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Polymerization of Transdimethylthiirane with Chiral Initiators

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ABSTRACT

In the polymerization of transdimethylthiirane using a chiral initiator an unusual phenomenon was observed : the sign of unreacted monomer changed at high conversions. A new kinetic equation is proposed to explain this behaviour.

1 - INTRODUCTION

The polymerization of 2,3 disubstituted heterocycles has not been yet extensively studied, most of the work having been performed by VANDENBERG (1969, 1972, 1976). These monomers have the particularity to present in the cycle two asymmetric carbons in α position.

In his studies on the polymerization of cis and trans dimethyloxiranes and dimethylthiiranes VANDENBERG has used cationic and modified coordinated initiators. It was demonstrated that the polymerization occurs, whatever is the initiator,with a complete inversion of configuration of the asymmetric carbon involved in the ring-opening process. In particular, an optically pure trans dimethyloxirane leads to an optically inactive polymer due to the inversion of configuration of the asymmetric carbons during the ring-opening process. The fact that both carbon atoms are chemically equivalent indicates that the structure of the polymer is determined only by the enantiomeric choice. The latter could be promoted if one uses an optically active initiator. As a consequence, such a preferential choice should enrich the unreacted monomer in one of the antipodes.

It seemed to us interesting to develop such a study with a special emphasis on the resolution reaction of a racemic monomer, here trans 2,3-dimethylthiirane,using optically active initiators.

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2 - POLYMERIZATION WITH DIETHYLZINC-3,3 DIMETHYL 1,2 BUTANE-DIOL INITIATOR SYSTEM

It was previously shown that when a racemic monomer is polymerized with a chiral initiator one of the antipodes could be preferentially incorporated into the polymer chain and the unreacted monomer is enriched in one of the enantiomers (SIGWALT 1976, SEPULCHRE 1976, SPASSKY 1977). This is the so-called "stereoelective" polymerization.

We have used as initiator the system obtained by reaction between diethylzinc and R(-) 3,3 dimethyl 1,2- butanediol (R(-) DMBD) which has been up to now the most efficient in the stereoelective polymerization of thiiranes. Polymerizations were run in bulk at room temperature and stopped at various conversions. In all cases, in agreement with the mechanism of Vandenberg, optically inactive polymers were obtained. On the other hand, the optical activity of unreacted monomers varied during the reaction. A negative monomer i.e. enriched in SS enantiomer is isolated at the beginning, then a change of the sign occurs around 60 % conversion and positive monomers, enriched in RR enantiomer are isolated (Fig. 1)*.

2-1) Kinetic equation

Up to now, two classes of monomers have been distinguished according to their kinetic behaviour i.e. the shape of the curve of the optical purity of unreacted monomer. With conversion they followed the so-called first and second order kinetic equations in which the ratio of the relative consumption rates of the two enantiomers was proportional to their first or second order concentration. However, the sign of unreacted monomer was always the same at various conversion. According to Fig. 1, the stereoelective behaviour of trans dimethylthiirane differs completely from the previous one. A particularity is observed for the first time, the change of the sign of residual monomer at a definite conversion. Such a phenomen is only possible if the two enantiomers polymerize according to different kinetics laws.

We have tested several possibilities and have found that the best interpretation of kinetic results in a large range of conversion is obtained when the ratio of the relative consumption rates of the stereoisomers obeys the following relationship :

$$\frac{d\,|RR|}{d\,|SS|} = \gamma\,|RR|^2 \qquad (1)$$

This equation must be integrated, if one considers that γ is constant during all the process,as previously observed for other thiiranes, leading to :

$$\frac{1}{|RR|_{\circ}} - \frac{1}{|RR|} = (|SS| - |SS|_{\circ}) \qquad (2)$$

where $|RR|_{\circ}$ and $|SS|_{\circ}$ are the initial concentrations of the antipodes.

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* The optically pure (RR) enantiomer is dextrorotatory with a specific rotatory power $|\alpha|_D^{25} = +135$ (SALVADORI 1967).

