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

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Abstract
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)lac-tones with other well-controlled polymerization mechanisms such as anionic, cationic, free radical, and metathesis polyadditions of unsaturated comonomers, as well as polyconden-sations, 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.

Contents

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

1. Introduction

Biodegradable polymers have attracted widespread attention during the last few years [I]. 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 poly-condensation, 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 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 alkanoic acids) (PHA). The high stereoselectivity of the enzymatic synthesis produces as a rule polyesters with high crystallinity which have attracted a great deal of attention during the last few years [3].

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	$T_g(X)$	T_m (^{0}C)
	Polylactone		
	Poly(ω-hydroxy acid)		
R=- -(CH$_2$)$_2$-βPL, β-propiolactone	PβPL	-24	93
R=- -(CH$_2$)$_3$-γBL, γ-butyrolactone	PγBL	-59	65
R=- -(CH$_2$)$_4$-δVL, δ-valerolactone	PδVL	-63	60
R=- -(CH$_2$)$_5$-εCL, ε-caprolactone	PεCL	-60	65
R=- -(CH$_2$)$_2$-O-(CH$_2$)$_2$-DXO, l,5-dioxepan-2-one	PDXO	-36	-
R=- -(CH$_2$-CH(CH$_3$))-βBL, β-butyrolactone	PβBLisotactic[a]	5	180
	PβBL atactic	-2	-
R=- -(C(CH$_3$)$_2$-CH$_2$)-PVL,pivalolactone	PPVL	-10	245

Rl　^-　　　　　　II

	Polydilactone		
	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-L A./L-LA (50-50) D$_5$L-LA, (D,L) racemic lactide	PDLLA	45-55	—

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

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

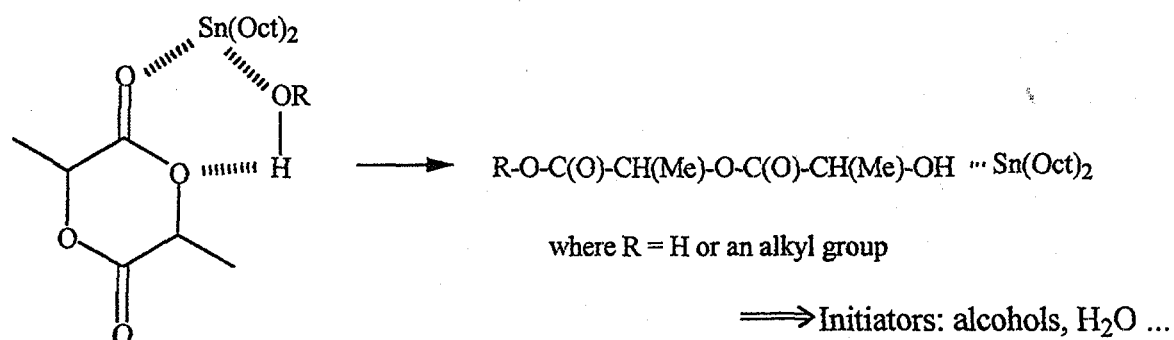| Mechanism	Initiator and/or catalyst
Cationic	Protonic acids: HCl, HBr, RCOOH, RSO_3H
	Lewis acids: $AlCl_3$, BF_3, $FeCl_2$, $ZnCl_2$
	Alkylating agents: $CF_3SO_3CH_3$, Et_3O^+ "BF_{4j} $(CH_3)_2I^+$ "SbF_6
	Acylating agents: $CH_3C(O)^+$ 'OCl_4
Anionic	Alkoxides: $RO^{-+}M$ (M=alkali metal, complexed or not by crown ether)
	Carboxylates: $RCOO^{-+}M$ (M=alkali metal)
	Alkali metal: naphthalenides
	Alkali metal supramolecular complexes
	Grafitides: 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 *p, d,* or /orbitals **of a** favorable energy)
	Carboxylates: RCOOM (M=metal with free p, d, or *f* orbitals of a favorable energy)
	Metal oxides and halogenides (mainly of Sn and transition metals)
Enzymatic	Lipase

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-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.
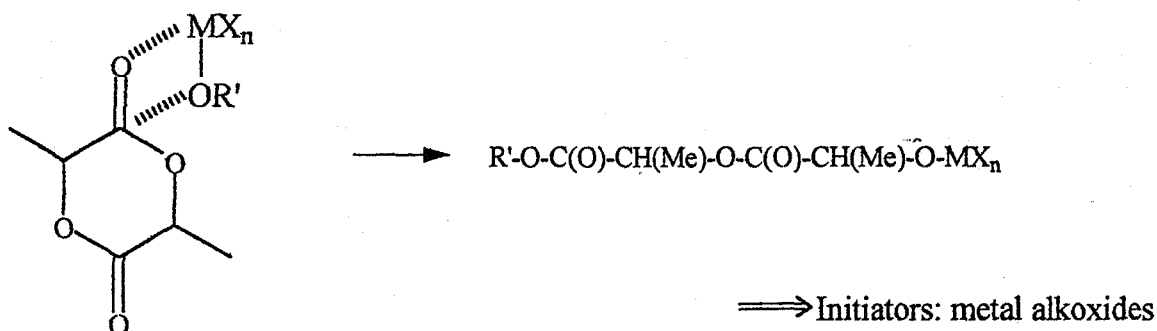
2. Aluminum Alkoxides Mediated Ring Opening Polymerization of Lactones and Lactides

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)lac-tone [H]. Polymerization is assumed to proceed through an insertion mechanism, the details of which depends on the metal compound (Scheme Ia). The most frequently encountered Lewis acid catalyst is undoubtedly the stannous 2-ethylhexanoate, currently referred to as stannous octoate ($Sn(OCt)_2$). On the other hand, when metal alkoxides containing free *p-, d-,* or *f-* orbitals of a favo poxide [13-15], tetraphenylporphinato aluminum alkoxides [16], and diethyl aluminum methoxide [17], respectively. Confirming the observed living character of the polymerization promoted by aluminum alkoxides, the extent of side reactions, mainly the "back-biting" ones, has been studied by Penczek et al., who have quantitatively described the degree of livingness by the so-called selectivity parameter (β). β is defined as the ratio of the rate constant of propagation to the rate constant of side reactions (β=kp/ks) and shows the highest value in ROP initiated by $Al(OfPr)_3$ [18]. Recent works have reported on the living polymerization of εCL and LA as initiated by lanthanide alkoxides. Although these initiators look very promising because of the very high polymerization rate, their selectivity appears to be much less than in the case of aluminum trialkoxides [19-21].

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

R-O-C(O)-CH(Me)-O-C(O)-CH(Me)-OH ··· $Sn(Oct)_2$

where R = H or an alkyl group

$\Longrightarrow$ Initiators: alcohols, H_2O ...

(b) Metal (with free p-, d- and f- orbitals) alkoxides : $R'O-MX_n$

R'-O-C(O)-CH(Me)-O-C(O)-CH(Me)-O-MX_n

$\Longrightarrow$ Initiators: metal alkoxides

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

This section aims at reviewing recent advances in ROP of cyclic (di)esters initiated by aluminum alkoxides. The controlled synthesis of high molecular weight polymers with narrow molecular weight distribution obtained by ROP initiated by $Al(OfPr)_3$ will be discussed first. Next, the preparation of random and diblock copolymers, α- and α,ω-functional (co)polyesters, will be presented. Then the different factors which affect the polymerization kinetics will be analyzed. Finally, our attention will be devoted to the synthesis and subsequent polymerization of functional monomers, the main objective being the straightforward preparation of aliphatic polyesters bearing functional pendant groups all along the main backbone.

2.1. Homopolymerization of Cyclic (Di)esters as Initiated by Al(OZPr)$_3$

Aluminum isopropoxide has proved to be a very effective initiator for the polymerization of lactones: βPL, δVL, εCL, DXO, and βBL and dilactones: D,L- and L-LA, and GA. It is worth noting that cyclic carbonates, e.g., 2,2-dimethyltri-methylene carbonate (DTC) and cyclic anhydrides such as adipic anhydride (AA) have also been polymerized by aluminum trialkoxides with the unique possibility to control the molecular parameters of the polycarbonate (PDTC) and polyanhydrides (PAA). This is illustrated in Scheme 2 and the preferred reaction conditions are given in Table 3.
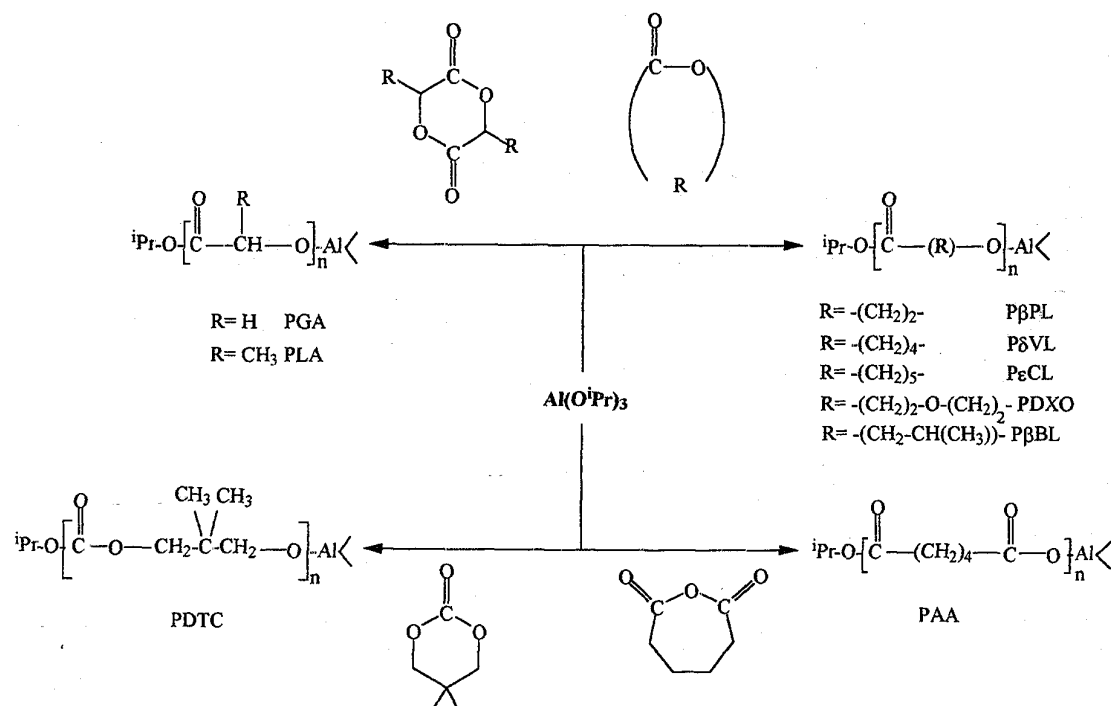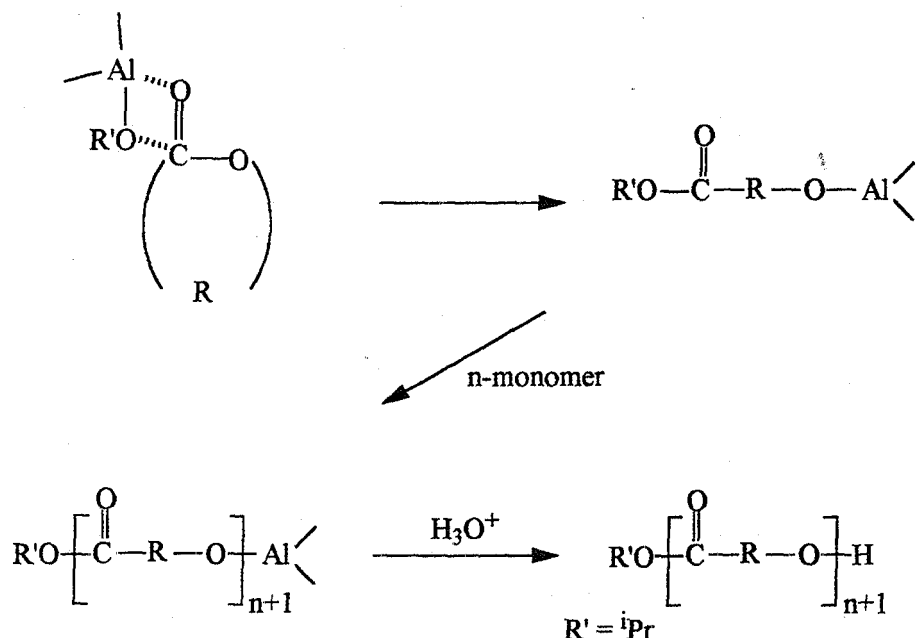

Scheme 2

Table 3. *Preferred reaction conditions for the ROP of different monomers as initiated by Al(OiPr)$_3$*

Monomer	Solvent	Temperature ^{0}C	Reference
βPL	Toluene THF	40	[22]
OVL	Toluene THF	0-25	[22]
εCL	Toluene THF	0-25	[22-24]
βBL	Toluene	75	[25]
DXO	Toluene	25	[26]
GA^a	Toluene	40	[27]
D$_5$L-LA	Toluene	70	[28]
L,L-LA	Bulk	110-180	[29-31]
AAa	Toluene CH$_2$Cl$_2$	25	[32, 33]
TMC	Toluene	25	[34]

^{a} Due to very limited solubility of PGA and PAA chains in toluene, it is advised to initiate the polymerization by living PCL oligomers, [iPrO-PCL-O]$_3$Al, as prepared by εCL ROP promoted by Al(OfPr)$_3$.

