

ADVANCES IN POLYMER SCIENCE

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D. Mecerreyes · R. Jérôme
P. Dubois

Novel Macromolecular
Architectures Based on Aliphatic
Polyesters: Relevance of the
"Coordination-Insertion"
Ring-Opening Polymerization

J. L. Hedrick · J. W. Labadie
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Nanoscopically Engineered
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Controlled Macromolecular
Architectures

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Macroporous Thermosets
by Chemically Induced Phase
Separation



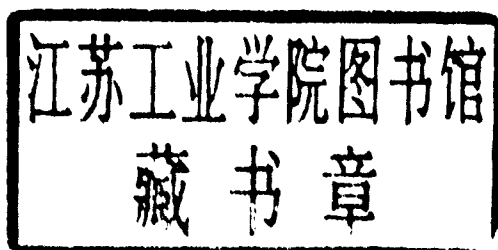
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**Macromolecular
Architectures**

Macromolecular Architectures

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P. Dubois, C. J. Hawker, J. L. Hedrick,
J. G. Hilborn, R. Jérôme, J. Kiefer,
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Preface

Thanks to recent advances in the chemistry of preparing polymers, an increasing number of tools are at our disposal for the design of polymer materials. The design level ranges from monomer synthesis, controlled stepwise or chainwise polymerization, block copolymer synthesis, over branching to crosslinking reactions. Depending on the structure of the individual polymer chains formed these will be organized in the bulk to give specific properties. Hence, this gives us two architectural levels: *The structure of individual macromolecules and the microstructure of the material produced*. While both of these organization levels may contribute to the design of materials properties we would ultimately like to be able to tailor our material to suit desired applications in which surface properties, mechanical or thermal behavior, processability, optical or electrical characteristics etc. are crucial. The next decades should see an enormous advance in nanoscopic and supramolecular chemistry leading to novel predetermined properties. Molecular manipulation of nano and microstructures paves the way to organic polymer materials by design. Such architectures comprise both the synthesis and the kinetic and thermodynamics of macromolecular organization and is the theme of this volume.

The book consists of four articles reviewing the literature based on the authors own experiences over the last decade in this field. It does not claim to be exhaustive nor to provide complete coverage of the very extensive literature in this field. Instead, it focuses on the currently intense areas of research namely living polymerization, block copolymer synthesis, synthesis of dendrimers and finally macroporous thermosets. Hopefully, this volume will not only serve as a book on the design of macromolecular architectures but also as a source of inspiration to produce polymers combining several functional properties.

In the first chapter by P. Dubois and D. Mecerreyes, living polymerization to produce precisely defined linear polyesters is outlined and also compared to other living polymerization techniques. In chapter two, C. Hawker describes the synthesis of polymeric dendrimers which are organic globular-like nanoscopic entities of exact molecular mass and functionality synthesized either by the convergent or divergent approach. How block copolymers are produced to define micromorphology in high performance polymers and thereby tailoring their thermal, chemical, mechanical and dielectrical properties is the content of chapter three by J. Hedrick. The book concludes with a fourth chapter by J. Kiefer on the importance of kinetic and thermodynamics for microstructural organization in thermosets.

The editor would also like to acknowledge the valuable input from Professor Stanislaw Penczek, Professor Bernard Sillion, Professor Anders Hult, and Professor Vipin Kumar who served as referees for the above contributions.

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Jöns G. Hilborn

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Novel Macromolecular Architectures Based on Aliphatic Polyesters: Relevance of the “Coordination-Insertion” Ring-Opening Polymerization

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Recent developments in the macromolecular engineering of aliphatic polyesters have been overviewed. First, aluminum alkoxides mediated living ring opening polymerization (ROP) of cyclic (di)esters, i.e., lactones, lactides, glycolide, is introduced. An insight into this so-called “coordination-insertion” mechanism and the ability of this living polymerization process to prepare well-defined homopolymers, telechelic polymers, random and block copolymers is then discussed. In the second part, the combination of the living ROP of (di)lactones with other well-controlled polymerization mechanisms such as anionic, cationic, free radical, and metathesis polyadditions of unsaturated comonomers, as well as polycondensations, is reported with special emphasis on the design of new and well-tailored macromolecular architectures. As a result of the above synthetic breakthrough, a variety of novel materials have been developed with versatile applications in very different fields such as biomedical and microelectronics.

