Polymer Bulletin 13, 223–227 (1985)

Polymer Bulletin

Stereoelective Polymerization

Polymerization of Racemic Methylthiirane Using a Chiral Initiator Prepared with a Diastereoisomeric 1,2-Diol

M. Sepulchre and N. Spassky

Laboratoire de Chimie Macromoléculaire, Associé au C.N.R.S.,
Université Pierre et Marie Curie, 4 – Place Jussieu, F-75230 Paris Cedex 05, France

SUMMARY

The stereoelective polymerization of methylthiirane was studied with the $ZnEt_2$/(2S,3S)3-methyl 1,2-pentanediol initiator system. The stereoelectivity depends upon the diastereoisomeric purity of the diol and the experimental conditions of the initiator preparation. The presence of an additional asymmetric centre in the alkyl substituent significantly increases the stereoelectivity ratio as compared to that observed with the usual standard initiator system : $ZnEt_2$/(R) 3,3-dimethyl 1,2-butanediol.

INTRODUCTION

In the course of our investigations in the field of "chiral assistances" in the enantioasymmetric (stereoelective) polymerization of methylthiirane, we were interested to study the influence on the stereoelectivity of chiral factors coming from the initiator itself. We have previously demonstrated that when using our standard initiator system $ZnEt_2$/(R)3,3-dimethyl 1,2 - butanediol [DMBD] (molar ratio 1/1) the stereoelectivity of the process was greatly enhanced when the polymerization was carried out with enantiomerically enriched monomers as compared with the racemic one. An enhancement was also observed when using racemic monomer but in the presence of optically active compounds (external chiral agents) used as additives or solvents (1). In this paper we want to report some results concerning the stereoelectivity obtained with an initiator prepared with (2S,3S) 3-methyl-1,2-pentanediol [MPD] , a 1,2-diol including in its alkyl substituent an additional asymmetric centre which is able to act as an internal chiral agent.

EXPERIMENTAL

Materials

The preparation of (2RS,3S)-(α_D^{25} = -8.58° (neat, 1dm)) and (2S,3S) - (α_D^{25}= -3.75° (neat, 1dm)) 3-methyl 1,2-pentanediols has been already described (2). Their diastereoisomeric compositions (2S,3S)/(2R,3S) are supposed to be very close to those determined for the corresponding oxiranes i.e. are estimated to be equal to 50/50 and 85/15 respectively. Diols with other compositions are prepared by mixing determined amounts of these two diols. Diethylzinc is a commercial (ORGMET) solution in n-heptane. Toluene is purified under vacuum over calcium hydride and sodium mirrors . (S) - methylthiirane : α_D^{25} = -26.2° (neat, 1dm) is obtained from (R) 1,2 - propanediol : α_D^{25} = -14.6° (neat, 1dm) according to (3) and is diluted with racemic compound to give a monomer with α_D^{25}= -18.07° (neat, 1dm) which is dried over sodium mirrors.

Initiators

All the experiments are carried out under high vacuum in sealed glass apparatus. Reagents are stored in graduated tubes and are transfered in the reaction vessel by distillation using the breakseal technique. Diethylzinc (1.4-2 mmol) and 1,2-diol (1.4-2 mmol) are reacted in toluene ($\sim$12ml) 0.5hr at room temperature, then 2hr at the desired temperature. The solvent and the excess of reagents are after that evaporated and the reaction products are dried 2.5hr under vacuum at the same temperature.

Polymerizations

Toluene ($\sim$22ml) and methylthiirane (37-40 mmol) are successively introduced in the reaction vessel containing the dried initiator and the polymerization is run at room temperature. At the end of the polymerization the solvent and the unreacted monomer are evaporated and trapped in liquid nitrogen. The polymer is dissolved in toluene with a few drops of acetic acid. After elimination of zinc acetate by centrifugation, the polymer is recovered by precipitation in methanol. Pure methylthiirane ($\geq$ 99 % by GC) is obtained by fractionnal distillation of the evaporated toluene solution on a spinning band column.

Measurements

Optical activities are measured with a Perkin-Elmer 241 Polarimeter equipped with thermoregulated cells (for polymers $[\alpha]_D^{25}$ in benzene, c = 0.4 $g.dl^{-1}$; for recovered monomer α_D^{25}(neat, 1dm)). Intrinsic viscosities of polymers are determined in benzene at 25°C.

