

## **Mechanism of the Anionic Polymerization of Lactones, Initiated by Intercalation Graphite Compounds**

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### **SUMMARY**

The anionic polymerization of  $\beta$ -propiolactone (PL)-oxethane-2-one, pivalolactone (PVL) - 3,3-dimethyloxethane-2-one and  $\epsilon$ -caprolactone (CL) - oxepane-2-one, initiated by binary and ternary intercalation compounds (IC) of lithium and potassium in graphite is investigated. The polymerization is carried out in bulk or in xylene. It is established that the lactones penetrate in IC and polymerize in their interlayer spacings. The polymerization causes a delamination of IC. High polymers of the lactones can be obtained by the action of some IC investigated.

### **INTRODUCTION**

It is known that in the homogeneous anionic polymerization of CL polymer products with molecular masses about 10 000 are obtained, only when the monomer concentration is above a determined critical value (DEF-FIEUX AND BOILEAU 1976, ITO ET AL. 1977, ITO AND YAMASHITA 1978). In all cases the polymers are accompanied by cyclic oligomers (dimers, trimers etc.), which are result of intra- and intermolecular transesterifications.

Recently it was established that IC of the alkali metals initiate the polymerization of a great number of vinyl and cyclic monomers (PANAYOTOV AND RASHKOV 1972, 1973; PANAYOTOV ET AL. 1975). In the process of our investigations it was announced by MAZIER ET AL. (1980) that in tetrahydrofuran (THF) or toluene (Tol) high polymers from CL were obtained under the action of some IC. The determination of the molecular masses of the polymers obtained was made however after precipitation in diethyl ether. In this way the low molecular fractions were removed by the solvent. It was interesting to prove directly that the lactone polymerization proceeds in the interlayer spacings of IC. For this purpose the polymerization of PL, PVL and CL was investigated. It was initiated by IC of lithium and potassium -  $\text{LiC}_{12}$ ,  $\text{KC}_8$ ,  $\text{KC}_{24}$ ,  $\text{KHgC}_8$ ,  $\text{KC}_{28}$  DMSO and

KC<sub>24</sub>DME<sub>2</sub> (DMSO - dimethylsulfoxide, DME - dimethoxyethane). We also tried to find conditions under which minimum oligomer products from CL would be formed.

### EXPERIMENTAL

The binary and ternary IC were prepared from Madagascar graphite (MG) with particle size 100-125  $\mu\text{m}$  or from highly oriented pyrolytic graphite (HOPG) with plate size 5 x 4 x 0,3 mm  $\pm$  0,05 mm in vacuo according to HEROLD (1955), MAKRINI ET AL. (1980) and RASHKOV (to be published). The polymerization was carried out in vacuo and terminated with 0,1 N HCl. The products obtained were isolated by solvent evaporation and investigated by GPC. The dilatometric measurements were performed with KC<sub>24</sub> (HOPG) in vacuo. The increase of the plate thickness was determined along the "C" axis.

### RESULTS AND DISCUSSION

#### A. Polymerization in bulk

In the bulk polymerization, initiated by IC (20°C, 8 hours, MG) the polymer yield decreases in the following order: CL (80-100 %), PL (70-80 %) and PVL (10-20 %). The yield does not significantly depend on the interlayer distance or on the nature of the intercalated in IC organic molecule (Table 1). It is influenced by the granulometry of IC. For instance, when KC<sub>24</sub> (MG) is used, the polymer yield from PL after 8 hours is 80 %, while for KC<sub>24</sub>(HOPG) it is lower than

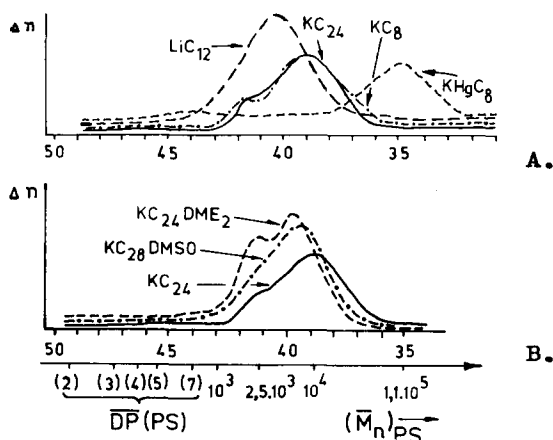
TABLE 1  
Bulk polymerization of CL under the action of IC  
(20°C, 8 hours, MG, [CL] : [KI] = 90)