Keywords. Lactones, Lactides, Aliphatic polyesters, Ring opening polymerization, Living polymerization, Macromolecular engineering

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List of Symbols and Abbreviations

ATRP	atom transfer radical polymerization
BD	butadiene
DM(T)A	dynamic mechanical (thermo)analysis
DMAP	dimethylaminopyridine
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
EA	ethyl acrylate
MA	methyl acrylate
MMA	methyl methacrylate
MWD	molecular weight distribution
NMR	nuclear magnetic resonance
PCEVE	poly(chloro vinyl ether)
PCL	poly(ϵ -caprolactone)
PCS	photon correlation spectroscopy
PDI	polydispersity index
PEO	poly(ethylene oxide)
PLA	polylactide, including (D,L) and P(L)LA
PMCP	poly(methylene-1,3-cyclopentane)

PNB	polynorbornene
PS	poly(styrene)
ROP	ring opening polymerization
ROMP	ring opening metathesis polymerization
RT	room temperature
SAXS	small angle X-ray scattering
TEM	transmission electron microscopy
TEOS	tetraethoxysilane
THF	tetrahydrofuran
T _g	glass transition temperature
TGA	thermal gravimetric analysis
T _m	melting temperature
TMC	trimethylene carbonate
TMEDA	tetramethylethylenediamine
UV	ultraviolet
VP	vinyl pyrrolidone

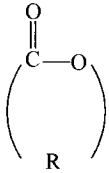
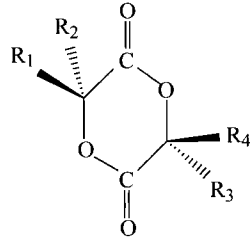
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Introduction

Biodegradable polymers have attracted widespread attention during the last few years [1]. This important research effort has been driven by the need for specific single-use materials in the biomedical field and by the search for biodegradable substitutes of conventional commodity thermoplastics, in answer to the increasing discarded plastic waste in landfills. Among the various families of biodegradable polymers, aliphatic polyesters have a leading position since hydrolytic and/or enzymatic chain cleavage yields ω -hydroxyacids which in most cases are ultimately metabolized. As will be discussed later, aliphatic polyesters can be prepared from a large variety of starting (natural) materials and synthetic routes. By a judicious choice of the repetitive ester unit(s), one can play at will with the material properties such as crystallinity, glass transition temperature, toughness, stiffness, adhesion, permeability, degradability, etc.

Polyesters are currently synthesized by a step-growth process, i.e., a polycondensation, from a mixture of a diol and a diacid (or a diacid derivative), or from a hydroxy-acid when available. Ring opening polymerization (ROP) of cyclic esters and related compounds is an alternative method for the synthesis of aliphatic polyesters. Comparison of these two mechanisms is clearly in favor of the polyaddition process [2]. Molecular weight of the polycondensates is usually limited to a few tens of thousands ($M_n < 30,000$), and the only way to control it in this limited range of chain length is the use of terminating (monofunctional) agents. Even though conversion of the hydroxyl and acid groups is close to completion, any departure from the reaction stoichiometry has a very detrimental effect on the chain length. Furthermore, polycondensation of ω -hydroxy acids leads to the formation of side-reaction by-products, and it requires long reaction

Table 1. Monomer structures and polymer melting point and glass transition temperatures of the most common aliphatic polyesters obtained by ROP [2, 7]

Monomer	Polymer	T _g (°C)	T _m (°C)
	Poly(lactone) Poly(ω -hydroxy acid)		
R=-(CH ₂) ₂ - β PL, β -propiolactone	P β PL	-24	93
R=-(CH ₂) ₃ - γ BL, γ -butyrolactone	P γ BL	-59	65
R=-(CH ₂) ₄ - δ VL, δ -valerolactone	P δ VL	-63	60
R=-(CH ₂) ₅ - ϵ CL, ϵ -caprolactone	PeCL	-60	65
R=-(CH ₂) ₂ -O-(CH ₂) ₂ -DXO, 1,5-dioxepan-2-one	PDXO	-36	-
R=-(CH ₂ -CH(CH ₃))- β BL, β -butyrolactone	P β BLisotactic ^a P β BL atactic	5 -2	180 -
R=-(C(CH ₃) ₂ -CH ₂)-PVL, pivalolactone	PPVL	-10	245
	Poly(dilactone) Poly(α -hydroxy acid)		
R ₁ =R ₂ =R ₃ =R ₄ =H GA, glycolide	PGA	34	225
R ₁ =R ₄ =CH ₃ , R ₂ =R ₃ =H L-LA, L-lactide	PLLA	55-60	170
R ₁ =R ₄ =H, R ₂ =R ₃ =CH ₃ D-LA, D-lactide	PDLA	55-60	170
R ₁ =R ₃ =CH ₃ , R ₂ =R ₄ =H meso-LA, meso-lactide	PmesoLA	45-55	-
D-LA/L-LA (50-50) D,L-LA, (D,L) racemic lactide	PDLLA	45-55	-

