

Optically active poly[thio-1-(*N,N*-diethylaminomethyl) ethylene]

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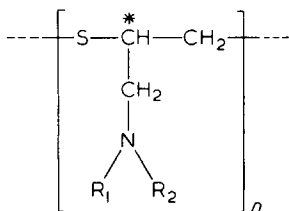
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Poly[thio-1-(*N,N*-diethylaminomethyl) ethylene] [poly(TDAE)] of different optical purities were prepared by stereoselective polymerization of racemic *N,N*-diethyl-*N*-(thiirane-2-ylmethyl) amine (TDAE) using a (1:1) $\text{ZnEt}_2/\text{R}(-)$ 3,3-dimethyl 1,2-butanediol (*R*(-)-DMBD) chiral initiator system. Optically enriched TDAE samples were isolated as residual monomers. These monomers were thermally polymerized to give optically active poly(TDAE) with randomly distributed *R* and *S* repeat units in various proportions. The configuration of the enantiomer preferentially incorporated into growing chains during the stereoselective polymerization was determined as *R* on the basis of the presence of a positive Cotton effect at 260 nm in the c.d. spectrum of residual monomers. This configuration agrees well with the known homosteric character of the $\text{ZnEt}_2/(-)$ DMBD initiator system. ^{13}C n.m.r. spectra of the different optically active poly(TDAE) samples and those of more or less stereoregular racemic ones were compared. It was found that the carbon atom of the main chain methine group is the only one which is stereosensitive. Observed triad effects were used to determine the degree of isotacticity of optically active poly(TDAE)s prepared by thermal polymerization of partly enriched monomers. The stereoselectivity of the initiator system and the optical activity of optically pure TDAE and poly(TDAE) were deduced. Side-chain nitrogen atoms did not show any competitive effect with sulphur atoms in the coordination process to the chiral initiator system.

INTRODUCTION

Over the last few years, chiroptical properties of optically active macromolecules undergoing a chemical reaction have been considered in detail in order to distinguish respective effects of chemical and conformational modifications on o.r.d. and c.d. spectra of polymers¹.

As a first step of the study of optically active weak polybases, which can be reversibly protonated by strong acids, poly[thio-1(*N*- R_1 -*N*- R_2 -aminomethyl) ethylenes] have been prepared by ring-opening polymerization of disubstituted aminomethylthiiranes². These polymers have a polythioether backbone and *N,N*-disubstituted amino groups in side chains according to the formula:



Such a macromolecule can be rendered optically active either by enriching main-chain chiral centres in one of the

two possible configurations or by introducing chiral centres in side-chains through one of the nitrogen substituents. The latter leads to polydiastereoisomers.

Chiroptical properties of optically active poly[thio-1-(*N,N*-diethylaminomethyl) ethylene] ($\text{R}_1 = \text{R}_2 = \text{ethyl}$) [poly(TDAE)] having achiral side chains, and main chain asymmetric carbon atoms partly enriched in one of the antipodes, have already been described³. However, neither the preferred configuration nor the stereoregularity of main chains have been determined.

In this paper, we wish to report the synthesis of a series of different optically active poly(TDAE) samples by stereoselective polymerization of the racemic monomer or by thermal polymerization of enantiomerically enriched monomers. Chiroptical characteristics of such monomers and ^{13}C n.m.r. spectra of polymers are used in order to determine the tacticity and the optical purity of polymer chains. An evaluation of the optical activity of optically pure monomer and polymer is proposed.

EXPERIMENTAL

The racemic monomer *N,N*-diethyl-*N*-(thiirane-2-ylmethyl) amine was prepared from epichlorhydrin and diethylamine

Table 1 Stereoselective polymerization of racemic *N,N*-diethyl-*N*-(thiirane-2-ylmethyl)amine

Run	Solvent	<i>C/M</i>	<i>t</i> (h)	Yield (%)	$[\alpha]_D^{25}$ polymer ^a			α_D^{25} Residual monomer ^b	$[\eta]^{25}$ 100 cm ³ g ⁻¹	\bar{M}_n ^d
					Benzene	Dioxane	H ₂ O(HCl)			
I	bulk	6.2	3	29	-15.8	- 9.7	+35.0	-2.3	1.8	340 000
II	bulk	6.2	6	44	-19.4	-12.4	+40.0	-4.8	2.5 ^e	600 000
III	bulk	6.3	14	54	-14.0	- 8.7	+29.0	-8.2	1.15	-
IV	toluene	8.1	61.5	69	-11.9	- 7.5	+25.0	-	0.9	-
V	toluene	4.3	240	28	-25.0	-16.0	+50.5	-	1.32	-