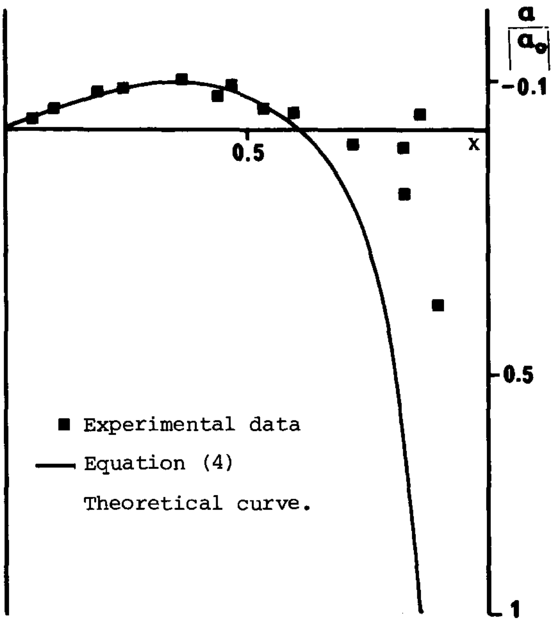

Fig. 1 - Dependence of the optical purity of unreacted monomer on the conversion in stereoelective polymerization of trans dimethylthiirane using $ZnEt_2$-(-)DMBD initiator.

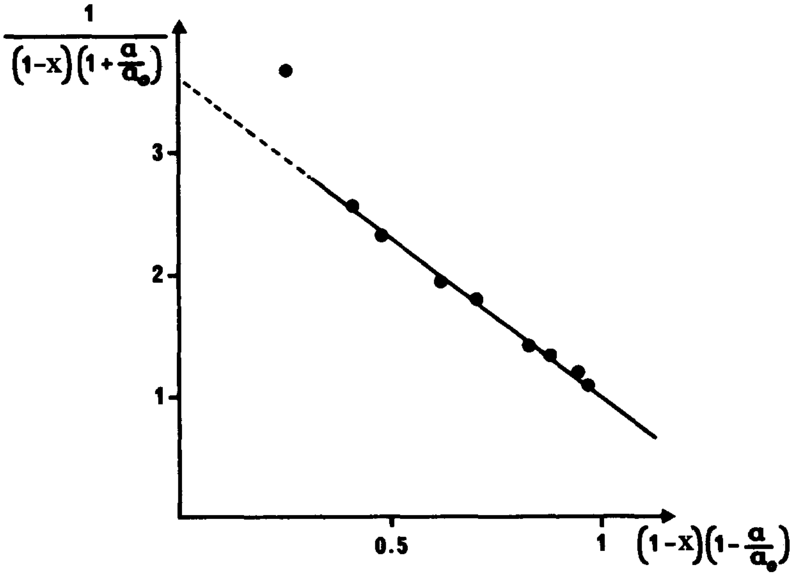

Fig. 2 - Experimental verification of stereoelective equation (4)

If one introduces into equation (2), the conversion x and the optical purity α/α_o of the unreacted monomer

$$x = 1 - \frac{|RR| + |SS|}{|RR|_o - |SS|_o} \qquad o.p. = \frac{|RR| - |SS|}{|RR| + |SS|} = \frac{\alpha}{\alpha_o}$$

one obtains the following general equation (3) :

$$\frac{1}{(1 + \frac{\alpha}{\alpha_o})(1-x)} = - \frac{\gamma}{4} (|RR|_o + |SS|_o)^2 (1 - \frac{\alpha}{\alpha_o})(1-x) + \gamma |RR|_o \, |SS|_o \, \frac{|RR|_o + |SS|_o}{2 \, |RR|_o} + \frac{|RR|_o + |SS|_o}{2 \, |RR|_o} \qquad (3)$$

that may be simplified when one starts from a recemic monomer $|RR|_o = |SS|_o = \frac{|M|_o}{2}$

For polymerization in bulk $|M|_o = 10{,}2$ moles/l, and the final equation takes the form :

$$\frac{1}{(1 + \frac{\alpha}{\alpha_o})(1-x)} = - 26{,}01 \, \gamma \, (1 - \frac{\alpha}{\alpha_o})(1-x) + 26{,}01 \, \gamma + 1 \qquad (4)$$

We have verified that equation (4) applies to the polymerization of trans dimethylthiirane. If one plots its first terme $1/(1 + \frac{\alpha}{\alpha})(1 - x)$ against $(1 - \frac{\alpha}{\alpha_o})(1-x)$ one finds that the experimental points fit well on a straight line at least up to 60 % conversion (Fig. 2). From the slope and the ordinate at the origin, one obtains the same value for γ equal to 0.102 mole^{-2} l^{2}. One can also see that the experimental data are fitting satisfactorily on the theoretical curve using the $\frac{\alpha}{\alpha_o}$, x plotting (Fig. 1) up to 60 % conversion. For higher conversions, the large scatter observed might be due either to catalyst aging (after more than ten days) or to a change of mechanism at high conversions.

