STEREOELECTION AND STEREOSELECTION IN THE RING-OPENING POLYMERIZATION OF EPOXIDES AND EPISULFIDES

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Abstract—Polymerizations of racemic mixtures of epoxides or episulfides may lead to stereoregular polymers through a stereoselective process, and to optically active polymers through a stereoelective process that gives either atactic or isotactic polymers. Monomers that have been most studied are propylene oxide, propylene sulfide and *t*-butyl thiirane, and their polymerization with insoluble initiators such as alcoholates of Zn is discussed, and also the polymerization of thiiranes in homogeneous phase using cadmium thiolates.

Polymers obtained in some conditions may be fully isotactic, and in the case of *t*-butylthiirane, optically active polymers could be fractionated, giving a racemic and a pure enantiomeric fraction.

Stereoelection laws differ according to monomers, being either first or second order in enantiomers concentration, and showing or not a temperature effect and a "memory effect" of the initial enantiomeric composition of the monomer mixture. An interpretation is proposed for these various behaviours, that may lead to high optical yields for some systems (with stereoelectivity ratios up to 8).

Stereoselective and stereoelective polymerizations (the latter also called asymmetric selective) are polymerizations involving a steric control for the incorporation of monomer units into the polymer chains when the monomer is a mixture of at least two enantiomers. The individual active sites, or the whole catalytic system, may choose preferentially one enantiomer, giving polymer chains with a different composition from the starting mixture of R and S monomers. Most of the work done in this field has been made using racemic mixtures of R and S that are obtained more easily, but one may also start from a relatively pure enantiomer or from optically active mixtures of various compositions.

Three families of monomers have been studied and the results have been described in recent review:[1,2] asymmetric α olefins, N carboxyanhydrides, substituted oxiranes and thiiranes (see Fig. 1). In the case of olefins, the chiral group is a substituent to the double bond and becomes after polymerization a pendant group to the polymer chain, but in the other cases, the chiral carbon is included into the heterocycle and later into the main polymer chain. If no

Fig. 1. Polymerization of chiral monomers.

steric control occurs during the growth, an atactic statistical copolymer of R and S enantiomers is obtained.

In a stereoselective polymerization, polymer molecules are obtained from a mixture of enantiomeric monomer molecules with incorporation of only one type of enantiomer into one growing *polymer chain*. In the case of cyclic monomers having a chiral group (no inversion) this selection of enantiomers R and S on two types of sites gives birth to a stereoregular polymer formed of poly R and poly S chains:
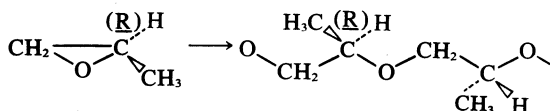

Starting from a monomeric racemic mixture for example, a racemic polymer mixture $(R_n + S_n)$ is obtained.

The definition given is relative to a perfect process, but in most systems there is only partial stereoselection—and partial stereoregularity—either because some growing chains may incorporate to a lesser extent the other enantiomer, or because there are more than two types of sites, more or less stereospecific.

The situation is more complex in the case of the α-olefins mentioned above, since the selection of the chiral monomers might occur without having a stereospecific polymerization, but it seems that initiators used with olefins and leading to stereoselection are generally also stereospecific.

It is also interesting to note that a regular opening of a *pure cyclic enantiomer* on the same bond (without isomerization) gives an optically active isotatic polymer, and that does not necessitate a stereospecific catalyst that is necessary in order to have stereoselection, starting from a racemic mixture.

It has also been possible to obtain optically active polymers starting from a racemic mixture and using chiral initiators. This has been shown in the case of epoxides,[3,1] N carboxyanhydrides,[4] α olefins[5] and episulfides.[6–8] This type of polymerization has been called asymmetric selective or stereoelective. In the ideal case, this corresponds to the formation of polymer molecules from
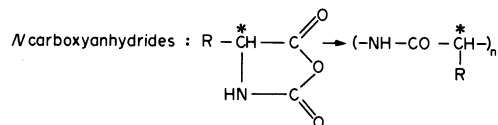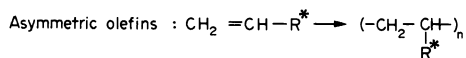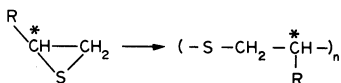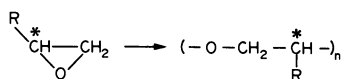
a mixture of two enantiomers with incorporation of only one type of enantiomer (R or S) into the *polymer sample.* This is the consequence of the presence of only one type of site, giving for example poly R chains, and the other enantiomer not being polymerized. This perfect process should give also stereoregular polymers (if the conditions are already described are respected) but in all systems known until now, there is only partial stereoelection, either because some chains may include the other enantiomer to a lesser extent, or because there is more than one type of site. In all cases, the residual monomer is enriched into the non elected enantiomer, and the situation is similar to a copolymerization.

The optical yield and the percentage of stereoelection may be defined:

Optical yield: $\dfrac{[R] - [S]}{[R] + [S]} \times 100$

% stereoelection: $\dfrac{[R]}{[R] + [S]} \times 100.$

These values may be calculated from the polymer composition in R and S units or from the residual monomer composition, but as polymer optical activity is not always proportional to the excess of R over S units, it is better to refer to residual monomer, for which the optical yield may be easily measured:

Optical yield: $\dfrac{\alpha_{(sample)}}{\alpha^{0}_{(pure\ enantiomer)}} \times 100.$

It is possible to define reactivity ratios similar to those for a copolymerization between two different monomers (here R and S). We shall see that for several stereoelective systems studied, the reactivity of monomers is corresponding to an ideal copolymerization. In this case, $r_1 = (1/r_2)$ and the relative rate of incorporation of the two monomers is independent of the nature of the last added unit, which means that it is possible to use only one reactivity ratio r

$$r = \frac{k_{RR}}{k_{RS}} = \frac{k_{SR}}{k_{SS}}$$

giving the relative preference of the system for one enantiomer.

The r values obtained until now for asymmetric α olefins and N carboxyanhydrides are relatively low (1.2–1.7) but they may be higher for epoxides and specially for episulfides (2.4 and higher), and I shall discuss in this paper polymerizations of those two monomer families, giving polymers that are either stereoregular or optically active, or both together. Before discussing the mechanisms, we shall examine some experimental results concerning stereospecific polymerizations of oxiranes and thiiranes (epoxides and episulfides.)

