Preparation of Optically Active Poly β-Propiolactones

I. Polymerization of Racemic α-Methyl α-n-Propyl β-Propiolactone with Zinc and Cadmium Chiral Glycolates

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ABSTRACT

   Racemic α-methyl-α-n-propyl-β-propiolactone is readily polymerized with zinc and cadmium chiral glycolates leading to optically active polyesters. The stereoelectivities observed are lower than for oxiranes and thiiranes with the same initiator system. A value of rotatory power for pure enantiomer α_0 is deduced from NMR measurements in the presence of chiral solvent. The structure of polymers is discussed on the basis of NMR results.

INTRODUCTION

   "Stereoelective" polymerizations are convenient for the preparation of optically active polymers, mainly when enantiomers are not easily available by usual synthetic methods. Racemic monomer mixtures are polymerized using a chiral initiator with a preferential incorporation of one of the enantiomers into the polymer chain and this method was successfully applied in the case of three-membered ring monomers such as oxiranes and thiiranes as reviewed by SEPULCHRE (1976) and SPASSKY (1977).
   Preliminary reports (SPASSKY (1978)) indicate that such a stereoelective procedure could also be applied in the case of a four-membered ring monomer, namely α-methyl-α-n-propyl-β-propiolactone (MPPL).
   Racemic α,α disubstituted β-propiolactones were polymerized using anionic initiators (THIEBAULT (1962), HALL (1969), LENZ (1974)) leading to partially crystalline polymers. Only two preparations of optically active polyesters starting from resolved monomers have been described : JARM and FLES polymerized

α-(p-substituted benzene sulfonamide)-β-lactones, while D'HONDT and LENZ prepared poly(α-ethyl-α-phenyl-β-propiolactone from the corresponding monomer using tetraalkylammonium carboxylates as anionic initiator.

In this paper, various features of the stereoelective polymerization of racemic MPPL using zinc and cadmium glycolates are reported. A determination of optical activity of pure enantiomer α_0 is described. Preliminary results on polymer tacticity are given.

EXPERIMENTAL

MPPL was synthetized according to the method described by FISCHER (1959). Chiral initiators were obtained by reacting diethylzinc or dimethylcadmium with R(-) 3,3 dimethyl 1,2 butanediol (DMBD) or S(+) phenyl 1,2 ethanediol (PED). All polymerizations were run in apparatus sealed under high vacuum according to usual techniques described previously for thiirane polymerizations (DEFFIEUX).

POLYMERIZATION OF MPPL WITH CHIRAL INITIATORS

1 - ZnEt$_2$-R(-) DMBD system

As shown in table I the polymerization in bulk at room temperature of racemic MPPL with ZnEt$_2$-R(-) DMBD system leads to optically active polymers, levorotatory in chloroform solution, the optical activity of which decreases with conversion. All polymers are crystalline with a melting point close to 110°C. At the same time, the unreacted monomer is continuously enriched in levorotatory enantiomer.

According to general rules found for three-membered ring monomers (SEPULCHRE (1976)) one can expect an "homosteric" type process i.e. a polymerization proceeding with a preferential choice of the R enantiomer.

Thus, the residual levorotatory MPPL should be of S-configuration. A negative Cotton effect located at 207 nm which is typical of ester $n \rightarrow \pi^*$ transition was found in the CD spectrum of the monomer.

The magnitude of the choice depends on the polymerization temperature. As shown in Fig. 1, the rotatory powers α_m of residual monomers increase when polymerizations were carried out at a lower temperature (-10°C). Such an effect may be explained by a stronger coordination of the chosen enantiomer at low temperature.

The rates of polymerization observed for MPPL, based on conversion at a given time, are lower as compared with monosubstituted thiiranes, but much higher than those of oxiranes polymerized with the same initiator.

It should be also pointed out that the usual stereospecific initiator ZnEt$_2$-H$_2$O shows a very low efficiency for MPPL polymerization (19 % conversion in two weeks at room temperature)

TABLE 1

POLYMERIZATION OF RACEMIC MPPL WITH $ZnEt_2$/R(-) DMBD
INITIATOR SYSTEM IN BULK AT ROOM TEMPERATURE

Initiator prepared by reacting components 2 hr
at room temperature.

C/M moles %	Time polym. (hr.)	Yield (%)	Unreacted monomer α (neat,dm)	Polymer $[\alpha_p]$ (CHCl$_3$)
4.8	24	17	− 0.41	− 2.4
7.5	24	22.4	− 0.69	− 1.6
8.6	14	42	− 0.94	− 1.2
5.6	32	49	− 0.47	− 1.7
8.4	24	61	− 1.29	− 0.6
7.8	50	79	− 4.35	− 0.5
7.3*	29	87	− 4.80	$\sim$ 0

*) initiator prepared by reacting components 2 h
at 80°C.

