$$-RT \ln \frac{\sigma}{1-\sigma} = \Delta(\Delta G^{\ddagger}) = \Delta G_{\mathrm{i}}^{\ddagger} - \Delta G_{\mathrm{s}}^{\ddagger} \qquad (7)$$

$$-\frac{\mathrm{d} \ln [\sigma/(1-\sigma)]}{\mathrm{d}(1/T)} = \frac{\Delta(\Delta H^{\ddagger})}{R} \qquad (8)$$

Here, $\Delta G_{\mathrm{i}}^{\ddagger}$ and $\Delta G_{\mathrm{s}}^{\ddagger}$ express the free energes of activation for coisotactic and cosyndiotactic additions, respectively. An Arrhenius plot of the data in Table IV enables us to estimate the values of $\Delta(\Delta H^{\ddagger})$ as 1.8 ± 0.5 kcal/mol and $\Delta(\Delta S^{\ddagger})$ as 3.6 ± 1.4 eu (Figure 1). These may be compared with the values of $\Delta(\Delta H^{\ddagger}) = 1.07$ and $\Delta(\Delta S^{\ddagger}) = 1$ eu obtained by Fox and Schnecko[7] for homopolymerization of MMA. Elias and Goldi have collected a number of other values showing the temperature dependencies of tacticities in various homopolymerizations.[8]

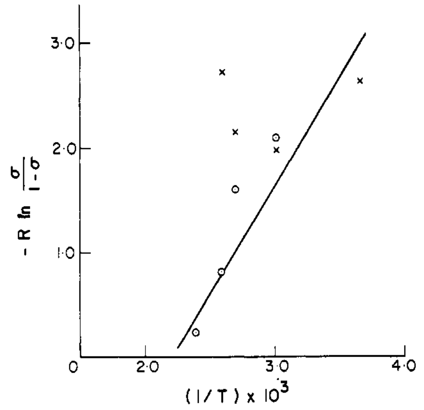

Figure 1. An Arrhenius plot of the data in Table IV: ⊙, our analysis; ×, analysis of Ito and Yamashita.

It is important to recognize that the reasonable value of temperature dependence of σ is dependent on *both* the nmr assignments *and* the reversible kinetic scheme (including its parameters). An irreversible treatment of the kinetic scheme yields an unrealistic temperature dependence of σ, as is seen in the third column of Table IV. While this cannot be taken as proof of the validity of the reversible treatment,[3] it does tend to further confirm it. As Berger and Kuntz[9] pointed out a number of years ago, sequence distribution analysis is superior to composition analysis for discriminating between alternate kinetic schemes in copolymerization.

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Highly Stereoelective Polymerization Processes[1]

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ABSTRACT: The initiator resulting from the reaction of diethylzinc with (*R*)-(−)-3,3-dimethyl-1,2-diol is a highly stereoelective system for the polymerization of propylene sulfide. Starting from racemic mixture, monomers of optical purities up to 90% could be obtained using this system. An equation linking the conversion and the optical activity of unreacted monomer has been established. The ratio, $r = \Sigma K_{iR}/\Sigma K_{iS}$, of rate constants for the consumption of the two antipodes was found equal to 3.5. It was also shown that the optical purity of a pure enantiomer of propylene sulfide has a higher value than the one previously obtained by direct synthesis. This polymerization process can be used as a method of preparation of enantiomers of high optical purity and also in order to determine their absolute optical purity.

We have reported recently[2] that products of reaction between diethylzinc and substituted optically active 1,2-diols are very suitable initiators for stereoelective polymerization of propylene sulfide. In a stereoelective process, as defined by Pino,[3] there is a preferential polymerization of one of the enantiomers of a racemic monomer. In the present work we report more detailed data concerning the use of one of these initiators resulting from the reaction between diethylzinc and (*R*)-(−)-3,3-dimethyl-1,2-butanediol.

