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Binod B. De[a]; Swaminathan Sivaram[a]; Pradeep K. Dhal[ab]
[a] Division of Polymer Chemistry National Chemical Laboratory, Pune, India [b] Material Research Laboratory, Polaroid Corporation, Cambridge, MA

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CHIRAL POLYMER MATERIALS: ELUCIDATION OF THE EFFECT OF COMONOMERS ON COPOLYMER OPTICAL ACTIVITY DURING ASYMMETRIC COPOLYMERIZATION OF 1,2-DISUBSTITUTED OLEFINS†

BINOD B. DE, SWAMINATHAN SIVARAM, and PRADEEP K. DHAL*,‡

Division of Polymer Chemistry
National Chemical Laboratory
Pune 411008, India

Key Words: Chiral polymers; Asymmetric induction; Main-chain chirality; Protecting group chemistry

ABSTRACT

Asymmetric copolymerization of styrene derivatives (**1a** and **2a**) with 1,2 disubstituted vinyl monomers, viz., *N*-substituted maleimide and citraconimide derivatives (**2** and **3**), was carried out. Asymmetric induction was brought about by the chiral auxiliaries linked to the styrene monomer in the form of a reversible azomethine protective group. Facile and quantitative removal of these moieties makes it possible to estimate the extent of asymmetric induction unequivocally. Spectroscopic and chiroptical techniques were employed to study the chiral structures of these copolymers. The effect of the nature of the comonomers on the asymmetric induction is discussed.

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†NCL Communication Number 5758.

‡Present address: Material Research Laboratory, Polaroid Corporation, 750 Main Street - 5C, Cambridge, MA 02139.

INTRODUCTION

Syntheses of optically active functional vinyl copolymers with chirality originating from main chain chiral configuration and conformation are of contemporary research interest [1-3]. Structural requirements for obtaining configurationally chiral optically active polymers involve incorporation of local molecular asymmetry along the polymer chain [4]. Fundamentally, two different approaches are available to realize such polymer structures: 1) copolymerization of 1,2-disubstituted vinyl monomer and 2) generation of defined asymmetric *n*-ad (viz., diad, triad, tetrad, etc.) homopolymer and copolymer structures along the polymer chain. Significant literature is available pertaining to the synthesis of the first type of configurationally chiral polymers [5-7]. Synthesis of such polymers often involves the covalent linkage of the chirality-inducing agents (chiral auxiliary or template) to one of the comonomers which are subsequently removed (after polymerization). Such chemical linkages between the monomers and chiral auxiliaries are usually through robust bonds, viz., ester, ether, imide, etc. This gives rise to difficulties for quantitative removal of the chiral auxiliary and hence makes the assessment of asymmetric inductions in these polymers ambiguous [8]. This is particularly important since some recent findings indicate unusual influences of the side chain substituents (chiral or achiral) on the overall observed optically activity of polymer chains [9, 10].

In order to achieve quantitative removal of the chiral auxiliaries, we adopted the principle of *protective group chemistry* for reversibly linking the chiral auxiliaries to functional monomers and their copolymerization with 1,2-disubstituted vinyl monomers [11]. This protective group strategy enabled us to deprotect the auxiliaries quantitatively from the polymer chains, and the optical activities of the resulting template-free copolymers could be estimated. As a part of our efforts in this direction to elucidate further the factors governing asymmetric inductions in these polymers, we pursued our studies with monomers possessing different types of structures. As the chiral template monomer, we used both the antipodes of the styrenic azomethine derivative **1** (**1a** and **1b**). *N*-Cyclohexyl maleimide (**2**) and *N*-phenyl citraconimide (**3**) were used as the 1,2-disubstituted vinyl monomers. The cyclohexyl group in monomer **2** is transparent to UV (unlike phenyl maleimide) above 210 nm, and hence the UV absorbance of this component would not overlap with that of phenyl ring of the accompanying chiral monomer (**1**). This would enable us to map the CD structural features of the copolymers more precisely. Monomer **3** with a methyl substituent on the olefinic double bond lacks the C_2 symmetry that is present in its maleimide counterpart. Furthermore, this would provide some degree of rigidity to the polymer backbone. Thus, the optical activities of the copolymers obtained with this monomer are anticipated to provide some guidelines on the role of such structures on the asymmetric inductions in the polymer backbone during chain propagation.

EXPERIMENTAL

The solvents used in these experiments were reagent grade and were purified by adopting standard purification procedures prior to use. All the reagents were analytical grade obtained from Aldrich and were used as received.

Chiral Monomers

The chiral monomers used in this study are *N*-(4-vinyl benzylidene) *R*(+)-1-phenylethylamine (**1a**) and the corresponding *S* isomer (**1b**). These two monomers were synthesized by reacting 4-vinyl benzaldehyde with the corresponding amines following our previously reported procedure [11].