The ring-opening proceeds through a "coordination-insertion" mechanism which involves the insertion of the monomer into the "Al-O" bond of the initiator (Scheme 3). The acyl-oxygen bond of the cyclic monomer is cleaved in a way which maintains the growing chain attached to aluminum through an alkoxide bond.

Polymerization is currently stopped by hydrolysis of the active aluminum alkoxide bond which leads to the formation of a hydroxyl end-group. Rather as an exception, the active growing species in polymerization of adipic anhydride is not an aluminum alkoxide, but an aluminum carboxylate, which leads to a car-boxylic acid end-group after ultimate hydrolytic deactivation. The second chain extremity is capped with an ester carrying the isopropoxy radical of the initiator. Note that as far as the ROP of DTC is concerned, this second end-group turns out to be an isopropoxy carbonate function.

Scheme 3

Whatever previously listed monomer is considered, the "living" character of the polymerization has been confirmed by kinetic studies, where polymerization is first order in both monomer and initiator. Moreover, the molecular weight can be predicted by the monomer-to-initiator molar ratio, the molecular weight distributions are narrow (PDI= 1.05-1.20), and the monomer resumption experiments are quantitative. Worthy of particular mention is the "living" mechanism reported for the bulk polymerization of lactide in absence of any solvent [29]. Actually, P(L- and D,L-)LA chains of M_n higher than 100,000 can be synthesized in bulk at a temperature ranging from 110 to 180 ^{0}C. Again, the degree of polymerization is in close agreement with the starting feed monomer-to-Al(OfPr)$_3$ ratio. However, some limitations have been observed in ROP of βBL. At βBL monomer-to-initiator ratios higher than 150, a competition between propagation and (inter- and intra-molecular) transesterifications, and elimination reactions, i.e., proton abstraction with the concomitant formation of crot-onic ester, takes place and the control over the PβBL molecular structure is lost definitively [25].

2.2. Random and Block Copolymerization

Generally, when two or more monomers of similar reactivity polymerize according to the same "living" mechanism, their simultaneous polymerization leads to random copolymers and their sequential polymerization to block copolymers. Accordingly, copolymerization of εCL with δVL [35], TOSUO [36], and γBL [37] initiated with Al(OfPr)$_3$ in toluene at 25 ^{0}C leads to highly statistical copolymers as confirmed by triad analysis by ^{13}C NMR spectroscopy. At the same time, the control over the molecular parameters and the narrow molecular weight distributions already observed in the respective homopolymerizations are maintained. Of particular interest is the case of γBL, the five-membered cyclic ester, usually classified as a lactone unable to be ring-opening polymerized under conventional experimental conditions. However, in the presence of freshly distilled Al(OzPr)$_3$, i.e., predominantly aluminum isopropoxide associated in trimer known for being the most active species in ROP, γBL has proved to oli-gomerize up to a DP of ca. 10, in toluene at RT. Furthermore, γBL copolymerizes with εCL up to about 50 mol% of γ-oxybutyryl units content, with high and controlled molecular weights and narrow MWD [37].
Interestingly, the lactones copolymerization is responsible for a decrease in both T_m and degree of crystallinity of the copolyesters when compared to the parent homopolymers. This behavior is illustrated in Fig. 1 in the case of
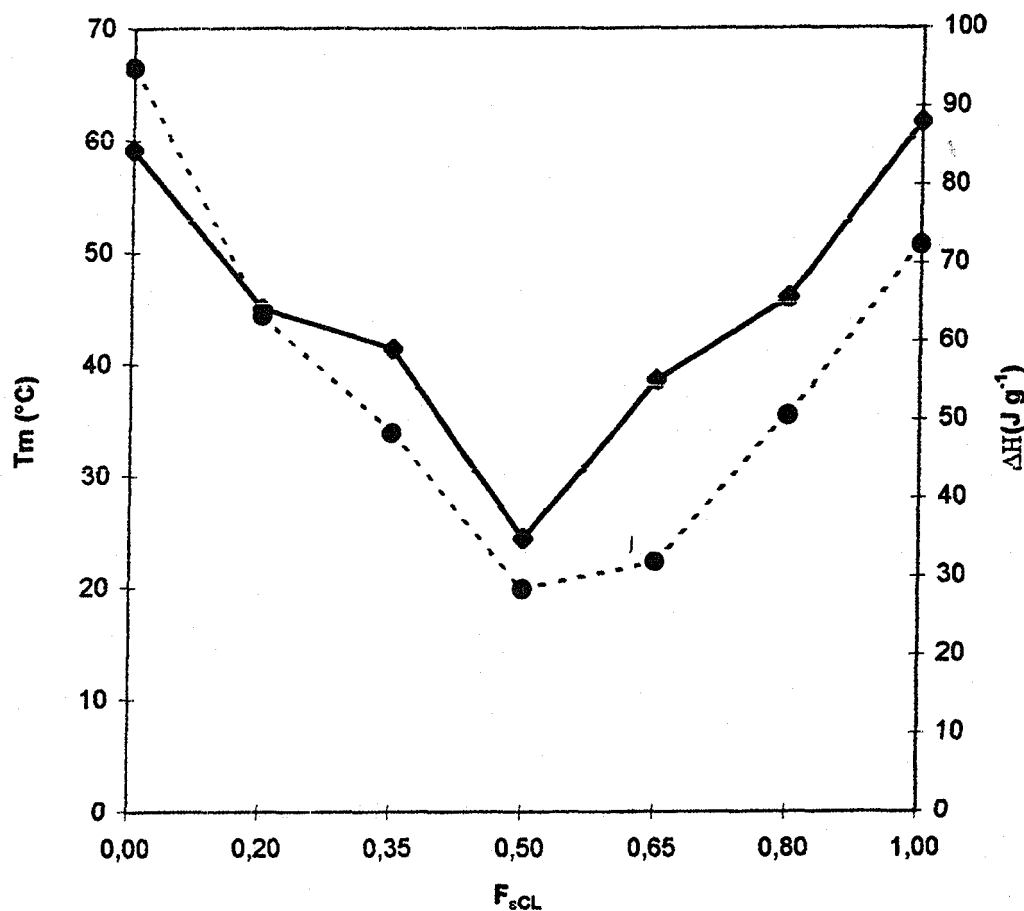
po-ly(εCL-co-δVL) random copolymers [35].

Fig. 1. Melting temperature (—,T_m) and enthalpy (--,ΔH) of poly(εCL-co-δVL) random copolymers at different compositions, as synthesized by "coordination-insertion" ROP initiated with Al(OzPr)$_3$ in toluene at 0 ^{0}C. $F_{εCL}$ is the molar fraction of εCL in the copolyester. (T_m and ΔH were determined by DSC at a heating rate of 10 °C/min).

On the other hand, when εCL is copolymerized with dilactones such as GA [38] and (D- and D,L-)LA [39], tapered or pseudoblock copolymers are obtained with a reactivity ratio much in favor of the dilactone. As an example, the reactivity ratios in the copolymerization of εCL and D,L-LA in toluene at 70 ^{0}C are T_1= 0.92 (ε-CL) and r_2=26.5 (D-L-LA). Very similar reactivity ratios were calculated for copolymerization between εCL and L-LA, other experimental conditions being kept unchanged. However the control over the polymerization is lost due to transesterification side reactions perturbing the propagation step. Such a behavior is characterized by the broadening of molecular weight distributions (PDI~2), the formation of cyclic oligomers, and the randomization of the comonomer units along the polyester chain, as the monomer conversion increases and approaches completion.

Block copolymers have been prepared by sequential addition of the comon-omers as well. So far several combinations have been attempted by copolymerizing successively different lactones or mixtures of them, e.g., (poly(εCL-fr-δVL), poly[εCL-*b*-(εCL-co-δVL)] [35] and poly(εCL-*b*-DXO) [26]. In every one of the above-mentioned cases, perfectly well-tailored diblock copolyesters are prepared whatever the nature of the comonomer that is polymerized first. It is worth recalling that sequential copolymerization involving l,5-dioxepan-2-one (DXO, see Table 1) forms a block copolymer in which one block is nothing but an alternating poly(ester-alt-ether). As will be discussed in Sect. 2.5, diblock copolyesters with one block selectively functionalized by ethylene ketal groups spread all along the backbone can be readily prepared through the sequential copolymerization of εCL with l,4,8-trioxa(4,6)spiro-9-undecanone (TOSUO) [40]. The resulting poly(εCL-b-TOSUO) copolyesters offer the advantage of being easily converted in block copolymers with one sequence bearing either ketone or alcohol pendant functions, by successive and highly selective ketal de-protection and ketone reduction reactions, respectively. More detail is made available in the "synthesis and (co)polymerization of functional cyclic ester monomers[5]" section. As far as the sequential copolymerization of

lactones and dilactones is concerned, block copolymers (poly[εCL-*b*-(D,L-LA)] and po-ly(εCL-b-GA)) have been recovered with the exclusive condition that the lac- tone was added first, followed by the addition of the dilactone after complete consumption of εCL [27,41]. The same methodology has led successfully to the synthesis of block copolymers between εCL and adipic anhydride AA, that is poly(εCL-*b*-AA). The polymerization of εCL is initiated first by $Al(OzPr)_3$ and then AA is added to the living PCL chains. Reverse addition is forbidden since the ROP of cyclic, anhydrides proceeds through aluminum carboxylate growing species, which are known to be totally inactive in promoting the polymerization of εCL. Furthermore, PAA chains are poorly soluble in apolar solvent so that above an M_n of ca. 5000 the polyanhydride as directly initiated by $Al(OfPr)_3$ would precipitate quite rapidly. Starting the polymerization with εCL is a key solution to overcome this drawback, the living PCL preformed chains responsible for keeping the whole P(εCL-fr-AA) growing copolymer soluble in toluene [33].

The exclusive formation of the block copolymer has been confirmed by selective fractionation, NMR spectroscopy, and SEC analysis. For instance, the copo-lymerization of εCL and δVL has been followed by SEC. Figure 2 compares the SEC chromatograms of the first PCL block and the final poly(εCL-*b*-δVL) diblock copolymer. The molecular weight of the macroinitiator is shifted towards higher values in close agreement with the theoretical value expected from the comonomer-to-$Al(OiPr)_3$ molar ratio, and the MWD remains very narrow during the copolymerization process (PDI=LlO).

Interestingly, the ROP of GA by living PCL macroinitiators as initiated by aluminum alkoxides has led to PGA chains of unprecedented molecular weights (M_n as high as 70,000). Note also that symmetrical triblock copolyesters which present interesting elastomeric properties (see Sect. 4.1), have also been prepared by sequential addition of the εCL and DXO comonomers as will be discussed in Sect. 4.1.
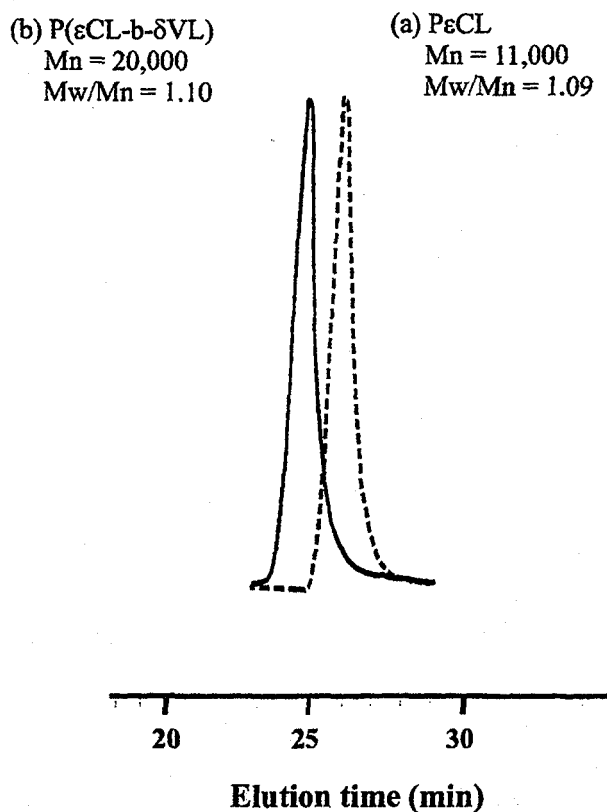

(b) P(εCL-b-δVL)
Mn = 20,000
Mw/Mn = 1.10

(a) PεCL
Mn = 11,000
Mw/Mn = 1.09

20   25   30

Elution time (min)

Fig. 2. SEC traces of PCL macroinitiator (curve a) and poly(εCL-b-δVL) block copolymer (curve b).
Polymerization conditions: [monomer]$_0$=l mol/l; ([εCL]$_0$+([δVL]$_0$)/[Al(OiPr)$_3$]$_0$= 200; toluene at 0 °C.