It must be noticed that according to equation (4), the optically pure monomer should be obtained at 86 % conversion.

2-2) Influence on the polymerization temperature

It was observed in previous studies that the temperature had no or little effect on the stereoelective behaviour of monomers obeying a first order kinetic law, such as methylthiirane (SEPULCHRE 1976), but a great dependence was found in the case of monomers obeying the second order law such as t-butylthiirane (DUMAS 1978).

In the case of trans dimethylthiirane, as shown in table 1 the stereoelectivity of the process is varying with the temperature.

TABLE 1

EFFECT OF THE TEMPERATURE ON THE POLYMERIZATION OF TRANS DIMETHYLTHIIRANE USING $ZnEt_2$-(-) DMBD INITIATOR SYSTEM

All polymerizations carried out in bulk.

TEMPERATURE (°C)	C/M % (moles %)	TIME (hr)	CONVERSION (%)	$\lvert\alpha\rvert_D^{25}$ unreacted monomer
25	4.9	15	5	- 4.07
25	4.2	113	24	-11.90
25	4.7	480	83	+18.10
40	4.9	25	6.9	- 0.45
40	5.0	20	14	- 0.69
40	4.9	170	88	+20.70
50	4.6	3	5.7	- 0.75
50	5.6	41	27	+ 3.2
50	5.3	144	90	+50.50
80	4.7	2.25	36	+ 0.25

At higher temperature (40,50°C) the stereoelection follows the same type of kinetic behaviour as at room temperature with a change of the sign of unreacted monomer above a definite conversion. The maximum value of the curve seems to be lowered and the change of the sign occurs at a lower conversion.

3 - INFLUENCE OF THE NATURE OF THE CHIRAL COMPONENT OF THE INITIATOR

It is known that the magnitude of resolution for stereoelective processes is depending on the nature of the chiral component and particularly on the bulkiness of the substituent of the asymmetric carbon.

We have used two other 1,2 diols systems in order to compare their efficiency with that of R(-) DMBD.

3-1) Diethylzinc-R(-) 1,2 propanediol system

R(-) 1,2 propanediol |(-) PD| has the same configuration as R(-) DMBD, thus a direct comparison of the effect of substituents could be made.

As shown in table 2, the rate of polymerization with $ZnEt_2$-(-) PD system is much smaller than with the previous system. Moreover, the sign of residual monomer was found to be positive on a large range of conversions and no tendency for inversion seemed to occur.

TABLE 2

EFFECT OF THE NATURE OF THE CHIRAL COMPONENT OF THE INITIATOR ON THE POLYMERIZATION OF TRANS DIMETHYLTHIIRANE

Polymerizations carried out in bulk.

Diol	Temperature	C/M (moles %)	time (days)	conversion (%)	$\lvert\alpha\rvert_D^{25}$ unreacted monomer
R(−)PD	21	4.9	3.8	16	+ 0.03
	21	4.5	14	28	+ 0.55
	50	4.9	5	69	+ 2.85
R,R(−)BD	21	5.4	14	5	− 0.65
	21	5.5	33	11	− 1.80

It seems therefore possible that the kinetic equation for this system is quite different from that of the (−) DMBD system. In the case of methylthiirane the use of (−)PD just lowered the stereoelectivity but didn't modify the behaviour (SEPULCHRE 1976).

3-2) Diethylzinc R,R(−) 2,3 butanediol system

R,R(−) 2,3 butanediol |(−)BD| has a steric similarity with trans dimethylthiirane (two identical neighbouring asymmetric carbons with methyl groups in α to the heteroatom) and for this reason the polymerization of the latter with this system was performed. As shown in table 2 the rate of polymerization is much smaller than with (−)PD and only low conversions could be obtained in reasonable time.

It was found, that the residual monomer was negative. It is not clear however if this behaviour is similar to that of (−) DMBD or again different.

One must recall that in the case of methylthiirane these three diols gave the same type of steric choice but with decreasing stereoelectivities in the order tBu > Me > Me,Me (DEFFIEUX 1974). Thus the change of the chiral component could modify more or less the stereoelective process depending on the nature of the monomer.

In the present case the $ZnEt_2$-R(−)DMBD initiator system showed the best resolution and also the most unusual behaviour with a change of the sign at a given conversion.

These results show the complexity of the interactions between chiral compounds bearing several asymmetric centers.

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