Comonomers

N-Cyclohexyl maleimide (**2**) and *N*-phenyl citraconimide (**3**) were synthesized following literature procedures [12].

Polymer Synthesis

The copolymerization reactions were carried out at 70°C under a nitrogen atmosphere by mixing the appropriate amounts of the monomers in toluene (15% solution w/v) using AIBN (1% w/w of monomers) as the free radical initiator. After achieving the desired conversions, the polymerization reaction mixtures were poured into excess methanol. The polymers were purified by repeated (three cycles) dissolution and reprecipitation from THF and methanol, respectively. The samples were finally dried under vacuum to constant weight.

Removal of the Chiral Template Residues (1-phenyl ethyl amine) from the Copolymers

In a typical hydrolysis experiment, to 20 mL of the polymer solution (0.5 g copolymer dissolved in 20 mL THF) cooled to 5°C, 3 mL of 2 N HCl was added dropwise with constant stirring. The resulting reaction mixture was allowed to stir for 24 hours at 25°C and subsequently poured into excess water. The operation was repeated twice, and finally the polymer was dissolved in THF, followed by precipitation from petroleum ether. It was then dried to constant weight under vacuum.

Characterization

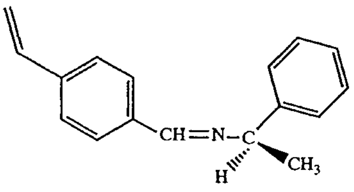
The melting points were measured with a Buchi 510 melting point apparatus. Elemental analyses were carried out at the National Chemical Laboratory, Pune microanalytical facility. ^{1}H- and ^{13}C-NMR spectra were recorded with a General Electric QE 300 spectrometer using $CDCl_3$ as the solvent and TMS as the internal reference. Infrared (IR) spectra were recorded with a Perkin-Elmer 1600 FT-IR spectrometer with the samples in the form of thin films on NaCl plates. Gel permeation chromatography (GPC) was carried out using a Waters GPC II liquid chromatograph fitted with μ-styragel columns and a refractive index detector. THF was used as the mobile phase. Optical rotations were measured in THF at 25°C using a JASCO DIP 181 polarimeter at a sample concentration of 2 $mg \cdot mL^{-1}$. Circular dichroism (CD) spectra were recorded at 25°C with a JASCO J-600 automatic recording spectropolarimeter in dioxane at a sample concentration of ~ 1 $mg \cdot mL^{-1}$ using a cell having a path length of 0.1 cm. UV spectra were recorded at 25°C in

THF using a Hitachi model 220 UV-Vis spectrophotometer. The sample concentration was 5–15 mg·mL^{-1}, and the path length of the UV cell was 0.1 cm.

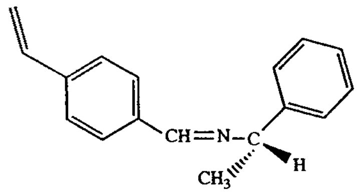
RESULTS AND DISCUSSION

Synthesis of Monomers and Copolymerization

Both the antipodes of the Schiff base of 4-vinyl benzaldehyde with *R*(+) and *S*(−) 1-phenyl ethylamine (**1a** and **1b**) were used as the chiral template monomer.



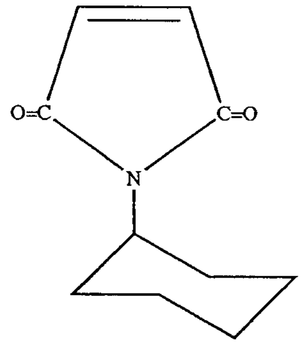
1a



1b

The choice of this type of polymerizable chiral auxiliary is based on our experience with our earlier study [11]. In the earlier investigation we tried to evaluate the asymmetric induction efficiency of different types of chiral auxiliaries such as α-methylbenzyl amine, tartarate derivatives, etc. Among the different types of auxiliaries tested, α-methylbenzyl amine gave the highest asymmetric induction. As 1,2-disubstituted vinyl comonomers, we used *N*-cyclohexyl maleimide (**2**) and *N*-phenyl citraconimide (**3**) in the present study. While comonomer **2** offers a UV transparent substituent, comonomer **3** results in a C_2 nonsymmetric structure in the polymer backbone (vide infra).