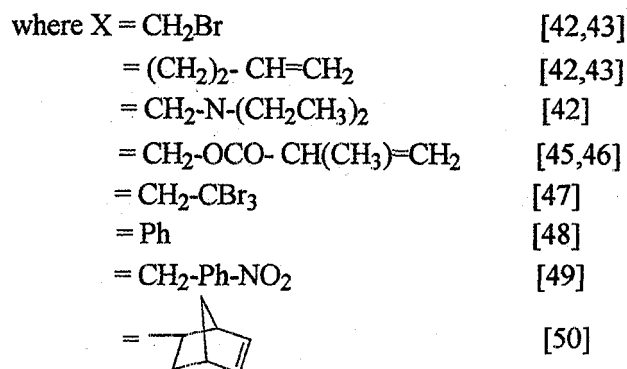2.3.Selective End-Functionalization

The synthesis of end-reactive polymers (telechelic macromolecules) of a precisely controlled molecular weight is an important step for any macromolecular engineering. In this regard, Al derivatives containing p (p=l,3) functional alkox-ide groups associated with 3-p inactive alkyl groups have proved to be highly effective. In agreement with the "coordination-insertion" mechanism discussed above, the functional group (OCH_2X) of the aluminum alkoxides is selectively attached to the α-chain end via an ester linkage, whereas a hydroxyl end group is systematically present in the ω- position, as the result of the hydrolytic deactivation of the propagating

aluminum alkoxide species (Scheme 4).
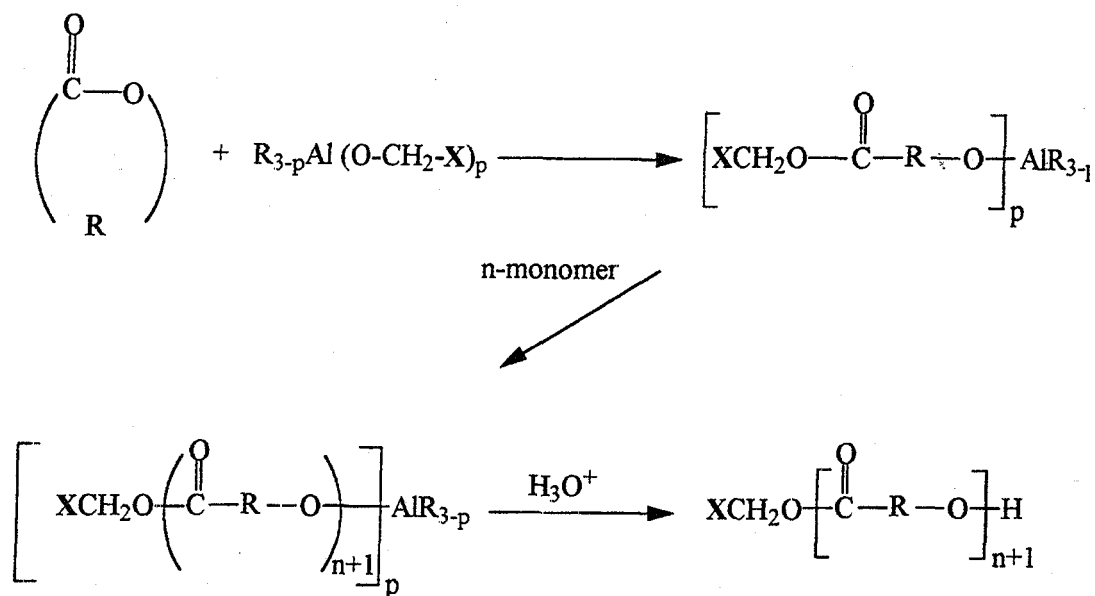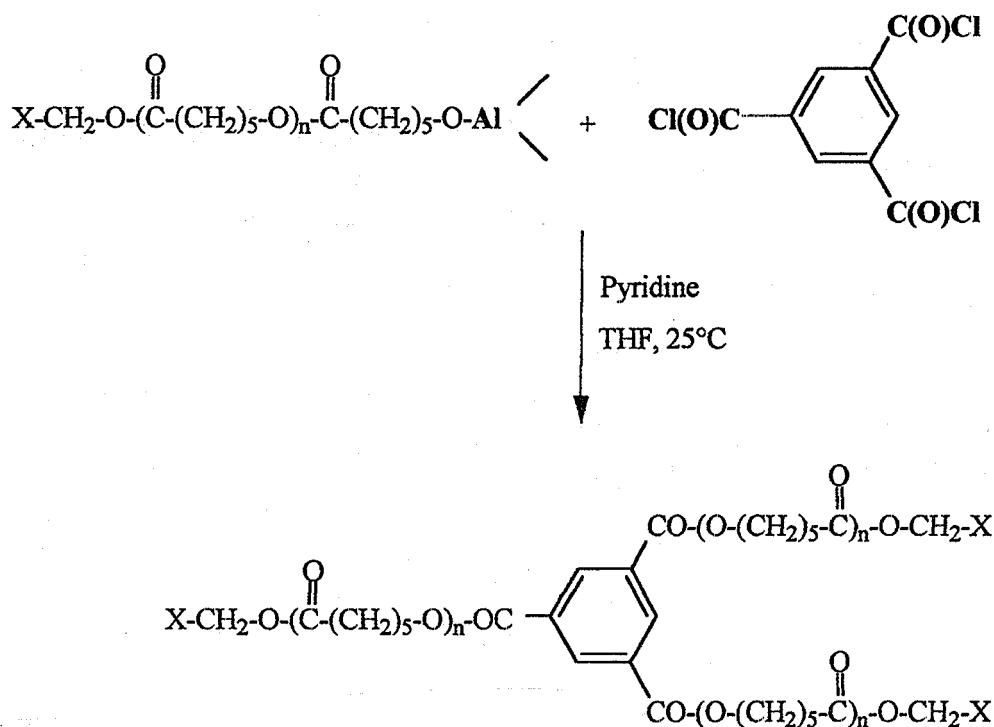

Scheme 4

Functional diethyl aluminum alkoxides have been prepared by reaction of $AlEt_3$ with an equimolar amount of the corresponding alcohol (XCH_2OH). The reaction equilibrium is favorably displaced by formation and elimination of ethane [42, 43]. On the other hand, aluminum trialkoxides have been synthesized by substituting the three alkoxy groups of $Al(OiPr)_3$ by the selected functional alcohol. Distillation of the toluene/2-propanol azeotrope allows the substitution to be complete (Scheme 5) [44].

$$Et_3Al + HO\text{-}CH_2\text{-}X \xrightarrow{\text{toluene}} Et_2\text{-}Al\text{-}O\text{-}CH_2\text{-}X + C_2H_6 \uparrow$$

$$(^iPrO)_3Al + 3\ HO\text{-}CH_2\text{-}X \xrightleftharpoons{\text{toluene}} (X\text{-}CH_2\text{-}O)_3Al + 3\ ^iPrOH$$

where X = CH_2Br [42,43]
= $(CH_2)_2\text{-}CH{=}CH_2$ [42,43]
= $CH_2\text{-}N\text{-}(CH_2CH_3)_2$ [42]
= $CH_2\text{-}OCO\text{-}CH(CH_3){=}CH_2$ [45,46]
= $CH_2\text{-}CBr_3$ [47]
= Ph [48]
= $CH_2\text{-}Ph\text{-}NO_2$ [49]
= [50]
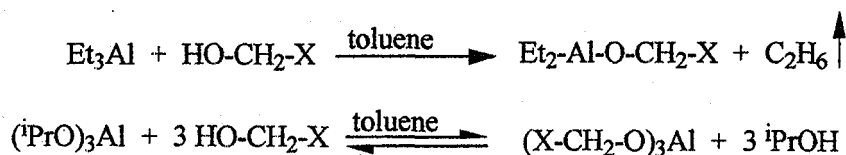
Scheme 5

Polymerization of ε-CL and (L- or D,L-)LA is perfectly "living" when initiated with any of the aforementioned functional aluminum alkoxides in toluene at 25 and 70 ^0C, respectively. This is supported by the close agreement between the mean degree of polymerization (DP) at total monomer conversion and the monomer-to-initiator molar ratio, the narrow molecular weight distributions (PDI= 1.1-1.3), and the quantitative end-group functionalization as detected by NMR spectroscopy. Clearly a great variety of asymmetric telechelic α-functional ω-hydroxy PGL and PLA have been recovered owing to the great versatility of the initiators that can be used. Similarly, the preparation of symmetric telechelic α,ω-hydroxy polyesters has been accomplished by using alkylaluminum di-alkoxides as difunctional initiators, e.g., $Et_2Al\text{-}O\text{-}X\text{-}O\text{-}AlEt_2$ where X is either an aliphatic

group or a polymer chain (Scheme 6) [51].

$$HO-X-OH \quad + \quad 2 \, AlEt_3 \longrightarrow Et_2Al-O-X-O-AlEt_2 \quad + \quad 2 \, C_2H_6 \uparrow$$

$$Et_2Al-O-X-O-AlEt_2 \quad + \quad \text{(caprolactone)} \longrightarrow Et_2Al-(O-(CH_2)_5-\overset{O}{\overset{\|}{C}})_n-O-X-O-(\overset{O}{\overset{\|}{C}}-(CH_2)_5-O)_n-AlEt_2$$

$$\overset{H_3O^+}{\swarrow}$$

$$H-(O-(CH_2)_5-\overset{O}{\overset{\|}{C}})_n-O-X-O-(\overset{O}{\overset{\|}{C}}-(CH_2)_5-O)_n-H$$

with X = -(CH_2)_4- ; -(CH_2)_2-N(CH_3)-(CH_2)_2-; -(CH_2)_2-[O-CH_2-CH_2]_n-O-(CH_2)_2-
or -(CH_2)_3-[Si(CH_3)_2-O]-Si(CH_3)_2-(CH_2)_3-.

Scheme 6

A hydroxyl group is selectively attached at both chain ends as demonstrated by FTIR and ^{1}H NMR spectroscopies, and confirmed by titration of the derived α,ω-dicarboxylic acid polyesters. Diethylaluminum dithiolates have also been investigated as initiator for the ROP of εCL. Dithiols have been reacted with a two-fold molar excess of, AlEt$_3$, making Al dithiolates available for the controlled synthesis of hydroxy telechelic PCL [51]. Synthesis and use of H$_2$N-(CH$_2$)S-OAlEt$_2$ as an initiator also deserve interest, since the nucleophilic addition of the amino group onto the carbonyl of the monomer is nothing but an initiation process in addition to the aluminum alkoxide itself. This is another way to prepare α,ω-hydroxy PCL in a living manner [51]. Another general approach to end-functional polyesters relies upon the proper control of the termination step instead of the initiation one. In this regard, the aluminum alkoxide propagating species or the resulting ω-hydroxy end group after hydrolytic deactivation can be readily modified by reacting with carboxylic acid derivatives such as acid chlorides, acid anhydrides, or isocyanates. By this method, different ω-functional polyesters have been prepared [10,43,51]. The main advantage of this method is being able to avoid the preparation of the functional aluminum alkoxide. However, the functionalization may not be quantitative, specially when molecular weight is relatively high (Scheme 7).

$$R'-O-(\overset{O}{\overset{\|}{C}}-R-O)_n-\overset{O}{\overset{\|}{C}}-R-O-\overset{O}{\overset{\|}{C}}-NH-X \quad \xleftarrow{OCN-X}$$

$$R'-O-(\overset{O}{\overset{\|}{C}}-R-O)_n-\overset{O}{\overset{\|}{C}}-R-O-Al \overset{\diagup}{\diagdown} \text{ or H} \quad \xrightarrow{Cl-\overset{O}{\overset{\|}{C}}-X} \quad R'-O-(\overset{O}{\overset{\|}{C}}-R-O)_n-\overset{O}{\overset{\|}{C}}-R-O-\overset{O}{\overset{\|}{C}}-X$$

$$\xrightarrow{\text{(anhydride)}} \quad R'-O-(\overset{O}{\overset{\|}{C}}-R-O)_n-\overset{O}{\overset{\|}{C}}-R-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-OH$$

Scheme 7

A more general strategy to approach symmetrical telechelic polyesters consists of the control of both initiation and termination steps. Indeed, combination of a functional initiator for the (di)lactones ROP with an effective coupling agent, such as terephthalic acid chloride, quantitatively yields an α,ω-functional polyester of a two fold molecular weight [52]. Similarly, end-functional tri-arm star-shaped PCLs have been prepared using a trifunctional coupling agent (Scheme 8) [53].

X-CH₂-O-(C-(CH₂)₅-O)ₙ-C-(CH₂)₅-O-Al + Cl(O)C—[benzene ring]—C(O)Cl / C(O)Cl

Pyridine
THF, 25°C

X-CH₂-O-(C-(CH₂)₅-O)ₙ-OC—[benzene ring]—CO-(O-(CH₂)₅-C)ₙ-O-CH₂-X / CO-(O-(CH₂)₅-C)ₙ-O-CH₂-X

Scheme 8

2.4. Kinetic Aspects of the "Coordination-Insertion" ROP

Significant advances in the understanding of the "coordination-insertion" ROP mechanism have been made owing to the kinetic studies by Duda and Penczek.

