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Soluble Bimetallic μ-Oxoalkoxides. IX. ϵ-Caprolactone and β-Propiolactone Block Copolymerization

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Synopsis

The fast and living ring-opening polymerization of lactones by bimetallic μ-oxoalkoxides in homogeneous organic phase has led to successful block copolymerization. The catalyst is coordinatively associated in organic media; however, interaction with lactones can induce, following their nature, different rearrangements of the catalytic aggregates, depending on the nature of these lactones. Consequently, ϵ-caprolactone and β-propiolactone block copolymers are quantitatively obtained only in the presence of a completely dissociated catalyst.

INTRODUCTION

In previous papers,[1–7] the catalytic behavior of bimetallic μ-oxoalkoxides in lactone-opening polymerization has been analyzed. These compounds have the general formula I:

$$(\mathrm{RO})_{p-1}\text{—}\mathrm{M}_2^{(p)}\text{—O—}\mathrm{M}_1^{(\mathrm{II})}\text{—O—}\mathrm{M}_2^{(p)}\text{—}(\mathrm{OR})_{p-1}$$

where the nature of metals $\mathrm{M}_1^{(\mathrm{II})}$ (Zn, Co, Mo, Fe, Cr, Mn), $\mathrm{M}_2^{(p)}$ ($\mathrm{Al}^{\mathrm{III}}$, $\mathrm{Ti}^{\mathrm{IV}}$) and alkoxide groups (practically any *n*-, *sec*- or *tert*-alkoxy group) can be easily modified. The principal characteristic of these compounds is their high solubility in different organic media due to their coordinative association.[3,5,7] The mean size of these aggregates is largely controlled by the catalyst composition, the temperature variations, and the presence of an additional organic ligand; for example, a stoichiometric amount of alcohol is sufficient to dissociate the catalyst completely.

The bimetallic μ-oxoalkoxides are highly active catalysts in the lactone-opening polymerization; the chain growth process obeys a very simple coordinative insertion of the monomer into the $\mathrm{M}_2^{(p)}$—OR bond, due to a selective acyl–oxygen cleavage of the lactone ring.[2,3,5,6] The propagation step has a perfectly living character, which is the required condition successfully to prepare block copolymers. Furthermore, the number of growing chains per trimetallic unit may vary between 1 and 2 ($p - 1$), depending on the main degree of catalyst association; the more aggregated the catalyst, the lower that number. On the contrary, in a completely dissociated catalyst, all of the 2($p - 1$) $\mathrm{M}_2^{(p)}$—OR bonds are available for chain initiation.[3,5,7]

The ease with which the lactone-opening polymerization initiated by bimetallic μ-oxoalkoxides is achieved has led to several attempts to prepare well-defined block copolymers. In addition to their technological interest as both pure and additive materials, well-defined block copolymers are highly sought as model compounds in fundamental studies of polymers morphology. It is well known that the sequential arrangement encountered in these block copolymers is responsible for unexpected and very interesting behavior in relation to the heterogeneous character of these materials.[8–11]

On the other hand, it may be worthwhile to determine the influence of the heterophase structure of such a block-type product on the general behavior of its own sequences, in particular on the crystallization of a semicrystalline block. To undertake such a basic analysis, it is necessary to control accurately the copolymer composition (proportion, length, and polydispersity of the sequences), which is responsible for the environmental conditions in which the crystallization will take place.

In this report, the sequential polymerization of two different lactones by metallic μ-oxoalkoxides will be described. It will give an example of the broad potentialities of these catalysts in the field of block copolymerization since, unlike simple alkoxides, they are able to polymerize several other types of monomers.[12] Using ϵ-caprolactone (CL) and β-propiolactone (PL), both sequences are semicrystalline, and the corresponding block copolymer can be used as a model compound for studying the crystallization phenomena in sequential structures.

EXPERIMENTAL

Reagents

Lactones were commercial reagents (pure grade), dried over CaH_2 at room temperature and purified by distillation under reduced pressure (ca. 10^{-2} mm Hg). Benzene (or toluene) and n-butanol (analytical grade) were dried by refluxing over $LiAlH_4$ and CaH_2, respectively, and distilled under argon atmosphere.