The polymerization of racemic propylene sulfide by this initiator at different conversions produces a dextrorotatory polymer (in C_6H_6 or $CHCl_3$ solution); unreacted monomer is levorotatory (neat value). This corresponds to a preferential consumption of the *R* monomer over the *S* monomer. It was established previously that the *S* monomer is levorotatory.[4]

Experimental Section

The preparation of the standard initiator was carried out in toluene solution at room temperature by treating diethylzinc with the glycol with a molar ratio 1:1.2. The polymerization proceeds in this case in an apparently homogeneous medium. At the end of the polymerization, unreacted monomer and solvent are evaporated under vacuum and the distillate is fractionated through a spinning-band column, giving the pure monomer. The polymer is dissolved in benzene, separated from remaining initiator by centrifugation, and then precipitated in an excess of methanol. Another technique of preparation of the initiator was also used: after allowing diethylzinc and glycol to react for 2 hr in toluene solution, the solvent was evaporated and the catalyst dried 2 hr under vacuum. Then a

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(1) Paper presented at the XXIII IUPAC Meeting, Boston, Mass., July 1971.

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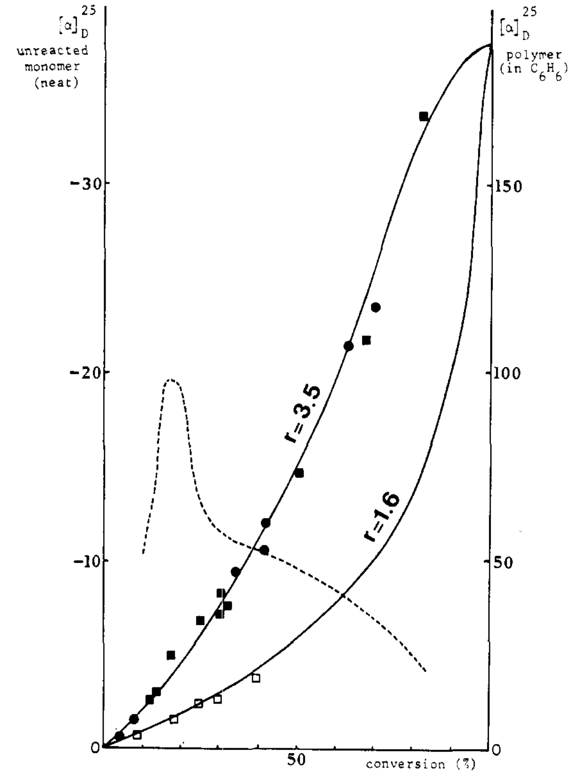

Figure 1. Stereoelective polymerization of racemic propylene sulfide using $ZnEt_2$–(*R*)-(−)-3,3-dimethyl-1,2-butanediol initiator: ■, unreacted monomer, standard initiator; ●, unreacted monomer, initiator prepared using drying technique; □, unreacted monomer, Furukawa's data[8] for $ZnEt_2$-L-leucine; ----, polymer (this work); —, theoretical curves for unreacted monomer optical activity according to eq 5.

new volume of toluene was added and the polymerization carried out in heterogeneous medium. In this case, the rates of polymerization were strongly increased, but the optical yields at corresponding degrees of conversion remained unchanged. All the experiments were carried out in all-sealed apparatus using high vacuum techniques.

Results and Discussion

The optical activity of unreacted monomer is increasing with increasing conversion (see Table I). The variation follows an S-shape curve (Figure 1) which is comparable with that observed in kinetic resolutions of a racemic mixture by consumption of one of the antipodes.

Making the following assumptions, it was possible to establish an equation in agreement with the experimental results. (a) The stereoelection is not dependent upon the nature of the last monomer unit. This was shown by Kumata, *et al.*,[5] to be the case for stereoelective polymerization of propylene oxide using the diethylzinc-*l*-menthol system. (b) At a definite time, for an active center concentration [C], the consumption of enantiomers is expressed by eq 1. (c)

$$-\frac{d[R]}{dt} = k_R[C][R]$$
$$-\frac{d[S]}{dt} = k_S[C][S] \qquad (1)$$

TABLE I
STEREOELECTIVE POLYMERIZATION OF RACEMIC PROPYLENE SULFIDE BY DIETHYLZINC–(*R*)-(−)-3,3-DIMETHYL-1,2-BUTANEDIOL (1:1.2)[a]