As mentioned above, the major advantage of aluminum alkoxide mediated ROP when compared with most anionic and cationic processes is its living character. Transesterification side reactions or termination reactions are fully depressed at least until complete monomer conversion, and polyesters with predictable molecular weight and narrow MWD, are obtained. However, aluminum alkox-ides, like other metal alkoxides, are known to be aggregated in solution. This aggregation plays an important role in the polymerization kinetics. Fpr instance, polymerizations are characterized by an induction period of time before the initiation step which appears to correspond to a monomer/initiator co-ordinative rearrangement [10]. This fact can also determine the initiation efficiency. For example, $Al(OfPr)_3$ in toluene leads to a coordinative aggregation equilibrium between tetramers (A4) and trimers (A3). Depending on the monomer and reaction conditions both species (A3+A4) can act as initiators for the polymerization (case LA in toluene at 70 ^{0}C) or only the more reactive A3 can be involved (case εCL) [54]. On the other hand, the aggregation of some aluminum alkoxides was also observed during the propagation step. For instance, in the polymerization of εCL initiated in apolar solvent with dialkyl aluminum monoalkoxides, R_2AlOR', the covalent "Al-O" growing species proved to associate and form inactive aggregates. The type and size of the aggregates depend on the solvent polarity, the nature of the alkyl R substituents, and the presence of coordinative ligands such as amines and alcohols. Actually, only the small fraction of disassociated aluminum alkoxides (in equilibrium with the aggregates) are active in ROP of (di)lactones. This polymerization behaves as a "living-dormant" polymerization, often known as "pseudoliving" polymerization (Scheme 9) [55].
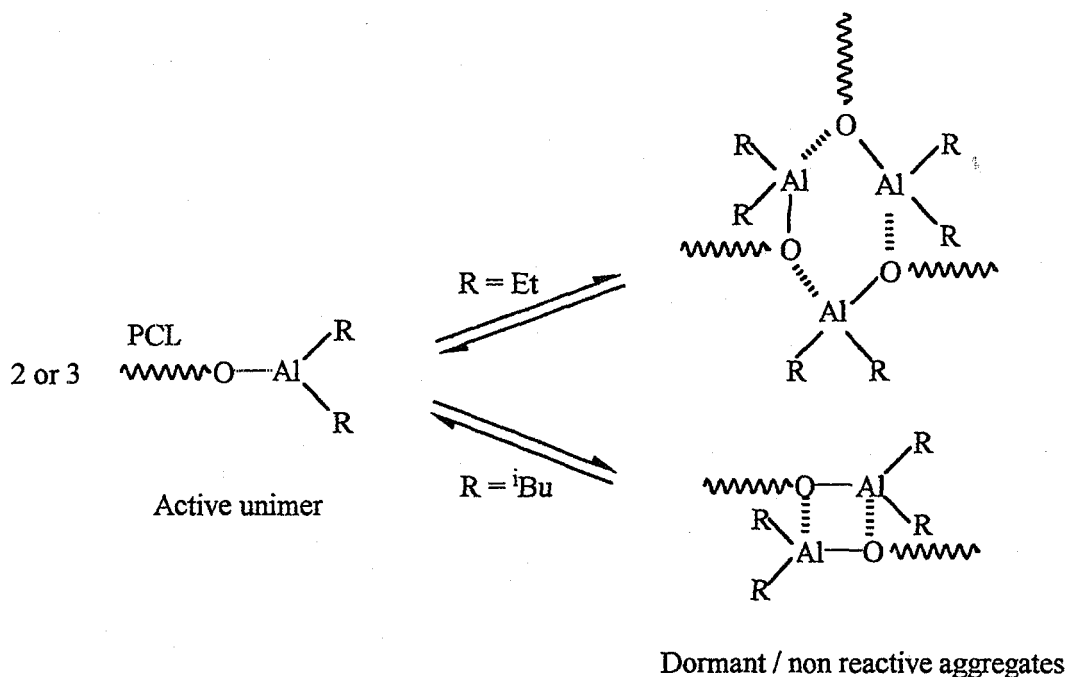
Scheme 9

Apart from the alkoxides aggregation, the different factors which affect the kinetics of the (di)lactones ROP initiated by aluminum alkoxides might be summarized as follows.

a) Nature of the alkoxides: aluminum trialkoxides propagate faster than dialkyl aluminum monoalkoxides due to the higher ionicity of the Al-O bond in the former case [56].

b) Temperature: as expected, the overall polymerization rate increases with temperature. However, at high temperature the transesterification side reactions may occur, limiting the molecular weight, broadening the MWD, and yielding cyclic oligomers [56].

c) Solvent: the polymerization proceeds faster in non-polar solvents. This is explained by the fact that polar solvents compete with the monomer in coordinating the reaction sites, i.e., the aluminum atom of the growing species. In other words, the solvent prevents or at least limits the access of the monomer to the reaction site, thus decreasing the overall rate of polymerization [56,57].

d) Additives: external additives can modify the rate of polymerization by three different mechanisms.

1   By acting as transfer agents. It has been established by kinetic studies that low-molecular weight alcohols and diols, which have been introduced into the polymerization mixture of εCL and Al(OfPr)$_3$, operate as chain-transfer agents. Accordingly, they participate in the initiation step in such a way that the total initiation species equals three isopropoxy groups of Al(OfPr)$_3$, plus the added alcohol (diol) molecules. Moreover, they can also act either as decelerators in polymerization initiated with highly active Al(OfPr)$_3$ trimers (A3), or as accelerators in polymerization initiated with much more stable and accordingly less active Al(OfPr)$_3$ tetramers (A4). Alcohols actually modify and shift the equilibrium between the A3/A4 aggregates, facilitating the transformation of the low reactive A4 into A3 (or other more reactive initiating species) [58].

2   By provoking the complete deaggregation of the growing chains as initiated by R$_2$AlOR'. This is the case of secondary amines, the addition of which increases the overall rate of polymerization [55].

3 By increasing the Al-O bond reactivity. This effect has been observed when Lewis bases, such as pyridine, picoline, and nicotine, were added to the reaction mixture in equimolar amount relative to the Al alkoxide active species [30-33], This kinetic effect is triggered by a specific coordination of the Lewis base onto the Al atom of the growing site which may increase the ionicity of the Al-O bond (Scheme 10a). These additives have to be added in the right amounts. An excess generally produces a decrease in the polymerization rate. The ligand does not act as an activator any more but rather blocks the growing sites, preventing the monomer from coordinating the aluminum alkoxide. It is worth noting that Inoue et al. have recently reported on the kinetic activation of δVL polymerization initiated by tet-raphenylporphinato (TPP)Al alkoxide in the presence of bulky Lewis acid compounds [59]. In that precise case, the extremely fast polymerization has been attributed to the coordinative interaction between the monomer and the bulky Lewis acid (Scheme 10b).

(a)   **(b)**
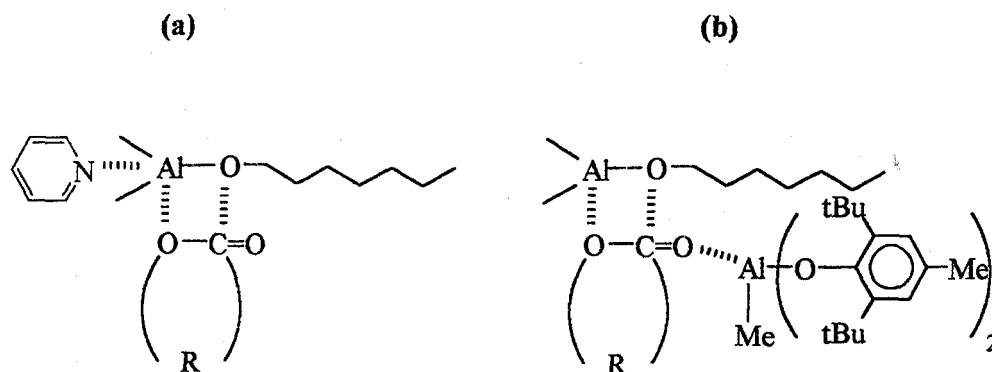
Scheme 10

2.5.Synthesis and (Co)poiymerization of Functional Cyclic Ester Monomers

Special attention has been paid to the preparation of biodegradable polymers bearing functional pendant groups. The availability of functional pendant groups is highly desirable for the fine tuning of properties like crystallinity, glass transition temperature, hydrophilicity, and chemical reactivity in view of, e.g., attachment of drugs, improvement of biocompatibility, and promotion of bioad-hesion. Several examples of functional monomers and their (co)polymerization have been reported in the literature (Scheme 11).
Although important efforts have been devoted to the synthesis of functipnal-ized monomers, which is very often complex and tedious, only one example of controlled/living (co)polymerization has been reported so far. This is the case of the 5-ethylene ketal ε-caprolactone, precisely l,4,8-trioxa(4,6)spiro-9 undecan-one (TOSUO), which is readily synthesized by a one-step oxidation reaction of the commercially available monoethylene ketal of the 1,4-cyclohexanedione [36]. TOSUO has proved to homopolymerize in a "living" way when initiated by $Al(OfPr)_3$ in toluene at 25 ^{0}C (Scheme 12) [66].
As a result, well-defined homo PTOSUO, but also random and block copolymers with εCL, were prepared [36, 40]. Treatment of the (co)polyester chain with $(C_6Hg)_3CBF_4$ in CH_2Cl_2 at RT allows for the quantitative deprotection of the pendant ketone functions. Furthermore the reduction of the formed ketone into hydroxyl groups has been performed selectively by $NaBH_4$ in CH_2Cl_2/Et0H solvent mixture at RT. Importantly, no chain scission has been detected by SEC and ^{1}H NMR spectroscopy, neither after the deprotection step nor after the reduction one. Thus aliphatic polyesters bearing either ketone pendant groups or hydroxyl pendant groups can be readily synthesized, which opens new application prospects. It is worthwhile pointing out that the controlled copolymerization between TOSUO and lactides has also been successfully performed. Aliphatic polyesters with hydroxyl groups highly reactive toward $AlEt_3$ provided a macroinitiator for (di)lactones polymerization, so that synthesis of biodegradable functional comb, graft, and dendri-graft aliphatic polyesters has been possible (see Sect. 3.1). The poly(εCL-co-TO-SUO) copolyesters have proved to be easily redispersed in water. Compared to pure PCL in the same molecular weight range that gives a crude precipitate, both homo PTOSUO and copolymers with εCL provided stable dispersions in water of a mean size below 100 nm (see Sect. 4.4). On the other hand, poly(εCL-co-TO-SUO) copolymers with at least 15 mol% TOSUO units statistically distributed along the backbone displayed a low T_g of ca. -40 ^{0}C, making them valuable rubbery materials to be used in combination with semicrystalline PCL. Therefore, poly[εCL-*b-(*εCL-co-TOSUO*)-b*-εCL] symmetrical triblock copolyesters represent potential biodegradable and biocompatible thermoplastic elastomers.
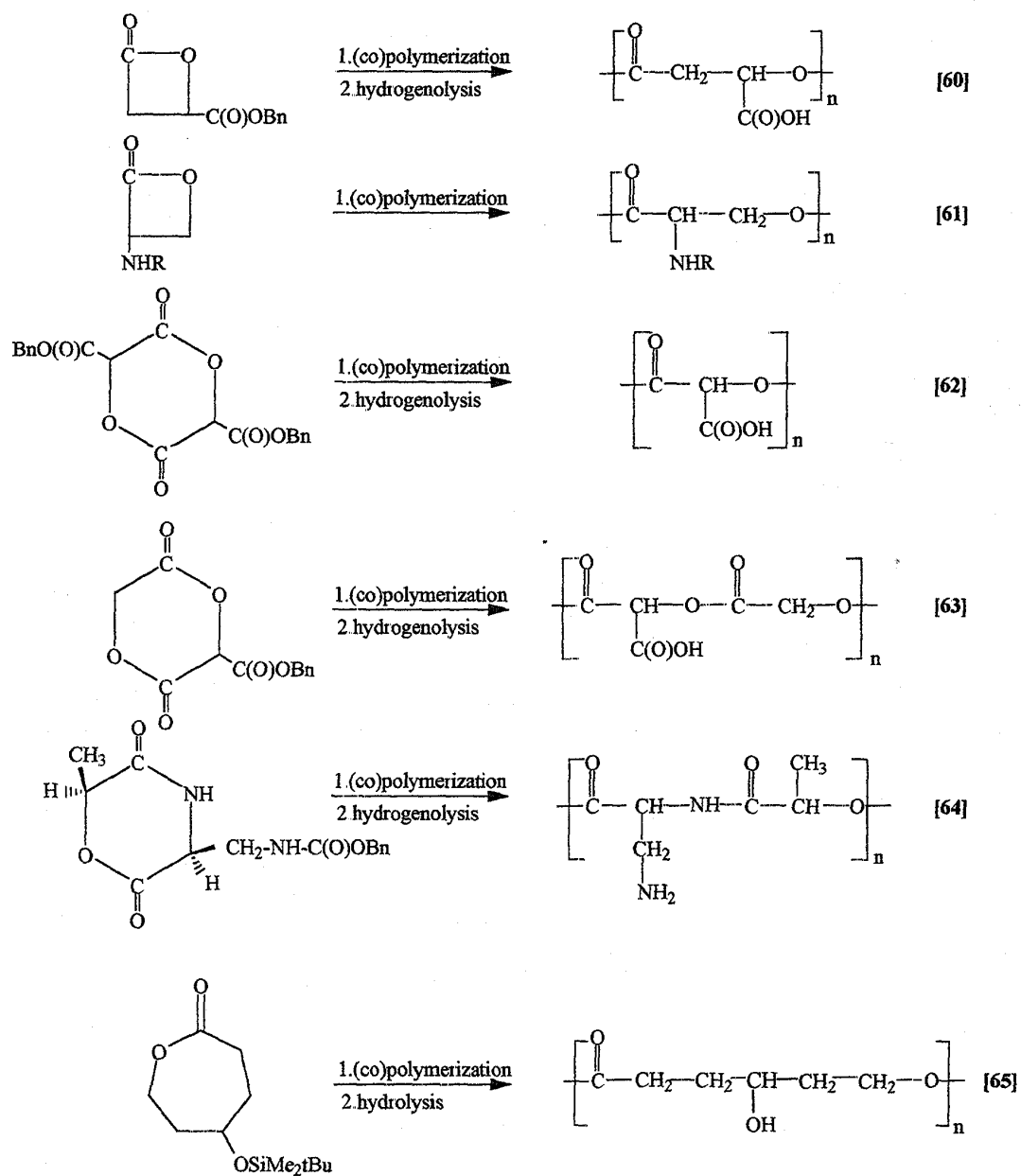
Scheme 11
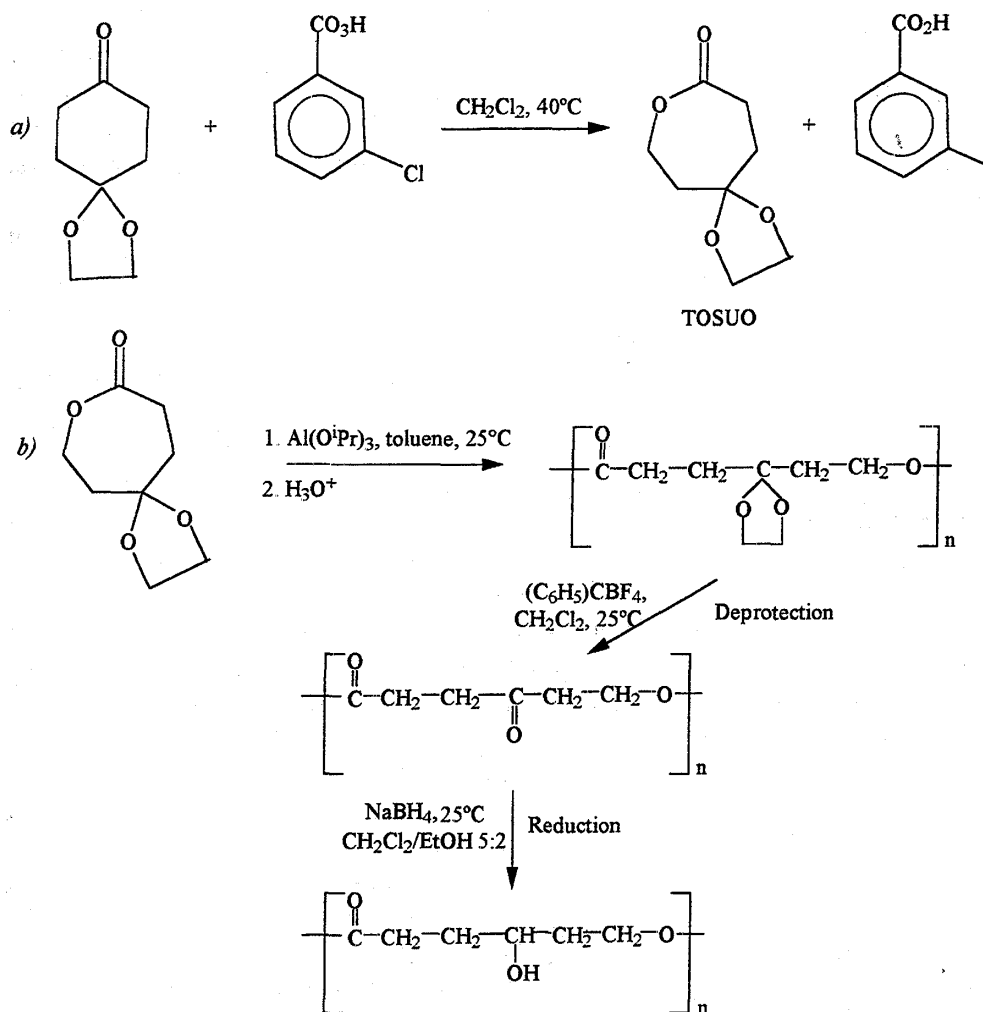
Scheme 12