Both the antipodes of the chiral template monomer **1** were copolymerized with the comonomers **2** and **3** separately, offering a total of four series of copolymers (viz., **1a** + **2**, **1a** + **3**, **1b** + **2**, and **1b** + **3**). Each series of copolymers consisted



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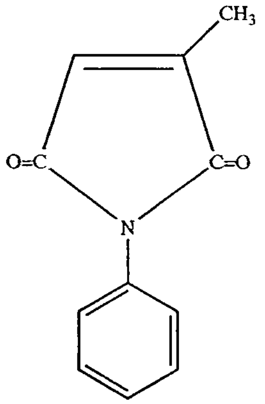

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TABLE 1. Results on Synthesis and Chiroptical Behavior of Copolymers of **1a** and **1b** with **2**

Entry	Chiral monomer	Mole fraction of chiral monomer in the reaction mixture	Mole fraction of chiral monomer in the copolymer	$[\alpha]_D^{25}$ Before hydrolysis	$[\alpha]_D^{25}$ After hydrolysis
1	**1a**	0.20	0.32	+7.8	−1.1
2	**1a**	0.30	0.39	+33.0	−1.2
3	**1a**	0.50	0.59	+79.6	−1.6
4	**1a**	0.65	0.72	+100	−1.8
5	**1b**	0.20	0.30	−7.2	+1.0
6	**1b**	0.30	0.42	−32.0	+1.5
7	**1b**	0.50	0.61	−75.0	+2.2
8	**1b**	0.65	0.71	−100.0	+1.8

of four different copolymers of varying comonomer compositions prepared with different molar ratios of the monomers. All the copolymers thus obtained were soluble in common organic solvents such as THF, toluene, chloroform, etc. The compositions of these copolymers were determined by elemental analysis and complemented by ^{1}H-NMR spectroscopy. Their composition data are presented in Tables 1 and 2. Although styrene and maleic anhydride are well known for undergoing alternating copolymerization under free radical conditions [13], the present systems, though closely similar, deviate from such a type of chain structure. However, the relative reactivities of these comonomers are fairly similar. Molecular and struc-

TABLE 2. Results on Synthesis and Chiroptical Behavior of Copolymers of **1a** and **1b** with **3**

Entry	Chiral monomer	Mole fraction of chiral monomer in the reaction mixture	Mole fraction of chiral monomer in the copolymer	$[\alpha]_D^{25}$ Before hydrolysis	$[\alpha]_D^{25}$ After hydrolysis
1	**1a**	0.10	0.25	+9.0	−1.8
2	**1a**	0.20	0.31	+17.2	−2.2
3	**1a**	0.30	0.38	+41.2	−1.1
4	**1a**	0.52	0.58	+58.4	−2.6
5	**1a**	0.58	0.65	+80.2	−1.1
6	**1b**	0.10	0.24	−8.4	+1.6
7	**1b**	0.20	0.30	−16.4	+2.4
8	**1b**	0.30	0.37	−40.6	+1.2
9	**1b**	0.50	0.57	−59.3	+2.8
10	**1b**	0.60	0.67	−79.8	+0.9

tural characterization of these copolymers were carried out by ^{1}H- and ^{13}C-NMR spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and gel permeation chromatography (GPC). In the IR spectra, the polymers show the presence of the characteristic band at 1644 cm^{-1} due to the azomethine linkage. This attests to the intactness and stability of the azomethine linkage during chain propagation and subsequent work-up conditions. This is further supported by the ^{1}H-NMR spectra where the peak due to the azomethine proton at 8.2 ppm is present and no indication of the aldehyde proton peak at 9.8 ppm is evident. In addition, the peak due to the methine proton of the α-methylbenzyl amine moiety of the Schiff base is present at 4.6 ppm. Typical FT-IR and ^{1}H-NMR spectra of a representative copolymer of **1a** with **3** are shown in Figs. 1(a) and 2(a), respectively. Gel permeation chromatography reveals that the polymers possess moderate molecular weights, with the number-