^a hydrochloride form in water, amine form in benzene and dioxane (*C* ≈ 1.0%)

^b neat, dm

^c measured at 25°C in benzene (amine form)

^d in toluene at 25°C

^e $\eta_{sp}/c = 2.5 \times 100 \text{ cm}^3 \text{ g}^{-1}$ (*C* = 0.5%) for the hydrochloride form in water without salt

Table 2 Thermic polymerization of partially enriched (–) *N,N*-diethyl-*N*-(thiirane-2-ylmethyl) amines (in bulk at –30°C)

Poly(TDAE)	α_D^{25} Monomer ^a	$[\alpha]_D^{25}$ Polymer ^b	η_{sp}/c 100 cm ³ g ⁻¹ ^c
VI	-2.3	+ 5.4	3.3
VII	-4.8	+10.4	9.7
VIII	-8.2	+16.5	1.5

^a neat, dm (*d* = 0.94)

^b polyamine form in benzene (*C* ≈ 1.0%)

^c hydrochloride form in water (*C* ≈ 0.5%)

according to a procedure described previously⁴.

C.d. spectra were recorded on a Jasco J40B spectrophotometer and ¹³C n.m.r. spectra were obtained by using Jeol PFT100 and WH 90 Bruker spectrometers, the latter being operated by the Research Commun Center of the University of Rouen. Samples of polymers (200 mg) in solvent (3 ml) were studied.

RESULTS AND DISCUSSION

Synthesis of optically active poly(TDAE)

Stereoselective polymerization of racemic monomer

Optically active polymers may be prepared by stereoselective polymerization of racemic monomers using chiral initiators. In this type of polymerization, one of the two enantiomers is preferentially incorporated in growing chains, while the residual monomer becomes optically active by enrichment in the opposite antipode.

The stereoselective polymerization of thiiranes has been widely studied in recent years and several reviews have been published^{5,6}. So far, the initiator obtained by reacting equimolar amounts of diethylzinc and R(–)-3,3-dimethyl-1,2-butanediol (R(–)DMBD) has been found to be one of the most efficient. Depending on the monomer, this initiator system allows more or less stereoregular optically active products to be prepared⁶. This initiator was used to polymerize the racemic *N,N*-diethyl-*N*-(thiirane-2-ylmethyl) amine (TDAE) in bulk and in toluene solution at room temperature. Experimental data are listed in *Table 1*.

Optically active poly(TDAE) samples of high molecular weight were obtained. Their specific optical rotatory power $[\alpha]_D^{25}$ decreased as the yield increased with the exception of run I. This exception probably resulted from a lower stereoselective efficiency of the initiator. In contrast, the optical activity of the residual monomer increased with conversion.

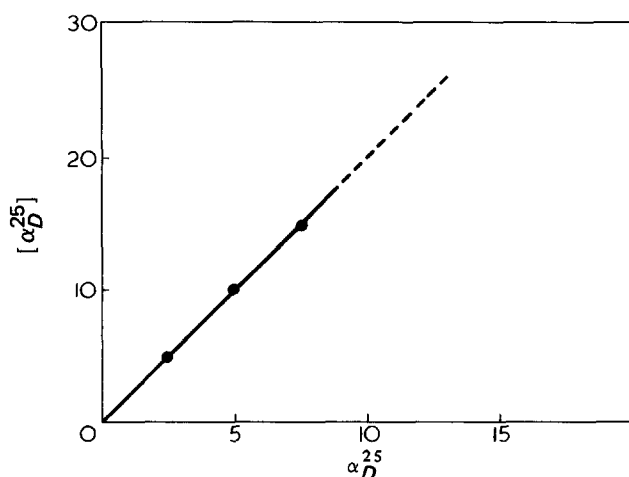


Figure 1 Variations of specific rotatory power $[\alpha]_D^{25}$ of thermally polymerized poly[thio-1-(*N,N*-diethylaminomethyl) ethylenes] [poly(TDAE)] as a function of specific rotatory power α_D^{25} of starting monomers

These findings are in good agreement with previous results obtained for monosubstituted oxiranes and thiiranes⁵.