2 - $ZnEt_2$-S(+) PED system

As expected in this case the S type enantiomer
is preferentially incorporated into the polymer chain, the re-
sidual monomer being enriched in dextrorotatory enantiomer.
For example at 5 % conversion one obtains α_m = + 0.66 (neat,
dm) and $[\alpha_p]$ = + 3,4 (C = 0.4, CHCl$_3$). The residual monomer
(α_m = + 0.66) was polymerized again using the $ZnEt_2$-R(-)DMBD
system of opposite chirality and after 23,6 % conversion the
unreacted monomer showed an optical activity of α_m = − 0,19
(neat,dm) which clearly indicates that again in the latter
case dextrorotatory enantiomer is preferentially consumed.

3 - $CdMe_2$-R(-)DMBD system

MPPL is very easily polymerized with this ini-
tiator system as shown in Table 2. The residual monomer is
dextrorotatory, which corresponds to the preferential choice
of levorotatory enantiomer during the polymerization process.
Such a behaviour, i.e. inversion in enantiomeric choice as
compared to zinc initiator, was previously observed in the case
of thiiranes and has been explained by the predominance in the
cadmium initiator of alkylalkoxide type species over the dial-
koxide one (SEPULCHRE (1976)). This corresponds to the so-
called "antisteric" process, i.e. the enantiomer of configura-
tion opposite to that of the chiral initiator is preferen-
tially chosen.
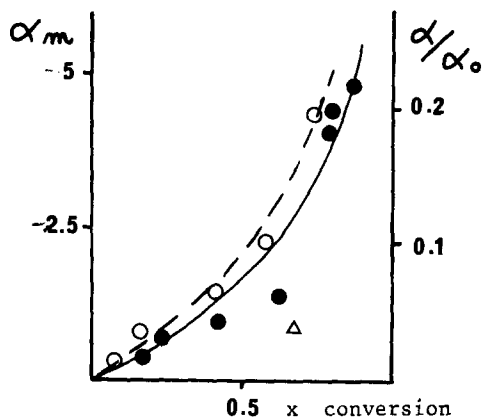
α_m

α/α_o

Fig. 1 Dependence of the rotatory power and the
optical purity of unreacted monomer on the conversion.
Experimental data of polymerizations carried out at :
   O - 10°C   ● room temp.   Δ 80°C

Theoretical curves : — — r = 1.35   ——— r = 1.25

TABLE   2

POLYMERIZATION OF RACEMIC MPPL IN BULK
WITH Me$_2$Cd/R(-)DMBD INITIATOR SYSTEM.

C/M	Time	Temperature	Yield	Residual monomer α_m
(mole %)	(hours)	(°C)	(%)	(neat, dm)
8.5	24	- 4	24.4	+ 0.06
7.5	42 / 24	- 5 / -30	73.5	+ 0.71

It must be recalled that cadmium initiators were unable
to polymerize oxiranes, while they readily initiate the polymeri-
zation of MPPL.
   The optical activities of residual monomers are lower at
corresponding conversions than with the zinc alkoxide initiator.

In order to evaluate the magnitude of the choice one must know the optical activity α_0 of a pure enantiomer. The latter has not yet been synthetized and therefore indirect methods should be used, such as NMR studies in the presence of chiral agents.

OPTICAL PURITIES (α/α_0) OF MPPL ENANTIOMER MIXTURES

The optical purities of enantiomerically enriched MPPL monomers were determined by high resolution ^{1}H NMR at 250 MHz in the presence of optically active chiral alcohol namely (-)2,2,2 trifluoro 1 naphtyl ethanol. This reagent was already used by PIRKLE for enantiomeric purity determinations, although the same author chose the anthryl derivative in the case of γ-lactone determinations. Spectra of racemic and enantiomerically enriched MPPL monomers were run in CCl_4 solution in the absence and in the presence of the chiral alcohol. The protons H_A and H_B of methylene cyclic group and those of methyl substituent were found to show non-equivalence. The singlet signal of methyl protons becomes a doublet with a shift of 3,25 Hz ($\Delta\delta$ = 0,013 ppm) the upfield signal being higher in the case of levorotatory monomer.
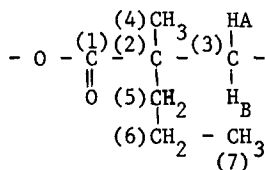
Enantiomeric purity is easily obtained from integration of signals and according to our findings α_0 of a pure (S)(-)MPPL should be equal to - 22° ± 2° (neat, dm).