### EXPERIMENTAL RESULTS FOR STEREOSPECIFIC POLYMERIZATIONS OF OXIRANES AND THIIRANES

Two main families of initiators may realize the stereospecific polymerization of *Propylene oxide* (PO). The complex $FeCl_3$–PO has been used first by Pruitt and Baggett[9] and then by many others with some modifications, and has given a polymer of which a fraction insoluble in actone is very crystalline. However, an important racemization of the monomer units occurs (as shown by using optically active monomer with the same initiator). There are also probably several different mechanisms occuring, and we shall not discuss this system further.

The other family of initiators first described by Furukawa *et al.*[10] is obtained by reaction between a dialkylzinc and water or alcohols, and they are mainly formed by zinc oxide or zinc alcoholates. The polypropylene oxides obtained may be fractionated into a crystalline fraction (about 20% of polymer obtained at room temperature) and an amorphous fraction, both of high molecular weights. The alcoholate systems generally do not lead to much monomer isomerization, as the results obtained with optically active monomers show.

Polymerization of *propylene sulfide* (PS: methyl thiirane) using the same initiator family has been studied by our group. The polymers have a higher bulk crystallinity than polypropylene oxide, but could not be fractionated.[11,12] For the system diethylzinc-water, the percentage of isotactic diads is at least 80%. However, studies with the optically active monomer[13] have shown some racemization. But the iso diads content may be much higher when some cadmium derivatives are used (that do not polymerize PO) and with cadmium tartrate for example, is at least 95%.[14] Well oriented fibers could be prepared and the X-ray study gave the unit cell, space group and factor structure, and confirmed the isotactic structure.[15] An important result is that an identical structure (and the same melting point) have been found for an optically active isotactic polymer obtained starting from a monomer sample very rich in one enantiomer. In the case of polypropylene oxide, the crystalline structure of the racemic polymer only has been determined,[16] but is very likely identical for the optically active polymer since the melting points are close.

The isotactic structure has been confirmed by NMR studies for racemic polyoxides and polysulfides, and also for optically active polypropylene sulfide. Until recently, monomers selectively deuterated on the tertiary carbon had to be used in order to obtain simple PMR spectra:
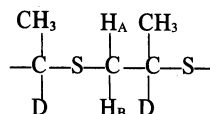
The H_A protons of the methylene group are stereosensitive to the configuration of the next asymmetric carbon.[17] But the yields of deuterated monomer synthesis are low and this complicates the study.

We have shown using Fourier transform NMR of ^{13}C that in the case of polypropylene sulfide the asymmetric carbon is stereosensitive[18] and the use of deuterated monomer is no longer necessary. It may be seen on Fig. 2 that there is only one peak at 41.1 for an isotactic polymer obtained in bulk with cadmium allyl thiolate at $-20°C$, that is split for an atactic polymer obtained with an anionic initiator (carbazyl Cs). In these two cases, the ring opening occurs exclusively between CH_2 and S and the polymer has regular head to tail linkages. Irregular head to head structures occur if a cationic initiator ($AlCl_3$ for example) is used. Several groups in Japan and France have found similar results in the case of polypropylene oxide.[19-21]

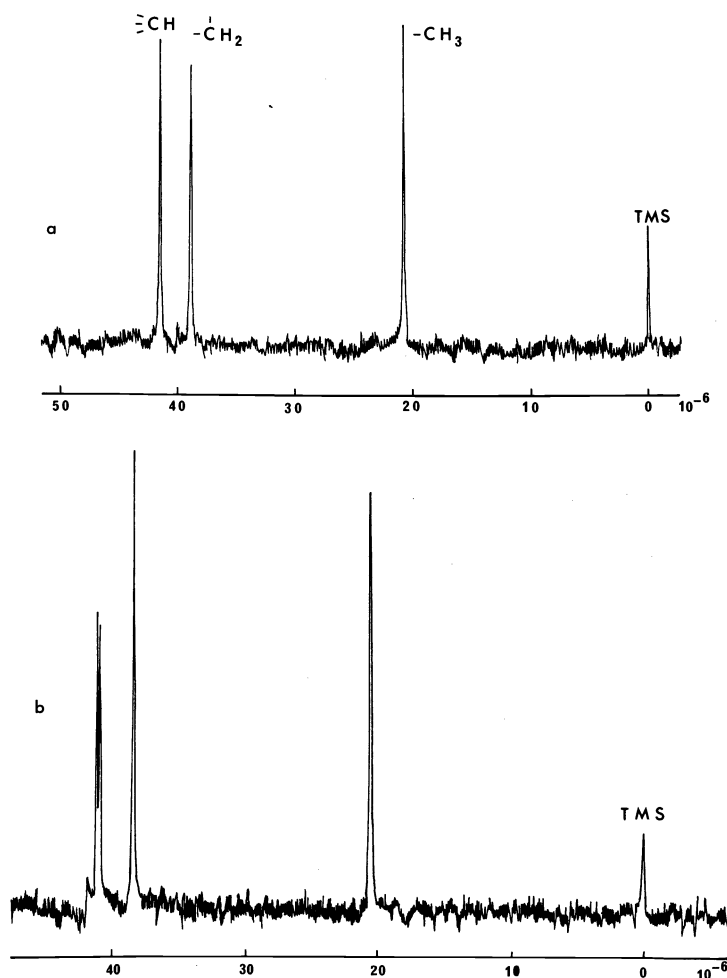The case of the polymer of tertiobutylthiirane CH_2—CH—C$(CH_3)_3$ presents some similarities and some

Fig. 2. ^{13}C NMR spectra of poly(propylene sulfide) (a) Isotactic polymer obtained with cadmium allyl thiolate (in bulk at 0°C). (b) Atactic polymer obtained with carbazyl cesium (in THF solution at −30°C).

differences. Polymerization of the racemic monomer with classical anionic initiators gives an amorphous polymer showing NMR triad effects for tertiary and secondary carbons and diad effects for the quaternary carbon.[22] Stereospecific initiators (ZnEt$_2$–H$_2$O or alcoholates) give isotactic crystalline polymers.[23] With ZnEt$_2$–H$_2$O, there is some isomerization of the optically active monomer. But the polymer obtained has a similar melting point and X-ray diagram identical to those of the polymer obtained with a pure enantiomer and a nonstereospecific anionic initiator. The melting points are much lower than that of the racemic crystalline polymer, that has also a completely different X-ray diagram. This shows that the crystalline structure for the optically active and the racemic polymers are different, even if their structure (isotactic) is identical, as may be seen on the NMR spectra (see Fig. 3).