3. Synthesis of Block and Graft Copolymers by Combination of (Di)lactones Ring Opening Polymerization with Other Living/Controlled Polymerization Processes
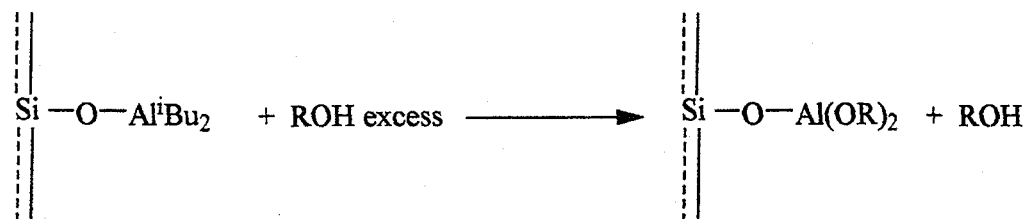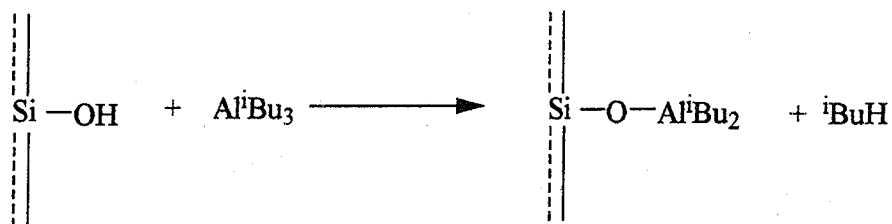
Macromolecular engineering is the ultimate goal of the polymer chemist when he has a monomer or a family of monomers at his disposal. Once each step of the polymerization process is carefully controlled, every molecular parameter of the polymer is predictable: molecular weight, tacticity, molecular weight distribution, nature of the end groups, microstructure, and composition, and block length in the case of copolymers. Like pieces of a construction set, these properly-tailored macromolecules can then be used to design new polymeric materials [67,68]. Block and graft copolymers are convincing examples of well-controlled molecular architectures that comprise at least two polymeric components and lead to original materials, e.g., thermoplastic elastomers, polymeric emulsifiers, surface modifiers, etc.
With the idea of extending the scope of the macromolecular engineering of aliphatic polyesters, the "coordination-insertion" ROP of lactones and dilac-tones has been combined with other polymerization processes. This section aims at reviewing the new synthetic routes developed during the last few years for building up novel (co)polymer structures based on aliphatic polyesters, at least partially.
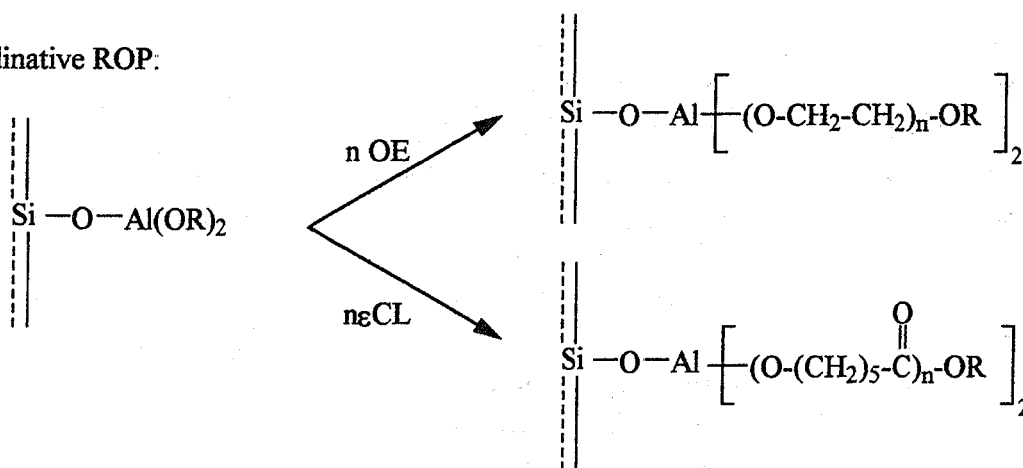
3.1. Ring Opening Polymerization

Considerable effort has been carried out by different groups in the preparation of amphiphilic block copolymers based on poly(ethylene oxide) PEO and an aliphatic polyester. A common approach relies upon the use of preformed ω-hy-droxy PEO as macroinitiator precursors [51, 70]. Actually, the anionic ROP of ethylene oxide is readily initiated by alcohol molecules activated by potassium hydroxide in catalytic amounts. The equimolar reaction of the PEO hydroxy end group(s) with triethyl aluminum yields a macroinitiator that, according to the
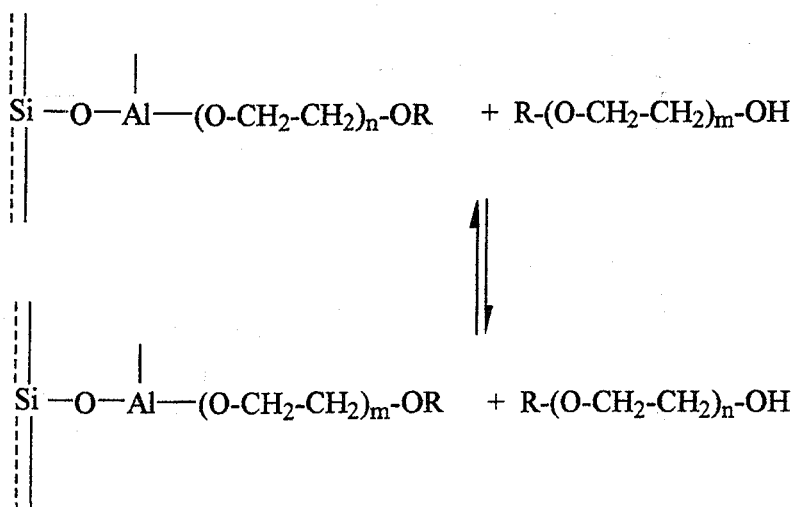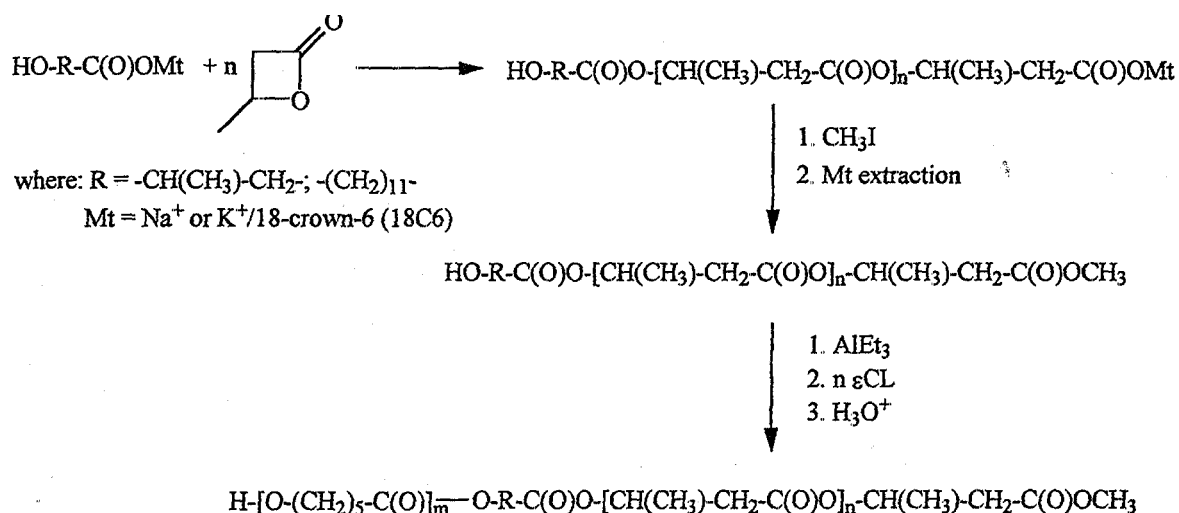
coordination-insertion mechanism previously discussed (see Sect. 2.1), is highly active in the εCL and LA polymerization. This strategy allows one to prepare di- or triblock copolymers depending on the functionality of the PEO macroin-itiator (Scheme 13a,b). Diblock copolymers have also been successfully prepared by sequential addition of the cyclic ether (EO) and lactone monomers using tetraphenylporphynato aluminum alkoxides or chloride as the initiator [69]. Of special interest is the heterogeneous catalytic coordination ROP process recently proposed by Hamaide et al. [117-119]. The catalytic system was obtained by grafting alkyl aluminum moieties onto silica. Porous silica (surface area: 320 m^2/g) was reacted with triisobutylaluminum in order to replace all the si-lanol groups by Si-O-AlR$_2$ bridges (Scheme 14a). Adding alcohol in excess caused the formation of aluminum alkoxides and allowed the catalytic mode, because of a rapid exchange reaction between the grafted active centers and the free alcohols present in the medium. AU the polymer chains were end-capped by these alcohol molecules, which gave functionalized oligomers (Scheme 14b).

The catalytic systems based on aluminum alkoxide grafted onto silica has proved to be efficient in ROP of epoxides, such as ethylene oxide (EO) and propylene oxide (PO), lactones (εCL) and lactides [118]. Despite the fact that heterogeneous catalyst generally results in a dispersion of properties, the exchange reaction between alcohols and active alkoxide species averages the structures of the chains and allows narrow MWD (Scheme 14c). Not only tailor-made ω-func-tionalized oligomers but also random and block (oligo)copolymers have been produced. Note that a continuous process has been set up and that the recycling of the catalyst can be performed after washing the support [119].

Block copolymers of (R,S)-β-butyrolactone and εCL have been synthesized by combining the anionic ROP of the first monomer with the coordinative ROP of the second one (Scheme 15) [71]. The first step consisted of the synthesis of hydroxy-terminated atactic PβBL by anionic polymerization initiated by the alkali-metal salt of a hydroxycarboxylic acid complexed with a crown ether. The hydroxyl end group of PβBL could then be reacted with AlEt$_3$ to form a macroin-itiator for the εCL ROP.