Polymerization rates were much larger in bulk than in solution. They are comparable to those found for other thiiranes except methylthiirane⁷ and methoxymethylthiirane⁸, which polymerize faster.

Thermal polymerization of enantiomerically enriched monomers. In order to prepare optically active poly (TDAE) samples having a statistical distribution of R and S repeat units, partly enriched (–) TDAEs, isolated as residual monomers from previous stereoselective polymerizations (runs I, II and III in *Table 1*), were polymerized using thermal initiation at –30°C in darkness for several weeks (*Table 2*) in sealed ampoules under vacuum.

While the stereoselective polymerization gave *laevo*-rotatory polymers from the preferentially elected *dextro*-rotatory monomers (*Table 1*), thermal polymerization of *laevo*-rotatory residual monomers yielded *dextro*-rotatory poly(TDAE)s VI, VII and VIII, (*Table 2*). The optical activity of these thermally polymerized poly(TDAE) samples increased linearly as a function of the optical activity of monomers, as shown in *Figure 1*. C.d. spectra of polymers VII and VIII in dioxane are represented in *Figure 2*. Except for the magnitudes of c.d. bands, these spectra are similar to those already reported for polymers prepared under different experimental conditions³. The 242 n.m. c.d. band has been

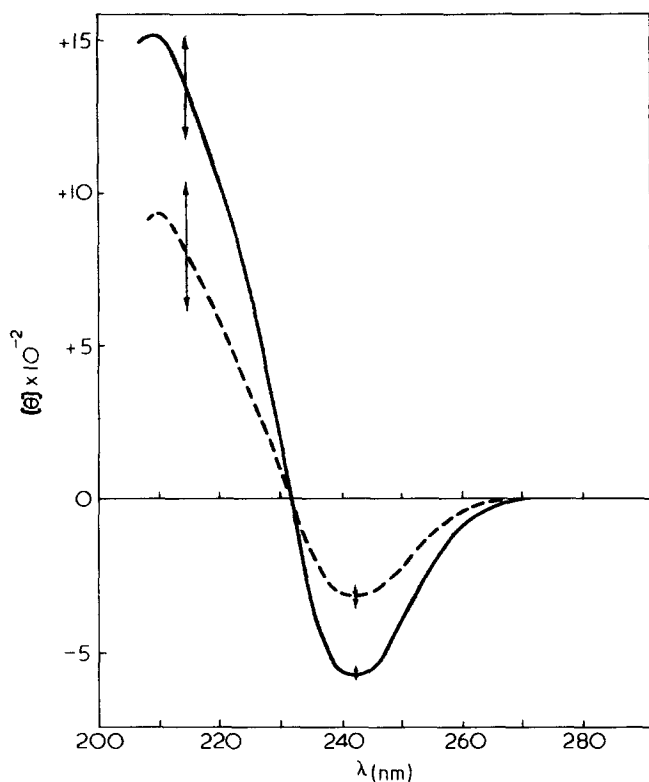


Figure 2 C.d. spectra of thermally polymerized poly(TDAE)s VII and VIII in dioxane (VII ---, VIII —)

assigned to the $n \rightarrow \sigma$ electronic transition of the sulphur chromophore in thioether groups. The 210 nm c.d. band was shown as resulting from the overlapping of the $n \rightarrow \sigma$ Cotton effect due to the nitrogen chromophore in amino groups and of the Cotton effect corresponding to the second electronic transition of the sulphur chromophore usually observed below 200–210 nm in polythiiranes.

Configuration of the elected enantiomer during the stereoselective polymerization

For thiiranes, the configuration of the elected enantiomer can be easily determined from the chiroptical properties of the residual monomer. Indeed, for all thiiranes studied so far, the presence of a positive Cotton effect at about 260 nm in the c.d. spectrum has been correlated to an S absolute configuration of the asymmetric carbon atom of the heterocycle^{9–11} except for *t*-butylthiirane. In this case, a special contribution due to the modification of the charge distribution by one of the methyl groups accounts for the negative Cotton effect associated to the S configuration¹². The c.d. of *laevo*-rotatory TDAEs (Table 1, run II) was investigated in methanol. In this solvent, three c.d. bands were found, a positive one at 265 nm, a negative one at 220 nm and the beginning of a positive one, the maximum of which is located below 210 nm (Figure 3). It is likely that the two low wavelength bands come from the overlapping of the second thiirane Cotton effect (found at 204 nm in methylthiirane – Figure 2) and the $n \rightarrow \sigma$ transition of the amine chromophore known to be located at 206 nm in (+)-*N*-methyl-2-aminobutane³. The 265 nm c.d. band, very similar to that of methylthiirane, can be assigned to the $n \rightarrow \sigma$ electronic transition the thiirane chromophore¹².