Configurational correlations related to field position of peaks are presently under study.

NMR STUDIES ON POLYMERS

In our previous paper (SPASSKY (1978)) we reported that we have not observed any stereosensitivity in ^{13}C NMR spectra at 25,12 MHz in $CDCl_3$ solution. All carbons gave only one single peak.

Presently working at 50,29 MHz in the same solvent, we have found that the methylene chain carbon C(3) and the methyl carbon C(4) appear as doublets, the former being substantially resolved ($\Delta\delta$ = 0,10 ppm). Chemical shifts observed (in ppm from Me_4Si) : C(1) = 174.21 ; C(2) = 46.26 ; C(3) = 68.84 and 68.74 ; C(4) = 19.76 and 19.71 ; C(5) = 38.04 ; C(6) = 17.43 ; C(7) = 14.30

$$- O - \overset{(1)}{\underset{\overset{\|}{O}}{C}} - \overset{(2)}{\underset{\overset{|}{(5)CH_2}}{C}} \overset{(4)CH_3}{-} \overset{(3)}{\underset{\overset{|}{H_B}}{C}} \overset{HA}{-}$$

$$(6)CH_2 - CH_3 \quad (7)$$

In the case of the optically inactive polymer prepared by anionic initiator both peaks of the $C_{(3)}$ doublet are equiva-

lent, while a substantial difference in magnitude is observed in the optically active polymer (Fig. 2). The downfield peak increases with the rotatory power of the polymer and therefore can be assigned to an isotactic enchainment, the upfield peak corresponding to a syndio-dyad. These findings support the presence of both types of enantiomeric units in the polymer chain and in the case of optically inactive polymers a statistical distribution of both types of dyads, iso and syndio, is found. This is in disagreement with a pure syndiotactic structure recently proposed for the crystalline part of the polymer on the basis of crystallographic determinations (MARCHESSAULT (1978)). No predominance of syndiotactic dyads were found in anionically initiated optically inactive polymers. Presently we are studying the correlation between optical activity and tacticity in various polymers prepared by stereoelective procedures.

The same polymers were also examined by ^{1}H NMR at 250 MHz in orthodichlorobenzene solution at 110°C. Protons H_A and H_B of the methylene chain group appear as the most stereosensitive giving a well resolved pattern of 6 to 8 peaks (Fig. 3). As may be seen, when going from the optically inactive polymer to an optically active one ($|\alpha_D|$ = + 3,4 ($CHCl_3$)). Again, a dyad effect (a quadruplet for each proton) is observed, which confirms the conclusions of the ^{13}C NMR analysis.

DISCUSSION

From the experimental data reported above it appears that zinc and cadmium chiral glycolates are convenient initiators for the stereoelective polymerization of MPPL.

The determination of the rotatory power α_o of optically pure MPPL (α_o = 22° (neat, dm)) by a NMR chiral solvent method allowed us to obtain informations on the magnitude of the stereoelection, during the polymerization.

According to the shape of the stereoelective curve (Fig. 1 α/α_o versus conversion) the resolution kinetics follow the so-called "first-order law" (SEPULCHRE (1977)) which corresponds to the theoretical equation

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

where α/α_o is the optical purity of unreacted monomer at a given conversion x and r the stereoelectivity ratio corresponding to the preference of the initiator for one enantiomer.

The experimental data obtained at − 10°C and at room temperature with zinc initiator seem to fit well with theoretical curves corresponding to values of r equal respectively to 1.35 and 1.25 (Fig. 1). These values are lower than those usually observed for oxiranes and thiiranes with the same initiator (SEPULCHRE (1976) SPASSKY (1977)). Although stereoelectivity seems to depend on the temperature, the experimental data are not consistent with a
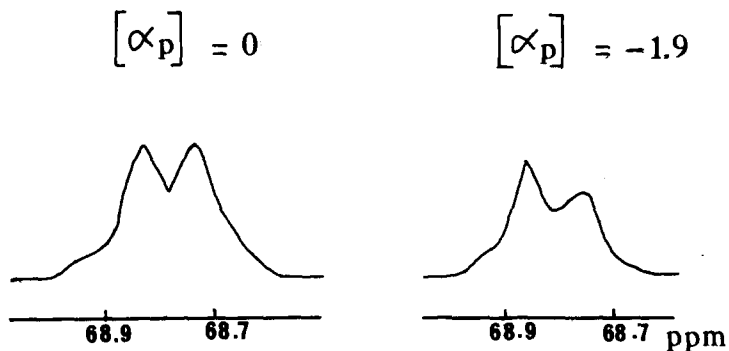
$$\left[\alpha_p\right] = 0 \qquad\qquad \left[\alpha_p\right] = -1.9$$