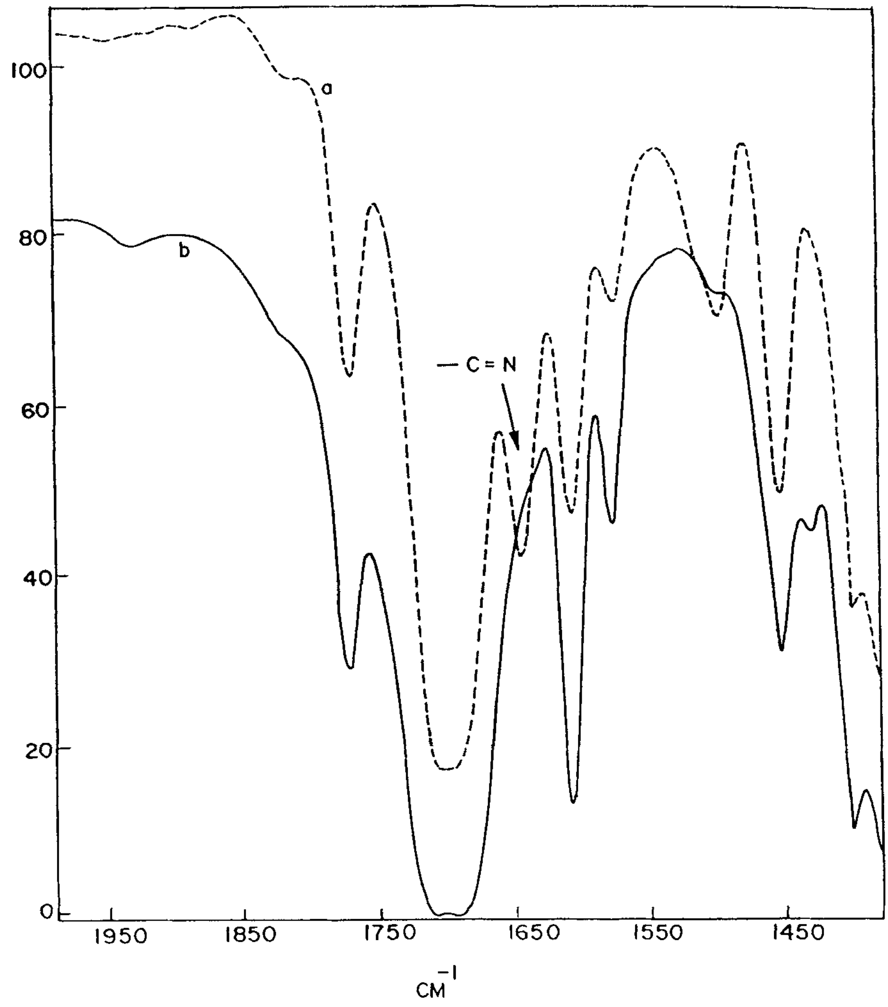


FIG. 1. Infrared spectra of the copolymer of **1a** with **3** (58:42): (a) before removal of the chiral auxiliary and (b) after removal of the chiral auxiliary.

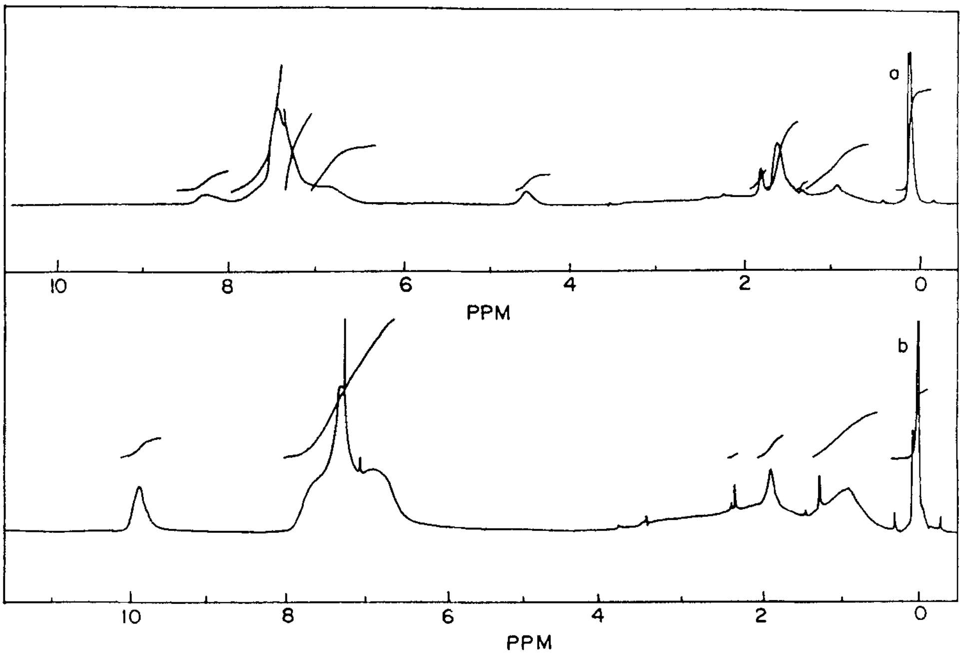


FIG. 2. ^{1}H-NMR spectra of the copolymer of **1a** with **3** (58:42): (a) before removal of the chiral auxiliary and (b) after removal of the chiral auxiliary.

average molecular weight in the 25,000 to 30,000 range. The samples are somewhat polydisperse (typically PDI = 2.8). The composition of the copolymer does not significantly influence the molecular weight.