MECHANISM OF STEREOSPECIFIC POLYMERIZATIONS OF OXIRANES AND THIIRANES

The formation of stereoregular polymers from racemic mixtures of chiral oxiranes and thiiranes does not involve necessarily a stereoselective mechanism (Mechanism (1)—see Fig. 4), and other possibilities might be imagined.

A mechanism (2), stereoregulative, could give an isotactic polymer indifferently from both enantiomers (if

an inversion of configuration occurs for one unit out of two on the average). But this mechanism may be excluded since the same initiators gave isotactic optically active polymers when starting from one entiomer, and the polymers had optical activities similar to those obtained from the same monomer using classical anionic non-stereospecific initiators.[24] If the stereoregulative mechanism was operative, the polymer obtained with an optically active monomer should have been inactive.

A mechanism (3) leading to an alternated copolymerization of R and S enantiomers, would give a polymer (R–S)$_n$. But this may excluded for all the cases studied until now as it would lead to a syndiotactic polymer whereas the obtained stereoregular polymers are isotactic.

It may be concluded that stereospecific polymerizations of racemic mixtures are stereoselective, which means there are two types of sites choosing preferentially either the R or the S enantiomer.

In some cases, some sites are fully stereospecific and lead to the crystalline fraction of the sample, and others are partly stereospecific and give the amorphous fraction. This occurs for example with epoxides. The formation of isotactic chains and of chains rich in one enantiomer has been explained in this case by Furukawa[26] and Tsuruta[25] by an enantiomorphic catalyst sites control mechanism, similar to that also proposed for Ziegler Natta initiators.
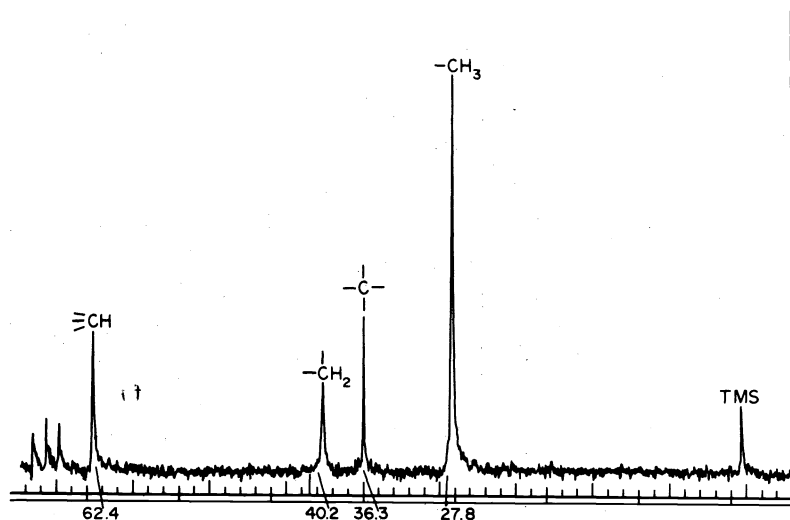
Fig. 3. ^{13}C NMR spectrum of isotactic poly(t-butyl thiirane). Racemic monomer polymerized using DMBD–Zn(C$_2$H$_5$)$_2$ as initiator. A polymer prepared with a pure enantiomer using potassium tertiobutylate as initiator gives an identical spectrum.

Fig. 4. Possible modes of formation of stereoregular poly(alkyl oxiranes) and poly(alkyl thiiranes).

Tsuruta has assumed the existence of two groups of enantiomorphic sites, one group involving chiral sites with various degrees of R nature and the other those with various degree of S nature, that may give polymer chains with rather different stereoregularities. The same explana-

tion may be valid for the formation of polypropylene sulfide when the samples obtained are not fully isotactic (with ZnEt$_2$–water or ZnEt$_2$–alcohol systems).

One of the mechanistic problems for stereospecific polymerizations is that of the influence of the initiator surface, that plays an important part in the polymerization of monoolefins. The initiators already mentioned for stereoselective polymerization (Zn and Cd oxides, alcoholates or tartrates) are insoluble, and moreover the relative concentration of active centers is a very small part of the whole initiator. It has been shown however that some cadmium thiolates are good stereospecific initiators for propylene sulfide polymerization[27] and we have studied the mechanism of this polymerization.[28] The initiator may be fully consumed giving an homogeneous solution and the active centers concentration is equal to initiator concentration, the polymers obtained being living polymers with one living end per Cd atom. According to the temperature and solvent used, polymers may be amorphous or crystalline, crystalline polymers being generally obtained for $t < +10°$, and that even in some polar solvents such as THF (see Table 1). However, the tacticity of polymers obtained in solution is lower than that of polymers obtained in bulk with cadmium tartrate or with Cd thiolates, which are completely isotactic. It is then possible to have a fully stereoselective polymeriza-
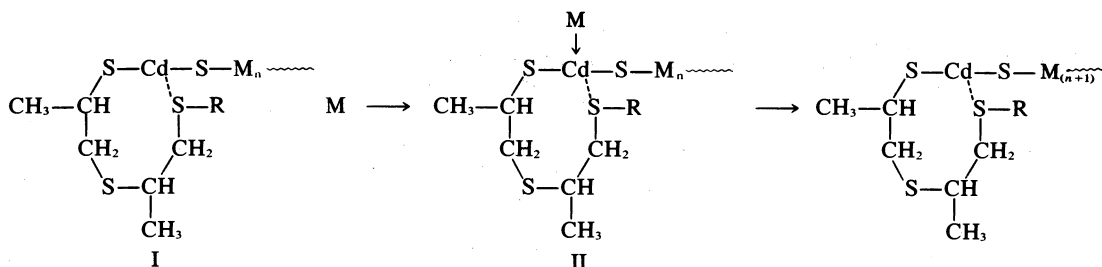
Table 1. Influence of the solvent and monomer concentrations on polymer crystallinity and tacticity[37] (polymerization of propylene sulfide at 0°C)