The amine $n \rightarrow \sigma$ electronic transition is known to be

blue-shifted in strong acids because of a protonation which involves the non-bonding electrons of nitrogen atoms^{13,3}. In the case of TDAEs, the protonation of the amino group can explain the modification of the c.d. spectrum in the 200–230 nm region which leaves a positive band at 202 nm similar to that observed for methylthiirane. In contrast, the weakness and the splitting of the 265 nm band are still not well understood.

Nevertheless, the positive sign of the thiirane $n \rightarrow \sigma$ Cotton effect found in methanol is in favour of an S configuration for the asymmetric carbon atom of the *laevo*-rotatory monomer. Therefore, an R type configuration can be assigned to the antipode which is preferentially polymerized in the presence of ZnEt₂/R(-)-DMBD initiator.

For all the thiiranes and the oxiranes studied so far, the R enantiomer was always preferentially elected when using the ZnEt₂/R(-)-DMBD initiator system. This kind of election was named 'homosteric'^{5,14}. Therefore, the R configuration attributed to the elected monomer is in good agreement with the homosteric character of the initiator system used to polymerize the racemic monomer in runs I to V (Table 1).

Evaluation of tacticity and optical purity of poly(TDAE)s from ¹³C n.m.r. spectra

A typical ¹³C n.m.r. spectrum of a poly(TDAE) prepared by stereoselective polymerization (sample II) is shown in Figure 4. Chemical shifts are given in ppm as compared with the internal standard TMS. Assignments of the different

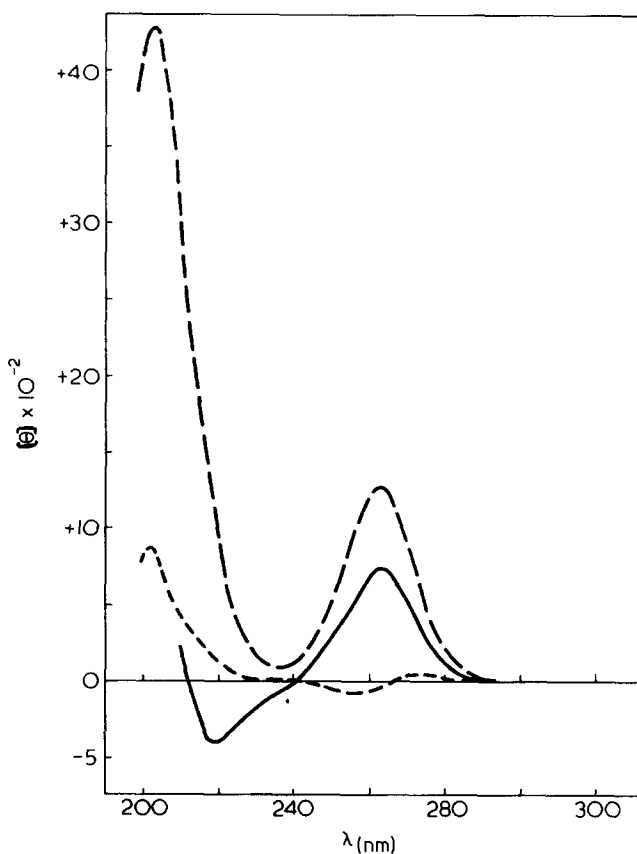


Figure 3 C.d. spectra of optically enriched *N,N*-diethyl-*N*-(thiirane 2-ylmethyl) amine (TDAE) (obtained as residual monomer from the stereoselective polymerization of a racemic mixture; run II; Table 1) in methanol (amine form) —, (hydrochloride form) --- and of S(-) methylthiirane (O. P. ~52%) in methanol - - - -

