Primary structure and chiroptical properties of polydiasteriomers obtained by stereoelective polymerization of N-[(S)-sec-butyl] and N-[(R)-sec-butyl-N-methyl-N-(R,S)-thiirane-2-ylmethyl] amine isomers

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Stereoisomers of *N*-(sec-butyl)-*N*-methyl-*N*-((R,S)-thiirane 2-ylmethyl) amine ((S)-sec-butyl, optical purity O. P. ~94% and (R)-sec-butyl, O. P. ~26%) were polymerized using a chiral initiator system (1:1) ZnEt$_2$/R(−)3,3-dimethyl-1,2-butanediol (R(−)BMBD) (stereoelective polymerization). In agreement with the homosteric character of this initiator, the configuration of the asymmetric centre located in the heterocycle of the elected diastereoisomer is shown to be R from c.d. spectra of residual monomers, whatever the configuration of the asymmetric centre located in the pendant group. O.r.d. and c.d. spectra of stereoelected polydiastereoisomers are described and compared to those of corresponding polydiastereoisomers bearing racemic main-chain chiral centres. ^{13}C n.m.r. spectra of different polydiastereoisomers are reported. The stereosensitivity to tacticity of the main-chain carbons is poor but some of the side-chain carbon atoms are very sensitive to the presence of two asymmetric centres per repeat unit. The optical purity of main-chain chiral centres is deduced from the split resonance of one of these carbons atoms. It is shown that chiroptical properties of polydiastereoisomers primarily depend on configurations of the two chiral sites without obvious contributions from macromolecular conformations. The 242 nm c.d. band assigned to the $n \rightarrow \sigma^*$ electronic transition of sulphur chromophores is sensitive only to the optical purity of main-chain chiral centres and can be used to evaluate the configurational enrichment due to the stereoelective polymerization.

INTRODUCTION

As a part of our investigation of chiroptical properties of reactive optically active polymers other than biopolymers, we have been interested in studying poly[thio-1-(*N*–R$_1$–*N*–R$_2$-aminomethyl)ethylene], a series of new optically active polyamines[1]. These weak polybases were synthesized by ring-opening polymerization of corresponding thiiranylalkylamines[1], according to classical methods already used for other thiiranes[2]. There are several possible ways of obtaining optically active polymers from this type of monomer. We have already reported the case of poly[thio-1-(*N*–R$_1$–*N*-methylaminomethyl)ethylene] (I) in which the optical activity came from a predominant configuration of asymmetric carbon atoms located in side-chain R$_1$ substituents, while for main-chain asymmetric carbon atoms equal amounts of R and S configurations were statistically distributed along the chain ('racemic' chain)[1]. We have also reported the case of poly[thio-1-(*N*,*N*-diethylaminomethyl) ethylene] (II) in which main-chain chiral centres were configurationally enriched by stereoelective polymerization, side-chain substituents being achiral[3].


(I)   (II)
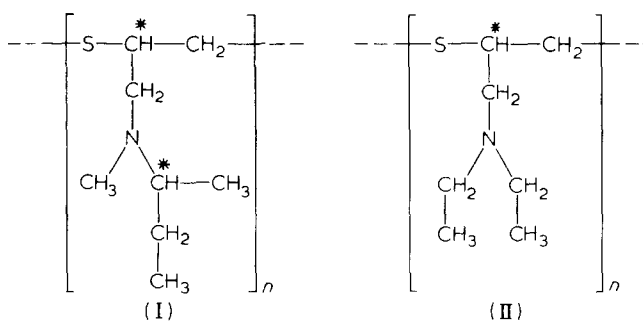
Chiroptical properties of these optically active polyamines were discussed with regard to chromophores present in the backbone and in the side-chain[4].

In polythioethers, the $n \to \sigma^*$ electronic transition of sulphur chromophore is usually located aroung 240 nm[5]. For optically active polyamine (II) in dioxane, the magnitude of this c.d. band was found to be proportional to the optical purity of main-chain chiral centres[3]. In contrast, no c.d. band appeared in the 230–250 nm spectral range for polydiastereoisomers (I) in which the main-chain was 'racemic'[4]. In the latter case, chiral centres located well inside the pendant groups seemed to be unable significantly to perturb main-chain thioether chromophores, at least in the selected solvent.

These features suggested that, in the case of polydiastereoisomers with 'non-racemic' main-chain, the 242 nm c.d. band should become optically active and, thus, should reflect the optical purity of these main-chain chiral centres[4].

The confirmation of this hypothesis requires the preparation of polydiastereoisomers with different configurational compositions in the main-chain. As the corresponding thiirane monomer (III) is not yet available in optically pure diastereoisomeric forms, the stereoelective polymerization method[6] has been used to prepare monomers (III) and the corresponding polymers (I) with different optical purities.

(III)   (IV)
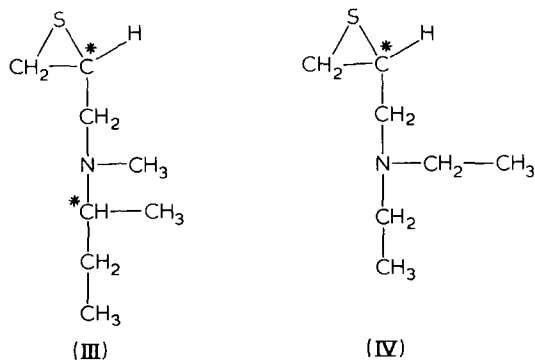
In this paper the results are reported of the stereoelective polymerization of stereoisomers of N-(sec-butyl)-N-methyl-N ((R,S)-thiirane 2-ylmethyl) amine (III) [(III)$^S_{R,S}$†: (S)-sec-butyl, O. P. $\simeq$ 94%; (III)$^R_{R,S}$†: (R)-sec-butyl, O. P. $\simeq$ 26%]. Chiroptical properties of resulting polymers and residual monomers are analysed with regard to sulphur and nitrogen chromophores and compared to those of parent compounds (II) and (IV). The observed results are correlated to main- and side-chains chiral centre configurations.