Solvent	Initiator C	$[C] \cdot 10^3$ (mol/l)	$[M]$ (mol/l)	State of polymer	σ†
toluene	Cd(SCH$_2$CH=CH$_2$)$_2$	3	4	crystalline	0.76
tetrahydrofuran	Cd(SCH$_2$CH=CH$_2$)$_2$	3	3.9	crystalline	0.76
tetrahydrothiophen	Cd(SCH$_2$CH=CH$_2$)$_2$	3	4	crystalline	0.78
HMPA	Cd(SCH$_2$CH=CH$_2$)$_2$	3	3.9	amorphous	0.50
toluene	Cd(SCH$_2$CH$_2$SBu)$_2$	2.5	1.2	amorphous	0.50
toluene	Cd(SCH$_2$CH$_2$SBu)$_2$	2.6	5.3	crystalline	0.70
toluene	Cd(SCH$_2$CH$_2$SBu)$_2$	2.5	12.8 (in bulk)	crystalline	1.00

† $\sigma = (h_{41.3}/h_{41.1} + h_{41.3}) \, h_{41.1}$ and $h_{41.3}$ peaks height corresponding respectively to iso diads and syndio diads (see Ref. (41) on the calibration of ^{13} NMR with ^{1}H NMR).

tion in homogeneous phase, and the increase of tacticity with monomer concentration (see Table 1) may be explained by a coordination equilibrium of the monomer on the active site. This would also be in agreement with the increase of stereoregularity when temperature is lowered, and with the negative influence of strongly solvating agents (such as HMPA in low concentration) on tacticity.

A simple scheme may be proposed that takes into account the results mentioned, and for which the polymer growth occurs only on one side of the Cd atom, the other side being blocked by the formation of a stable cycle formed by intramolecular coordination with a sulfur atom after the incorporation of one or two monomer units on the other Cd side:

$$(1-x)^{r-1} = \frac{1+(\alpha/\alpha_0)}{(1-(\alpha/\alpha_0))^r} \frac{2^{r-1}[S]_0^r}{[R]_0([R]_0+[S]_0)^{r-1}}. \quad (3)$$

When polymerization is realized with a racemic mixture, $[R]_0 = [S]_0$ and eqn (3) simplifies into (4):

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

For low yields, $\alpha \ll \alpha_0$ and the equation may be further simplified, giving[30] eqn (5):

$$\alpha = \alpha_0 \frac{r-1}{r+1} \log(1-x). \quad (5)$$

An approximate value of r may be deduced from a few

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We shall see however that some stereoelection experiments show that this scheme is too simple to explain all the results.

EXPERIMENTAL RESULTS FOR STEREOELECTIVE (OR ASYMMETRIC SELECTIVE) POLYMERIZATIONS OF OXIRANES AND THIIRANES

With several systems leading to stereoelective polymerizations the enriching of residual monomer into one enantiomer could be related with monomer conversion in a simple manner, assuming that stereoelection is depending only on the nature of the active site and independent of the nature of the last monomer unit. The global rate constants for R and S consumption are

$$k_{RR} = k_{SR} = k_{CR}$$
$$k_{RS} = k_{SS} = k_{CS}$$

if C represents any active site. If monomer consumption follows a first order law,

$$-\frac{d[R]}{dt} = k_{CR}[R]$$

$$-\frac{d[S]}{dt} = k_{CS}[S]$$

and

$$\frac{d[R]}{d[S]} = r_R \frac{[R]}{[S]} \quad (1)$$

or

$$\frac{[R]}{[R]_0} = \left(\frac{[S]}{[S]_0}\right)^{r_R} \quad (2)$$

with $r_R = (k_{CR}/k_{CS})$ characterizing the relative preference of the system towards the R antipode (over the S antipode). If x is the polymer yield, α the optical activity of unreacted monomer, α_0 that of a pure R enantiomer, and $[R]_0$ and $[S]_0$ the initial concentrations of enantiomers R and S, eqn (3)[29] may be deduced from (2)

experiments (and even from one result only) using eqn (5), but the error is large and it is better to trace the whole $\alpha = f(x)$ curve and to determine the best theoretical curve based on eqn (4) that fits with experimental results.

The first example of stereoelective polymerization has been given by Tsuruta et al. for propylene oxide polymerized using the system $ZnEt_2$–(+) borneol.[3,4] From the optical yields obtained at low conversions, r values of about 1.6 may be deduced. Propylene sulfide with the same system and with other monoalcohols has given $r \sim 1.3$.[31] But we also found that using systems based on chiral diols, much higher optical yields could be obtained. For example, with propylene sulfide and the system $ZnEt_2$–(−) 3,3-dimethyl 1,2-butane diol', values of r as high as 2.4 have been obtained. (With $\alpha_0 = 51°$, the value 3.5 given in a previous publication[29] was based on an incorrect reference value α_0 for the pure enantiomer.) This means that the optical purity of unreacted monomer is 60% for 80% conversion, corresponding to a residual monomer composition 80% R/20% S.

Figure 5 shows the good agreement between experimental data and theoretical curves obtained for r_R values of 1.4 ($ZnEt_2$(+)tBuCHOHCH$_3$) and 2.4 ($ZnEt_2$(−)tBu CHOH CH$_2$OH). These polymerizations are giving the levorotatory enantiomer. On the same figure may be seen the results obtained with the system $Cd(Me)_2$–(−)tBu CHOH CH$_2$OH for with the same chiral diol was used but that gave a good stereoelection of *the other enantiomer* (with $r_S = 1.9$).[31]

It was possible to find a relationship between the absolute configuration of the chiral alcohols used, the composition of the reaction product formed with the organometallic derivative and the preferentially chosen enantiomer.