Scheme13

a) Catalyst preparation:

$$\text{Si} - \text{OH} \quad + \quad \text{Al}^i\text{Bu}_3 \quad \longrightarrow \quad \text{Si} - \text{O} - \text{Al}^i\text{Bu}_2 \quad + \quad {}^i\text{BuH}$$

$$\text{Si} - \text{O} - \text{Al}^i\text{Bu}_2 \quad + \quad \text{ROH excess} \quad \longrightarrow \quad \text{Si} - \text{O} - \text{Al(OR)}_2 \quad + \quad \text{ROH}$$

b) Coordinative ROP:

$$\text{Si} - \text{O} - \text{Al(OR)}_2 \quad \xrightarrow[\quad n\varepsilon\text{CL} \quad]{\quad n\,\text{OE} \quad}$$

$$\text{Si} - \text{O} - \text{Al} \left[\text{(O-CH}_2\text{-CH}_2\text{)}_n\text{-OR} \right]_2$$

$$\text{Si} - \text{O} - \text{Al} \left[\text{(O-(CH}_2\text{)}_5\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{)}_n\text{-OR} \right]_2$$

c) Rapid alcohol-alkoxide exchange reaction (e.g., for PEO-OH)

$$\text{Si} - \text{O} - \text{Al} - \text{(O-CH}_2\text{-CH}_2\text{)}_n\text{-OR} \quad + \quad \text{R-(O-CH}_2\text{-CH}_2\text{)}_m\text{-OH}$$

$$\updownarrow$$

$$\text{Si} - \text{O} - \text{Al} - \text{(O-CH}_2\text{-CH}_2\text{)}_m\text{-OR} \quad + \quad \text{R-(O-CH}_2\text{-CH}_2\text{)}_n\text{-OH}$$

Scheme 14

HO-R-C(O)OMt + n [structure: β-lactone with O and C=O] → HO-R-C(O)O-[CH(CH$_3$)-CH$_2$-C(O)O]$_n$-CH(CH$_3$)-CH$_2$-C(O)OMt

where: R = -CH(CH$_3$)-CH$_2$-; -(CH$_2$)$_{11}$-
Mt = Na$^+$ or K$^+$/18-crown-6 (18C6)

1. CH$_3$I
2. Mt extraction

↓

HO-R-C(O)O-[CH(CH$_3$)-CH$_2$-C(O)O]$_n$-CH(CH$_3$)-CH$_2$-C(O)OCH$_3$

1. AlEt$_3$
2. n εCL
3. H$_3$O$^+$

↓

H-[O-(CH$_2$)$_5$-C(O)]$_{\overline{m}}$—O-R-C(O)O-[CH(CH$_3$)-CH$_2$-C(O)O]$_n$-CH(CH$_3$)-CH$_2$-C(O)OCH$_3$

Scheme 15

Using the opposite strategy, preformed co-aliphatic primary amino PCL has been shown to be an efficient macroinitiator for the ROP of γ-benzylglutamate JV-carboxy anhydride (BG-NCA) leading to original biodegradable P(εCL-*b*-BG) diblock copolymers. Interestingly, the polybenzylglutamate segment can be selectively hydrogenated into polyglutamic acid, i.e., a hydrophilic polypeptide block, making available new biocompatible and biodegradable block copolymer surfactants (Scheme 16a) [72]. The key problem for the successful block copolymerization of εCL and amino acid-NCAs was the synthesis of ω-aliphatic primary amino PCL. As previously reported (see Sect. 2.3), initiation of εCL polymerization with an aluminum alkoxide containing a primary amino group leads to an α,ω-hydroxy PCL instead of the expected OC-NH$_2$, ω-OH polymer. An initiator that contains a masked amine was then proposed. In this respect, a bromine-containing diethylaluminum alkoxide, Br(CH$_2$)I$_2$OAlEt$_2$, has proved to be a valuable candidate, since it is easily converted into the expected primary amine (Scheme 16b). The polypeptide (PBG) block is thus terminated with a primary amine so that a coupling reaction would lead to the related PCL-*b*-polypeptide-*b*-PCL triblock copolymer. After selective hydrogenation, this type of am-phiphilic triblock copolymers are precursors of physically cross-linked hydro-gels.

a)   PCL-NH$_2$ ÷   (BG-NCA) $\xrightarrow{\text{CHCl}_3,\ \text{RT}}$ PCL-NH-[C(O)-CH-NH]$_{\overline{m}}$H

O=C—O—C=O with —NH and C$_6$H$_5$-CH$_2$-O(O)C (BG-NCA)

BnOOC   (PCL-b-PBG)

↓ Hydrogenolysis

PCL-NH-[C(O)-CH-NH]$_{\overline{m}}$H

HOOC   (PCL-b-PGA)

b)   Br-(CH$_2$)$_{12}$-OAlEt$_2$ $\xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. εCL, toluene, RT}}$ Br-(CH$_2$)$_{12}$-O$\left[$C-(CH$_2$)$_5$-O$\right]_n$-H

Ac$_2$O, DMAP, NEt$_3$
THF, RT

N$_3$-(CH$_2$)$_{12}$-O$\left[$C-(CH$_2$)$_5$-O$\right]$-C-CH$_3$ $\xleftarrow{\text{NaN}_3,\ \text{DMF, RT}}$ Br-(CH$_2$)$_{12}$-O$\left[$C-(CH$_2$)$_5$-O$\right]$-C-CH$_3$

HCOO$^{(-)}$NH$_4^{(+)}$ / Pd-C (10%)
DMF, RT

H$_2$N-(CH$_2$)$_{12}$-O$\left[$C-(CH$_2$)$_5$-O$\right]$-C-CH$_3$

(PCL-NH$_2$)
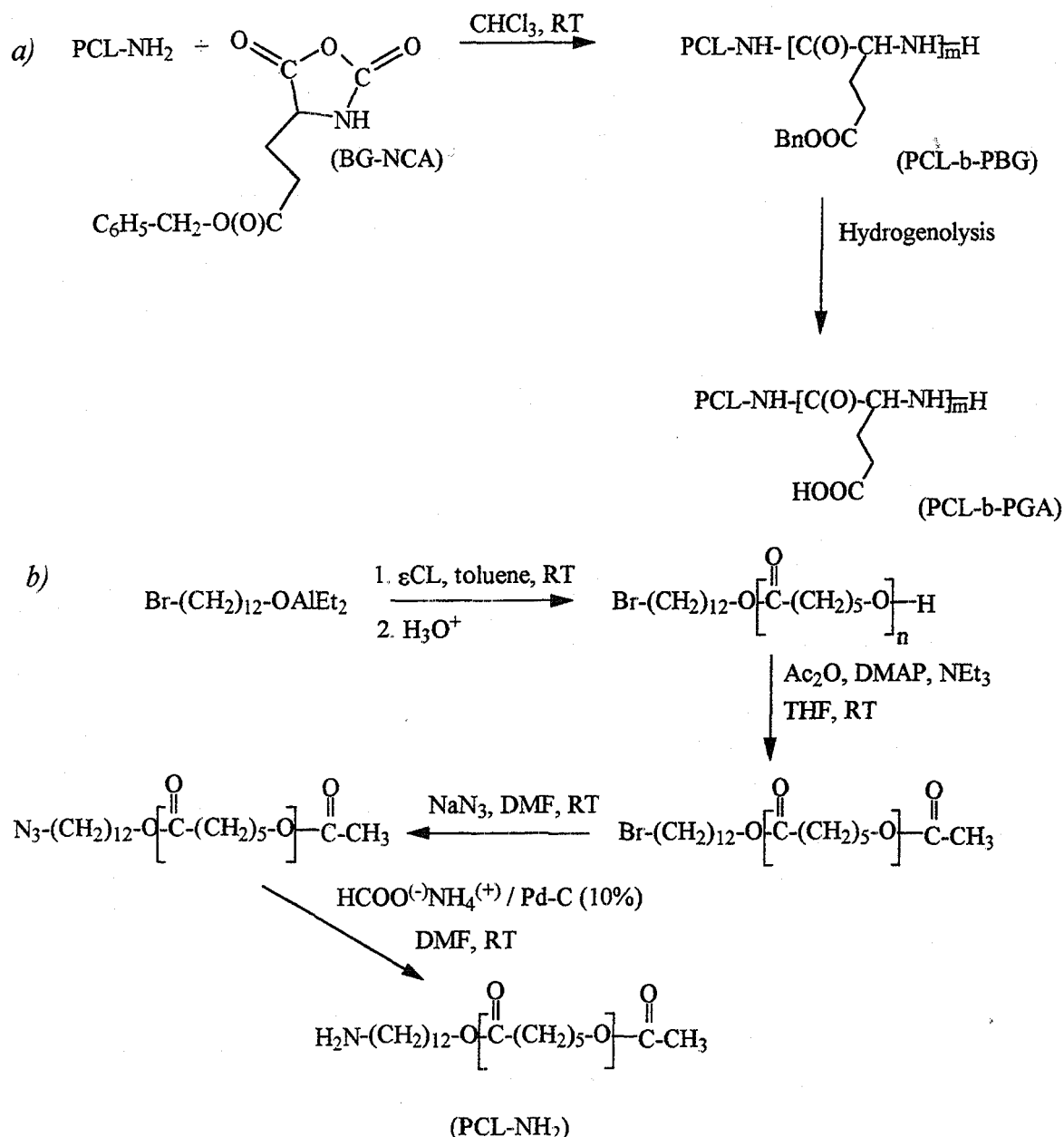
Scheme 16

Pitt et al. [65], and more recently, Albertsson et al. [73], have prepared chemically cross-linked aliphatic polyesters by ROP of the corresponding cyclic ester monomers in the presence of γ,Y-bis(ε-caprolactone)-type comonomers (Scheme 17). The cross-linked films displayed different swelling behaviors, de-gradability, and elastomeric properties depending on the nature of the lactone and composition of the comonomers feed. Recently, our laboratory reported on the first synthesis of fully biodegradable graft copolyesters by coordinative ROP. A PCL with pendant hydroxyl groups has been prepared by copolymerization with a few molar percent of TOSUO and subsequent ketone deprotection and reduction (see Scheme 12b). Reaction of the pendant hydroxyl groups with a slight excess of triethyl aluminum provides a multifunctional macroinitiator for the controlled ROP of εCL and lactides with formation of comb-like or graft copolymers, respectively (Scheme 18). If the grafts also contain TOSUO units, the release of the hydroxyl groups through the same procedure as previously, and their reaction with AlEt$_3$, allow an additional grafting reaction from being performed, leading to hyperbranched structures [74]. By judiciously controlling the lactone, e.g., εCL/TOSUO molar ratio and the initial content in Al(OiPr)$_3$ initiator, one has the possibility of tailoring the grafting density, the graft length, and the grafts distribution along the polyester backbone by, e.g., sequential addition of εCL and εCL/TOSUO comonomer mixtures.

Scheme 17

εCL + TOSUO

1. Al(O^{i}Pr)$_3$
2. H$_3$O$^+$

PCL

O O   O O

1. Deprotection
2. Reduction

PCL

OH   OH

nAlEt$_3$

PCL   + nC$_2$H$_6$

OAlEt$_2$ OAlEt$_2$

εCL   D,L-or L-LA   1. εCL / TOSUO
                                  2. Deprot / Reduct
                                  3. AlEt$_3$

PCL   PCL   PCL

PLA   OAlEt$_2$ OAlEt$_2$

Et$_2$AlO   Et$_2$OAl

Comb-like polyesters   Graft-copolyesters
                         e.g. P[CL-g-LA]   εCL

PCL

Hyperbranched PCL

Scheme 18 (next page)

3.2. Anionic Polymerization

ω-Hydroxy terminated polymers prepared by anionic polymerization, e.g., polystyrene (PS-OH) or polybutadiene (PBD-OH), have been transformed in efficient macroinitiators leading to the synthesis of poly(S-*b*-CL) or poly(BD-*b*-CL) diblock copolymers [75]. For that purpose, soluble zinc and aluminum µ-oxo-alkoxides

have been investigated as initiator precursors. One alkoxide group of the μ-oxo-alkoxides was substituted by either PS-OH or PBD-OH, all the other alkoxide groups being replaced by inactive carboxylate moieties as schematized hereafter (Scheme 19).

$$iPrO\!-\!Al(O iPr)\!-\!O\!-\!Zn\!-\!O\!-\!Al(O iPr)\!-\!O iPr \; + \; 3R\text{-}\overset{O}{\overset{\|}{C}}\text{-OH} \xrightarrow[(-3\,iPrOH)]{} \; iPrO\!-\!Al\!-\!O\!-\!Zn\!-\!O\!-\!Al$$

Pol-OH $\downarrow$ (- iPrOH)

$$\text{Pol-O}\!-\!\left[\overset{O}{\overset{\|}{C}}\text{-(CH}_2)_5\text{-O}\right]_n\!\!\text{H} \quad \xleftarrow[\text{2. H}_3\text{O}^+]{\text{1. n εCL}} \quad \text{Pol-O}\!-\!Al\!-\!O\!-\!Zn\!-\!O\!-\!Al$$

with Pol-OH = PBD-OH or PS-OH
and R = CH₃-(CH₂)₃-CH(Et)-
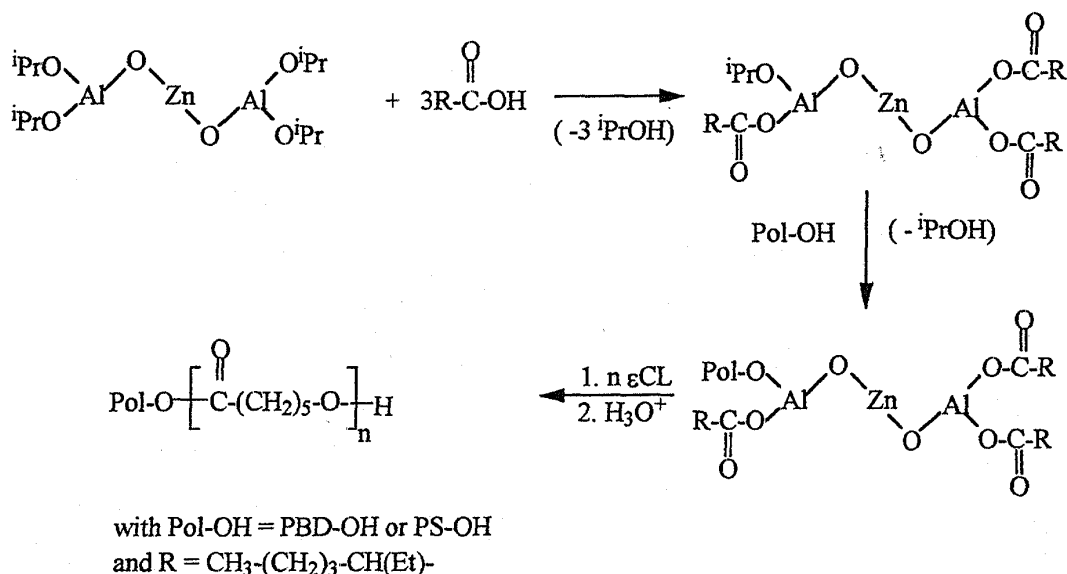
Scheme 19

