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# Effect of the Chiral Polymer Chain in the Anionic Polymerization of Styrene Oxide

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## ABSTRACT

Styrene oxide of different enantiomeric compositions was polymerized in bulk using a potassium alkoxide initiator. A preferential consumption of the enantiomer in excess was observed. The magnitude of this effect depends on the enantiomeric composition of the initial monomer : the more unbalanced is the latter, the stronger is the stereoelection observed. The stereoelective effect was almost completely suppressed by addition of complexing agents such as crown-ethers or cryptands. The observed phenomena are explained in terms of polymer-chain effects.

## INTRODUCTION

In the course of investigations of solvation effects of the polymer chain on active species (KAZANSKIJ (1977)) we were interested to study the influence of chiral polyether chain in anionic type ring-opening polymerizations. In such polymerizations, when using chiral monomers with various initial enantiomeric distributions, two types of behaviour were observed. In most of the cases, no variation between the optical activity of initial and of unreacted monomer was found and the resulting polymer has the same enantiomeric composition as the initial monomer. This means that the consumption of enantiomers depends only on the composition and there is no influence of chain end. Such a behaviour was observed for methyloxirane (TSURUTA 1965)), methylthiirane (SEPULCHRE (1974)), and t-butylthiirane (DUMAS (1977)).

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Recently, an "asymmetric-selective" effect was described (SATO (1975)) in the polymerization of unbalanced mixtures of (R) and (S)-t-butyloxiranes using potassium tert-butoxide as initiator. In this case the recovered unreacted monomer differed in enantiomer composition from the initial monomer. The stereoelective effect was ascribed to the formation of a chiral secondary structure around the metal cation (TSURUTA (1977)).

In this paper we wish to report preliminary results showing that a similar phenomenon is also observed in the polymerization of optically active styrene oxide (phenyl 1,2-epoxyethane).

Moreover, this stereoelective effect could be suppressed if using complexing agents such as crown-ethers or cryptands which trap the cation and isolate it from the influence of propagating chain.

## EXPERIMENTAL PART

Monomer. Optically pure (S)-Styrene oxide was prepared by the classical method starting from S(+) mandelic acid ($|\alpha|_D^{25}$ + 158 (C = 5, $H_2O$)) which was reduced by $LiAlH_4$ in ether solution into the corresponding 1,2 diol (yield = 83 % $|\alpha|_D^{25}$ + 40.1 (EtOH) (litt. $|\alpha|_D^{25}$ + 40,4 (EtOH) o.p. = 100 % PRELOG (1954)). The latter was tosylated and in a final step a cyclisation with sodium methoxide give a pure fractionated (S) styrene oxide (yield = 67 % $\alpha_{578}^{25}$ = - 36.10 (neat, dm) o.p. = 99 % litt. BERTI (R)-$|\alpha|_D^{25}$ + 34.24 (neat) i.e. $\alpha_D^{25}$ + 35.85 (neat,dm).

The monomer was purified before polymerization by drying on calcium hydride under high vacuum. Monomers of different optical purities were obtained by diluting the optically pure monomer with racemic one, commercially available, which was redistilled and purified in the same way.

Initiator. Potassium 3-oxa-1-heptaneolate was prepared by direct reaction of monobutylether of ethylene glycol in THF solution with a potassium mirror in a high vacuum apparatus. The evolving hydrogen was pumped out and the appearence of a blue colour substantiates the full consumption of alcohol.

Titrated stock solution (0.16 M) was divided in small portions, the solvent evacuated and the alkoxide kept in glass ampoules fitted with breakseals.The amounts of initiator in ampoules was again controlled by weight.

Polymerization. Polymerizations were carried out in bulk in apparatus sealed under high vacuum. Chosen amounts of monomer and initiator were mixed out and immediately a light brown colour appeared. After a given time of polymerization, the unreacted monomer is evaporated under high vacuum and its optical activity measured. The polymer is dissolved in toluene and then precipitated in excess of methanol. Oligomers were recovered by evaporation of the precipitation solution. Optical activities were measured on a Perkin-Elmer P 241 polarimeter.