Copolymerization Procedure

The catalyst was prepared by a condensation reaction between aluminum isopropoxide and zinc acetate in a 2:1 molar ratio at about 200°C in decalin. By refluxing the $(i\text{-}C_3H_7O)_4Al_2O_2Zn$ so obtained in decalin in the presence of a sufficient excess of n-butanol, replacement of the isopropoxy groups by n-butoxy groups takes place quantitatively while the 2-propanol is continuously distilled off. The catalyst preparation has been detailed elsewhere.[3,13]

Copolymerizations were carried out under stirring in a flask previously dried, flushed with argon, and kept at constant temperature (±1°C). Solvent (benzene or toluene), ϵ-caprolactone, and catalyst were added successively through a self-sealing device. Once the first lactone was completely polymerized, β-propiolactone was similarly added and the inlet tube then sealed off.

The copolymerization reactions were stopped by adding an excess (relative to the catalyst) of $2N$ HCl solution. The catalyst residues were extracted repeatedly with dilute HCl solutions, and the organic phase was then washed with water to neutral pH. The crude polymeric product was isolated from its benzene or toluene solution by precipitation in heptane; after filtration it was dried for 24 hr at room temperature under vacuum.

Fractionation of the Crude Copolymer

The fractionation procedure is based on the selective solubility of PCL in toluene, and the use of chloroform as common solvent and petroleum ether as common nonsolvent of PCL and PPL.

The crude polymeric product was stirred overnight in the presence of toluene. The insoluble part was separated by centrifugation, and similarly treated with toluene–$CHCl_3$ mixtures of increasing $CHCl_3$ content. The PPL content of the soluble fraction increased for each extraction, and finally pure PL homopolymer was isolated. On the other hand, the polymeric product, which is soluble in pure toluene, was fractionally precipitated by successive additions of petroleum ether; the last isolated fraction consisted of pure PCL.

Molecular Weight Determinations

Molecular weight determinations were carried out with a vapor-pressure osmometer (Knauer) in toluene at 45°C (for PCL) or in dichloromethane at 37°C (for PPL), the precision being about 5–10%, depending on the molecular weight value.

The molecular weight distributions were determined by gel-permeation chromatography (Waters model 200) on 0.25% solution in THF at room temperature.

RESULTS AND DISCUSSION

Characteristic Features of Polymerization of ϵ-Caprolactone and β-Propiolactone with Bimetallic μ-Oxoalkoxides

Before undertaking the block copolymerization of ϵ-caprolactone (CL) and β-propiolactone (PL), the homopolymerization of these two lactones by $(n\text{-}C_4H_9O)_4\,Al_2O_2Zn$ in toluene was systematically compared. Two main differences were observed: first, the rate constant of the β-PL polymerization is definitely lower; at 20°C and for a $1M$ initial monomer concentration, the rate constant rises to 2.4×10^{-4} and 109×10^{-4} min^{-1} for PL and CL respectively. Secondly, while the polymerization mechanism (in particular, the living character of the propagation step) remains unchanged, the mean number of growing chains per catalyst unit is different: 1 for CL and 2 for PL.[5] That difference in behavior can be qualitatively explained, knowing that neither the addition of CL nor the growth of the corresponding polyester chains has a measurable effect (by cryoscopic analysis) on the mean degree of catalyst association,[3,5,7] while the latter is reduced to half of its original value by the presence of PL.[14]

It is evident that this discrepancy in the interaction of the two lactones with the catalyst may be responsible for difficulties in their controlled sequential polymerization.

TABLE I
Block Copolymerization of ε-CL and β-PL with $(n\text{-}C_4H_9O)_4Al_2O_2Zn$[a]

	ε-Caprolactone	β-Propiolactone
$[M]_0$, mole/l.	1	1,38
[M]/[C]	140	210
Time	4 hr	6 days
Temperature, °C	20	30
Conversion, %	98	61

[a] Solvent, benzene; total conversion, 81%.

TABLE II
Composition of the Product Obtained from Copolymerization of CL and PL with $(n\text{-}C_4H_9O)_4Al_2O_2Zn$

	Weight %	$\overline{M}_n$ Calculated[a]	$\overline{M}_n$ Observed
PCL	40.5	16,000	16,000
PPL	27	4,600	4,000
Block copolymer	32.5	20,600	16,000 + 5,500

[a] Calculations based on the measured monomer conversion, assuming (as verified independently) 1 and 2 growing chain(s) per catalyst unit for CL and PL, respectively.