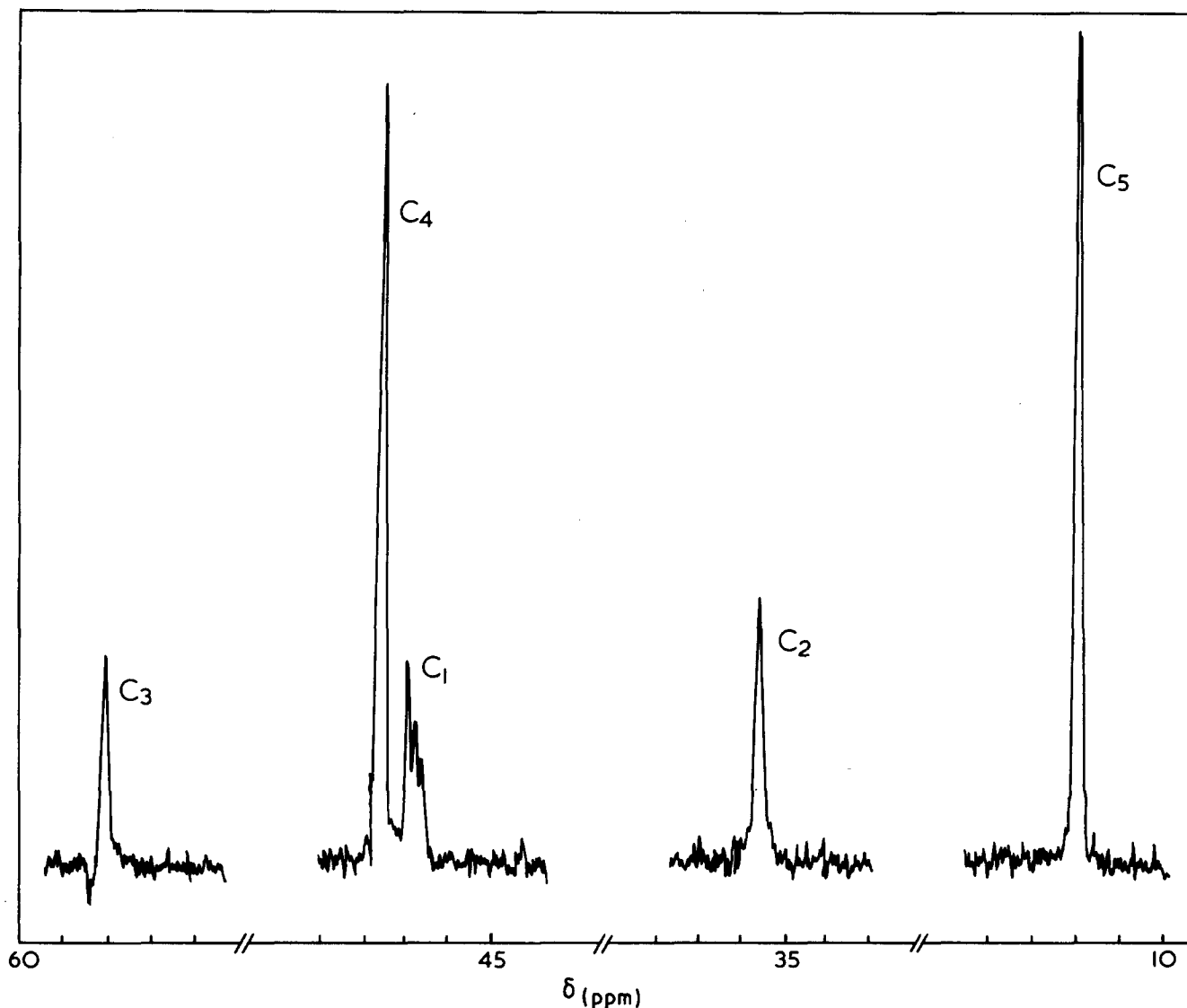
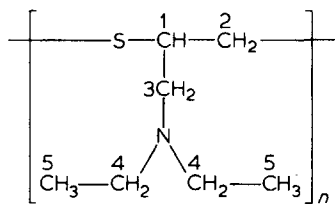


Figure 4 ^{13}C n.m.r. spectrum (22.63 MHz) in CDCl_3 at 25°C of optically active poly(TDAE) prepared by stereoselective polymerization (run II, Table 1) (10 000 scans; Sweep width 1620 Hz; reference signal TMS). The assignment was made from undecoupled spectra

peaks to carbon atoms, as referred to numbers on the scheme below, were made from undecoupled spectra.