One may define as having the same configuration an alcohol (or a diol) and a monomer for which the ordering of similar groups around the asymmetric carbon is identical. Similar groups are those for which steric hindrance and polar effects are similar, and this classification does not always lead to an order identical with that corresponding to the Cahn–Prelog rule for the
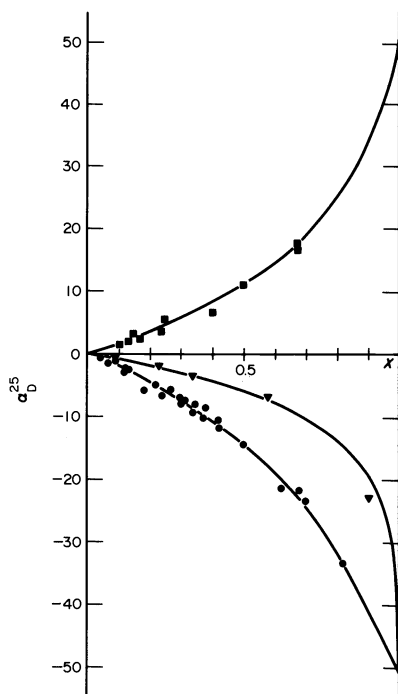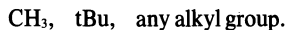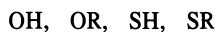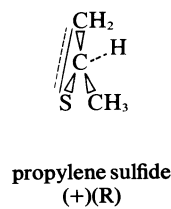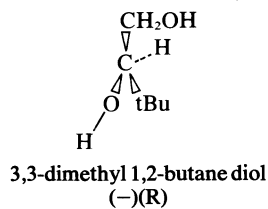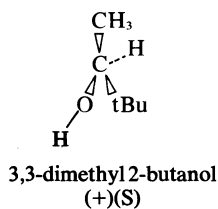
Fig. 5. Polymerization of propylene sulfide with various chiral initiators. Variation of the optical activity α_D^{25} (neat, dm.) of residual monomer with conversion x. Experimental points and theoretical curves based on eqn (4). Initiators: ● (−) (CH₃)₃CCHOHCH₂OH(DMBD)–Zn(C₂H₅)₂ (1/1) theoretical curve: $r_R = 2.4$; ■, (−) DMBD–Cd(CH₃)₂ (1/1); $r_S = 1.9$; ▲, (+) (CH₃)₃CCHOH CH₃–Zn(C₂H₅)₂(2/1); $r_R = 1.4$.

definition of R and S enantiomers. For example, one may consider the following series as similar groups:

$$CH_2OH, \quad CH_2SH, \quad CH_2S$$

$$OH, \quad OR, \quad SH, \quad SR$$

$$CH_3, \quad tBu, \quad \text{any alkyl group.}$$

In this respect, the following molecules may be considered to have the same absolute configuration

of behaviour have been found, particularly in the case of cadmium derivatives (see Fig. 5).

However, we have found that the nature of the metal was not the direct cause of the inversion of stereoelection observed for example when using the same chiral agent either with diethyl zinc or with dimethyl cadmium (Fig. 5). A more detailed study has shown that the election sign is depending mainly on the structure of the resulting catalyst, and more precisely on the ratio I_S of concentrations of alkyl alcoholate and dialcoholate:

$$I_S = \frac{(R-M_t-O)}{(O-M_t-O)}.$$

For the same alcohol, this ratio is depending on the metal, and also on the alkyl group, since the reactivity of organo metallic compounds decreases in the following order for primary alcohols: $ZnEt_2 > CdEt_2 > Et_2 > CdMe_2$, and I_S increases in the same sequence. It is depending also on the nature of the alcohol. With organo zinc derivatives, primary alcohols have a higher reactivity than secondary alcohols, but with organo cadmium compounds, reactivity is reversed. Moreover, there is also a strong decrease of reactivity for secondary alcohols with an increase of the substituent's bulkiness.

Many factors play a part in determining the I_S value, but it is easy to determine it by titration. It has been found that when $I_S \leqslant 1$ election was homosteric and that when $I_S > 3$ election was antisteric. For intermediate values, the election is very low and depending upon the system studied. An antisteric election could also be obtained for example with a ZnEt₂-diol system for a ZnEt₂/diol ratio equal to 2, leading to I_S values between 4 and 8 (whereas the Zn systems generally gives homosteric elections). And inversely, for (CdMe₂/diol) ratio of 0.5, values of I_S near one led to a small homosteric election.

A general observation is that monoalcohols lead to much lower stereoelections than corresponding diols. A comparison may be seen on Table 2 where it may be seen that for the series

$$(CH_3)_3C\ CHOH\ CH_2OH; \quad (CH_3)_3C\ CHOH\ CH_3;$$

$$(CH_3)_3C\ CHOH\ CH_2O\ CH_3$$

3,3-dimethyl 2-butanol
(+)(S)

3,3-dimethyl 1,2-butane diol
(−)(R)

propylene sulfide
(+)(R)

With the systems ZnEt₂-alcohol or ZnEt₂-diol prepared using equimolar amounts of Zn R and OH groups, it has been found that the enantiomer preferentially chosen by the active sites had the same absolute configuration as the chiral glycol used for the catalyst preparation. We have called such a choice an *homosteric stereoelection*. If there is agreement between the above definition of absolute configuration and the Cahn–Prelog definition, an R glycol chooses an R monomer, leaving a residual monomer enriched in S enantiomer. On the other hand, when the chosen enantiomer has a *configuration opposite* to the configuration of the chiral agent, this may be called an *antisteric stereoelection*.[31] Several examples of this type

the glycol gives a much higher r value. The ether alcohol gives a very low r value, and the same result has been obtained with the isomer (CH₃)₃C CH(OCH₃) CH₂OH. This particularly favorable result in the case of diols might be due to the presence of active cyclic or polymeric structures in the catalyst.[31]

The system ZnEt₂-3,3 dimethyl-1,2 butane diol has also been used for the polymerization of t-butyl thiirane, and polymerization could be realized in bulk as the rate is much smaller than for propylene sulfide. A very strong stereoelection is observed, giving at low and medium conversions residual monomers of optical purity still higher than in the case of propylene sulfide. But the

Table 2. Comparison of homosteric stereoelectivity ratios for propylene sulfide
according to the alcohol or diol associated with $An(C_2H_5)_2$

Initiator		Polymer	Monomer	r
$ZnEt_2 + R(-)\overset{tBu}{\underset{OH}{CH-CH_2OH}}$	(1:1)	(+)	(-)	2.4
$ZnEt_2 + S(+)\overset{tBu}{\underset{OH}{CH-CH_3}}$	(1:2)	(+)	(-)	1.4
$ZnEt_2 + R(-)\overset{tBu}{\underset{OH}{CH-CH_2OCH_3}}$	(1:2)	(+)	(-)	1.2

equation linking optical activity with conversion that was satisfactory for this monomer is no more valid for t-butyl thiirane, contrary to what has been written in a recent publication.[32] The former conclusion had been based on an insufficient number of experiments and to two faulty ones at high conversions, where the divergence with the calculations based on equation (4) are the highest. The experimental results may be however reconciled with a *second order law* for monomer consumption:

$$\frac{d[R]}{d[S]} = \rho\frac{[R]^2}{[S]^2}. \qquad (6)$$

This leads after integration to

$$\frac{1}{[R]} - \frac{1}{[R]_0} = \rho\left(\frac{1}{[S]} - \frac{1}{[S]_0}\right) \qquad (7)$$

and to

$$\frac{1}{(1-x)\left(1+\dfrac{\alpha}{\alpha_0}\right)} = \frac{\rho}{(1-x)\left(1-\dfrac{\alpha}{\alpha_0}\right)} + 1 - \rho \qquad (8)$$

for a racemic monomer.

