

Enantioasymmetric polymerization of racemic styrene oxide

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SUMMARY

The enantioasymmetric polymerization of racemic styrene oxide has been carried out in bulk with $\text{ZnEt}_2/(\text{R})$ 3,3-dimethyl 1,2-butanediol as chiral initiator system. The R enantiomer is preferentially polymerized and the magnitude of the choice is characterized by a stereoelectivity constant equal to 1.5. For comparison, the optical resolutions obtained in the polymerization of different oxiranes using the same initiator system are given.

INTRODUCTION

Optically active poly(styrene oxide)'s may be prepared by polymerization of optically active monomers (1,2) but also by enantioasymmetric (stereoelective) polymerization of the racemic monomer. In the only two examples of such a polymerization, $\text{ZnEt}_2/\text{borneol}$ (3) and $\text{ZnEt}_2/\text{menthol}$ (4) systems were used as chiral initiators. Only qualitative results were reported for the first system. The polymerization experiments carried out with the second system were stopped at relatively low polymer conversions and it can be deduced from the rotatory power of unreacted monomers that the stereoelectivity ratio which measures the preference of the initiator towards one of the enantiomers is not constant and increases with the polymer yield. In addition the optical activity of polymers was rather low and did not agree with the value expected from the optical balance.

In this paper, we want to report results concerning the bulk polymerization of racemic styrene oxide initiated with $\text{ZnEt}_2/(\text{R})$ 3,3-dimethyl 1,2-butanediol (DMBD) (molar ratio 1/1) system. This chiral initiator is known to successfully polymerize several oxiranes and thiiranes (5).

RESULTS AND DISCUSSION

The polymerization of racemic styrene oxide is carried out in bulk at room temperature at the beginning of the reaction and further at 80°C using an initiator prepared at 80°C in order to obtain more active species (6). It was observed in the case of monomers which polymerize rather slowly that the stereoelectivity constant is higher when the polymerization is started at room temperature instead of being directly carried out at 80°C (7). The experimental results are presented in Tab.1. The rotatory power of the unreacted monomer increases with the polymer conversion. From its sign, it can be concluded that the initiator preferentially polymerizes the R enantiomer. This choice is in agreement with the homochiral configurational rule (8). The stereoelectivity constant r related to this polymerization can be calculated from equation I (9)

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

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where α/α_0 is the optical purity of the unreacted monomer and x the polymer conversion.

Table 1

Bulk polymerization of racemic styrene oxide at 80°C^a using ZnEt₂/(R) 3,3-dimethyl 1,2-butanediol (molar ratio 1/1) as initiator system^b.

n°	POLYMERIZATION		α_D^{25} unreact. mon. (neat, dm)	$[\eta]^c$ dl.g ⁻¹	POLYMER			r ^e
	Time h	Yield %			$[\alpha_D]^{25}$ d			
					DOX	C ₆ H ₆	CHCl ₃	
1	48	32.7	- 3.2°	0.145	---	-32.5	---	1.52
2	47	46.7	- 4.95°	0.38	-30.8	-34	-31.6	1.50
3	72	71	-10.21°	0.74	-27.4	-28.2	-26	1.53
4 ^f	31	64.3	+ 2.85°	0.22	+10.3	+10.7	+10.2	1.15

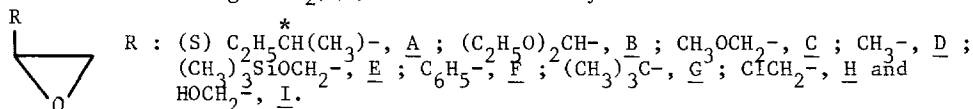
- a) The polymerization mixture is stirred for 3 days at room temperature before heating at 80°C.
- b) $[\text{Initiator}] / [\text{Monomer}] = 4.5 \text{ mol } \%$.
- c) In benzene at 25°C.
- d) Of precipitated solid polymer ; $c = 3 \text{ g.dl}^{-1}$.
- e) Stereoelectivity constant (see text), r_R for the experiments n° 1-3 and r_S for the experiment n°4.
- f) ZnEt₂/(S) 1-phenyl 1,2-ethanediol (molar ratio 1/1) as initiator system.