Removal of Chiral Amine Templates from the Copolymers

Protective group strategy for linking the chiral auxiliary to a functional monomer is advantageous due to the fact that the former could be removed quantitatively from the polymer chain, thus enabling elucidation of the extent of asymmetric induction (if any) on the polymer chain. All four sets of copolymers were subjected to hydrolysis in weakly acidified THF at room temperature for 24 hours. During this time all the azomethine linkages were disrupted, releasing the amines from the copolymer chains. This offers copolymers carrying free aldehyde groups. The template-cleaved copolymers were isolated by precipitating the polymer solution in aqueous methanol. Spectroscopic analyses (FT-IR and NMR) of the copolymers reveal complete cleavage of the protective groups. Thus, in the FT-IR spectra the 1644 cm^{-1} band (due to the azomethine group) has disappeared. Although the appearance of an aldehyde group is evident due to the increased intensity of the 1700 cm^{-1} band, overlapping of the imide carbonyl band in this region makes them indistinguishable. In the ^{1}H-NMR spectra, the peaks at 4.6 and 8.3 ppm of the unhydrolyzed copolymers are absent in the template-free copolymers. On the other hand, a new peak at 10.2 ppm due to the aldehyde proton is present in the spectra of the later copolymers. Typical FT-IR and ^{1}H-NMR spectra of the representative hydrolyzed copolymer are shown in Figs. 1(b) and 2(b). The degree of polymerization of these hydrolyzed copolymers (as determined by GPC) did not change significantly. This suggests the absence of any chain degradation during cleavage of the chiral auxiliary from the polymer chain.

Chiroptical Behavior of Template Linked and Template-Free Copolymers

All four sets of copolymers carrying the respective chiral template residues exhibit appreciable optical activity. The signs of specific optical rotations of these copolymers are the same as the chiral monomers used for the copolymerization. The specific rotation values of the copolymers are sensitive to their compositions. Results on the specific rotation values of these copolymers are summarized in Tables 1 and 2. Comparison of the composition of these copolymers with their specific optical rotation values indicates that there is no linear correspondence between the copolymer composition and specific rotation. Plots of observed and calculated specific optical rotations of the copolymers vs chemical composition for the copolymers based on **1a** with **2** and **3** are shown in Figs. 3 and 4, respectively. As can be seen from the plots, the calculated specific rotation values are always higher than the observed values. This behavior is probably due to a competitive effect of chirality of opposite sign due to the polymer backbone and side-chain chiral substituent (vide infra).

Measurement of the optical rotation values of the hydrolyzed (template-free) copolymers is particularly important since it would enable assessment of the asymmetric induction in the polymer backbone during chain propagation. All the hydrolyzed copolymers are optically active, and their specific optical rotation values are summarized in Tables 1 and 2, respectively. For the copolymers obtained using

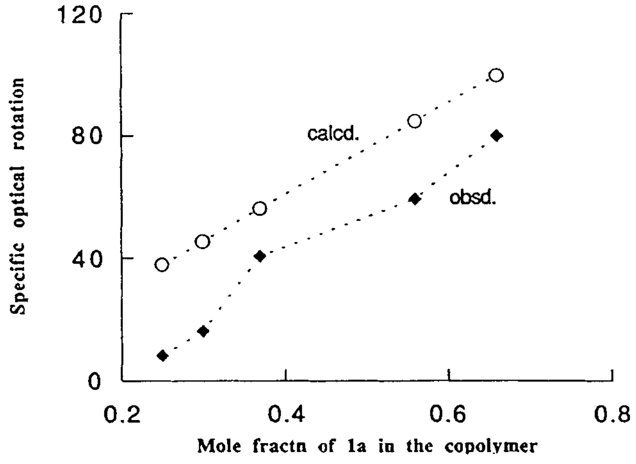


FIG. 3. Plots of calculated and observed specific optical rotations of the copolymers of **1a** with **2**.

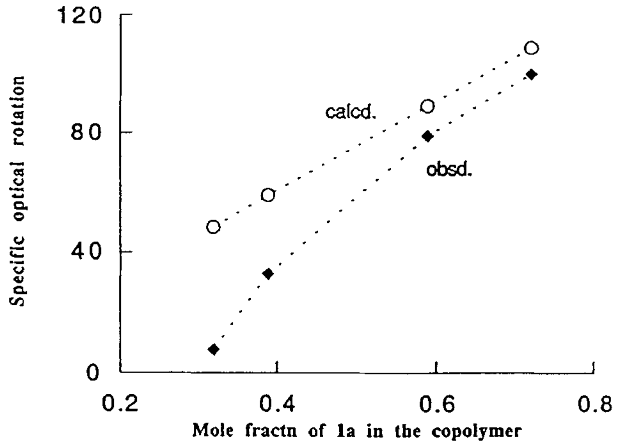


FIG. 4. Plots of calculated and observed specific optical rotations of the copolymers of **1a** with **3**.

