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Polymerization of γ-Benzyl Glutamate NCA with a Chiral Quaternary Ammonium Acetate

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SUMMARY :

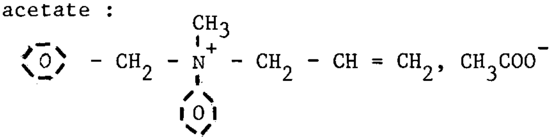
The polymerization of γ-benzyl D-, L-, and DL-glutamate NCA by d- and dl- methylallylbenzylphenyl ammonium acetate in dioxane was studied by a kinetic method and by the optical activity, IR and X-ray analyses of the resulting polymer. The kinetic data evidenced a high enantioseletivity in the polymerization and the polymer presented a good stereoregularity. There is no enantioelection. The chirality of the cation might have some influence on the selection but is not a predominant factor. The results were discussed on the basis of the NCA anion mechanism.

INTRODUCTION :

4 species take part in the polymerization of NCAs when the NCA anion mechanism ("activated monomer" mechanism) operates[1] : 1) the monomer; 2) the NCA anion; 3) the tadpole-type growing chain; 4) the catalyst whose cation, when the catalyst is ionic, would be always held close to the ionized monomer or the growing chain.

Among these 4 species, the last 2 ones might induce a stereochemical regulation. The present work deals with the part played by the catalyst, and more specifically with the influence of the chirality of the counter-ion on the stereochemical regulation in the polymerization of NCAS.

In this purpose we have previously synthesized dl- and d- methylallylbenzylphenyl ammonium acetate[2], which will be denoted by dl- or d-MABP acetate :



$$\langle O\rangle - CH_2 - \overset{CH_3}{\underset{\langle O\rangle}{N^+}} - CH_2 - CH = CH_2,\ CH_3COO^-$$

This compound has been chosen for various reasons :

1) The quaternary ammonium cation has a pecularly well defined asymmetry; 2) Contrary to a lot of ionic asymmetric species, the asymmetric center is the atom bearing the charge; 3) The acetate anion is not excessively basic, which prevents the cation from being decayed and the monomer from a possible racemization; 4) The polymerization induced by this catalyst is considered to be mainly due to the NCA anion mechanism[1,3].

Recently, PENCZEK and VOGL'S groups[4,5] synthesized a similar catalyst for the polymerization of chloral and β-propiolactone. Previously, SUZUOKI et al.[6] have used quaternary ammonium acetates (N-methyl-N-alkyl-α, α-dimethylpyrrolidinium acetate and N,N-dimethylpipecolinium acetate) whose nitrogen atom or the substituent on the nitrogen atom were asymmetric but which were not optically active. They observed that the disymmetry more than the asymmetry has an influence on the stereoregularity of the recovered poly-DL-alanine.

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EXPERIMENTAL RESULTS

γ-benzyl glutamate NCA (denoted by GBG-NCA) was polymerized in dioxane at 20°C. We carried out 6 experiments : DL-GBG-NCA was polymerized with d-MABP acetate (exp. 1), DL-GBG-NCA with dl-MABP acetate (exp. 2), L-GBG-NCA with d-MABP acetate (exp. 3), L-GBG-NCA with dl-MABP acetate (exp. 4), D-GBG-NCA with d-MABP acetate (exp. 5), D-GBG-NCA with dl-MABP acetate (exp. 6).

For each experiment, the conversion of monomer was kinetically followed (fig. 1). The reproducibility can be considered to be fairly good, as evidenced by exps. 3,4,5,6.

a) Exps. 3,4,5,6 are much faster (about 10 times as much at the initial time) than exps. 1 and 2. This means that the presence of D-GBG-NCA hinders the polymerization of L-GBG-NCA.

b) In exps. 3 and 4, the kinetic data of the 2 polymerizations are identical.

c) In exps. 1 and 2, the kinetic data of the 2 polymerizations are close (although not identical).

d) In exps. 5 and 6, the kinetic data of the 2 polymerizations are very close.

e) In exps. 3 (or 4) and 5 (or 6), the kinetic data of the 2 polymerizations are very close.

f) Exp. 1 : the polymer recovered after a conversion of 35 % (gravimetric determination) gave no optical rotation.