^a Also known as poly(3-hydroxybutyrate) [3]

times together with high temperatures. In contrast, ROP is usually free of these limitations. Under rather mild conditions, high molecular-weight aliphatic polyesters can be prepared in short periods of time. Table 1 presents the monomer structures, the related aliphatic polyesters as obtained by ROP, and their abbreviations. The thermal characteristic features, i.e., the glass transition and melting temperatures, are also reported. It is worth noting that in addition to the chemical methods, many bacteria synthesize, accumulate, and deposit in the cells aliphatic polyesters which are generally known as poly(hydroxy alkanolic acids) (PHA). The high stereoselectivity of the enzymatic synthesis produces as

Table 2. Different chemistries involved in the synthesis of aliphatic polyesters by ROP [2]

Mechanism	Initiator and/or catalyst
Cationic	Protonic acids: HCl, HBr, RCOOH, RSO ₃ H Lewis acids: AlCl ₃ , BF ₃ , FeCl ₂ , ZnCl ₂ Alkylating agents: CF ₃ SO ₃ CH ₃ , Et ₃ O ⁺ ·BF ₄ ⁻ , (CH ₃) ₂ I ⁺ ·SbF ₆ ⁻ Acylation agents: CH ₃ C(O) ⁺ ·OCl ₄ ⁻
Anionic	Alkoxides: RO ⁻ M (M=alkali metal, complexed or not by crown ether) Carboxylates: RCOO ⁻ M (M=alkali metal) Alkali metal: naphthalenides Alkali metal supramolecular complexes Graftides: KC ₂₄
Free Radical	Peroxides (monomers: cyclic ketene acetals)
Via Active Hydrogen	Amines and alcohols
Zwitterionic	Tertiary amines and phosphines
Coordination	Alkoxides: ROM (M=metal with free <i>p</i> , <i>d</i> , or <i>f</i> orbitals of a favorable energy) Carboxylates: RCOOM (M=metal with free <i>p</i> , <i>d</i> , or <i>f</i> orbitals of a favorable energy). Metal oxides and halogenides (mainly of Sn and transition metals)
Enzymatic	Lipase

a rule polyesters with high crystallinity which have attracted a great deal of attention during the last few years [3].

The first attempts at ROP have been mainly based on anionic and cationic processes [4, 5]. In most cases, polyesters of low molecular weight were recovered and no control on the polymerization course was reported due to the occurrence of side intra- and intermolecular transesterification reactions responsible for a mixture of linear and cyclic molecules. In addition, aliphatic polyesters have been prepared by free radical, active hydrogen, zwitterionic, and coordination polymerization as summarized in Table 2. The mechanistic considerations of the above-mentioned processes are outside the scope of this work and have been extensively discussed in a recent review by some of us [2]. In addition, the enzyme-catalyzed ROP of (di)lactones in organic media has recently been reported; however, even though this new polymerization procedure appears very promising, no real control of the polyesters chains, or rather oligomers, has been observed so far [6].

Above all, the discovery that some organometallic compounds are effective in the synthesis of high molecular weight PCL [7] promoted a renewed interest in the ROP of lactones, particularly with alkyl metals, metal halides, oxides, carboxylates, and alkoxides. These metal compounds were first classified as anionic

or cationic initiators [8]. Nevertheless, various studies have shown that most metal derivatives initiate the chain reaction through active covalent bonds [9]. Accordingly some authors classified those ROP as pseudoionic processes, which commonly involved coordination active species. Although this pseudoionic ROP allows the synthesis of polyesters of a high molecular weight, control of the polymerization is very difficult to achieve and is rather an exception. Actually depending on the structure of the organometallic derivatives, they can act either as catalyst, e.g., metal oxides, halides, and carboxylates, or as initiators, which is the case for metal alkoxides, the metal of which contains free *p*-, *d*-, or *f*- orbitals of a favorable energy (see next section). In the former case, the Lewis acid-type catalysts would not be chemically bonded to the growing chains, so that they can activate more than one chain. As a result, the average degree of polymerization is not directly controlled by the monomer-to-catalyst molar ratio. Moreover, transesterification side-reactions also perturb chain propagation which makes the molecular weight distribution broader ($PDI \sim 2$). On the other hand, the “active covalent” bonds of some of the above metal alkoxides display a good compromise of reactivity so that an acceptable control for the lactones ROP could be achieved. Among them, aluminum alkoxides have proved to promote a ROP with a restricted occurrence of termination, transfer, and transesterification side-reactions, showing a high degree of livingness and an unequal versatility in the preparation of high molecular weight polyesters and novel macromolecular architectures [10].