TABLE III
Block Copolymerization of CL and PL with Completely Dissociated $(n\text{-}C_4H_9O)_4Al_2O_2Zn$

	ε-Caprolactone	β-Propiolactone
$[M]_0$, mole/l.	1	1.1
$[M]_0/[C]$	200	237
Temperature, °C	20	30
Time, hr	13	264
Conversion, %	98	66
$(\overline{M}_n)$		
Calculated	5700	2800
Observed	5600[a]	—

[a] Measured before PL addition.

TABLE IV
Fractionation of CL/PL Block Copolymer

Fraction	Nature	Weight %	$\overline{M}_n$	$\overline{M}_{PCL}/\overline{M}_{PPL}$[a]	$\overline{M}_w/\overline{M}_n$
PCL before PL addition	—	—	5600	—	1.3
I	PCL	5	5400	—	1.3
II	PCL + PPL	48	8200	6500/1700	1.3
III	"	24	7800	4900/2900	1.4
IV	"	19	7600	3600/4000	—
V	"	4	7100	2800/4300	—

[a] Calculated from the $\overline{M}_n$ and elemental analysis of block copolymer fractions.

Block Copolymerization of ε-Caprolactone and β-Propiolactone by $(n\text{-}C_4H_9O)_4\text{-}Al_2O_2Zn$

A first block copolymerization attempt[5] was realized under the conditions summarized in Table I. Taking into account the slower PL polymerization rate, the CL was polymerized first, under conditions where its catalytic degradation[15] can be practically avoided.

The crude product resulting from the block copolymerization was separated into three principal components; the expected block copolymer and the two corresponding homopolyesters (Table II).

These results clearly indicate that all of the CL polymerization sites are not able to polymerize the second monomer, and that, after addition of the latter, new Al–n-butoxide bonds are now available for its conversion.

Consequently, this second monomer seems to be responsible for a rearrangement of the catalytic aggregates. This conclusion is still speculative, however, and requires a more detailed analysis of the polymeric catalyst behavior. However, the small difference between the calculated and observed molecular weight value of pure PPL (Table II) indicates that the mean number of two growing PPL chains per catalyst unit is not profoundly modified by the presence of polyester chains (PCL) on some catalytic sites. On that basis, the difference between the chain length of the PL homopolymer (4000) and the corresponding block sequence (5500) could be attributed to a kinetic effect in relation with the replacement of a n-butyl group by a polymeric one.

Block Copolymerization of ε-Caprolactone and β-Propiolactone by Completely Dissociated $(n\text{-}C_4H_9O)_4Al_2O_2Zn$

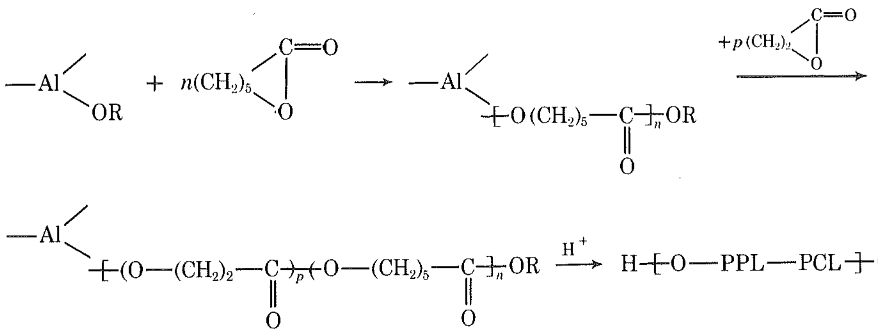
The preceding experiments showed that better results could be obtained by the complete dissociation of the catalytic aggregates before the first monomer addition. Indeed, every Al–n-butoxide bond having now initiated a PCL chain, the formation of PL homopolymer should be avoided. To confirm this assumption, CL and PL were sequentially polymerized by adding, before any polymerization, a stoichiometric amount of n-butanol to the Al–Zn n-butoxide catalyst solution;[5] Table III summarizes the conditions of this copolymerization experiment.

After catalyst hydrolysis, the product obtained is resolved into five fractions which have been characterized as indicated in Table IV. As expected, a completely dissociated catalyst allows the quasi-quantitative formation of block copolymer (the presence of a low amount of CL homopolymer may be tentatively attributed to a partial hydrolysis of catalyst when the second monomer is added). It is also apparent that the longer the PCL sequence, the shorter the PPL block associated with it; the crude fractionation of the copolymer results essentially from its heterogeneous composition rather than from its molecular weight distribution (MWD). The relative composition of the successive fractions indicates the coupling of a shorter PCL chain with a longer PPL one and vice versa. It could be assumed that the shorter the PCL living chain, the easier the second monomer (PL) initiation is. It is experimentally observed that PCL sequence and block copolymer have practically the same MWD; such an observation could be explained by the particular linking of the two sequences observed (Table IV).