The selection that we observe kinetically, was confirmed by the analysis of the polymers resulting from exps. 1 and 2, respectively denoted by "polymer I" and "polymer II", by IR spectroscopy according to AKAIKE et al.'s studies[7] and by X-ray diffraction.

IR data are reproduced on fig. 2 and X-ray patterns on fig. 3.

The stereoregularity of polymer I is high and of about 85 % (and maybe greater) according to our IR data. The X-ray diffraction confirms that this polymer is similar to a reference sample made from 50 % poly-D-GBG and 50 % poly-L-GBG. If our polymer is not a mixture of this type, at least it contains long poly-L-GBG and poly-D-GBG stereoblocks.

This result alone is interesting because there are few catalysts in the polymerization of NCAs, leading to a high stereoregularity, apart from nickel dl- (or d-) 2-methylbutyrate -tri-n-butylphosphine used by TANI et al.[8], triethylaluminium-(+) borneol complex used by TSURUTA et al.[9] and the previously mentioned catalysts used by SUZUOKI et al.[6]

On the contrary, polymer II is less stereoregular (around 65 % and maybe greater). The diffraction of X-rays shows that it is different from the reference sample made from a 50/50 mixture of poly-L-GBG and poly-D-GBG.

DISCUSSION

It is worth noting that the NCA anion mechanism involves an ionized ("activated") monomer and an electrically neutral polymer chain end instead of a permanently charged chain end and a neutral monomer.

We assume 1) that the polymerizations are contaminated to the same extent by secondary reactions and 2) that any way these reactions are not too much frequent, at least at the outset of the reaction. Then, the kinetic study shows off several interesting aspects of the polymerization.

First, as the initial rate of polymerization is much higher for chiral monomers than for the racemic monomer, we can assert that a stereoregulation operates in this polymerization.

Second, the kinetic data of the polymerization are identical or close for the optically pure salts and the racemic ones. Hence, the stereochemistry of the cation is primarily not involved in the polymerization.

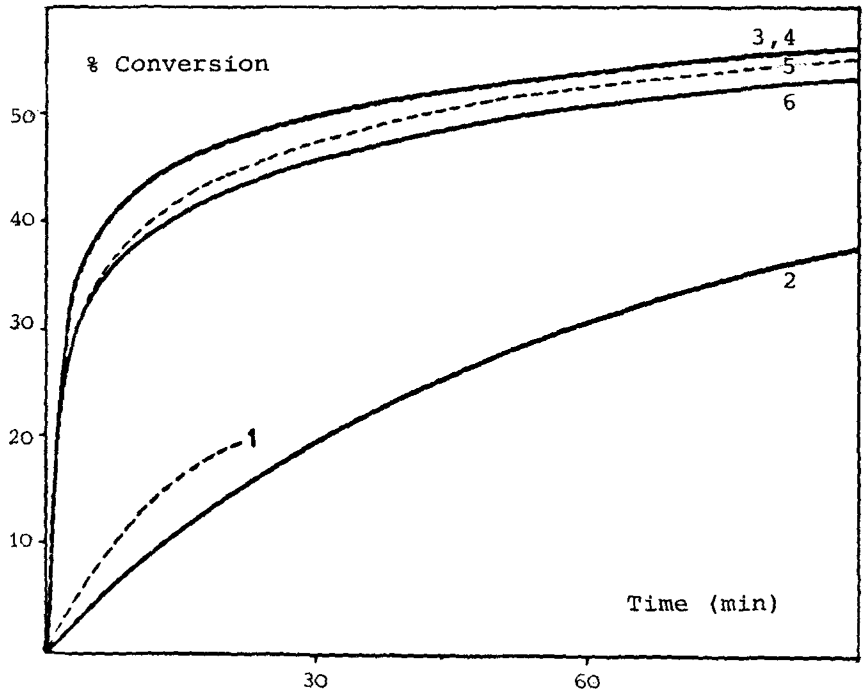
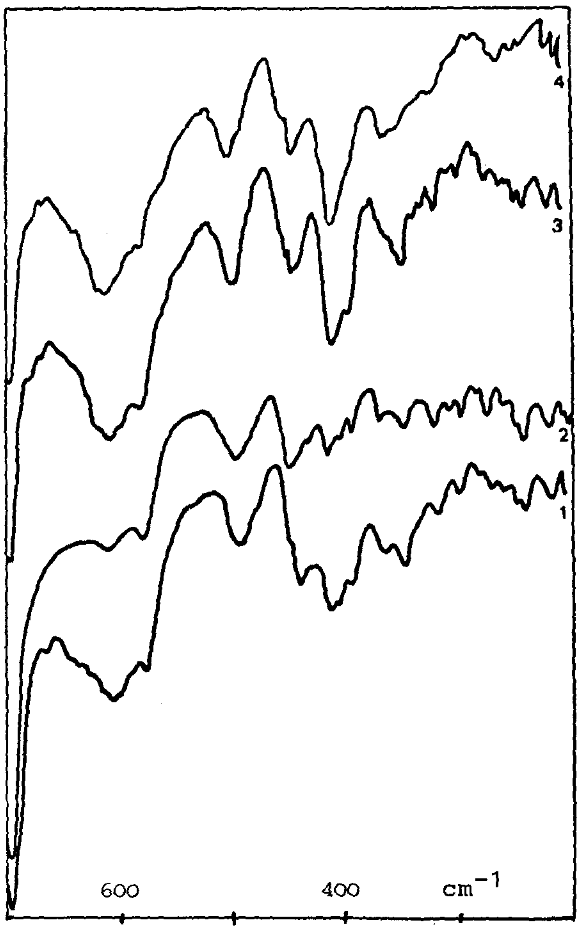