Equation (8) is verified by plotting $[1/(1-x) \; 1+(\alpha/\alpha_0)]$ as a function of $[1/(1-x)(1-(\alpha/\alpha_0))]$ (see Fig. 6). There is a satisfactory agreement between the slope $\rho = 7.5$ and the value of the ordinate to the origin, giving $(1-\rho)$.[33]

For such a consumption law, the limit of the optical activity of monomer for a complete conversion is no more equal to α_0 (as is the case with the first order law) but to $(\rho - 1/\rho + 1)\,\alpha_0$, corresponding for example in this case to an optical purity of 76% (see Fig. 7).

Another interesting difference with propylene sulfide is relative to the polymers. As those obtained from racemic *t*-butylthiirane by stereoselective polymerization, they are highly crystalline and isotactic, but the melting points are depending on the optical activity of the polymers. Those with low optical activities have m.p. of about 200° (similar to that of the racemic polymer obtained by stereoselection) and those with high optical activity a melting point of about 155° (close to that of the optically active polymer obtained from the pure enantiomer = 160°).

Those polymers obtained by stereoelection could be separated into different isotatic fractions, the melting points and the optical activities of which were close to those of the corresponding racemate and optically active
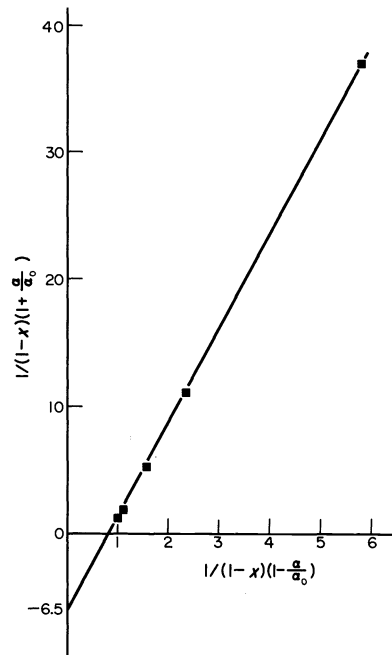
Fig. 6. Polymerization of *t*-butylthiirane at 20°C using DMBD–Zn $(C_2H_5)_2$ as initiator. Variation of $1/(1-x)(1+\alpha/\alpha_0)$ as a function of $1/(1-x)(1-\alpha/\alpha_0)$. $\alpha_0 = 43°$.

polymers. This was possible because the optically active polymer has a solubility that is higher (and a melting point lower) than for the racemate. Selective extraction and fractional precipitation have given fraction I soluble in benzene with a melting point of 157° and $[\alpha]_D^{25} = -167°$ in $CHCl_3$ (optically active polymer = m.p.: 160°. $[\alpha]_D^{25} = -189°$ in $CHCl_3$) and a fraction III insoluble in chloroform at 30° with no optical activity and m.p. = 204° (identical to that of the racemic polymer).

An interesting comparison could be made with polymers obtained by polymerizing with *non-stereoelective catalysts* monomers having various optical purities. Potassium tertiobutylate gave an atactic non-crystalline polymer (except with the pure enantiomer[23]), and $ZnEt_2$–H_2O gave crystalline polymers that could be fractionated in the same fashion as the polymers prepared by stereolection from a racemic monomer mixture.[32] This shows clearly that the mechanisms of stereospecific and stereoelective polymerizations are similar, with active sites choosing only one enantiomer.
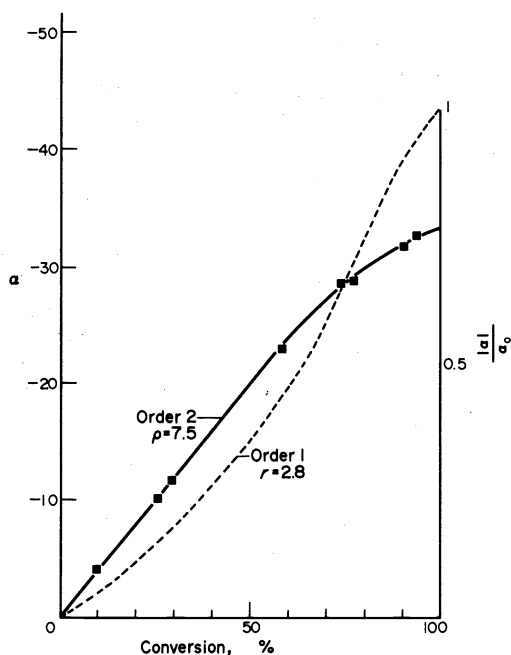
Fig. 7. Polymerization of t-butyl thiirane at 20°C using DMBD–Zn $(C_2H_5)_2$ as initiator. Variation of α and α/α_0 with conversion.
—— = theoretical curve according to eqn (7). $\rho = 7.5$. ------ = theoretical curve according to eqn (2). $r = 2.8$.

This type of fractionation cannot unfortunately be made with polymers obtained with propylene sulfide, since optically active and racemic polymer have the same crystal structure. But some other unexpected results have been observed when polymerizing optically active *propylene sulfide* mixtures of enantiomers with a stereoelective initiator such as ZnEt$_2$-(−)DMBD. The R enantiomer was chosen as in the case of a racemic mixture, but the r values were considerably enhanced compared to that case,[34,35] passing from 2.4 to 7 or 8 (see Table 3). Moreover, polymers were much more crystalline when R

Table 3. Stereoelective polymerization of propylene sulfide with Zn(C$_2$H$_5$)$_2$-DMBD. Influence of the optical purity of the monomer on stereoelectivity ratios (Polymerizations in toluene solution 1–1.6 M at room temperature)

$[\alpha]_D^{25}$ of monomer	R_0/S_0 monomer	Yield (%)	$[\alpha]_D^{25}$ unreacted monomer	r (based on mon.)
+ 23	72.5/27.5	46	+ 5.5	6.8
− 17.7	32.6/67.4	39	− 34.7	4.4
− 28.1	22.4/77.6	42	− 46.3	6.3
− 28.1	22.4/77.6	52.5	− 50.2	8.2

is in excess in the initial mixture, but were nearly amorphous when S is in excess.