N-cyclohexyl maleimide (**2**) as the comonomer, examination of these values (Table 1) indicates that these polymers exhibit small but distinct optical activity. In parallel with our earlier observation using *N*-phenyl maleimide [11], in the present case the sign of optical rotation values of the hydrolyzed copolymers are opposite to their unhydrolyzed precursors. This is probably the reason why the observed specific optical rotation values of the unhydrolyzed copolymers are lower than the calculated values. In a parallel study, Wulff et al. [9a] showed that the opposing effects of optical activities due to main chain configurational chirality and short-range conformational chirality of the pendant substituents significantly influence the observed optical activity of such polymers. In other words, the unhydrolyzed copolymers have to compensate for these buried values of opposite sign of the main chain. Furthermore, the specific rotation values of these hydrolyzed copolymers do not appear to be significantly influenced by the compositions of the copolymers. However, the small numerical values of specific optical rotations in the present case is a limiting factor for any quantitative comparison.

In order to elucidate the influence of the molecular structure of the 1,2-disubstituted olefins on the asymmetric induction in these copolymers, we chose *N*-phenyl citraconimide (**3**). It was anticipated that this monomer would serve two purposes. First, the presence of a methyl substituent (compared to a hydrogen atom in the case of the maleimide derivative) at the prochiral center would provide an additional restriction of rotation of the growing macroradical which might play a synergistic role in asymmetric induction. More importantly, the presence of a methyl substituent in this case compared with the maleimide derivative brings about further local molecular asymmetry. Thus, in the case of *N*-substituted maleimide-based systems, due to the presence of a C_2 symmetry axis, some amount of *meso* structures with a plane of symmetry is likely to be formed (since opening of the double bond can occur either in *cis* or *trans* fashion). On the other hand, when monomer **3** (lacking a C_2 axis of symmetry) is used, all the asymmetric centers in the resulting polymer backbone are chiral. As a result, the formation of any achiral *meso* structures can be minimized. The results on the specific rotation values of the hydrolyzed copolymers containing **3** are summarized in Table 2. Unfortunately, examination of these data reveal that there is no significant difference between the specific rotation values of these copolymers and those based on the corresponding maleimide derivatives. The reason for such behavior is unknown to us at the present time. Although their specific rotation values appear to be low compared to their template-bearing precursors, in the absence of knowledge of the absolute values of rotation (polymer chains with 100% enantiomeric structure of a given antipode) of such chains, it is difficult to assess the extent of asymmetric inductions (enantiomeric excess) in these polymer chains. Comparison of the chiroptical properties of these copolymers with those of appropriate low molecular weight model compounds with defined absolute configurations would probably answer these questions [14].

More information on the chiral structures of the polymer chains can be obtained by analyzing their circular dichroic (CD) spectra. We carried out CD measurements of both unhydrolyzed and hydrolyzed copolymers. Typical CD spectrum of an unhydrolyzed copolymer of **1a** and **2** is shown in Fig. 5(a), and the corresponding UV spectrum of this sample is shown in Fig. 6(a). The UV spectrum of this polymer shows a broad unresolved band in the 220 to 300 nm region. The higher wavelength part of the spectrum is due to the n-π^* transition of the aromatic C=N linkage while the lower part is due to the aromatic π-π^* transitions [15]. The CD spectrum of this polymer shows variety of structured bands. The CD spectrum shows a broad positive band with its maximum at 280 nm and a strong structured negative band with its maxima at 255 and 245 nm. This is followed by another weak positive band with its maximum at 225 nm. These copolymers exhibit positive optical rotations. Different electronic transitions of the chromophoric units associated with this polymer chain have been utilized to assign the CD peaks. The higher wavelength dichroic band pairs are due to the exciton coupled with the n-π^* transition of the C=N bond of the azomethine linkage [16]. Such type of exciton coupling behavior has been observed in the case of optically active vinyl copolymers bearing side-chain chiral substituents, where interaction between adjacent chiral substituents is attributed to such behavior [17]. The lower wavelength bands are a consequence of π-π^* transitions of the accompanying aromatic structures.