In order to determine tacticities and optical purities of the different optically active polymers, their ^{13}C n.m.r. spectra were compared to those of two different racemic poly(TDAE)s, a stereoregular sample obtained by polymerization with the stereospecific system $\text{ZnEt}_2/\text{H}_2\text{O}$ and an atactic sample prepared by anionic polymerization using a sodium metal film as initiator.

Chemical shifts in CDCl_3 and $\text{CCl}_4/\text{C}_6\text{D}_6$ at 25°C were

found not to be dependent on the initiator system. The carbon atom C_2 , corresponding to the main-chain methylene group, showed a single peak at 35.5 ppm while the methine carbon C_1 was stereosensitive showing a pattern with three peaks located at 46.9, 46.7, and 46.6 ppm. Other carbon atoms C_3 , C_4 and C_5 corresponding to side chains, were not found to be stereosensitive. They were located at 58, 47.5 and 11.9 ppm respectively.

In Figure 5 is shown the shape of the C_1 patterns found for typical polymers. Comparing optically active polymers (VI–VIII), the peak at 46.9 ppm was enhanced as the optical activity increased. On the other hand, this peak was found to be much larger for the polymer prepared using the stereospecific initiator $\text{ZnEt}_2/\text{H}_2\text{O}$ than for the other polymers. Consequently it has been assigned to isotactic triads i . The two other peaks of C_1 patterns have been attributed to heterotactic triads h_i and h_s and to syndiotactic triads s respectively. This assignment is in agreement with previous results found for other polythiiranes^{15,16}.

The proportion of isotactic triads for polymers prepared with different initiator systems as deduced from experimental curves deconvoluted in three peaks are given in Table 3.

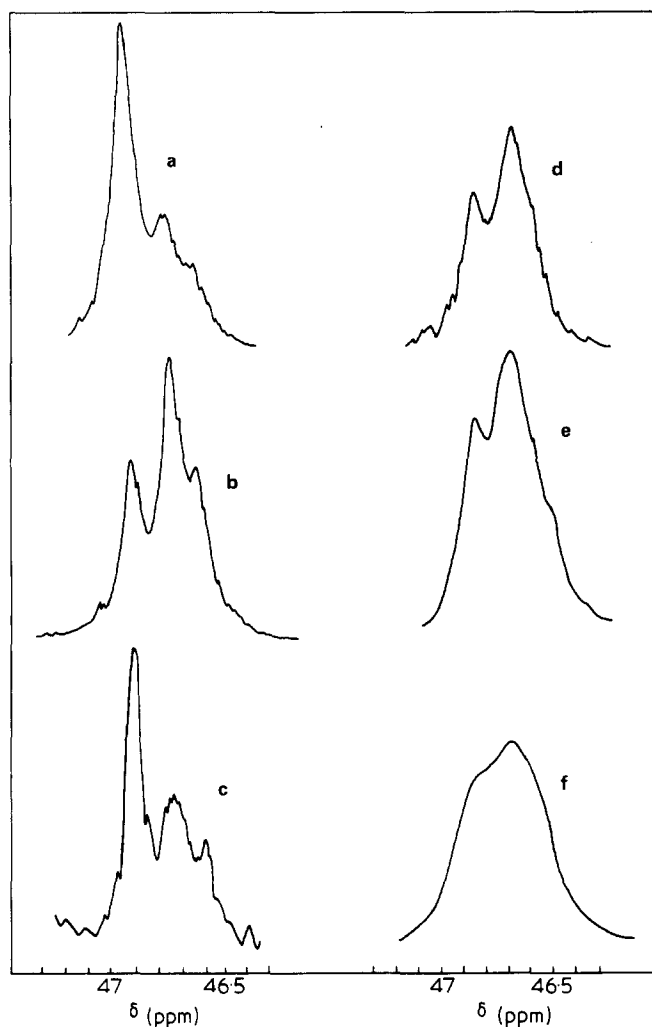


Figure 5 Shape of C_1 patterns found for racemic and optically active poly(TDAE)s derived from TDAEs polymerized with different initiator systems. (a) racemic TDAE ($ZnEt_2/H_2O$) (9400 scans); (b) racemic TDAE (Na) (90 000 scans); (c) racemic TDAE (1:1 $ZnEt_2/(-)$ DMBD) (Run I, Table 2, 10 000 scans); (d), (e), (f) partly enriched TDAE ($T = -30^\circ C$) run VI, VII and VIII, respectively (Table 2) (22 000, 7000 and 80 000 scans)