EXPERIMENTAL

Monomers

(III)$^S_{R,S}$ and (III)$^R_{R,S}$ were synthesized from epithiochlorhydrin and S(+) and R(−) N-methyl-sec-butylamines having O. P. = 94% and 26% respectively. The values of optical purities

were determined by ^{1}H n.m.r. on diastereoisomers obtained by reacting the two isomers of sec-butylamine with optically pure α-phenyl-α-trifluoromethyl-α-methoxyacetyl chloride.

Polymers

Optically active polydiastereoisomers (I) with configurational enrichment of asymmetric carbon atoms located both in main and in side-chains were prepared by stereoelective polymerization of monomers (III)$^S_{R,S}$ and (III)$^R_{R,S}$ using a (1:1) ZnEt$_2$/R(−) 3,3-dimethyl 1,2-butanediol mixture as the initiator system. Polymerizations were carried out in bulk at room temperature in sealed apparatus under high vacuum according to an experimental procedure already described for other thiiranes[6].

Measurements

Viscosimetric measurements were performed at 25°C with a FICA automatic viscosimeter equipped with an automatic dilution system.

O.r.d. spectra were recorded on a FICA Spectropol I spectropolarimeter thermostatted at 25°C.

C.d. spectra were obtained by using a JASCO J 40 B dichrometer at room temperature.

^{13}C n.m.r. investigations were carried out on a WH90 Brucker spectrophotometer operated by the Common Analysis Centre of the University of Rouen. Samples of polymers (200 mg) in CDCl$_3$ (3 ml) were studied.

RESULTS AND DISCUSSION

Stereoelective polymerization of N-(sec-butyl)-N-methyl-N(thiirane-2-ylmethyl) amines (III)$^S_{R,S}$ and (III)$^R_{R,S}$

Stereoelective polymerizations of monomers (III) were carried out by using the (1:1) ZnEt$_2$/R(−)3,3-dimethyl-1,2-butanediol (R(−) DMBD) chiral initiator system which gave the best results for several other thiiranes[6]. The residual monomer obtained from one of these polymerizations (run 2) was reused as starting monomer for another stereoelective polymerization (run 3). Experimental data are given in *Table 1*.

The slow polymerization observed for runs 1 and 2, with respect to runs 3 and 4 and to the case of monomer (IV)[3], is still not thoroughly understood. Anyway, high molecular weight polymers having similar intrinsic viscosities were obtained at comparable yields.

It was evident that polymers and corresponding residual monomers had optical rotations of the same sign. The optical rotatory power of the laevorotatory starting monomer increased in absolute value during the polymerization while that of the dextrorotatory one decreased. Since these variations of optical activity were obviously connected to the stereoelective choice of some of the diastereoisomeric molecules present in the reaction medium, we have tried to determine the configuration of residual monomers collected after the polymerization.

Determination of the stereoelective choice

From numerous examples of monosubstituted thiiranes and oxiranes, it has been shown that the (1:1) ZnEt$_2$/R(−) DMBD chiral initiator system preferentially incorporates the R isomer in polymer chains[6]. This feature was also observed for the stereoelective polymerization of racemic monomer (IV), a parent compound having only one chiral centre[3]. The results presented below demonstrate that a similar trend

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† In order to facilitate the understanding of diastereoisomeric species, we introduce the following notation: in brackets, the stereo isomer species (monomer or polymer unit); as superior index the predominant configuration of the side-chain, as inferior index the predominant configuration in the heterocycle or in the polymer main-chain. Thus a monomer (III) with a side-chain asymmetric carbon atom of pure S configuration and with balanced amount of both configurations in the heterocycle will be notated (III)$^S_{R,S}$. The polymer resulting from this monomer but enriched in R configuration in the main-chain will be written (I)^S_R

Table 1   Polymerization of monomers $(III)^S_{R,S}$ and $(III)^R_{R,S}$ using the (1:1) $ZnEt_2/R(-)$ DMBD initiator system. Polymerizations were carried out in bulk at room temperature

| | Initial monomer | | | | Polymerization | | Polymer | | | | |
| | | | C/M | | | | | | [α]$_D^{25}$ | | Residual monomer α$_D^{25}$ |
Run	Code	α$_D^{25}$ (neat)	mole %		yield %	time h	code[a]	(η)^{25} 100 cm^3 g^{-1} [b]	Benzene (C$_p$ = 0.9)	Dioxane (C$_p$ = 0.5)	(neat)
1	$(III)^S_{R,S}$	+28.7	4.7		29	180	$(I_1)^S_R$	0.90	+7.9	+17.2	+24.06
2	$(III)^S_{R,S}$	+28.7	4.9		32	216	$(I_2)^S_R$	0.92	+6.5	+13.8	+23.77
3	$(III)^{Sc}_S$	+23.77	4.3		26	2	$(I_3)^S_R$	0.90	+6.3	+13.0	+20.52
4	$(III)^R_{R,S}$	− 7.8	5.0		26	4	$(I_4)^R_R$	1.04	−18.2	−14.9	−14.05

[a] the nomenclature adopted here is justified *a posteriori* after examination of chiroptial properties of products.
[b] in benzene (amine form)
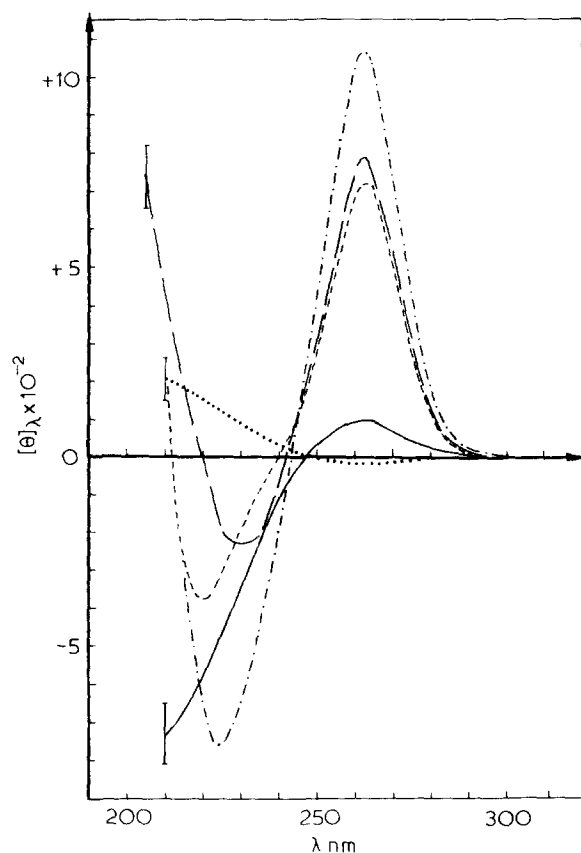[c] residual monomer of run 2