If the same type of experiment is made with *propylene oxide*, the R enantiomer is still chosen, but the stereoelectivity ratio decreases[35,36] (from 1.8 to about 1.3). Those observations show that the activities and relative proportion of active sites depend on the initial enantiomeric composition of the monomer. It has also been found with the same initiator that the prepolymerization of a small quantity of S propylene sulfide $(\alpha_D^{25} = -50.5)$ leads to an increase of stereoelectivity ratio (from 2.4 to 4) for the polymerization of a racemic monomer.[34]

Unfortunately, stereoelective initiators that have given the highest r values are based on glycols. They are insoluble and their complex structure could not be analysed. Initiators based on tertiary alcohols such as ZnEt$_2$-(+) dimethyl 3,3 butanol-2 (DMB) are soluble and could be studied by NMR.[31] The structure is still complex but a bulk formula could be assigned to an homosteric system: (EtZnOR, Zn(OR)$_2$)$_n$, and to an antisteric one: 6 EtZnOR, Zn(OR)$_2$. No significant correlation could be observed between the optical activities of complexes of these types and with the r values, that are also relatively low with these systems based on monoalcohols.

The active centres for the polymerization of propylene sulfide using cadmium thiolates could be much better identified as thiolate groups with one living end per Cd atom (see above). It was interesting to see if stereoelection could occur in this homogeneous system, for example by polymerizing first a small quantity of optically active monomer: a small but significant stereoelection on a racemic mixture was observed. No stereoelection was found in the presence of preformed optically active polymer (see Table 4). On the other hand, if the order of addition of the small quantities of optically active and racemic monomer is reversed, stereoelection is still observed.[37] This seems to indicate the influence of complexed *monomer* on the active sites and shows that the mechanism of selection on one site written on p. 261 is too simple to explain all the results.

If the election process is involving a coordination of the monomer on the metal, one would expect a favorable effect on stereoelection by lowering the temperature. The experimental results are quite different according to monomer and initiator. With the ZnEt$_2$-diol systems, for propylene oxide and propylene sulfide, there is very little or no effect of temperature on stereoelection. (Whereas an increase of stereoregularity, that is, of stereoselection, is observed.) On the other hand, for t-butyl thiirane and the same initiator, a very big influence of temperature has been found. The value of ρ increased from 7.5 at 20° to 15 at −7°. In that last case, an optical purity of 60% (that is 80% S/20% R) could be obtained at 50% yield! The decrease in election of the enantiomer with an increase of

Table 4. Influence of optically active monomer of polymer addition on stereoelective polymerization of propylene sulfide[37] (Initiator = Cd (S CH$_2$–CH=CH$_2$)$_2$. Polymerizations realized at 0°C in toluene solution. Racemic PS ~ 3.5 ml. Toluene ~ 3 ml)

Successive order of addition for seeds preparation	$[\alpha]_D^{25}$ (residual monomer)	Polymer yield (%)
Cd(SR)$_2$, (−)PS†	0.60	25
Cd(SR)$_2$, (±)PS, (−)PS†	0.63	24
Cd(SR)$_2$, (−)PS, (±)PS†	0.18	24
Cd(SR)$_2$, (±)PS,† (−)poly SP‡	0.00	32

†$\overline{DP}_n$ of each seed sequence ~110. Seeds were all prepared at room temperature with 0.1 g monomer per addition.
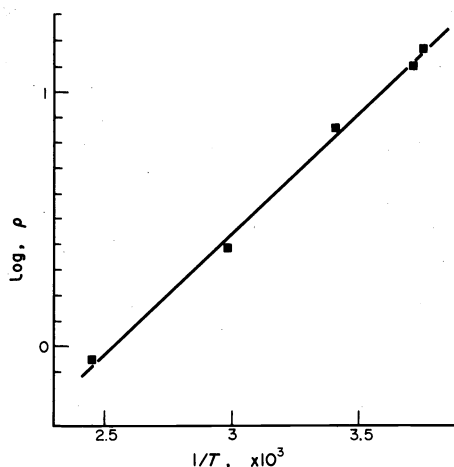‡0.1 g of (−)poly SP(DP ~ 1000).

Fig. 8. Polymerisation of t-butyl thiirane using DMBD–Zn $(C_2H_5)_2$ at initiator. Variation of ρ with absolute temperature.

temperature could even lead to a reversed election of the S enantiomer at a temperature of 135°C. The variation of $\log \rho = f(1/T)$ is linear and gives a value of $E_R - E_S \sim 5$ Kcal $\cdot$ mol^{-1} (see Fig. 8).

For propylene sulfide with cadmium thiolates as initiators, no election is observed at room temperature and there is a favorable effect of a lowering of temperature on the election.

MECHANISM OF STEREOELECTIVE POLYMERIZATIONS OF OXIRANES AND THIIRANES

The terms stereoelective and stereoselective are relative to initiating *systems* that choose in the first case only one enantiomer, and in the second case either one or the other according to the type of active site. If one considers only one site, no distinction can be made. The only explanation for a preferential choice of one enantiomer in a stereoelective system is the influence of an asymmetric counter ion on the anionic growing end, and a similar explanation for stereoselective polymerization seems to be likely.

This explanation of stereoelection is in agreement with the observation of the constancy of the preference of the system for one enantiomer during the whole polymerization (that is, the constancy of r or ρ). It may be added that for non stereospecific sites, this shows no influence of the last units of the growing chain end, the composition of which is changing continuously during a stereoelective polymerization. This could also be confirmed by several copolymerization experiments. There is no variation of the stereoelectivity ratio for the copolymerization of propylene oxide and ethylene oxide with ZnEt$_2$-alcohol[38] or for the copolymerization of propylene sulfide and ethylene sulfide with ZnEt$_2$-diol[39,8] or cadmium thiolate.[37] If a cooperative effect of the last units of the polymer chain influenced stereoelection, a decrease of stereoelection should have been observed with the incorporation of ethylene oxide or sulfide units.