Table 3 Proportion of isotactic triads for polymers prepared with different initiator systems

No	Initiator	α_D^{25} Initial ^a monomer	$[\alpha_p]_D^{25}$ ^b	i
—	Na	0	0	0.25
—	$ZnEt_2/H_2O$	0	0	0.65
II	$ZnEt_2/(-)$ DMBD	0	-19.4	0.51
VI	T(-30°C) ^c	-2.3	+5.4	0.25 _s
VII	T(-30°C) ^c	-4.8	+10.4	0.28
VIII	T(-30°C) ^c	-8.2	+16.5	0.33

a neat, dm

b amine form in benzene ($c \sim 1,0\%$)

c $T =$ thermic initiation

In order to minimize the inaccuracy of this determination due to the overlapping of peaks, i values were averaged from three recordings of the same spectrum.

The racemic polymer prepared using sodium initiator showed 25% isotactic triads in complete agreement with a Bernouillian statistical distribution for R and S configurations

of C_1 carbon atoms. The racemic polymer prepared with $ZnEt_2/H_2O$ showed a rather high stereoregularity (65% of isotactic triads). This tacticity is similar to that found for methylthiirane using the same initiator^{17,18}.

From the proportion of isotactic triads calculated as described above, it has been possible to evaluate the optical purity of poly(TDAE)s VI, VII and VIII assuming a Bernouillian distribution of R and S repeat units. This assumption was appropriated since no stereospecific effect has to be expected in this kind of initiation process. The same method was previously used in the case of methylthiirane¹⁸, isopropyl thiirane¹⁹ and methoxymethylthiirane⁸.

According to Bernouillian statistics, the distribution of different triads as a function of the molar fraction of R repeat units $\beta = R/R + S$ is given by equations (1):

$$i = RRR + SSS = \beta^3 + (1 - \beta)^3$$

$$h_i = RSS + SRR = \beta(1 - \beta^2) + \beta^2(1 - \beta)$$

$$h_s = RRS + SSR = \beta^2(1 - \beta) + \beta(1 - \beta)^2$$

$$s = RSR + SRS = \beta^2(1 - \beta) + \beta(1 - \beta)^2 \quad (1)$$

which can be simplified to:

$$i = 1 - 3\beta(1 - \beta) \quad (2)$$

$$h_i = h_s = s = \beta(1 - \beta) \quad (3)$$

The molar fraction of R repeat units β was determined from the proportion of isotactic triads i evaluated for polymers VI, VII and VIII obtained by thermal polymerization. The optical purity $S - R/R + S$ of their main-chain chiral centres and thus that of corresponding residual monomer were calculated. On the basis of experimental optical rotatory powers of partly enriched monomers and polymers, and of corresponding values of the optical purity deduced from ^{13}C n.m.r. spectra, optical rotatory powers α_0 and $[\alpha_p]_0$ of optically pure TDAE and poly(TDAE) were evaluated (Table 4). Averaging α_0 and $[\alpha_p]_0$ values calculated from data of polymers VI, VII and VIII, $\alpha_0^{25} = -25^\circ \pm 2.5$ and $[\alpha_p]_0^{25} = +51^\circ \pm 5$ are respectively proposed for optically pure S(-)-TDAE (neat) and (+)-poly(TDAE) (in benzene). Similarly, an evaluation of the c.d. spectrum of optically pure (+)-poly(TDAE) having S chiral centres in the main-chain was calculated. This spectrum is shown in

Table 4 Chiroptical characteristics of S (-)-TDAE and (+)-poly(TDAE) as deduced from thermally polymerized partly enriched (-) TDAEs (runs VI to VIII in Table 2)

Runs	α_D^{25} (neat, dm) Monomer	i^a	β^b	Optical purity ^c	α_D^{25} (neat, dm) Monomer	$[\alpha_p]_D^{25}$ Polymer ^d
VI	-2.3	0.25 _s	0.55	0.1	23	54
VII	-4.8	0.28	0.60	0.20	24	50.2
VIII	-8.2	0.33	0.66	0.32	25.6	51.5

a molar fraction of isotactic triads in corresponding polymers, averaged value from different spectra

b molar fraction of S enantiomer in monomer determined by using relations (2) and (3)

c $S - R/R + S$

d in benzene solution ($C_p \sim 1\%$)