Figure 1   C.d. spectra of starting monomers $(III)^S_{R,S}$ (———), $(III)^R_{R,S}$ (.........); of residual monomers obtained by stereoelective polymerization $(III_3)^S_S$ (— · — · — · —), $(III_4)^R_S$ (— — — —) (respectively runs 3 and 4 in Table 1); and of S(−) (IV) O.P. ≃ 20% (- - - - - - - -) in methanol

Cotton effect when the asymmetric carbon atom of the heterocycle has S configuration[5,7].

C.d. spectra of starting monomers $(III)^S_{S,S}$, $(III)^R_{R,S}$ and those of residual monomers (runs 3 and 4 in *Table 1*) are represented in *Figure 1*. These spectra are limited in the low-wavelength region by the solvent absorption. Several c.d. bands are observed in the accessible region above 195 nm. For monomer $(III)^S_{R,S}$ the 263 nm c.d. band is weak although the optical purity of the side-chain asymmetric centre is high. This feature shows that the sulphide chromophore in the thiirane ring is only slightly perturbed by the asymmetric centre localized well inside the dialkyl-aminomethyl substituent. In contrast, c.d. spectra of residual monomers obtained from stereoelective experiments show strong positive c.d. bands at 263 nm whatever the configuration of the chiral centre located in the pendant group. These positive c.d. bands are similar to that previously observed for partially enriched S (IV) in which the heterocyclic asymmetric carbon atoms is only present. Therefore, it is concluded that residual monomers are partially enriched in S configuration during the stereoelective process. Once again, the (1:1) $ZnEt_2/R(-)$ DMBD chiral initiator system preferentially polymerized the monomer molecules having R heterocyclic configuration.

It is difficult to decide whether or not the side-chain chiral centre affects the stereoelective process. Anyway, *Figure 1* suggests that the stereoelective choice remains the same whatever the configuration of the second chiral centre.

Other bands observed below 240 nm certainly result from the overlapping of the $n \to \sigma^*$ electronic transition of the amine chromophore, usually located at about 215 nm[4,8] with other electronic transitions of the sulphide chromophore, known to be present in this region of the spectrum[9].

For the 263 nm c.d. band, the effect of chiral centres located in pendant groups was neglected because they only slightly perturb the sulphide $n \to \sigma^*$ electronic transition. For lower-wavelength bands, both the heterocyclic [as shown for derivative (IV)] and the pendant group chiral centres contribute to the dissymmetric perturbation of sulphide and amine chromophores. The relative contributions of these two types of chromophores cannot be simply separated.

Chiroptical properties of polydiastereoisomers with a predominant configuration in the main-chain

In order to distinguish the effect of configurational enrichment on chiroptical properties, o.r.d. and c.d. spectra of
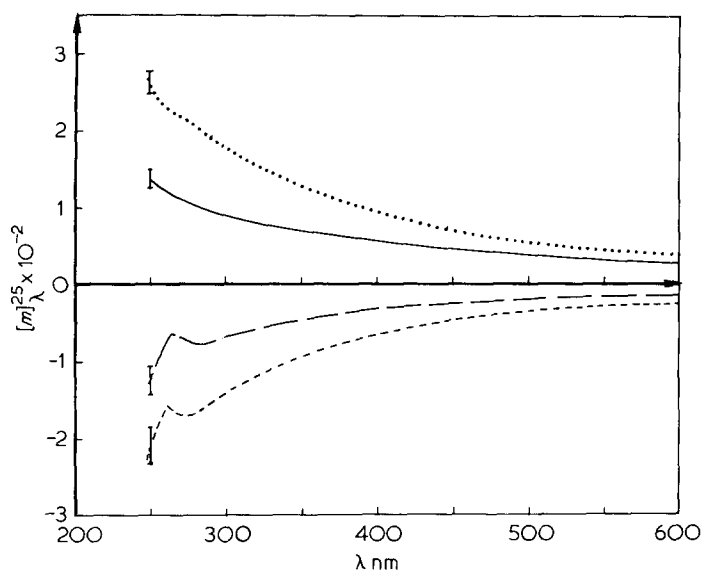
occurs for monomers $(III)^S_{R,S}$ and $(III)^R_{R,S}$ although two chiral centres are present in the same monomeric molecule.