Similar block copolymers, i.e., poly(S-*b*-CL), poly(BD-*b*-CL) as well as po-ly*(S-b-BD-b-CL)* ABC triblock copolymers have recently been prepared by Sta-dler et al. by sequential anionic polymerization (Scheme 20) [76]. Addition of 1,1-diphenylethylene is required in order to decrease down the too high reactivity of the polybutadienyl anions toward the initiation of the purely anionic ROP of εCL. Furthermore, due to the inevitable inter- and intramolecular transester-ification reactions in anionic ROP, especially at higher monomer conversion, the εCL polymerization time has been strictly controlled and the copolymerization was stopped by hydrolytic deactivation well before reaching quantitative εCL conversion.

$$\text{s-BuLi} + \text{(styrene)} \xrightarrow[\text{cyclohexane, RT}]{} \text{s-Bu}\!-\![\text{CH}_2\text{-CH}]_n\!-\!\text{CH}_2\text{-CH}^-\text{Li}^+$$

$\downarrow$ Butadiene 40°C

$$\text{s-Bu}\!-\![\text{CH}_2\text{-CH}]_n\!-\![\text{CH}_2\text{-CH=CH-CH}_2]\!-\!\text{CH}_2\text{-CH=CH-CH}_2{}^-\text{Li}^+{}_{m-1}$$

$\downarrow$
1. DPE, 40°C
2. εCL, RT
3. H₃O⁺

$$\text{s-Bu}\!-\!\left[\text{CH}_2\text{-CH}\right]_n\!-\!\left[\text{CH}_2\text{-CH=CH-CH}_2\right]_m\!-\!\text{CH}_2\text{-C(C}_6\text{H}_5)_2\!-\!\left[\overset{O}{\overset{\|}{C}}\text{-(CH}_2)_5\text{-O}\right]_o\!\!\text{H}$$
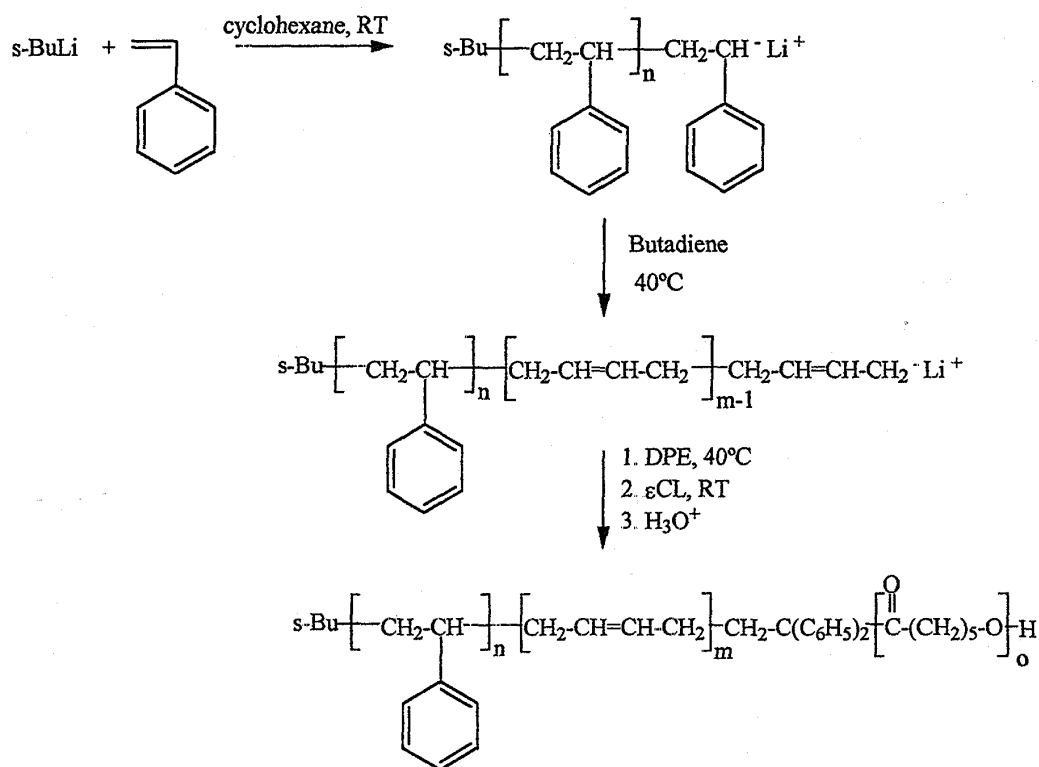
Scheme 20

Recently, our laboratory has developed a new method for the synthesis of po-ly(alkyl methacrylate-g-lactone) graft copolymers [77]. It consists of a set of two consecutive living polymerizations, i.e., an anionic polyaddition followed by a "coordination-insertion" ROP. In the first step, an alkyl methacrylate, e.g., methyl or 77-butyl methacrylate, was copolymerized with a few molar percent of (trimethylsiloxy)ethyl methacrylate via a living anionic (co)polymerization as promoted by 1,1-diphenylhexyllithium (DPHLi) in the presence of lithium chloride salt (LiCl) in THF at -78 ^{0}C. Deprotection of the hydroxyl function followed by the equimolar reaction with triethyl aluminum led to a multifunctional meth-acrylic macroinitiator for lactone ROP, with several initiating sites along the main backbone (Scheme 21). The second step consisted of the lactone ROP. The ROP was again perfectly well controlled and yielded graft copolymers of methyl and n-butyl methacrylates and lactones such as εCL, δVL, and TOSUO. The graft copolymers were characterized by a polymethacrylate main backbone and polyester grafts of predetermined molecular weight, a controlled branch density, and a narrow apparent polydispersity that ranged from 1.05 to 1.20. SEC analysis of the PoIy(MMA-g-CL) copolymer shows the expected increase in molecular weight with no remaining trace of unreacted starting macroinitiator (Fig. 3).

(b) Poly(MMA-g-CL)
Mn = 105000
Mw / Mn = 1.10

(a) Poly(MMA-co-HEMA)
Mn = 55000
Mw / Mn = 1.05

20   25

Elution time (min)
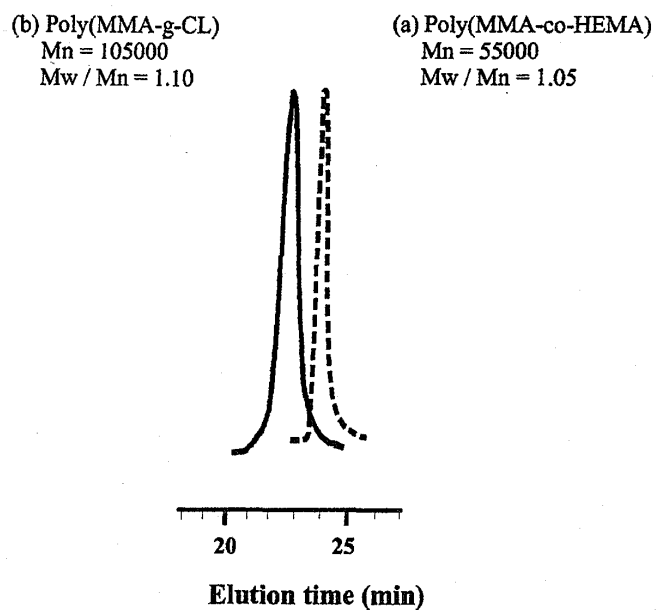
***Fig.** 3. Comparison of SEC traces for polyCMMA-co-HEMA) starting macroinitiator (curve a) and poly(MMA-g-CL) final graft copolymer (curve b). For synthetic conditions, see Scheme 21*
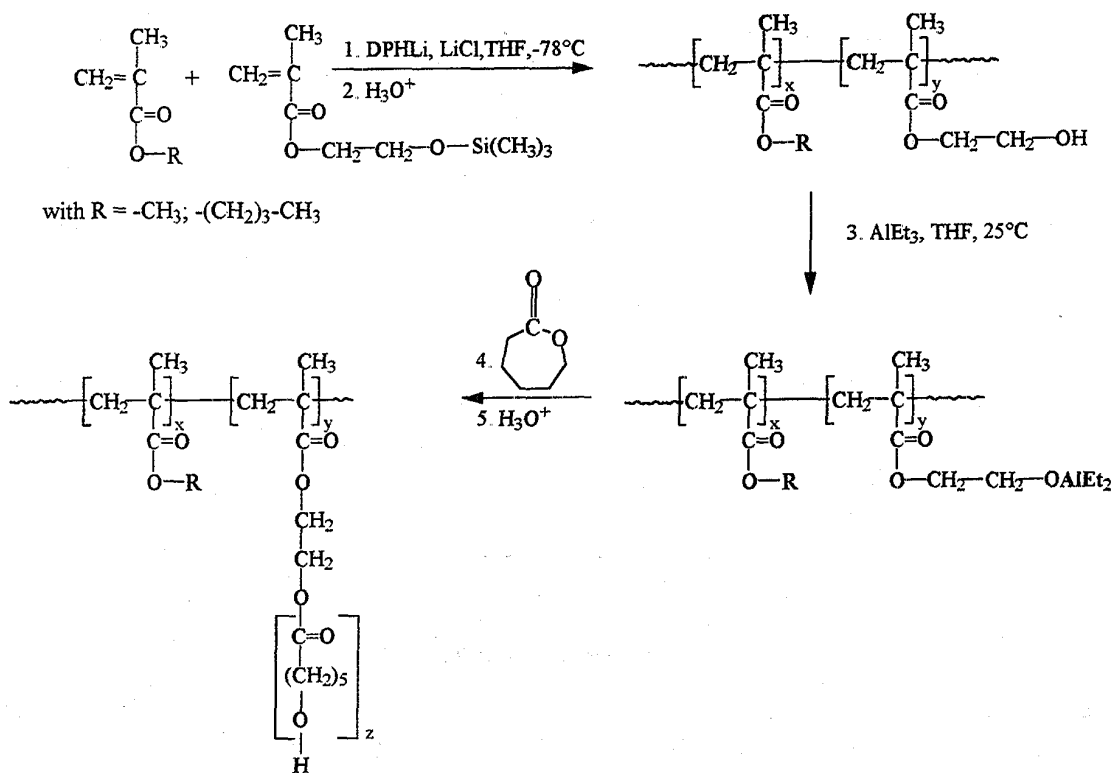
Scheme 21