Fig. 2. Enlarged signals of methylene chain carbon C(3) in ^{13}C 50,29 MHz NMR spectra of poly MPPL prepared by anionic ($\left[\alpha_p\right] = 0$) and stereoelective ($\left[\alpha_p\right] = -1,9$) initiation. (taken in CDCl$_3$ at 25°C, in ppm from TMS).
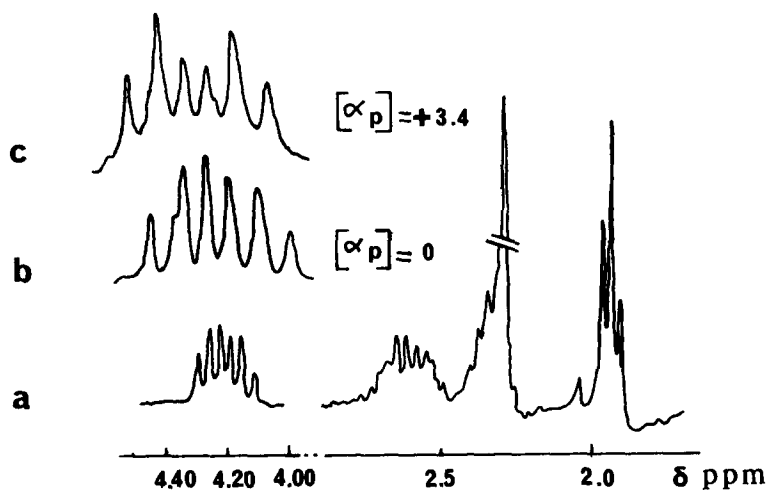

Fig. 3. ^{1}H 250 MHz NMR spectra of poly MPPL taken in O-dichlorobenzene solution at 110°C.
a. full spectrum of anionically initiated poly MPPL.
b. enlarged area of methylene protons of the chain in the previous spectrum
c. enlarged area of methylene protons of a stereo-elective type poly MPPL ($\left[\alpha_p\right] = +3,4$).

"second-order" kinetics (SEPULCHRE (1976)).

Other features of the stereoelective polymerization in dicate that MPPL has an original behaviour intermediate between the different classes established for the three-membered ring monomers.

Similarly to methyl thiirane, but contrarily to methyl-oxirane, MPPL is easily polymerized with cadmium glycolate according to the so-called "antisteric" process. On the other hand, the dependence of stereoelectivity on temperature is comparable with the behaviour of thiiranes with bulky substituents. Thus, more informations are necessary in order to propose a mechanism coherent with all the stereochemical features observed.

All the polymers we have prepared showed some degree of cristallinity, but the origin of the latter is still subject of discussion. According to NMR results no particular stereoregular structure was identified, in the non optically active polymers, for which a statistical distribution of enantiomeric units in the polymer chain seems probable.

Studies are now in progress in order to prepare polymers of high optical purities for structural determinations and further studies of physical properties.

Recent investigations indicate that the stereoelective procedure can be also applied to the case of other α and β substituted β-propiolactones which are presently under study.

REFERENCES

DEFFIEUX,A., SEPULCHRE M., SPASSKY N. and SIGWALT P.
    Makromol. Chem. 175/2, 339 (1974)
D'HONDT C. and LENZ R.W., J. Polymer Sci., Polymer Chem. Ed.,
    16, 261 (1978)
FISCHER N., Thèse d'Ingénieur Docteur, Paris (1959)
HALL H.K., Jr., Macromolecules 2, 488 (1969)
JARM V. and FLES D., J. Polymer Sci., Polymer Chem. Ed.,
    15, 1061 (1977)
LENZ R.W., Glasn. Khem. Drushtva Beograd, 39, 395 (1974)
MARCHESSAULT R.H., St PIERRE J., DUVAL M. and PEREZ S.
    Macromolecules 11, 1281 (1978)
PIRKLE W.H., SIKKENGA D.L. and PAVLIN M.S.
    J. Org. Chem. 42, 384 (1978)
SEPULCHRE M., SPASSKY N. and SIGWALT P.
    Israel J. of Chem., 15, 33 (1976)
SPASSKY N., in Ring-Opening Polymerization, T. Saegusa and
    E.J. Goethals Ed., ACS Symposium Series n°59,p.191(1977)
SPASSKY N., LEBORGNE A., REIX M., PRUD'HOMME R.E., BIGDELI E. and
    LENZ R.W., Macromolecules 11, 716 (1978)
THIEBAULT R., FISCHER N., ETIENNE Y. and COSTE J.
    Ind. Plast. Mod. 14 (2), 1 (1962)