The R-type stereoelection was effectively substantiated by c.d. spectra of residual monomers. Indeed, the rigid thiirane heterocycle gives to these molecules specific chiroptical properties directly related to the configuration of the heterocyclic asymmetric centre. It has been shown that the $n \to \sigma^*$ electronic transition of sulphide chromophore in thiirane heterocycles, usually observed at about 260 nm, gives a positive
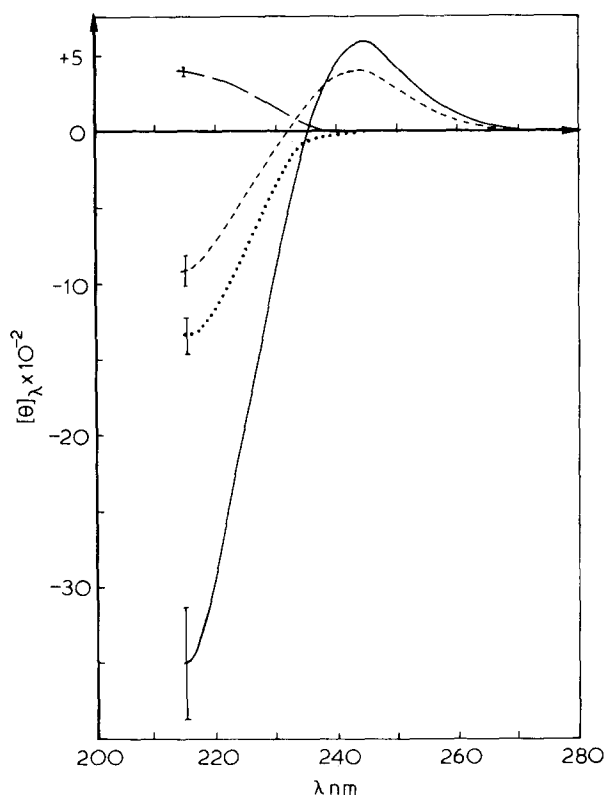
Figure 2 O.r.d. spectra in dioxane of stereoelected polydiastereo-isomers $(I_1)_R^S$ (————), $(I_4)_R^R$ (- - - - - -) as compared to o.r.d. spectra of polydiastereoisomers $(I)_{R,S}^S$ (. . . . .) and $(I)_{R,S}^R$ (— — — —) having racemic main chains

Figure 3 C.d. spectra in dioxane of steroelected polydiastereoisomers: $(I_1)_R^S$ (————), $(I_4)_R^R$ (- - - - -); as compared to c.d. spectra of poly-diastereoisomers: $(I)_{R,S}^S$ (. . . . . .) and $(I)_{R,S}^R$ (— — — —) having racemic main-chains

stereoelected polydiastereoisomers $(I)_R^S$ and $(I)_R^R$ were compared to those of polydiastereoisomers $(I)_{R,S}^S$ and $(I)_{R,S}^R$ having a 'racemic' main-chain. The latter were prepared by polymerizing monomers $(III)_{R,S}^S$ and $(III)_{R,S}^R$ with achiral initiators (sodium metal and $ZnEt_2/CH_3OH$ respectively).

O.r.d. spectra of the four polydiastereoisomers are given in *Figure 2*. Polymers derived from monomer $(III)_{R,S}^S$ showed positive o.r.d. curves whatever the initiator while

those prepared from monomer $(III)_{R,S}^R$ gave negative curves.

Corresponding c.d. spectra are represented in *Figure 3*. Polymers $(I)_{R,S}^S$ and $(I)_{R,S}^R$ show symmetrical spectra (with restriction due to the difference in optical purities). For both polymers, a c.d. band came out in the 215 nm region but no band was detected in the 240 nm region where the $n \to \sigma^*$ electronic transition of linear sulphide chromophore usually appears. In contrast, positive bands at 244 nm and negative ones at 215 nm were observed for stereoelected polymers $(I)_R^S$ and $(I)_R^R$ whatever the configuration of side-chain chiral centres. Since the 244 nm region of the spectrum does not present any band when the main-chain is 'racemic'[4] it is reasonable to conclude that the positive c.d. band observed for polymers $(I)_R^S$ and $(I)_R^R$ is mainly due to predominance of one configuration in main-chain chiral centres as was previously observed for other polythiiranes[5].

On the other hand, c.d. bands observed in the 215 nm region certainly result from the overlapping of Cotton effects related to both amine and sulphide chromophores. The relative contributions of each of these chromophores to the 215 nm band could not be simply distinguished because of overlapping.

For analogous polyamines[4], it has been shown that the contribution of amine chromophore is not observed in acidic aqueous solution (hydrochloride form). Indeed, the amine $n \to \sigma^*$ Cotton effect located at 215 nm shifts to lower wavelength when non-bonding electrons n are involved in a chemical bond between the nitrogen atoms and a proton. *Figure 4* shows c.d. spectra of protonated polymers (I) in water. As in dioxane solution, the c.d. spectra of stereoelected polymers are completely different as compared to those of polymers obtained using achiral initiators. C.d. spectra of polymers $(I)_{R,S}^S$ and $(I)_{R,S}^R$ are characteristic of two antipodes of different optical purities, while those of polymers $(I)_R^S$ and $(I)_R^R$ look similar in shape and in sign in spite of the opposite configuration of side-chain chiral centres. This trend, already noticed for amine forms in dioxane solution (*Figure 3*), agrees well with the prevalence in the main-chain of chiral centres
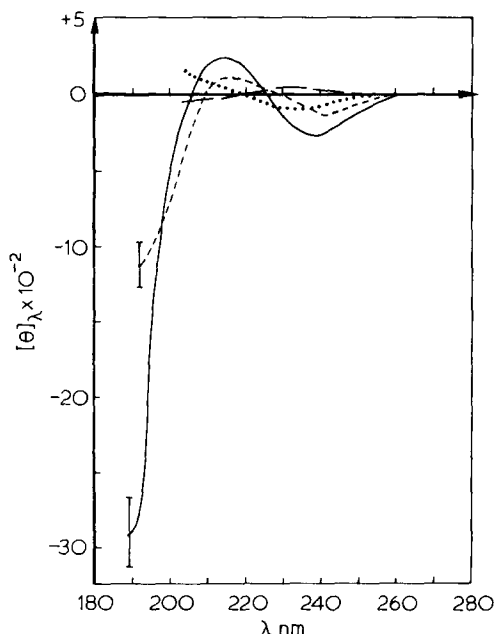