Initiator	Interlayer distance (Å)	Yield (%)	$\bar{M}_n$ (GPC)	$\bar{M}_w$ (GPC)	$\bar{M}_w/\bar{M}_n$
LiC <sub>12</sub>	3,7 <sup>a)</sup>	94	2700	7500	2,7
KC <sub>8</sub>	5,4 <sup>a)</sup>	77	4900	12600	2,6
KC <sub>24</sub>	5,4 <sup>a)</sup>	98	5400	11100	2,1
KHgC <sub>8</sub>	10,2 <sup>b)</sup>	100	39600 <sup>c)</sup>	114000	2,9
KC <sub>28</sub> DMSO	7,4 <sup>d)</sup>	84	3500	7400	2,2
KC <sub>24</sub> DME <sub>2</sub>	12,0 <sup>e)</sup>	94	2700	5600	2,0

a) NOVIKOV AND VOL'PIN (1971); b) MAKRINI ET AL. (1980)  
c) determined in o-dichlorobenzene because of the polymer insolubility in THF; d) RASHKOV (to be published); e) MERLE ET AL. (1978).

47 % after 24 hours.  $\bar{M}_v$  of the polymer obtained is 103 000 (determined in chlproform at 35°C according to the equation  $[\eta] = 4,2 \cdot 10^{-4} \cdot \bar{M}_v^{0,7}$  SHIOTA ET AL. 1967).

It should be noted that the poly-CL has the lowest molecular mass for the initiator with the smallest interlayer distance, and on the contrary it has the highest molecular mass for the initiator with the greatest interlayer distance (Table 1, Figure 1). But the great interlayer distance in the ternery IC  $KC_{28}DMSO$  and  $KC_{24}DME_2$  has not influenced the molecular masses of the polymers obtained and they are close to these, obtained with initiators  $LiC_{12}$  and  $KC_8$ . A well expressed monomodal molecular mass distribution (MMD) is observed only when  $LiC_{12}$  or  $KHgC_8$  are used (Figure 1 A.). Taking into account the high molecular mass of the poly-CL obtained with initiator  $KHgC_8$  and the lack of low molecular products, it may be assumed that the transesterification and the other destruction reactions are hampered to a great extent.

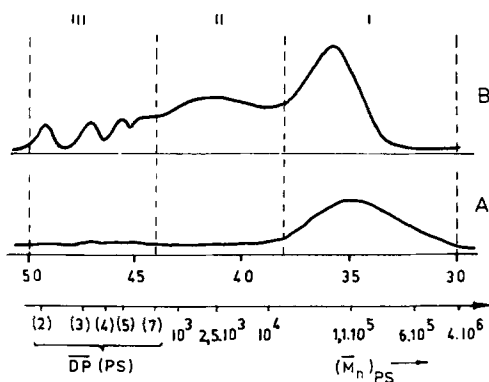


**Figure 1:** MMD of poly-CL, obtained in the bulk polymerization under the action of IC with different interlayer distance.

### B. Polymerization in solution

As a reaction medium xylene was preferred, because of its slower penetration into IC than THF and Tol. Xylene has lower polarity than CL and is a good solvent for the polymer obtained. During the polymerization in solution (20°C,  $[\text{monomer}] = 0,49 \text{ mol/l}$ ) the polymer yields were the same like these in the bulk polymerization, but the molecular masses of the polymers were considerably higher ( $\bar{M}_n \sim 100 \text{ 000}$ ). The molecular mass and MMD change with the time during the polymerization. When the initiator is  $KC_{24}$  (MG) the polymer, isolated from the reaction mixture after the

second hour of the reaction, has high molecular mass with monomodal MMD and trifle amounts of oligomers (Figure 2 A.). The polymer, isolated after the eighth hour is a mixture of oligomers (Figure 2 B.III), low molecular products and high polymers (Figure 2 B.II and B.I). If the polymer, obtained after 8 hours, is precipitated in diethyl ether, the oligomer fraction disappears in the GP-chromatogram. The same happens with the low molecular mass fraction, but according to MAZIER ET AL. (1980) MMD is bimodal. We found that in ether about 40 % of the polymerization products are dissolved. In the same way from the polymer, isolated after the second hour only about 10 % of low molecular products and oligomers are separated.



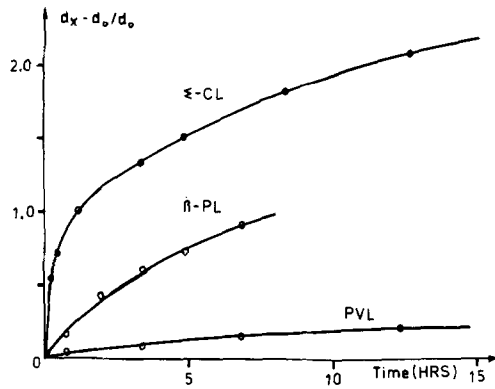
**Figure 2:** Dependence of MMD of poly-CL on the reaction time. Polymerization in solution (20°C, xylene,  $[CL] = 0,49 \text{ mol/l}$ ,  $[CL] : [K] = 68$ ).