Figure 1:
Polymerization of DL-, L- and D-GBG-NCA by d- and dl-MABP acetate
Exp. 1: DL-GBG-NCA + d-catalyst Exp. 2: DL-GBG-NCA + dl-catalyst
Exp. 3: L-GBG-NCA + d-catalyst Exp. 4: L-GBG-NCA + dl-catalyst
Exp. 5: D-GBG-NCA + d-catalyst Exp. 6: D-GBG-NCA + dl-catalyst
Polymerization conditions: [NCA] : 0.08 mol/l in dioxane
[NCA]/[Catalyst] : 8 % (mol/mol). Temperature : 20° C

Figure 2: IR data 1: polymer I 2: polymer II →
3: poly-L-GBG 4: poly-L-GBG + poly-D-GBG (1:1)



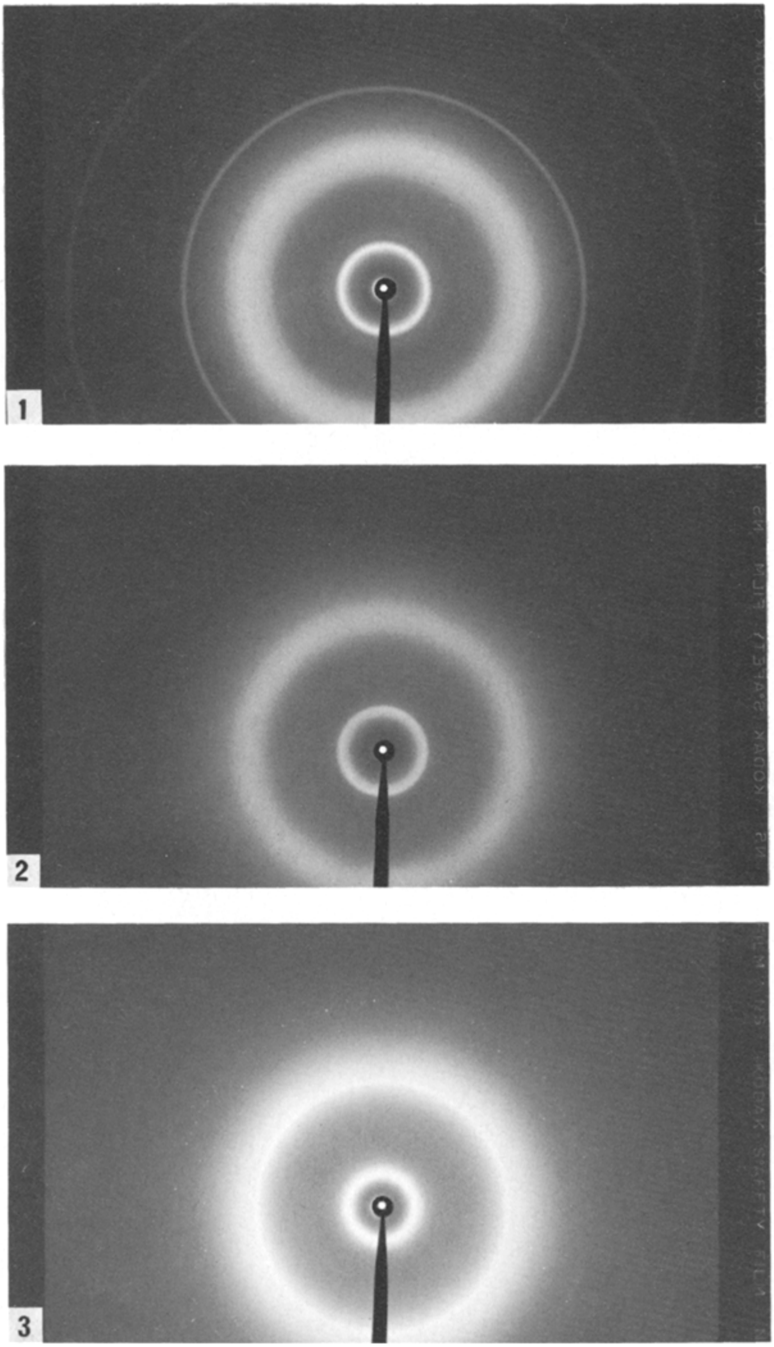


Fig. 3 : X-ray diffraction patterns : 1 : poly-L-GBG + poly-D-GBG (1:1) (The thin lines are due to internal standards of KCl and NaCl), 2 : polymer I, 3 : polymer II.

Consequently we are led to consider that the growing chain end controls alone the enantioselection, with possible participation of penultimate units.

In our recent work using catalysts having no asymetric center (sodium acetate, tetrabutylammonium acetate) as well as preformed polymers, which will be published separately, we obtained similar results as to the part played by the growing chain end. These results together with the above results evidence that the counter-ion does not participate in the stereoregulation.

However, the counter-ion can be considered to be located more or less close to the growing chain end constituted by three carbonyl groups, during the propagation, as it was pointed out for the similar case of the lactam polymerization[12].

Hence, the non-participation of the cation in the enantioselection can be interpreted either by the weakness of the interaction between the cation and the chain end or by the weakness of interaction between the NCA anion and the bulky ammonium cation or also its unsuitable size or shape for selection. Any way, the effect of the cation is considered to be so weak (if not inexistant) that the chain end effect conceals it completely.