Analysis of the CD spectra of the template-free polymers was also carried out to elucidate the chiral features of these copolymers. Particularly for the hydrolyzed copolymers of **1a** and **2**, the CD spectra are anticipated to offer clearer information. For such copolymers, UV-sensitive electronic transitions occur only due to the benzaldehyde chromophoric units since the associated substituents of monomer **2** (imide) are UV transparent in the region of measurement. A typical CD spectrum of the hydrolyzed copolymer of this series is shown in Fig. 5(b), and its UV spectrum is presented in Fig. 6(b). The CD spectrum reveals a broad negative dichroic band in the 335 to 265 nm range, with its maximum at 288 nm. This is followed by a structured weak bank in the lower wavelength region with, however, a more noisy structure. The higher wavelength negative peak is due to the n-π^* transition of the aromatic aldehyde units of the polymer arising from the hydrolysis of the azomethine linkage of monomer **1a**. The lower wavelength peak is an outcome of the π-π^* transition of the aromatic ring. However, unlike its precursor, this polymer does not reveal any exciton coupling effect. As such, the observed optical rotation of this

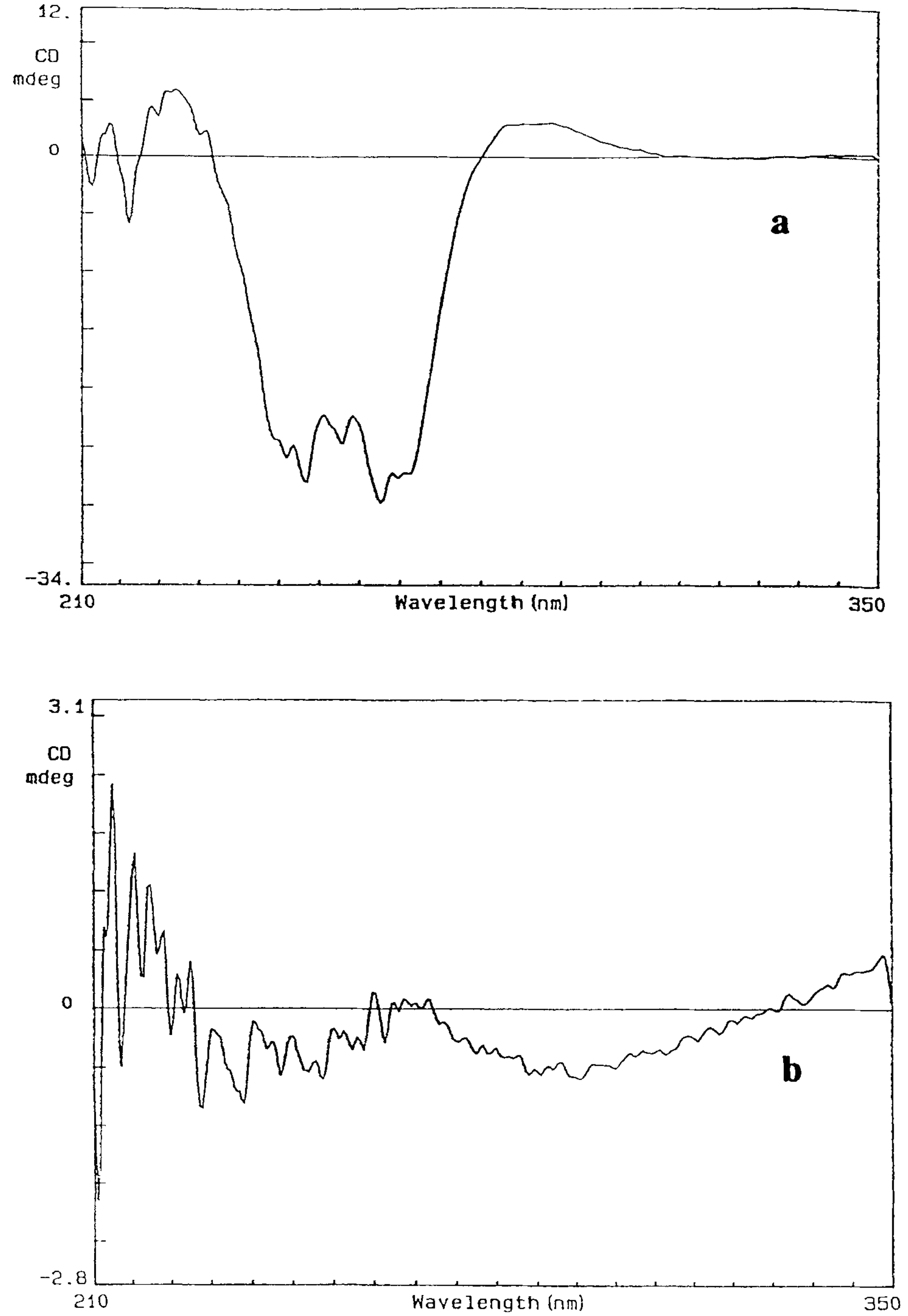
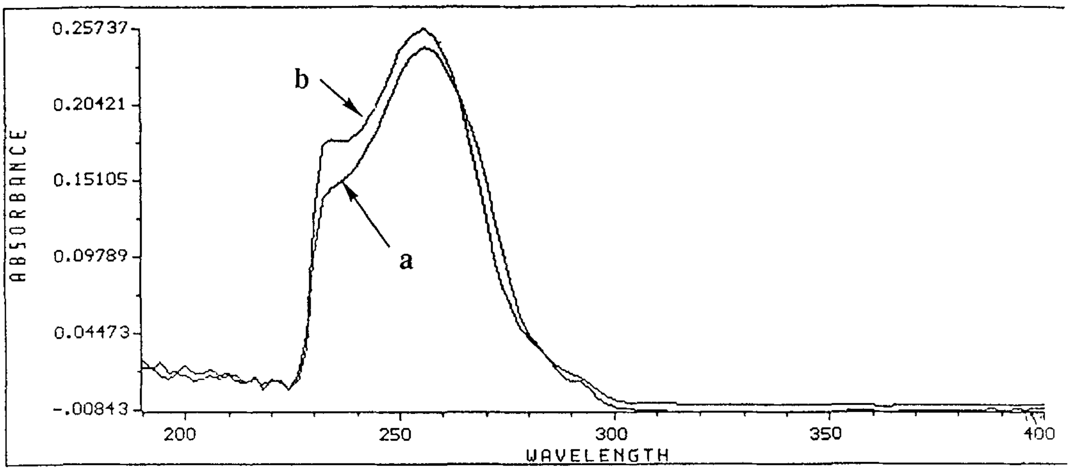