Figure 4 C.d. spectra in water (protonated from) of stereoelected polydiastereoisomers: $(I_1)_R^S$ (————), $(I_4)_R^R$ (- - - - - -), as compared to c.d. spectra of polydiastereoisomers: $(I)_{R,S}^S$ (. . . . . . .) and $(I)_{R,S}^R$ (— — — —) having racemic main-chains
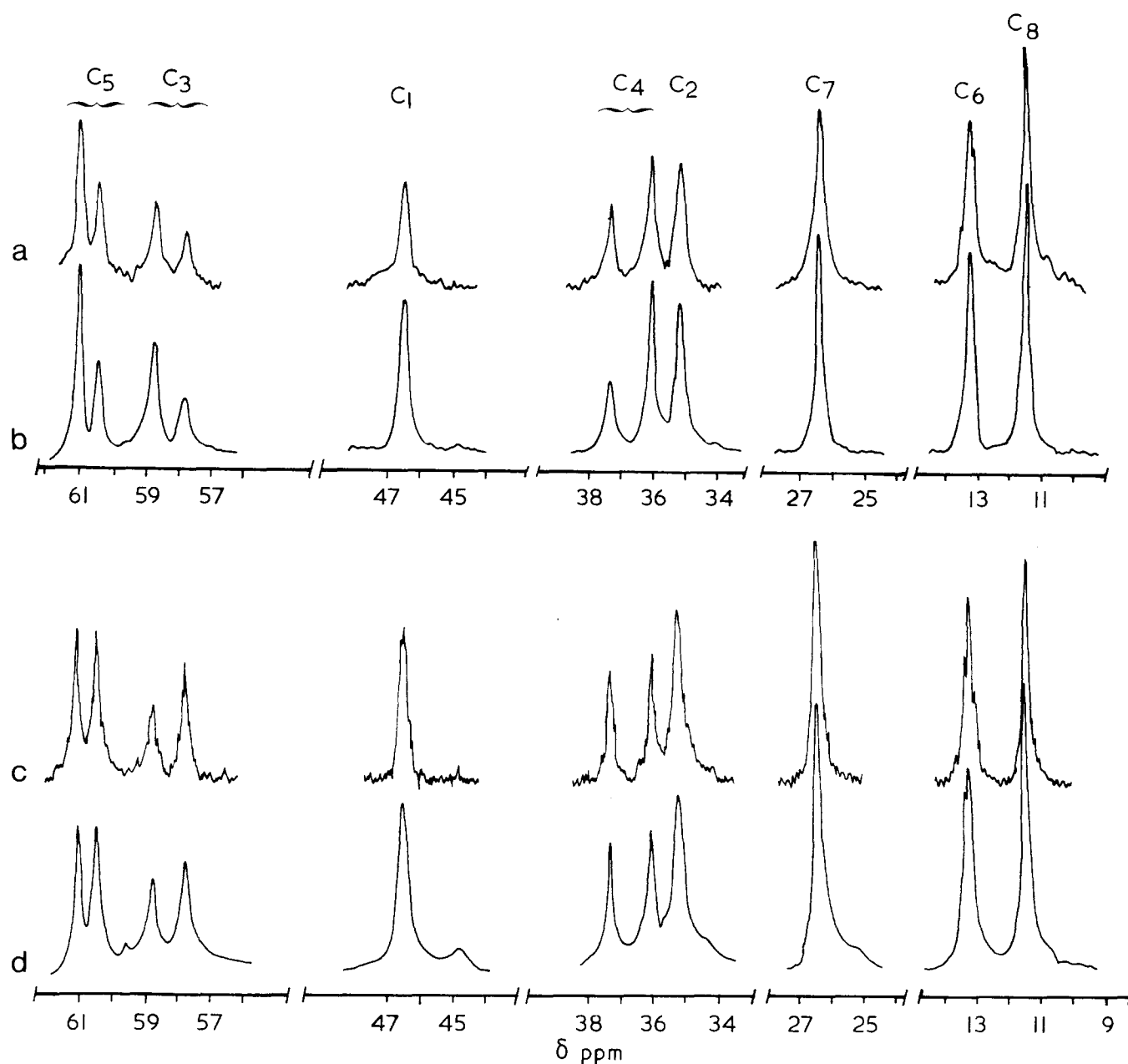
Figure 5 ^{13}C n.m.r. spectra (22.63 MHz) in CDCl$_3$ at 35° of different typical polydiastereoisomers (Sweep width — 1600 hz — reference signal TMS). (a) (I$_3$)^S_R 27 600 scans; (b) (I$_2$)^S_R 38 300 scans; (c) (I$_4$)^R_R 26 500 scans; (d) (I)$^{R,S}_{R,S}$ 41 000 scans (polymerized with ZnEt$_2$/H$_2$O system). The main-chain predominant configuration is given in inferior index while the side-chain one is given in superior index

of the same configuration in both stereoelected polymers (I)^S_R and (I)^R_R. When polymers (I)$^S_{R,S}$ and (I)$^R_{R,S}$ are in the amine form, the $n \to \sigma^*$ transition of the sulphur chromophore is optically inactive (*Figure 3*). For the hydrochloride form, a weak Cotton effect, slightly shifted to lower wavelengths, appears for both polymers.

The protonation reaction does not only suppress the amine $n \to \sigma^*$ Cotton effect in the c.d. spectrum, but it also drastically changes the contribution of sulphide chromophore. The 244 nm c.d. band, positive in dioxane, became negative in acidic water and, at the same time, a negative band appeared at 190 nm, both bands being separated by a small c.d. contribution.

These changes are still not well understood but similar behaviour was already observed for stereoelected polymers (II) which have no chirality in the side-chain[3]. In conclusion the similarities pointed out between c.d. curves of stereo-
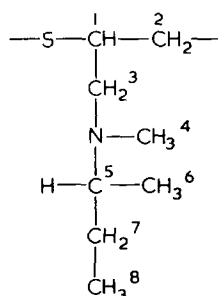
elected polymers (I)^S_R and (I)^R_R and c.d. curves of polymers (II), whatever the solvent, suggest that it is the main chain chiral cnetres which perturb predominantly amine and sulphide chromophores and not the side-chains ones. Thus optical purities of main-chain asymmetric centres had to be determined in order to check the previous statement more quantitatively.

Determination of the optical purity of main-chain asymmetric centres in polydiastereoisomers by ^{13}C n.m.r. spectrometric method

In the case of polymers (II) having no asymmetric carbon atoms in side-chains, the optical purity of main-chain chiral centres was determined from ^{13}C n.m.r. spectra by analysing the stereosensitivity to triads of the methine –CH resonance[3].