The highest optical activity reported for (S) styrene oxide prepared from (S) 1-phenyl 1,2-ethanediol is $[\alpha]_D^{20} = -37.1$ (neat) (10) which corresponds to $\alpha_D^{20} = -39^\circ$ (neat, dm) with $d = 1.051$. (S) 1-phenyl-ethanol prepared by reduction of (S) 2-hydroxy-2-phenyl ethyl p-toluene sulfonate, an intermediate compound in the synthesis of the oxirane, has the highest optical activity $[\alpha]_D^{20} = +48$ (neat) obtained up to now. The previously admitted optical activity $[\alpha]_D^{20} = +34.2$ (neat) (11,12) of a pure (R) styrene oxide was based on the comparison of the optical activity $[\alpha]_D^{23} = -44.3$ of 1-phenyl ethanol obtained by reduction and the value $\alpha_D^{25} = -44.2^\circ$ (13) reported in the literature for an optically pure product. Very recently, the enantiomeric composition of (R) styrene oxide with an optical activity of $[\alpha]_D^{15} = +33.2$ was calculated to be R/S = 96/4 (14) by ¹H-NMR using a chiral shift reagent and from this result it can be deduced that α^{15} should be close to 38° (neat, dm). Assuming $\alpha_{OD}^{25} = 39^\circ$ (neat, dm), the ^{OD} stereoelectivity constants r calculated from experimental data in Tab.1 are identical for the three experiments and equal to 1.5. The enantioselectivity does not change with the polymer conversion. In Tab.2 are given the stereoelectivity constants calculated from equation (I) related to all the polymerizations of racemic oxiranes carried out up to now with ZnEt₂/(R) DMBD initiators. The optical purity of unreacted monomer recovered at half-reaction (α/α_0) is also cited. The latter is a simple direct measure of the magnitude of the resolution reaction.

No obvious correlation can be found between the observed stereoselection and the nature of the substituent on the oxirane ring. It appears that styrene oxide occupies a middle position among all the monomers studied.

Table 2

Stereoelectivity constant r and optical purity of unreacted monomer at half-reaction $(\alpha/\alpha_0)_{x/2}$ observed in polymerization of racemic monosubstituted oxiranes using $\text{ZnEt}_2/(\text{R})$ DMBD initiator system.



OXIRANE	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
r	4	2	2	1.8	1.7	1.5	1.3	1.1	1.02
$(\alpha/\alpha_0)_{x/2} \%$	72/28 ^a	25	25	20	18.5	14	9.5	3.5	0.7
ref.	15	7	16	6	17	this work	18	19	17

a) Diastereoisomeric composition (2S, 3S)/(2R, 3S).

Kazanskij et al. (1) have found that in the polymerization of enantiomerically enriched styrene oxide with potassium alcoholate, the enantiomer in excess is preferentially consumed. This was explained as in the case of the copolymerization of R and S tert-butyloxirane with tert-BuOK (20) by the formation of a growing end chiral moiety around K^+ which preferentially adds the enantiomer of the same configuration. If a similar process acts in stereoelective polymerization simultaneously with the control by the chiral initiator, an increase of the stereoelectivity may be expected when one replaces in the initiator (R) DMBD by (S) 1-phenyl 1,2-ethanediol as chiral moiety. The latter can be considered indeed as a model of the monomer unit in the polymer chain. In fact a decrease of the stereoelectivity of about 24 % is observed ($r = 1.15$, Tab.1) as in the case of polymerizations of racemic methylthiirane using the same initiator (5). This confirms that in these polymerizations, the control by the initiator is predominant and that the initiator system based on (R) DMBD is the most efficient in the series.

The optical activities of prepared polymers are almost ten times higher than those reported for polymers obtained with ZnEt_2 /menthol system (4). They are even higher than the values expected from the optical balance of polymerization reactions assuming that $[\alpha]_D^{25} = -142$ (C_6H_6) for a pure poly (R) (styrene oxide). At the present time no satisfactory interpretation can be given for these findings. Only small variations of the optical activity are observed according to the solvent used (dioxane, benzene and chloroform) in contrast to that is observed in the case of polymethyloxirane (6,21). A similar behaviour was already reported for (+) 1,2-diethoxy-1-phenyl ethane (21), a model compound of the poly(styrene oxide) chain. Poly(styrene oxide) undergoes random chain scissions by aging. The optical activities of de-graded polymers appear only 6 % lower than that of freshly prepared polymers and are very close to those of the low molecular weight fractions of polymers. This shows that the polymer end groups have only a limited influence on the optical activity.

No melting point has been found by DTA measurements for crude poly(styrene oxide)'s and their acetone insoluble fractions though they are predominantly isotactic as shown by ^{13}C NMR analysis.

EXPERIMENTAL

Racemic styrene oxide (Dow) is purified by distillation under reduced pressure and dried under vacuum over CaH_2 . Optically pure (R) 3,3-dimethyl 1,2-butanediol, $[\alpha]_D^{25} = -28.5$ (CHCl_3 , $c = 0,6$), is prepared according to

(22). (S) 1-phenyl 1,2 ethanediol $[\alpha]_D^{25} = +39.2$ (EtOH, $c = 2.43$) is obtained by reduction of S(+) mandelic acid $[\alpha]_D^{25} = +156.7$ (H₂O, $c = 4.76$).

The polymerization experiments are carried out in sealed apparatus as already described (6). The polymer is recovered from its toluene solution by precipitation in methanol. The low molecular weight fractions (16 - 20 % of the whole polymer) remaining in suspension are isolated by centrifugation.

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