RESULTS AND DISCUSSION

In Table 1 are reported the results of polymerization of racemic methylthiirane initiated with $ZnEt_2$/(2S,3S) MPD (molar ratio 1/1) system prepared at room temperature. In these conditions, the choice of the initiator is "homosteric" as it can be deduced from the sign of the optical activity of unreacted monomer, the enantiomer preferentially incorporated in the polymer chain having the S configuration in agreement with the configurational rule previously established (4). It has been demonstrated that for methylthiirane (5) the stereoelectivity ratio r which defines in the present case the preference of the initiator towards the S enantiomer can be calculated from the equation :

$$(1-x)^{r-1} = \frac{(1 - \frac{\alpha}{\alpha_o})}{(1 + \frac{\alpha}{\alpha_o})^r} \frac{2^{r-1}\,[R]_o^r}{[S]_o(\,[R\,]_o+[S]_o)^{r-1}} \qquad (1)$$

Where $|\alpha|/|\alpha_o|$ is the optical purity of the unreacted monomer, x is the polymer conversion and $[R]_o$,$[S]_o$ are the initial enantiomeric concentrations of the monomer. When the starting monomer is racemic the equation (1) is simplified to

$$(1-x)^{r-1} = \frac{1 - \frac{\alpha}{\alpha_o}}{(1 + \frac{\alpha}{\alpha_o})^r} \qquad (2)$$

Using the experimental data reported in Table 1 and assuming that α_o =+ 52° (liq. 1dm) for pure R enantiomer (6), the stereoelectivity ratios r calculated from equation (2) were found to be relatively constant with an average value of 2.85. This value is a little higher than that obtained with $ZnEt_2$/(R)DMBD system (r_R = 2.3) (7). However one must notice that the latter initiator was prepared with an enantiomerically pure 1,2-diol which is not the case of the MPD we have used.

TABLE 1

Polymerization of racemic methylthiirane in toluene solution at room temperature using $ZnEt_2$/(2S,3S) MPD (molar ratio 1/1) initiator system prepared at room temperature.
$[I] / [M] = 3.5 - 5$ mol % ; $[M]_o = 1.5 - 1.8$ M/l

Polymerization		α_D^{25}	Polymer		Stereoelectivity
Time in hr	Yield in %	unreacted monomer	$[\alpha]_D^{25}$	$[\eta]$ in $dl.g^{-1}$	ratio r
23	19.5	+ 5.55°	-78.5	1.4	2.85
40	33.5	+ 9.82°	-65	0.87	2.65
48	53.5	+21.26°	-61	1	3.05
88.5	58.5	+23.02°	-51	1.78	2.85

TABLE 2

Polymerization of racemic methylthiirane in toluene solution at room temperature using $ZnEt_2$/MPD (molar ratio 1/1) initiator systems prepared at room temperature with MPD of different diastereoisomeric compositions.
$[I] / [M]$ = 3.6 mol % ; $[M]_o = 1.5 - 1.7$ M/l

MPD (2S,3S)/(2R,3S) molar ratio	Polymerization time in hr	Yield in %	α_D^{25} unreacted monomer	Polymer $[\alpha]_D^{25}$	$[\eta]$ in $dl.g^{-1}$	Stereoelectivity ratio r
50/50	46	23.7	+ 0.15°	- 1.4	1.71	1.02
72.8/27.2	45	22.5	+ 4.3°	-50	2.0	1.95
85/15	23	19.5	+ 5.55°	-78.5	1.4	2.85

The results in Table 2 show that the stereoelectivity ratios are largely depending upon the diastereoisomeric compositions of MPD. With MPD having almost equimolar amounts of (2S,3S) and (2R,3S) diastereoisomers an extremely low stereoelectivity is observed which is probably due to the very small excess of the (2S,3S) isomer. However it cannot be absolutely excluded that the presence of the additional asymmetric centre in α-position from that one bearing the hydroxyl group may play a role. The polymerization of methylthiirane initiated with achiral stereospecific systems modified by chiral additives generally does not occur with stereoelection except in the case of $ZnEt_2/H_2O$ system prepared in the presence of (6R,7S,9S,11S) sparteine (8). External chiral agents are considered to be not efficient enough to promote an unbalanced distribution of R and S active sites in an initially achiral initiator.

Furukawa (9) has shown on the example of the polymerization of racemic propylene oxide with the $ZnEt_2$/diethylglutamate system that the ratio $(r-1)/(r+1)$ is linearly varying with the enantiomeric excess of diethylglutamate. The same dependence seems to be observed with our initiator. From Figure 1 where the variation of $(r-1)/(r+1)$ is ploted versus the diastereoisomeric excess $[(2S,3S) - (2R,3S)] / [(2S,3S) + (2R,3S)]$ of MPDs, it can be deduced that the stereoelectivity ratio r should reach a value of 5.3 for optically pure (2S,3S) MPD.

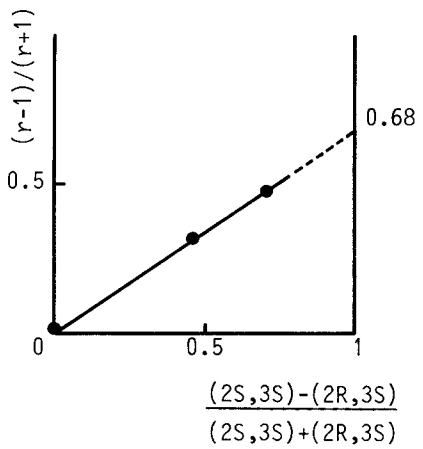

Figure 1. Variation of the stereoelectivity with the diastereoisomeric excess of MPD used in the preparation of the initiator.