FIG. 5. CD spectra of the copolymer of **1a** with **3** (58:42): (a) before removal of the chiral auxiliary and (b) after removal of the chiral auxiliary.



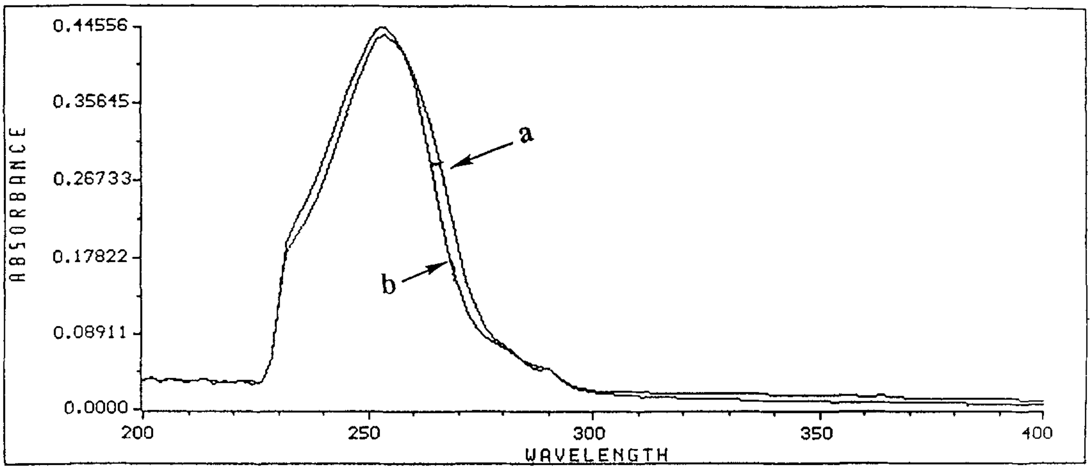


FIG. 6. (Top) UV spectra of the copolymer of **1a** with **3** (58:42): (a) before removal of the chiral auxiliary and (b) after removal of the chiral auxiliary. (Bottom) UV spectra of (a) azomethine of 4-methyl benzaldehyde with 1-phenyl ethylamine and (b) 4-methyl benzaldehyde.

negatively rotating polymer is considerably weaker (vide supra). This CD result suggests that 1-substituted vinyl monomer units of the copolymer chains are disposed in the chiral environment of this optically active polymer. In other words, it has been possible to bring about asymmetric induction in the polymer main chain by the associated chiral template during polymerization. Furthermore, it appears that by choosing appropriate substituents in the comonomer (in this case, the UV-transparent cyclohexyl group), it would be possible to assign the chiral components in such a type of main chain to optically active polymers.

CONCLUSIONS

Utilization of the principle of protective group chemistry has been useful for estimating asymmetric inductions with high precision in the polymer main chain during the free-radical-initiated copolymerization of 1,2-disubstituted vinyl monomers with 1-substituted vinyl monomers. The choice of appropriate substituents enabled us to ascertain the asymmetric inductions around different substituent groups. A variation of the comonomer structure in terms of molecular rigidity and symmetry does not appear to influence the asymmetric inductions. A more quantitative understanding of the asymmetric induction as well as the absolute configuration of the chain structure need to be investigated to further understand the mechanism of this asymmetric polymerization process. Our efforts are currently under way in this direction.

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