Freyss[16] and Kotaka[17] suggest indeed that the $\overline{M}_w/\overline{M}_n$ ratio of a block copolymer is always smaller than that of the more polydisperse sequence and often can be even smaller than either of the two sequences; these results are apparently due to a random linking of the two sequences in the block copolymer.

Several CL/PL copolymers with different sequences lengths (PCL/PPL = 2200/4800, 3800/4200, 14000/3500) have been also synthesized with completely dissociated Al_2/Zn μ-oxoisopropoxide and n-butoxide catalysts.[18] The physical properties and the crystallization behaviour of these block copolymers will be reported elsewhere.

As described in reaction scheme (1), the block copolymer chains are capped with a hydroxyl group at the end of the PPL sequence.



(1)

By a coupling reaction with a diisocyanate or a dichlorosilane compound, it is now easy to prepare the triblock copolymer PCL–PPL–PCL. Furthermore, by three successive lactone additions, the synthesis of triblock copolymers PCL–PPL–PCL and PPL–PCL–PPL could be considered. On the other hand, it is easy to exchange the alkoxide groups of the catalyst in an alcoholysis reaction using a less volatile (or less basic) alcohol and, in particular, an alcohol carrying an acetal end group. With the resulting catalyst, dihydroxylated homopolymers or block copolyesters are obtained after catalyst and acetal hydrolysis. The coupling of these diol PCL/PPL block copolymers could be used to synthesize the corresponding multiblock copolymers.

In conclusion, the bimetallic oxoalkoxides are very attractive lactone polymerization catalysts. Their easily controlled structure and composition, together with the living character of the corresponding propagation reaction, make possible facile block copolymerizations, with good control of the relative lengths and arrangement of the sequences in the copolymers obtained.

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References

1. M. Osgan and P. Teyssie, *J. Polym. Sci. B*, **8**, 319 (1970).
2. A. Hamitou, R. Jerome, A. J. Hubert, and P. Teyssie, *Macromolecules*, **6**, 651 (1973).
3. T. Ouhadi, Ph.D. Thesis, Univ. of Liège, 1973, and papers in preparation.
4. Ph. Teyssie, T. Ouhadi, and J.-P. Bioul, *Macromolecular Science-Physical Chemistry*, Series II, Butterworths, London–Boston, 1975, Vol. 8, p. 191.
5. A. Hamitou, Ph.D. Thesis, Univ. of Liège, 1975.

6. A. Hamitou, T. Ouhadi, R. Jerome, and P. Teyssie, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 865 (1977).
7. T. Ouhadi, A. Hamitou, R. Jerome, and P. Teyssie, *Macromolecules*, **9**, 927 (1976).
8. J. Moacanin, G. Holden, and N. W. Tschoegl, Eds., *Block Copolymers*, (*J. Polym. Sci. C*, **26**) Interscience-Wiley, New York, 1969.
9. S. L. Aggarwal, Ed., *Block Copolymers*, Plenum Press, New York, 1970.
10. G. E. Molau, Ed., *Colloidal and Morphological Behaviour of Block and Graft Copolymers*, Plenum Press, New York, 1971.
11. D. C. Allport and W. H. Janes, Eds., *Block Copolymers*, Wiley, New York, 1973.
12. N. Kohler, M. Osgan, and P. Teyssie, *J. Polym. Sci. B*, **6**, 559 (1968).
13. J-P. Bioul, Ph.D. Thesis, Univ. of Liège, 1973, and papers in preparation.
14. J. Heuschen, Masters Thesis, Univ. of Liège, 1973.
15. T. Ouhadi, C. Stevens, and P. Teyssie, *J. Appl. Polym. Sci.*, **20**, 2963 (1976).
16. D. Freyss, P. Rempp, and H. Benoit, *J. Polym. Sci. B*, **2**, 217 (1969).
17. T. Kotaka, T. Uda, T. Tanaka, and H. Inagaki, *Makromol. Chem.*, **176**, 1273 (1973).
18. G. Huynh Ba, Masters Thesis, Univ. of Liège, 1975.

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