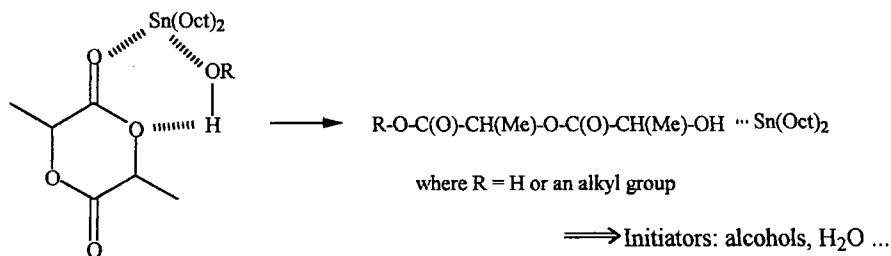
The purpose of this review is to report on the recent developments in the macromolecular engineering of aliphatic polyesters. First, the possibilities offered by the living (co)polymerization of (di)lactones will be reviewed. The second part is devoted to the synthesis of block and graft copolymers, combining the living coordination ROP of (di)lactones with other living/controlled polymerization mechanisms of other cyclic and unsaturated comonomers. Finally, several examples of novel types of materials prepared by this macromolecular engineering will be presented.

2

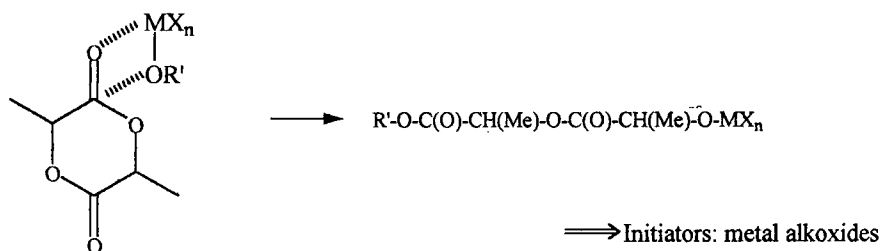
Aluminum Alkoxides Mediated Ring Opening Polymerization of Lactones and Lactides

Two different mechanisms have been proposed for the ROP of (di)lactones depending on the nature of the organometallic derivatives. Metal halides, oxides, and carboxylates would act as Lewis acid catalysts in an ROP actually initiated with a hydroxyl-containing compound, such as water, alcohol, or ω -hydroxy acid; the later would result more likely from the “in-situ” hydrolysis of the (di)lactone [11]. Polymerization is assumed to proceed through an insertion mechanism, the details of which depends on the metal compound (Scheme 1a). The most frequently encountered Lewis acid catalyst is undoubtedly the stannous 2-ethylhexanoate, currently referred to as stannous octoate ($\text{Sn}(\text{Oct})_2$). On the other hand, when metal alkoxides containing free *p*-, *d*-, or *f*- orbitals of a favo-

(a) Lewis Acid Catalysts: $\text{Sn}\phi_4$, SnBr_4 , $\text{Sn}(\text{Oct})_2$, $\text{Zn}(\text{acet})_2$,



(b) Metal (with free p-, d- and f- orbitals) alkoxides: $\text{R}'\text{O-MX}_n$



Scheme 1. Currently proposed insertion mechanisms in ROP of (di)lactones (schematized here for lactide monomers)

erable energy (Mg- , Sn- , Ti- , Zr- , Fe- , Al- , Y- , Sm- , Zn-alkoxides) are used as initiators, a two-step "coordination-insertion" mechanism would prevail, which consists of the lactone complexation onto the propagating species, i.e., the growing metal alkoxide, followed by a rearrangement of covalent bonds leading to the cleavage of the metal-oxygen bond of the propagating species and the acyl-oxygen bond of the cyclic monomer (Scheme 1b) [2, 12].

Although some organometallic compounds can allow for the synthesis of polyesters of a high molecular weight, control of the ROP process usually remains a problem. As an example, in the case of Lewis acid catalyst, molecular weights are difficult to predict and the molecular weight distribution is broad. M_w/M_n is close to 2 as the result of the occurrence of side transesterification reactions. On the other hand, Kricheldorf has studied different metal alkoxides and he has reported that "active covalent" bonds of the investigated metal alkoxides were reactive enough to generate intramolecular transesterification reactions – also known as "back-biting" reactions – yielding cyclic oligomers as by-products. Within the limits of the studied initiators, the reactivity would be $\text{Al}(\text{OiPr})_3 < \text{Zn}(\text{OnPr})_2 < \text{Ti}(\text{OnBu})_4 < \text{Bu}_3\text{SnOMe} < \text{Bu}_2\text{Sn}(\text{OMe})_2$. In agreement with these observations, some of us, and more recently Inoue and Penczek, have reported on the living polymerization of ϵ -CL, as initiated by aluminum alkoxides species such as bimetallic (Zn, Al) μ -oxo alkoxides and aluminum triisopropoxide.