## RESULTS AND DISCUSSION

Relatively few works were published on the polymerization of styrene oxide. Anionic polymerization using potassium methoxide as initiator was studied (SPIRIN (1972)) but only l.m.w. polymers were obtained. Coordinated anionic type initiators allowed the preparation of h.m.w. products (STILLE (1967) ALLEN (1967) TSURUTA (1968)). A stereoelective type polymerization was performed using chiral zinc alkoxides as initiator (KUMATA (1970)). No polymerization of optically active styrene oxide has yet been described. Optically pure styrene oxide has a relatively high rotatory power ($\alpha_o \approx 36{,}0$ (neat)) and for this reason it is very suitable for study of stereoelective effects, allowing to detect very small variations in enantiomeric composition. In this work, styrene oxide of different optical purities was polymerized in bulk using potassium alkoxide initiator. The experimental data are presented in table I. Polymerizations are very slow at room temperature but the rate is substantially increased when working at 82°C. The molecular weights obtained were somewhat lower than those expected from theoretical consideration. In some cases non negligible amounts of oligomers (up to 20 %) were obtained in the supernatant solution from precipitation, mixed with some unreacted monomer. The relative distribution of these products is presently under investigation. Thus, only the yield in h.m.w. products was considered. An important decrease of the optical activity of unreacted monomer is noticed in function of conversion as shown in Fig. 1 and in Table 1. The observed relative variation of the optical activity is much larger when starting with monomers of high optical purity. For example, in run n° 7 the optical purity of the monomer varied from 0.80 to 0.67, that means that the corresponding enantiomeric composition S/S+R changed from 0.90 to 0.83. As one can see, S-enantiomer, which was in excess in the initial mixture, was preferentially consumed during the polymerization.

The addition of complexing agents such as crown ether 18/6 (run n° 8) or cryptand |222| (runs n° 5 and 6) increases considerably the rate of polymerization which proceeds easily at room temperature.

The most interesting feature to be mentioned is that the use of complexing agents suppress almost completely the stereoelective effects observed in previous experiments. As seen, in runs n° 5, 6 and 8, the optical activity of unreacted monomer differs from that of initial monomer by less than 2 %.

The results reported above show that in the anionic polymerization of enantiomerically unbalanced styrene oxide a stereoelective effect occurs.

The magnitude of this effect is similar and even higher than that previously reported for t-butyloxirane using tBuOK as initiator (SATO (1975)).

The stereoelectivity is depending on the enantiomeric composition of initial monomer : the more unbalanced is the latter, the stronger is the effect.

The ratio of relative rates of consumption of both enantiomers i.e. the stereoelectivity ratio r , could be calculated from a previously established equation for stereoelective type po-

## TABLE I

## ANIONIC POLYMERIZATION OF OPTICALLY ACTIVE STYRENE OXIDE OF DIFFERENT ENANTIOMERIC COMPOSITIONS [(a)]

All polymerizations carried out in bulk.

| N° | Monomer | | Polymerization conditions | | | | Polymer | |
|---|---|---|---|---|---|---|---|---|
| | $\alpha_{578}$ init. (neat, dm) | $\alpha_{578}$ fin. (neat, dm) | $\frac{\lvert C\rvert}{\lvert M\rvert}$ % | time (hr) | temp. (°C) | additive | yield [(b)] % | $[\alpha_p]^{25}_{578}$ [(c)] |
| 1 | - 19.22 | - 17.32 | 1.33 | 83 | 82 | - | 55 | + 67 |
| 2 | - 19.22 | - 17.49 | 0.96 | 18 | 82 | - | 52 | + 66 |
| 3 | - 19.22 | - 18.05 | 0.92 | 8.3 | 82 | - | 34 | + 65 |
| 4 | - 19.22 | - 18.18 | 1.06 | 132 | 20 | - | 29 | + 64 |
| 5 | - 26.08 | - 25.8 | 1.52 | 4 | 20 | [222] [(d)] | 82 [(e)] | + 85 |
| 6 | - 26.08 | - 25.4 | 1.8 | 2 | 20 | [222] [(d)] | 80 | + 92 |
| 7 | - 29.46 | - 24.80 | 0.6 | 15 | 82 | - | 46 | + 98 |
| 8 | - 29.46 | - 29.08 | 0.8 | 38 | 20 | (18/6) [(f)] | 74 [(g)] | + 108 |
| 9 | - 36.10 | - | 2.3 | 168 | 82 | - | ~ 100 | + 118 |

(a) initiator : potassium 3-oxa-1-heptaneolate
(b) only h.m.w. polymers are taken into account
(c) h.m.w. polymer in dioxane
(d) Kryptofix [222] Merck ; $[222]/|C| \simeq 1$
(e) $M_{GPC} = 4000$
(f) dicyclohexyl-18-crown 6 Fluka ; $(18/6)/|C| \simeq 1$.
(g) $M_{osmo} = 7700$.