Let us examine what are the possible explanations for the equations giving the relative consumption of the enantiomers in stereoelective polymerizations. They have been verified up to high conversions in the case of propylene sulfide[29] and propylene oxide[36] (eqn (4) relative to a first order law) and in the case of t-butyl thiirane[33] (eqn (8) relative to a second order law). Equation 5 is also followed for stereoelective polymerization of N carboxy anhydrides.[40]

First order election law

It has been suggested that the preferential election of one enantiomer might depend upon an equilibrium of complexation of the enantiomers with the different sites. In that case, one would expect a significant effect of temperature on the equilibrium. This has not been observed for stereoelective polymerizations of propylene sulfide and oxide with the ZnEt$_2$-diol systems, but a strong effect of temperature has been found with t-butylthiirane that follows a *second order* law. A significant effect of temperature has also been found with propylene sulfide initiated with the Cd(SR)$_2$+(−) PS system, but the consumption law has not been verified yet in this case.

In the most general case, both stereoregular and non tactic chains are formed (for example, for propylene oxide and propylene sulfide with many initiators). It is necessary to take into account both stereospecific sites of concentrations C_R^* and C_S^* on which no cross propagation takes place and non stereospecific sites C* on which it may occur. For a first order law:

$$-\frac{dR}{dt} = k_R'[C^*][R] + k_R[C_R^*][R]$$

$$-\frac{dS}{dt} = k_S'[C^*][S] + k_S[C_S^*][S]$$

$$\frac{d[R]}{d[S]} = \frac{k_R'[C^*] + k_R[C_R^*]}{k_S'[C^*] + k_S[C_S^*]} \cdot \frac{[R]}{[S]}.$$

The verification of eqn (5) shows that in the systems studied

$$r = \frac{k_R'[C^*] + k_R[C_R^*]}{k_S'[C^*] + k_S[C_S^*]}$$

is a constant.

When the polymer could be fractionated (polypropylene oxide) into amorphous and crystalline fractions, the curves of the optical activity of the *polymer fractions* according to conversion obeyed also to eqn (4),[36] giving for example r values of 1.8 for the whole polymer, 1.6 for the amorphous fraction and 2.6 for the crystalline fraction.

For the crystalline fraction,

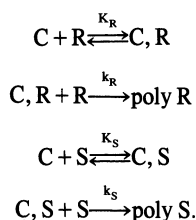$$r_{cr} = \frac{k_R}{k_S} \cdot \frac{[C_R^*]}{[C_S^*]}$$

and the simplest explanation is that $k_R = k_S$ for the stereospecific sites and that the election is resulting from the different concentrations of R and S sites. A limiting case could be that for which only stereoregular polymer is obtained, and the election would result only from the different amounts of R and S sites.

It is possible to consider another limit case for which cross propagation may occur on all sites, with different rates of addition of R and S leading to election ("kinetic choice"). There are a few examples of stereoelective initiating systems giving essentially amorphous polymers, but there is generally a change in the relative proportion of stereospecific and non stereospecific sites with polymerization conditions. This does not fit with the existence of identical sites but would agree with the suggestion made by Tsuruta of the existence of a whole spectrum of sites possessing various degrees of R and S nature, with

$$r_{am} = \frac{\sum_i k_{iR}'[C_i]}{\sum_i k_{iS}'[C_i]}.$$

Second order election law

It is possible to account for the second order law observed with *t*-butylthiirane by assuming that incorporation is realized only on sites already complexed by the monomer.

$$C + R \underset{}{\overset{K_R}{\rightleftharpoons}} C, R$$

$$C, R + R \overset{k_R}{\longrightarrow} \text{poly } R$$

$$C + S \underset{}{\overset{K_S}{\rightleftharpoons}} C, S$$

$$C, S + S \overset{k_S}{\longrightarrow} \text{poly } S.$$

This leads to

$$\frac{d[R]}{d[S]} = \frac{k_R K_R}{k_S K_S} \cdot \frac{[R]^2}{[S]^2} = \rho \frac{[R]^2}{[S]^2}.$$

Cross propagation may be neglected in this system since polymers show very high stereoregularities. It has also been found that ρ is not depending upon the optical purity of the monomer used: a value of $\rho = 7.7$ has been found using a monomer with an optical purity of 40% ($\rho = 7.5$ for the racemic mixture at 20°C). This is an agreement with the existence of pre-existing sites C that become active only after complexation with the monomer, the concentrations of R and S changing the relative number of *active* sites. This explains the strong variation of the election with temperature, that is due to a change of $(k_R K_R / k_S K_S)$.

It is possible now to discuss the difference of behaviour, using the same ZnEt₂-diol initiator, between *t*-butylthiirane on one hand and PO and PS on the other hand. With PO and PS, a strong influence of $([R]_0/[S]_0)$ ratio on stereoelection was found, and no effect of temperature. This may be understood if a complexation (or a reaction) of the monomer with pre-existing sites still occurs in this case, with the difference that there is no equilibrium or that it is strongly shifted to the right and practically independent of temperature. The active sites would be formed irreversibly at the beginning of the polymerization, with a concentration depending on the $([R]_0/[S]_0)$ ratio.

In the case of PS and cadmium thiolates, the effect of the addition of (−)PS in the seed is better explained by the occurence of an equilibrium of complexation, and this is in agreement with the observed influence of temperature on stereoelection and on stereoselection. More data are needed with this system in order to see whether it is really similar to that of *t*-butyl thiirane polymerized with a ZnEt₂-diol system.

CONCLUSION

Stereoelective and stereoselective anionic polymerizations of oxiranes and thiiranes that have been the most studied—that is, propylene oxide, propylene sulfide and *t*-butyl thiirane—are due to the asymmetric structure of the counter-ion that leads to the preferential incorporation of one of the two enantiomers into the polymer chains. Alcoholate or thiolate groups present in the initiator react with monomer to give active sites of different types, the relative concentration of which depends upon the nature of the monomer and on the relative concentration of the two enantiomers. In some cases—PO and PS with ZnEt₂-diol—the number and nature of active sites remains constant during the whole polymerization. This gives an election rate law first order in the concentration of the two enantiomers. In other cases—t-butyl thiirane with the same initiator—the active sites are formed through an equilibrium reaction with the monomer, and the concentration varies with conversion, giving an election rate second order in enantiomers concentration.

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