Typical ^{13}C n.m.r. spectra of different polydiastereoisomers (I) are shown in *Figure 5*. The assignments of the peaks

to specific carbon atoms were done using partial C–H decoupling.

$$-S-\underset{\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2^{\,7}}}{\underset{|}{C}^5-CH_3^{\,6}}}{\underset{|}{N}-CH_3^{\,4}}}{\overset{|}{\underset{|}{CH}}}-CH_2^{\,2}-$$

Chemical shifts are given using TMS as internal standard. According to the structure of these polymers, effects of tacticity as well of diastereoisomerism could be expected.

Main-chain methylene C_2 appears as a singlet at 35.1 ppm. The methine C_1 peak located at 46.6 ppm is slightly stereosensitive but the analysis of patterns in terms of triads was not reasonably possible. Therefore, the main-chain optical purity could not be estimated from methine patterns as was done previously for polymers $(II)^3$. No stereosensitivity to tacticity was observed for side-chain carbon atoms. However, it was found that carbons C_3, C_4 and C_5 directly bonded to nitrogen atoms gave rise, under the influence of the two asymmetric atoms present in each repeat unit, to well-resolved doublets located at 58.8–57.8, 37.3–36.0 and 61.0–60.4 ppm respectively. In the same way, carbon C_6 attached to the side-chain chiral centre C_5, gave a poorly resolved doublet located at 13.5–12.9 ppm. Carbon atoms C_7 and C_8 of the ethyl substituent were not at all stereosensitive and came out as singlets at 26.4 and 11.5 ppm respectively.

Chemical shifts of the different peaks do not vary when using different initiator systems and thus do not depend on configurations of main-chain chiral centres. Therefore, the relative intensities of C_3, C_4, C_5 and C_6 split signals are reliable to predominant configurations of the main and side-chain chiral centres. For stereoelected polydiastereoisomers $(I_2)_R^S$ and $(I_4)_R^R$ (run 2 and run 4, *Table 1*), all the doublets appeared unbalanced. The same situation was observed for C_3, C_4 and C_6 carbons in the polymer $(I)_{R,S}^{R,S}$ prepared with a non stereospecific achiral initiator from a monomer containing equal amounts of the four possible diastereoisomers. In this case, the main-chain is 'racemic' and equal numbers R and S configurational centres are randomly distributed in the side-chains *(Figure 5)*. The observed unbalancing can be due to differences in Nuclear Overhauser Effect reflecting the presence of non-equivalent side-chain conformers from the viewpoint of short range $^{13}C-^1H$ coupling. Finer experiments including reversed gate decoupling and investigations at higher frequencies are under examination in order to show whether these secondary effects are really connected to the mobility of side-chain atoms. Contrarily to doublets found for C_3, C_4 and C_6, the doublet assigned to the C_5 carbon atom is almost symmetrical for polymers $(I)_{R,S}^{R,S}$ and $(I)_R^R$ but significantly unbalanced for stereoelected polymers $(I_2)_R^S$ and $(I_3)_R^S$. This observation leads to the conclusion that the relative intensities of the two peaks of the C_5 doublet depend only on the main and side-chain chiralities.

Let us consider this problem in more detail. Starting monomers bear two asymmetric carbon atoms. In derived polydiastereoisomeric polymers, four different repeat units can be present with the following configurational structures:

(1S, 5S), (1R, 5R), (1S, 5R) and (1R, 5S)
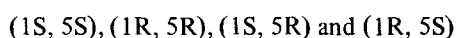
In contrast, to o.r.d. and c.d. spectra, n.m.r. is not able to distinguish between mirror images i.e. between (1S, 5S) and (1R, 5R) or between (1S, 5R) and (1R, 5S). Therefore, each peak of the C_5 split resonance can be assigned to one of these two couples of diastereoisomeric repeat units. Magnitudes A_1 and A_2 of these peaks are related to concentrations of the four diastereoisomeric units according to equations (1) and (2):

$$A_1 = [1S, 5S] + [1R, 5R] \qquad (1)$$

$$A_2 = [1S, 5R] + [1R, 5S] \qquad (2)$$

Naming σ and τ the molar fractions of R carbon atoms at the main-chain and at side-chains chiral sites, equations (1) and (2) become:

$$A_1 = (1 - \sigma)(1 - \tau) + \sigma\tau \qquad (3)$$

$$A_2 = (1 - \sigma)\tau + \sigma(1 - \tau) \qquad (4)$$

The molar fraction σ of R main-chain chiral centres is given by equation (5):

$$\sigma = \left[\frac{A_1}{A_1 + A_2} + \tau - 1\right] \bigg/ 2\tau - 1 = \left[\frac{A_2}{A_1 + A_2} - \tau\right] 1 - 2\tau \qquad (5)$$

Equation (5) shows that the relative magnitude of each peak of the C_5 split resonance depends on the configurational purity of both main-chain and side-chain chiral centres.

For stereoelected polydiastereoisomers $(I)_R^S$'s having almost pure S side-chain chiral centres $(1 - \tau = 0.97$ as determined by ^1H n.m.r. polarimetry of initial S(+) *sec*-butylamine), the well-contrasted observed A_1 and A_2 peaks primarily depend on the main-chain configurational purity, which can be evaluated from the weight of peaks by using equation (5).

It has been shown that the stereolective polymerization initiated by the $ZnEt_2/R(-)$ DMBD chiral initiator system, leads to a main-chain enrichment in the R configuration. Therefore, the larger peak of the C_5 doublet located at 61.0–60.4 ppm must be assigned to (1R, 5S) and (1S, 5R) diastereoisomeric repeat units, the latter being present in a very small proportion. For polymer $(I_2)_R^S$, the optical purity of the main-chain was evaluated to 0.30 ± 0.04 *(Figure 5)*. For polymer $(I_3)_R^S$, the doublet was slightly less unbalanced than for $(I_2)_R^S$ *(Figure 5)*. This fact well agrees with the presence of a larger amount of S configuration in the polymer main-chain due to a starting monomer enriched in that configuration (run 3 – *Table 1*). The optical purity of polymer $(I_3)_R^S$ main-chain was evaluated to 0.20 ± 0.04.