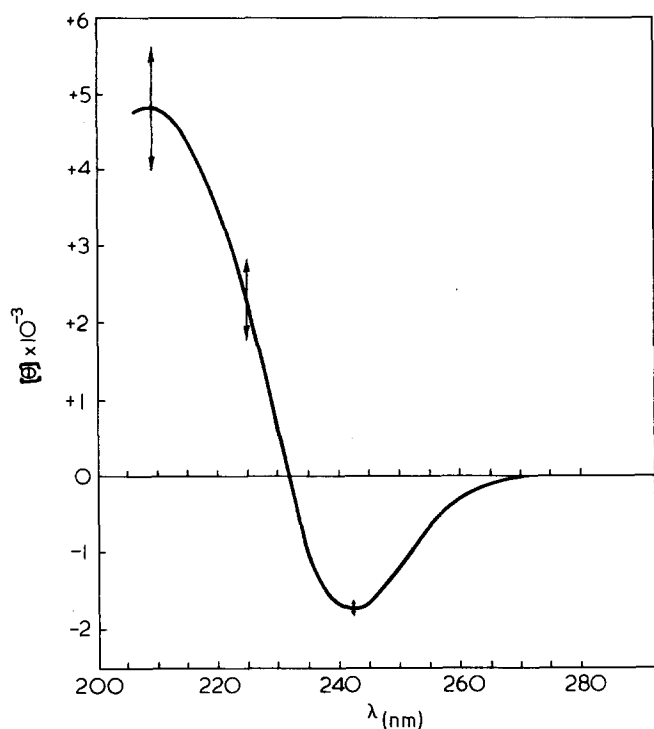


Figure 6 C.d. spectrum in dioxane of optically pure (+)-poly(TDAE) (Evaluated from ^{13}C n.m.r. and c.d. of optically enriched poly(TDAE)s VI, VII and VIII)

Figure 6. A better accuracy would have been obtained from partly enriched thermal polymers having higher optical purities than samples VI, VII and VIII but monomer with high optical purity is still not available. It should be obtainable through a stereoelective polymerization of an already optically enriched monomer as shown for other thiiranes⁵.

The stereoregularity is one of the factors known to favour the existence of ordered secondary structures for polymers in solution¹. An effect of the stereoregularity on the optical activity of optically active polymers has been shown in some cases²⁰. It is worth noting that it is now well established from numerous examples that the stereoregularity of optically active polythiiranes and polyoxiranes as well, has no effect on optical activity which depends on the optical purity of monomeric units only. Therefore, the optical activity of a partly enriched poly(TDAE) must be directly related to the optical purity of its chiral centres whatever the stereoregularity.

If poly(TDAE) II, prepared by stereoelective polymerization (Table 1), resulted from a random distribution of R and S repeating units, the molar fraction of isotactic triads i would have been 0.38 according to a value of β evaluated from the optical rotatory power of optically pure (+)-poly(TDAE). Actually, the value $i = 0.51$ (Table 3) confirms the partly stereoelective character of the $\text{ZnEt}_2/\text{R}(-)$ -DMBD initiator system^{7,18}.

Using the proposed optical rotatory power of S(-)-TDAE, ($\alpha_{\text{D}}^{25} = -25^\circ$ neat), it was also possible to determine a value for the degree of stereoelectivity r from experimental data

reported in Table 1. It was assumed that racemic TDAE, like racemic methylthiirane and other thiiranes, fits the first order kinetic law^{5,6}:

$$(1-x)^{r-1} = \frac{1-\alpha/\alpha_0}{(1+\alpha/\alpha_0)^r} \quad (4)$$

where x is the conversion and α/α_0 is the purity of the residual monomer. A value $r \sim 2.0$ was obtained. This value is close to $r \sim 2.4$ found for methylthiirane using the same initiator system¹⁴. Accordingly, it is concluded that nitrogen atoms present in side chains have practically no effect on the stereoelective process. In contrast, side chain oxygen atoms of methoxymethylthiirane were found to compete with heterocyclic sulphur atoms in the coordination process to metal atoms of initiating species⁸.

The absence of any effect due to side chain nitrogen atoms on the stereoelective polymerization of TDAE is in agreement with previous results showing that the stereoelective polymerization of methylthiirane was not perturbed by the addition of large amounts of a tertiary amine⁴.

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