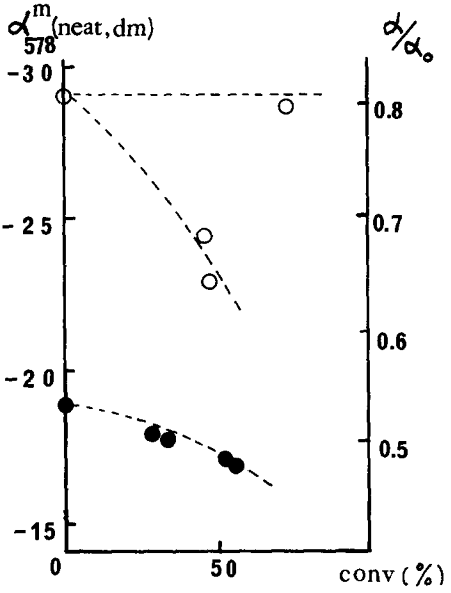

Fig. 1 Dependence of rotatory power and optical purity of unreacted monomer on conversion.

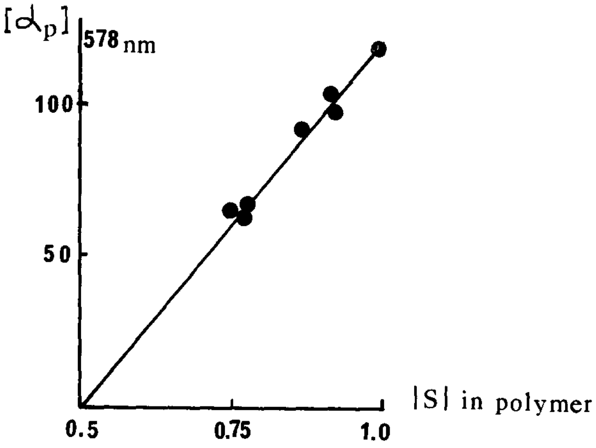

Fig. 2 Correlation between the measured rotatory power of the polymer and the calculated enantiomeric composition.

lymerizations (SEPULCHRE (1972)).

For runs n° 1 to 4, one finds an average value of $r_S$ = 1,20, which seems not depend very much on the conversion. This value is very close to that one obtained in the polymerization of t-butyloxirane of similar optical purity (TSURUTA (1977)).

When starting with a monomer of higher optical purity (run n° 7 o.p. = 80 %), the stereoelectivity is substantially increased and reaches a value close to $r_S = 5$.

It is not clear presently if the stereoelectivity would remains constant up to very high conversions or would decrease due to enrichment in opposite antipod of the unreacted monomer. Further experiments are now in progress in order to understand completely this behaviour.

The most reasonable explanation of the observed features seems to be an effect of the polymer chain. Indeed, it is known that a cation like potassium could be strongly solvated by polyethers (PANAYOTOV). In the present case, from the beginning of the polymerization one forms a polyether chain containing a great excess of one of the enantiomeric units e.g. S/R = 9/1 for an initial monomer of 80 % optical purity. Therefore, as proposed previously by TSURUTA (1977) in the case of t-butyloxirane, a growing end chiral moiety could be formed around the counterion $K^+$. The preferential consumption of S enantiomer during the process is in agreement with the chirality of this center. The increase in stereoelectivity with increase of optical purity of the initial monomer is also substantiating the influence of the chirality of active center moiety (PONOMARENKO).

The almost complete absence of stereoelectivity when using complexing agents, i.e. crown-ethers or cryptands, could be explained in the following way. First, the rates of polymerization reactions are very much increased in the presence of complexing agents, which could be a defavorable factor for selectivity (GIESE). Although, the main reason seems to be due to the trapping by the complexing agent of the counter-ion, which is no more able to be chelated by the polymeric chain and, thus, to be influenced by its chirality. Similar chelated structures were previously proposed in anionic polymerization of various epoxides (PRICE). A substantial decrease in stereoselectivity was observed when working in highly polar solvents such as DMSO or HMPA or by adding 18/6 crown ether.

The stereoregularity of our polymers is presently under study and should provide supplementary informations on the polymerization process. It must be pointed out that the optical activity of prepared polymers is in good agreement with enantiomeric composition calculated from the conversion (Fig. 2) and this seems to be a good evidence against any racemization during the polymerization process. The chiroptical properties of all prepared products are under examination.

Further studies on the effects of chiral polymer chains are now in progress.

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