A. Polymerization time 2 hours.

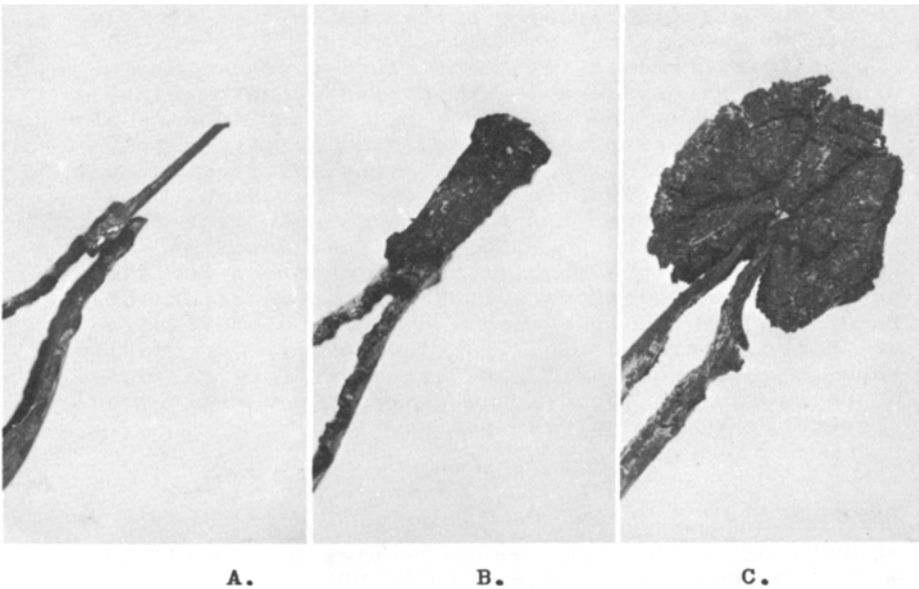
B. Polymerization time 8 hours.

### C. Changes in IC during the interaction with lactones

Contacting with lactones, the binary and ternary IC change their characteristic colour from golden yellow ( $KC_8$ ) and dark blue ( $LiC_{12}$ ,  $KC_{24}$ ,  $KC_{24}DME_2$ ) to black. As a result of the interaction with lactones IC undergo increase of their size along the "C" axis (Fig. 3). It should be noted that the thickness increasing rate of IC decreases in the same order as the polymer yield of the investigated lactones decreases during the bulk polymerization. When IC interacts for a long time with lactones, delamination of the initiator takes place, which is so great that it can be really observed with naked eye (Figure 4).



**Figure 3:** Time dependence of the IC thickness along the "C" axis of  $KC_{24}$  (HOPG) on interaction with lactones.



**Figure 4:** Infringements in the lamellar structure of  $KC_{24}$  (HOPG) under different polymerization conditions:

- A.  $KC_{24}$  (HOPG)
- B.  $KC_{24}$  (HOPG) after an interaction with xylene solution of CL ( $[CL] = 0,49 \text{ mol/l}$ ; 24 hours)
- C.  $KC_{24}$  (HOPG) after an interaction with CL (24 hours)

## CONCLUSIONS

Because of their high dielectric constants the lactones penetrate with high rate in the interlayer spacings of IC. In this way the reorganisation of the crystalline structure is prevented and probably this is leading to an infringement of the lamellar structure of IC in the initial stadium. When the interlayer distances are small these infringements will be considerable. This decreases the probability the propagating living end to remain immobilized between the graphite layers. Thus the decomposition reactions of the macromolecules will be enhanced. Indeed, the initiators with small interlayer distance -  $\text{LiC}_{12}$ ,  $\text{KC}_8$  and  $\text{KC}_{24}$  give polymers with low molecular masses. When initiators with greater interlayer distances are used, the preparation of polymers with higher molecular masses is possible. This suggestion was confirmed in the case of  $\text{KHgC}_8$ . The presence of organic molecules, which solvate the potassium in the ternary IC  $\text{KC}_{28}\text{DMSO}$  and  $\text{KC}_{24}\text{DME}_2$  is a possible reason for the low molecular masses of the polymers obtained, inspite of the great interlayer distances in these initiators.

The infringements in the lamellar structure are avoided to a considerable extent in the polymerization of CL in xylene (Figure 4 B.). After 2 hours of such polymerization we isolated high molecular poly-CL with 97 % yield. It contained insignificant amount of low molecular fractions. On the other hand, the changes in MMD after the second hour show that the polymer chains, though slowly, diffuse into the solution, where all the conditions are apparent for the decomposition reactions to take place. Reactions of this kind for the homogeneous anionic polymerization of CL are described by ITO ET AL. (1977). Our results show, that the use of IC as initiators for the lactone polymerization shifts the ring-chain equilibrium preferably to the polymer chains.

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