The optical purity of the monomer recovered at half-reaction using the latter initiator would be 50 % instead of 30 % with the $ZnEt_2$/(R)DMBD system. The bulkiness of substituents in the 1,2-diols favorably influences the stereoelectivity as it was shown in the case of methylthiirane (10). However this factor cannot explain the more than doubled value of r as compared with r = 2.3 found for 3-methyl 1,2-butanediol or 3,3-dimethyl 1,2-butanediol.

The isotactic diad content of polymers obtained with $ZnEt_2$/MPD system is quite similar to that of polymers prepared with $ZnEt_2$/(R)DMBD system. Thus we must consider that the asymmetric centre in the alkyl substituent favours a new chiral arrangement of species in the initiator in which S type active sites become much more prevailing.

The behaviour of $ZnEt_2$/MPD system is however somewhat different from that of $ZnEt_2$/DMBD. For example, if (S) enantiomerically enriched methylthiirane (e.e. 35 %) is polymerized with $ZnEt_2$/(2S,3S)MPD, no increase in the stereoelectivity is observed (r = 2.75 calculated from equation (1)) contrary to what is obtained with $ZnEt_2$/(R)DMBD (1). In the present case the stereoelectivity is also depending upon the temperature of preparation and drying of the initiator ; as seen in Table 3,r is greatly decreasing when the temperature is increased. Simultaneously the rate of polymerization and the intrinsic viscosities of prepared polymers are both increasing. A partial racemization of the diol seems to be excluded e.g. a prolonged heating (68hr) of the neat diol at 100°C does not significantly change its optical activity. We rather consider that at higher temperature the arrangement of species and the distribution of the two types (R and S) of sites are probably modified leading to less stereoelective initiator systems.

T A B L E 3

Polymerization of racemic methylthiirane in toluene solution at room temperature using $ZnEt_2$/(2S,3S)MPD (molar ratio 1/1) initiator systems prepared at different temperatures.
$[I]/[M] = 3.8 - 5.2$ mol % ; $[M]_o = 1.6 - 1.7$ M/l

Initiator preparation T°C	Polymerization time in hr	Yield in %	α_D^{25} unreacted monomer	Polymer $[\alpha]_D^{25}$	Polymer $[\eta]$ in dl.g^{-1}	Stereoelectivity ratio r
25	40	33.5	+ 9.82°	-65	0.87	2.65
50	3	35.4	+ 8.60°	-54	1.64	2.2
>50,<70	2.75	46	+ 7.94°	-33	3.73	1.65
≃100	0.5	53	+ 6.7°	-19.5	5.7	1.4

In conclusion, the behaviour of chiral $ZnEt_2$/1,2-diol initiator system is modified by the presence, in the alkyl substituent of the diol, of an additional asymmetric centre located in α-position of the C-O-Zn- bonds. In particular its ability to chiral discrimination is increased when prepared in usual conditions. This finding may be compared with the enhanced stereoelectivity observed in the case of the polymerization, initiated with $ZnEt_2$/(R)DMBD system, of (2RS,3S) 1,2-epoxy 3-methyl pentane (11) involving an asymmetric centre in α-position of the oxirane moiety.

REFERENCES

1. N. Spassky, A. Leborgne, M. Sepulchre, Pure and Appl.Chem. 53, 1735 (1981).
2. M. Goguelin, M. Sepulchre, Makromol.Chem. 180, 1215 (1979).
3. N. Spassky, P. Sigwalt, Bull. Soc.Chim. Fr. 1968, 3541.
4. N. Spassky, A. Leborgne, A. Momtaz, M. Sepulchre, J. Polym.Sci., Polym. Chem. Ed. 18, 3089 (1980).
5. M. Sepulchre, N. Spassky, P. Sigwalt, Macromolecules 5, 92 (1972).
6. M. Sepulchre, N. Spassky, C. Mark, V. Schurig, Makromol.Chem., Rapid Commun. 2, 261 (1981).
7. A. Deffieux, M. Sepulchre, N. Spassky, P. Sigwalt, Makromol. Chem. 175/2, 339 (1974).
8. M. Sepulchre, P. Sigwalt, N. Spassky, IUPAC Int. Symp. on Macromolecules, Dublin, Polymer Proceedings 1, 141 (1977).
9. J. Furukawa, T. Saegusa, S. Yasui, S. Akutsu, Makromol.Chem. 94, 74 (1965).
10. M. Sepulchre, N. Spassky, P. Sigwalt, Isr. J. Chem. 15, 33 (1976-77).
11. M. Goguelin, M. Sepulchre, Makromol. Chem. 180, 1231 (1979).

Accepted March 14, 1985