For the polydiastereoisomer $(I_4)_{R,S}^R$, A_1 and A_2 peaks were almost identical in spite of the main-chain configurational enrichment *(Figure 5)*. The rather low side-chain configurational purity accounts for the poor sensitivity of the method in this case, in agreement with the introduction of $\tau = 0.63$ in equation (5).

Starting from the above measured diastereoisomeric compositions of stereoselected polymers, it was possible to evaluate the stereoelectivity ratio r of the polymerization process (r is representing the preferential choice of the initiator for one of heterocyclic stereoisomers). Assuming that the polymerization obeys to a first-order kinetic law, i.e. the

relative rates consumption ratio is expressed by $d[R - S]/d[S - S] = r[R - S]/[S - S]$, the stereoelectivity ratio r could be obtainable from equation (6):

$$(1 - x)^{r-1} = \frac{\alpha - \alpha_{(S-S)}}{(\alpha_{(R-S)} - \alpha)^r} \times \frac{(\alpha_{(R-S)} - \sigma_{(S-S)})^{r-1}}{2}$$

(6)

which was previously established in the case of the polymerization of a 50/50 (2R, eS)/(2S, 3R) diastereoisomeric mixtures mixtures of *sec*-butyl oxiranes[10]. Indexes $(R - S)$ and $(S - S)$ were introduced to distinguish the diastereoisomers. The first letter indicates the configuration at heterocyclic (for monomers) or at main-chain (for polymers) chiral sites while the second letter gave the configuration at side-chain ones. In equation (6), x is the polymer yield, α is the optical activity of the unreacted monomer and $\alpha_{(R-S)}$ and $\alpha_{(S-S)}$ are the optical activities of pure $(R - S)$ and $(S - S)$ diastereoisomeric monomers respectively. x and α are experimental data (see *Table 1*). $\alpha_{(R-S)}$ and $\alpha_{(S-S)}$ were calculated from the polymer composition and from α_i and α rotatory powers of the starting and unreacted monomers respectively, as shown in the following equations reflecting:

(i) the polymer composition at conversion x

$$[R - S]^p + [S - S]^p = x([R - S]_i^m + [S - S]_i^m)$$ (7)

(ii) the optical purity in the main-chain of the prepared polymer

$$O.P. = \frac{[R - S]^p - [S - S]^p}{[R - S]^p + [S - S]^p}$$ (8)

(iii) the compositions in each stereoisomeric unit of the polymer

$$\left.\begin{array}{l}[R - S]^p = [R - S]_i^m - [R - S]^m \\[6pt] [S - S]^p = [S - S]_i^m - [S - S]^m\end{array}\right\}$$ (9)

(iv) the optical activities of initial monomer and unreacted monomer at conversion x

$$\alpha_i = \frac{\alpha_{(R-S)}[R - S]_i^m + \alpha_{(S-S)}[S - S]_i^m}{[R - S]_i^m + [S - S]_i^m}$$

$$\alpha = \frac{\alpha_{(R-S)}[R - S]^m + \alpha_{(S-S)}[S - S]^m}{[R - S]^m + [S - S]^m}$$ (10)

In the above equations, the superior index p and m are used to distinguish between expressions relative to monomer and polymer.

From data corresponding to run 2 (*Table 1*), $\alpha_{(S-S)}$ and $\alpha_{(R-S)}$ were evaluated to $-6°$ and $+63.5°$ respectively. The value of stereoelectivity ratio r calculated from run 1 and run 2 is equal to 2.05. This value is very close to that found when polymerizing monomer (IV)[3] ($r = 2.0$), or other mono-substituted thiiranes, using the same chiral initiator system[6]. Therefore, the presence of one asymmetric carbon atom located in the side-chain does not substantially modify the stereoelection at the heterocyclic site. On the contrary, for *sec*-butyl-oxirane, a monomer in which the two asymmetric

centres (cyclic and extra-cyclic) are in α-position, the stereoelectivity ratio was enhanced[10].

Relative contribution of the two different asymmetric centres to chiroptical properties of polydiastereoisomers

We have already mentioned that chiroptical properties of stereoelected polydiastereoisomers (I) resembled very much those of optically active polymers (II) which have no asymmetric carbon atom in side-chains.

It is shown below that in 'stereoelected' polydiastereoisomers (I), the two types of chiral centres, e.g. main-chain and side-chain ones perturb the amine and the sulphur chromophores almost independently.

In a previous work[3] the molar ellipticity of 242 nm c.d. band was found to be equal to 1700 ± 100 deg.cm. dmol^{-1} for pure poly (R) (II). The optical purity of polydiastereoisomer $(I_2)_R^S$ and $(I_3)_R^S$ main-chains has been estimated to 0.30 ± 0.04 and 0.20 ± 0.04 respectively, from ^{13}C n.m.r. spectra. The molar ellipticity $[\theta]_{242}$ was equal 470 ± 40 deg.cm. dmol^{-1} for $(I_2)_R^S$ and 310 ± 40 deg.cm. dmol^{-1} for $(I_3)_R^S$.

For all the optically active polythiiranes and polyoxiranes studied so far, the optical activity was directly proportional to the main-chain optical purity. Assuming this is also true for the 242 nm c.d. band of polydiastereoisomers (I), the molar ellipticity $[\theta]_{242}$ for pure poly R (I) was evaluated from the c.d. spectrum and using the determined optical purities of polymers $(I_2)_R^S$ and $(I_3)_R^S$. Coherent values $([\theta]_{242} = 1570 \pm 140$ and $[\theta]_{242} = 1550 \pm 200)$ were obtained from the two sets of data.

It is noteworthy that these values are almost similar to that found for pure poly R (II) the side-chains of which are achiral. It is inferred that the 242 nm c.d. bands of polydiastereoisomers (I) reflects almost solely the optical purity of main-chain chiral centres.

In the case of polydiastereoisomer $(I_4)_R^R$, we were unable to determine the optical purity of the main-chain from ^{13}C n.m.r. spectra for reasons given in the previous chapter. Nevertheless, one can propose 0.22 as value of optical purity on the basis of the magnitude of the 242 nm c.d. band $([\theta]_{242} = 340 \pm 40$ deg. cm. dmol$^{-1})$. This value is close to that found for $(I_3)_R^S$, which can be substantiated by the fact that these both polymers were prepared by stereoeletive polymerization stopped at the same conversion, e.g. 26%.