[C]/[M], % (mol: mol)	Time, hr	Yield, %	$[\eta]^b$ (100 ml/g)	$[\alpha]^{25}D$, deg, polymer (C_6H_6)	$[\alpha]^{25}D$, deg, unreacted monomer (neat)	Optical yield[e] of unreacted monomer, %
3.7	21.0	12.0	2.4	64.0	−2.5	6.7
3.7	22.5	13.2	2.5	54.8	−2.9	7.7
3.7	17.0	24.0	3.1	74.7	−7.0	18.7
3.7	45.0	29.0	2.3	52.9	−8.7	23.2
3.7	46.0	31.6	3.3	44.8	−7.5	20.0
3.7	42.0	50.0	2.7	52.4	−14.7	39.2
8.5	5.5	17.5	2.6	97.2	−6.2	16.5
7.9	72.0	76.0	2.3	34.6	−33.8	90.1
7.1	20.0	21.5	3.0	61.2	−5.0	13.3
7.6[c]	15.0	62.0	4.0	37.4	−21.5	57.3
7.3[d]	3.0	34.0	6.3	52.5	−9.5	25.3

[a] Polymerizations carried out in toluene at room temperature. Monomer concentration 1.8–2.0 *M*. The initiator was prepared by reacting diethylzinc and glycol 2 hr at room temperature in toluene. [b] Measured in benzene at 25°. [c] The initiator was prepared according to drying techniques at room temperature. [d] The initiator was prepared according to drying techniques; drying temperature 55°; polymerization at −10°. [e] Assuming $[\alpha_0]^{25}D$ −37.5° (neat) for optically pure monomer.

The values of the rate constants k_{iR} and k_{iS} might be different for each site *i*, but the relative preference toward *R* antipode (over *S* antipode) is constant during the polymerization. That means that $r = \Sigma k_{iR}/\Sigma k_{iS}$ is constant.

With these assumptions, one obtains eq 2, of the same type

$$\frac{d[R]}{d[S]} = r\frac{[R]}{[S]} \qquad (2)$$

as the composition equation for an "ideal" copolymerization. Integration of this equation gives eq 3.

$$\frac{[R]}{[R]_0} = \left(\frac{[S]}{[S]_0}\right)^r \qquad (3)$$

From experimental data, one knows the optical activity of the unreacted monomer (α), the yield of polymerization (x), and the initial concentrations of the enantiomers $[R]_0$ and $[S]_0$.

$$\alpha = \alpha_0\frac{[R] - [S]}{[R] + [S]}$$

$$x = 1 - \frac{[R] + [S]}{[R]_0 + [S]_0}$$

It follows that

$$\frac{[R]}{[R]_0} = \left(1 + \frac{\alpha}{\alpha_0}\right)(1 - x)\frac{[R]_0 + [S]_0}{2[S]_0}$$

$$\frac{[S]}{[S]_0} = \left(1 - \frac{\alpha}{\alpha_0}\right)(1 - x)\frac{[R]_0 + [S]_0}{2[S]_0}$$

These parameters can be introduced in eq 3, giving eq 4.

$$(1 - x)^{r-1} = \frac{1 + (\alpha/\alpha_0)}{(1 - (\alpha/\alpha_0))^r}\,\frac{2^{r-1}[S]_0^{\,r}}{[R]_0([R]_0 + [S]_0)^{r-1}} \qquad (4)$$

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(5) Y. Kumata, J. Furukawa, and T. Saegusa, *Makromol. Chem.*, **105**, 138 (1967).

TABLE II
STEREOELECTIVE POLYMERIZATION OF OPTICALLY ACTIVE PROPYLENE SULFIDE BY DIETHYLZINC-(R)-(−)-3,3-DIMETHYL-1,2-BUTANEDIOL (1:1.2)[a]

Yield, %	$[\eta]$[c] (100 ml/g)	$[\alpha]^{25}\text{D}$, deg polymer (C_6H_6)	$[\alpha]^{25}\text{D}$, deg unreacted monomer (neat)	Optical purity,[b] %	$[\alpha]^{25}\text{D}$, deg unreacted monomer, calcd[d]
18.3	2.7	−28.3	−33.2	88.5	−32.0
43.2	3.4	−36.6	−35.9	95.7	−35.0

[a] Experimental conditions as in Table I. Optical activity of the starting monomer −29.7° (neat); optical purity 79.2%.[b] Initiator concentration [C]/[M] = 10% (mol:mol). [b] Based on α_0 −37.5° (neat). [c] Measured in benzene at 25°. [d] Based on α_0 −37.5° (neat) and $r = 3.5$.

When the starting mixture is racemic ($[\text{R}]_0 = [\text{S}]_0 = [\text{M}]_0/2$) the equation is simplified and one finds the equation given by Furukawa.[6]

$$(1 - x)^{r-1} = \frac{1 + (\alpha/\alpha_0)}{(1 - (\alpha/\alpha_0))^r} \tag{5}$$

If x, α, α_0, $[\text{R}]_0$, and $[\text{S}]_0$ are known, the value of r for which the experimental data are satisfied can be determined by trial and error.