On the other hand, the kinetic study reveals that no enantioelection occurs under the present conditions : if it were the case, the D-NCA (exps. 5, 6) and the L-NCA (exps. 3,4) would not polymerize with the same rate. This was confirmed by the measurement of the optical activity of polymer I. Again, the unfitness of the cation for stereoregulation in the propagation is confirmed.

However, the analysis of the recovered polymer leads us to consider that the stereoregularity varies with the catalyst employed : smaller for polymer II than for polymer I.

This is consistent with the small discrepancy observed between the curves 1 and 2, but not with the other kinetic data (equality of the rate of polymerization of monomer D and L with either cation). Hence our partial results do not allow us to know at this stage whether and how the chirality of the cation is actually involved in the enantioselection which is mainly controled by the growing chain end with or without the participation of penultimate units.

EXPERIMENTAL

Reagents :

D-, L- and DL-GBG-NCA were prepared according to IKEDA and SMETS' procedure[10]. The NCA was repeatedly recristallized in a mixture of ethyl acetate and petroleum ether (b.p. 40-65° C) until the chlorine content was less than 0,1 mol. %.

d- and dl-MABP acetate were prepared as described in ref. 2.

Dioxane was repeatedly dried and distilled over sodium until water content was less than 20 ppm by Karl-Fisher titration.

Measurements :

The polymerization was carried out by the addition of a solution of the NCA in dioxane to a solution of the catalyst by the same technique as described in ref. 11 and was followed by volumetry at constant pressure.

Polarimetric measurements were made with a Perkin-Elmer 241 polarimeter, with polymer I dissolved in trifluoroacetic acid.

IR spectroscopic data were obtained with a Perkin-Elmer 225 spectrophotometer, in the region 700-200 cm^{-1}. The polymer was dissolved in chloroform and was cast into a film on a cesium iodide disc.

X-ray diffraction was performed on the dry-frozen polymer in an Anton Paar A-8054 Graz apparatus.

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