While 242 nm c.d. bands of polydiastereoisomers $(I_3)_R^S$ and $(I_4)_R^R$ are very similar in magnitude, 215 nm c.d. bands differ substantially (*Figures 6* and *7*). It is suggested that the difference comes from the contribution of the side-chain chiral centres, which are almost optically pure S for the former and only enriched in R for the latter. In order, to demonstrate this point, a simulation of c.d. curves of polyme $(I_3)_R^S$ and $(I_4)_R^R$ was made by adding the contribution due to main-chain chiral centres (calculated from poly(II) with O. P. $\simeq$ 0.20 and 0.22 respectively) and the contribution due to side-chains (as in poly(I) with a 'racemic' main-chain and side-chain of corresponding optical purities). Simulated curves are represented in *Figures 6* and *7* together with experimental ones. The curves are in good agreement in the 240 nm region while the fitting is far brom being perfect in the 210–215 nm region. However, discrepancies are not larger than that one would expect from high experimental uncertainties due to the absorbance of the solvent (dioxane) whose cut-off is located at 210 nm at the selected pathway. On the other hand, we were dealing with model compounds only. From this simulation, only the trend to additivity of
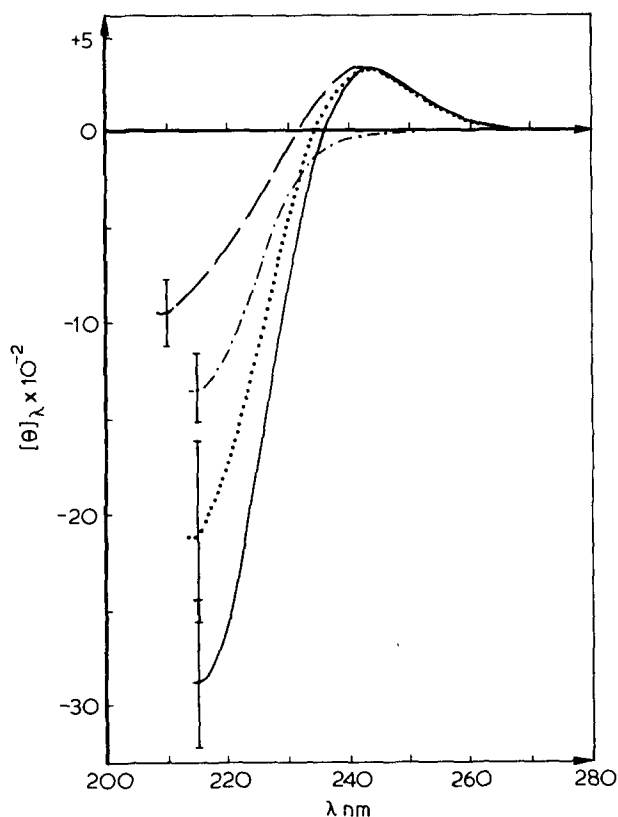
Figure 6 Comparison of the experimental c.d. spectrum of poly-diastereoisomer $(I_3)_R^S$ (———) in dioxane with a simulated one (. . . . . .) obtained by adding the c.d. spectrum of polydiastereoisomer $(I)_{R,S}^S$ (— · — · — · —) to that of a polymer (II) (— — — —) partially enriched in R configuration (O.P. ≃ 20%)

Figure 7 Comparison of the experimental c.d. spectrum of poly-diastereoisomer $(I_4)_R^R$ (———) in dioxane with a simulated one (. . . . .) obtained by adding the c.d. spectrum of polydias-tereoisomer $(I)_{R,S}^R$ (— · — · — · —) to that of a polymer (II) (— — —) partially enriched in R configuration (O.P. ≃ 22%)

main-chain and side-chain chiroptical contributions must be retained.

It seems at present difficult to perform reasonable theoretical calculations of o.r.d. and c.d. spectra on such non-rigid macromolecules using available structural parameters in order to bear out these findings.

In conclusion, one can ascertain that chiroptical properties of polydiastereoisomers are primarily depending on the configurational distribution of main and side-chain chiral centres without any obvious contribution assignable to macromolecular conformations.

The presence in monomer molecules of second asymmetric centre located well-inside the pendant groups does not affect the magnitude and the choice of stereoelective process.

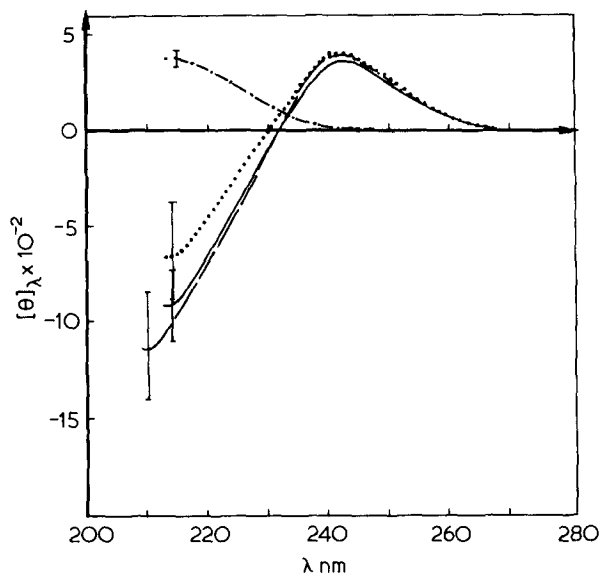However, by their specific effects on ^{13}C n.m.r. spectra, side-chain asymmetric centres, allowed us to show, at last,

that the 242 nm c.d. band observed in dioxane can be used to evaluate the optical purity of main-chain chiral centres in this type of polydiastereoisomers. The introduction of asymmetric carbon atoms in side-chains of functional optically active polymers with true chiral centres in the main-chain could be an useful method to determine configurational structures by n.m.r.

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