We have realized two series of polymerizations: one starting from a racemic mixture, another starting from optically active levorotatory enantiomer. The initiator used is preferentially consuming the R antipode, so that the unreacted monomer is enriched in S antipode (levorotatory). As can be seen from Tables I and II, the optical activities of unreacted monomer for high yields of polymerization could be as high as −36.0° (neat value), which is higher than the optical activity of the purest enantiomer obtained until now by direct synthesis (−32.6°).[7] This means that there is some racemization during the two-step synthesis used starting from optically pure *l*-propylene glycol. From the shape of the stereoelective curve one can estimate that the optical activity of the pure (S)-propylene sulfide must be in the vicinity of −37 or −38° (neat).

If one takes −37.5° for α_0, the experimental data are fitting satisfactorily with a value of r equal to 3.5 (Figure 1). The results obtained with the optically active monomer (Table II) confirm this hypothesis.

The variation of the optical activity of the resulting polymer (Table I; Figure 1) depends on the conversion and cannot be interpreted yet. However, it is rather unexpected to find a maximum for the optical activity around 20% conversion. One might have expected a progressive decrease of optical activity with increasing conversions. An explanation could be that the most stereoelective active species are not formed from the beginning. This would mean that k_R/k_S varies at the beginning of the polymerization, and the fact that the optical activity of unreacted monomer varies according to eq (5), with r equal 3.5, from the beginning of the reaction, is not in favor of this hypothesis. It is also probable that the optical activity of the polymer does not depend only on the R and S unit ratio but also on the sequence distribution of enantiomer units, the preferential conformations in solution being different. We have not yet enough information on this subject. It can be seen that a polymer obtained from the optically active monomer has also a low optical activity (for example, $[\alpha]^{25}\text{D} = -36.6°$ (C_6H_6) compared with the activity of the polymer prepared with the same monomer and cadmium tartrate catalyst $(\alpha)^{25}\text{D} = -114°$ (C_6H_6)). This can be understood since the stereoelective system used has a preference for the enantiomer with the lowest concentration, and the election and concentration effects cancel each other, but the effect of the monomer unit sequence distribution perhaps also occurs.

We have tried to test the validity of eq 5 in the case of results obtained by others in the field of stereoelective polymerization of heterocycles with similar types of initiators. The system diethylzinc-L-leucine used by Furukawa[8] in the case of propylene sulfide is much less stereoelective, with an r value close to 1.6.

It would be necessary to have yields higher than 97% in order to obtain an optical purity of 90% for the unreacted monomer (Figure 1). Such a system does not seem suitable for the prepartion of a pure enantiomer.

In the case of asymmetric selection polymerization of propylene oxide, Furukawa, *et al.*,[6] made similar assumptions and found for r a value of 1.37, using a simplified equation that can be used for low conversions. Using eq 5 we find 1.33 for this system. For the system diethylzinc-*d*-borneol used by Inoue, *et al.*,[9] we find $r = 1.9$.

For these two series of results, however, there are not experiments carried out at high conversions. It would be very interesting to see in this case, using systems of high stereoelectivity, if the value of $[\alpha]\text{D}$ −15° (neat) obtained for the purest enantiomer available corresponds to absolute optical purity.

Conclusion

We have found that diethylzinc-(R)-(−)-3,3-dimethyl-1,2-butanediol initiator is a very efficient stereoelective system for propylene sulfide polymerization and can give a residual monomer of optical purity up to 90%, starting from a racemic mixture.

The ratio of rate constants for the consumption of the enantiomers has a value around 3.5, and this resolution reaction is at least as efficient as the classical methods of synthesis now available for the preparation of enantiomers of the highest optical activity.

A kinetic scheme has been proposed that is perhaps oversimplified but explains satisfactorily the variation of the optical activity of residual monomer with conversion. It was also possible to show that the enantiomers obtained by direct synthesis are not optically pure and that their purity could be increased using the polymerization resolution.

This method is then potentially interesting for the determination of the optical purity of enantiomers for which the use of classical physicochemical techniques has not been possible. However, a comparison with the results obtained independently using a more direct method (such as nmr measurements on complexes) would be most interesting, and we are working in that direction.

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