3.3. Cationic Polymerization

Harris and Sharkey have converted isobutylene polymers into thermoplastic elastomers by the grafting of semi-crystalline polypivalolactone segments, the melting temperature of which is of ca. 245 ^{0}C [78]. The "grafting-from" technique was investigated on poly(isobutylene-co-*p*-methylstyrene) random copolymers, which were synthesized by cationic copolymerization. Active initiation species were generated by metalation of the benzylic carbons, followed by a car-boxylation reaction and then formation of ammonium carboxylate pendant groups (Scheme 22). The ROP of PVL was initiated by those carboxylic acid salts positioned all along the polyisobutylene backbone. Nevertheless, the control over the graft copolymers parameters was very poor.
In a similar way, the "grafting-from" technique has been applied to the synthesis of poly(chloroethylvinylether) chains by grafted PCL segments, i.e., poly(CEVE-g-CL) graft copolymers. Purposely cationically prepared PCEVE were partially modified by the introduction of 5-10% hydroxyl groups [79]. An equi-molar reaction of the pendant hydroxyl functions with HAIfBu$_2$ provided di-isobutyl aluminum monoalkoxides dispersed along the polyether backbone, which again proved to be active in coordinative ROP of εCL. Substitution of PCEVE macrocycles for the PCEVE linear chains led to novel "sun-like" graft copolymers with well-defined molecular parameters (Scheme 23) [80].
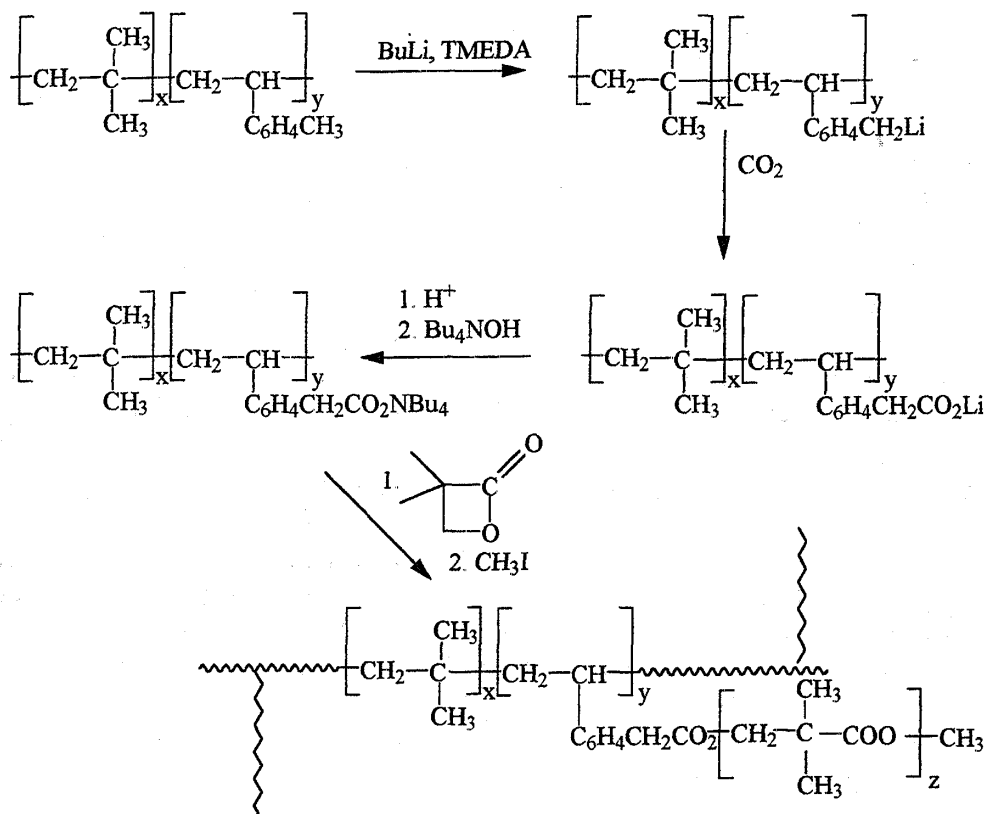
Scheme 22
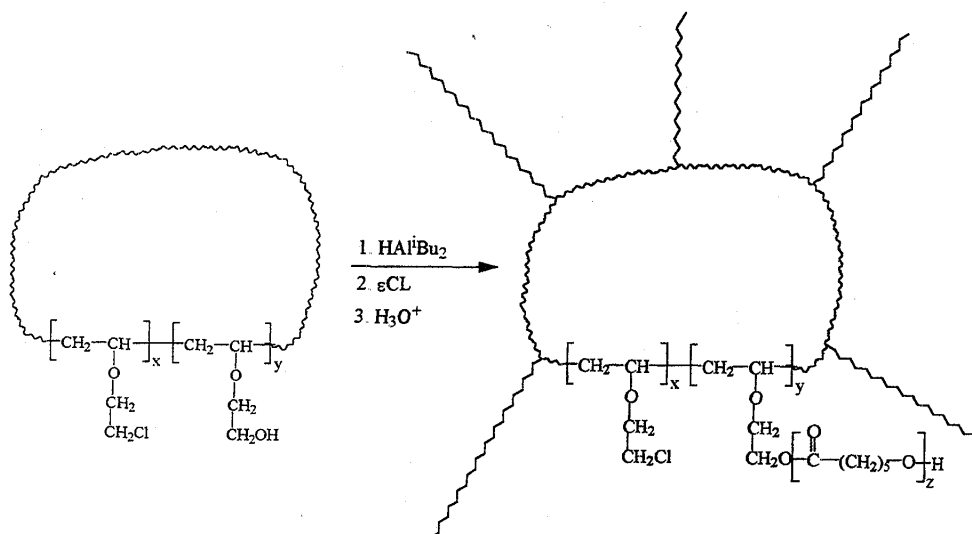
Scheme 23

3.4. Radical Polymerization

The last decades have witnessed the emergence of new "living"/controlled polymerizations based on radical chemistry [81, 82]. Two main approaches have been investigated; the first involves mediation of the free radical process by stable nitroxyl radicals, such as TEMPO while the second relies upon a Kharash-type reaction mediated by metal complexes such as copper(I) bromide ligated with 2,2'-bipyridine. In the latter case, the polymerization is initiated by alkyl halides or arenesulfonyl halides. Nitroxide-based initiators are efficient for sty-rene and styrene derivatives, while the metal-mediated polymerization system, the so called ATRP (Atom Transfer Radical Polymerization) seems the most robust since it can be successfully applied to the "living"/controlled polymerization of styrenes, acrylates, methacrylates, acrylonitrile, and isobutene. Significantly, both TEMPO and metal-mediated polymerization systems allow molecular weight and chain end functionality to be controlled accurately, while poly-dispersity remains narrow (PDRl<1.5). In collaboration with

Hawker et al., we have recently combined this new radical chemistry with aluminum alkoxide initiated ROP of lactones in order to obtain well-defined block and graft copolymers. Quite interestingly, we introduced the original concept of performing simultaneous dual living polymerizations as a novel one-step approach to block copolymers [83]. For example, from a hydroxy functionalized alkoxyamine initiator, both living ROP of εCL catalyzed by Sn(OCt)$_2$ and controlled free radical polymerization of styrene take place without the need for any intermediate steps (Scheme 24). It means that two different chains, i.e., PCL and PS chains, are growing away from the "biheaded" initiator, simultaneously and via two drastically different mechanisms.
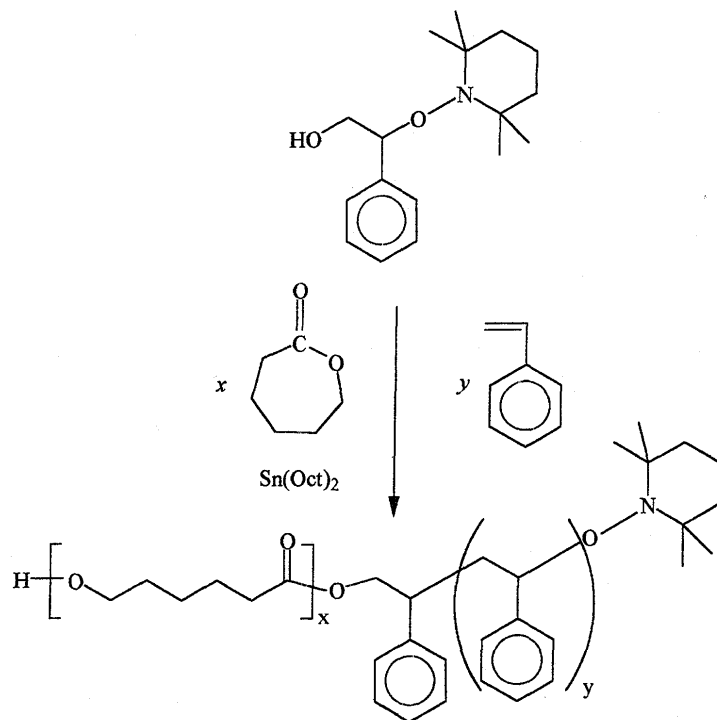
Scheme 24

In a very similar way, hydroxy functionalized ATRP initiators such as 2,2,2-tribromoethanol can be used for the simultaneous polymerization of εCL and MMA (Scheme 25) [83]. Purposely, the ROP of εCL is promoted by Al(OzPr)$_3$ added in catalytic amount so that the rapid alcohol-alkoxide exchange reaction (see Sect. 2.4) activates all the hydroxyl functions. In order to avoid initiation by the isopropoxy groups of Al(OfPr)$_3$. The in-situ formed iPrOH is removed by distillation of the zPrOH/toluene azeotrope. On the other hand, the ATRP of MMA is catalyzed by NiBr$_2$(PPh$_3$)$_3$. The two aforementioned one-step methods provide block copolymers with controlled composition and molecular weights, but with a slightly broad MWD (PDI=1.5-2).

CBr₃CH₂OH

Scheme 25 content:

$$x \quad \text{(methacrylate)} \qquad \text{CBr}_3\text{CH}_2\text{OH} \qquad y \quad \text{(caprolactone)}$$

NiBr₂(PPh₃)₃ \qquad Al(OⁱPr)₃

H₃O⁺

$$\text{Br}\left[\begin{array}{c}\text{CH}_3\\|\\\text{C}-\text{CH}_2\\|\\\text{COOCH}_3\end{array}\right]_x\text{CBr}_2\text{CH}_2\text{O}\left[\begin{array}{c}\text{O}\\\|\\\text{C}-(\text{CH}_2)_5-\text{O}\end{array}\right]_y\text{H}$$
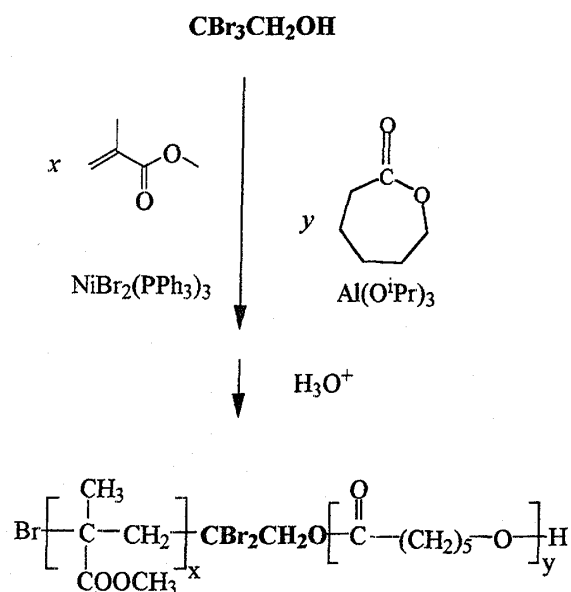
Scheme 25

In a more conventional approach, poly(S-*b*-CL) and poly(MMA-*b*-CL) block copolymers have been prepared from the same components as described previously, but in a two-step process via macromolecular initiators [47]. In a first step, α-hydroxy PS and α-hydroxy PMMA have been prepared by controlled radical polymerization. After transformation of the hydroxyl end groups into aluminum alkoxide functions, these polymeric initiators can be used to initiate the ROP of εCL (Scheme 26, shown for poly(MMA-*b*-CL) copolymers). On the other hand, α-TEMPO and OC-CBr₃ PCL prepared by living coordinative ROP initiated with the hydroxy functionalized alkoxyamine and CBr₃CH₂OH have been able to initiate quantitatively the controlled polymerization of styrene and methyl methacrylate, respectively. By this two-step method, block copolymers with controllable composition and molecular weight for each blocks were recovered with narrow MWD (PDI= 1.1-1.3). This strategy has been extended successfully to other monomers such as D,L-LA and L-LA and functional methacrylates,e.g., 2-hydroxyethyl methacrylate [84]. Furthermore, the isolated diblock copolymers are again potential macroinitiators for additional ROP of (di)lactones or ATRP of unsaturated monomers, paving the way to novel ABC triblock or other multiblock copolymers.

CBr₃CH₂OH

NiBr₂(PPh₃)₃ \qquad Al(OⁱPr)₃

$$\text{Br}\left[\begin{array}{c}\text{CH}_3\\|\\\text{C}-\text{CH}_2\\|\\\text{COOCH}_3\end{array}\right]_x\text{CBr}_2\text{CH}_2\text{OH} \qquad \text{CBr}_3\text{CH}_2\text{O}\left[\begin{array}{c}\text{O}\\\|\\\text{C}-(\text{CH}_2)_5-\text{O}\end{array}\right]_y\text{H}$$

AlEt₃ \qquad NiBr₂(PPh₃)₃

$$\text{Br}\left[\begin{array}{c}\text{CH}_3\\|\\\text{C}-\text{CH}_2\\|\\\text{COOCH}_3\end{array}\right]_x\text{CBr}_2\text{CH}_2\text{O}\left[\begin{array}{c}\text{O}\\\|\\\text{C}-(\text{CH}_2)_5-\text{O}\end{array}\right]_y\text{H}$$
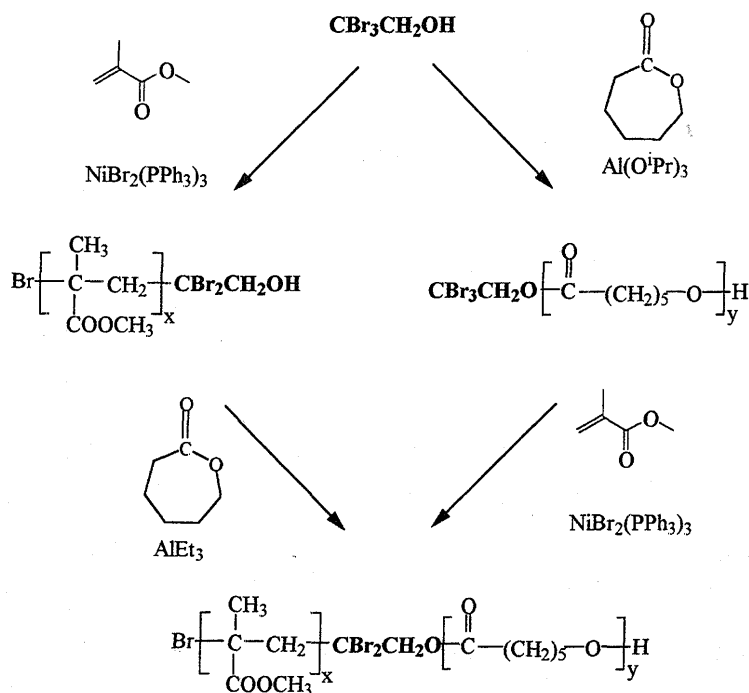
Scheme 26

Concerning the synthesis of graft copolymers, Jedlinski et al. have prepared poly(MMA-g-βBL) copolymers via anionic grafting of βBL from a modified PMMA backbone [85]. PMMA chains were partially saponified by potassium hydroxide and complexed by 18C6 crown ether so as to act as multifunctional macroinitiators for the βBL anionic polymerization (Scheme 27). Although the graft efficiency was high and the branch density easily predetermined by the degree of saponification, the use of poorly defined PMMA backbones, actually obtained by a conventional non-controlled free radical polymerization, yielded graft copolymers with broad MWD. In a similar approach, Caywood et al. prepared po-ly (ethylacrylate-g-pivalolactone) copolymers which displayed interesting thermoplastic elastomer properties [86].
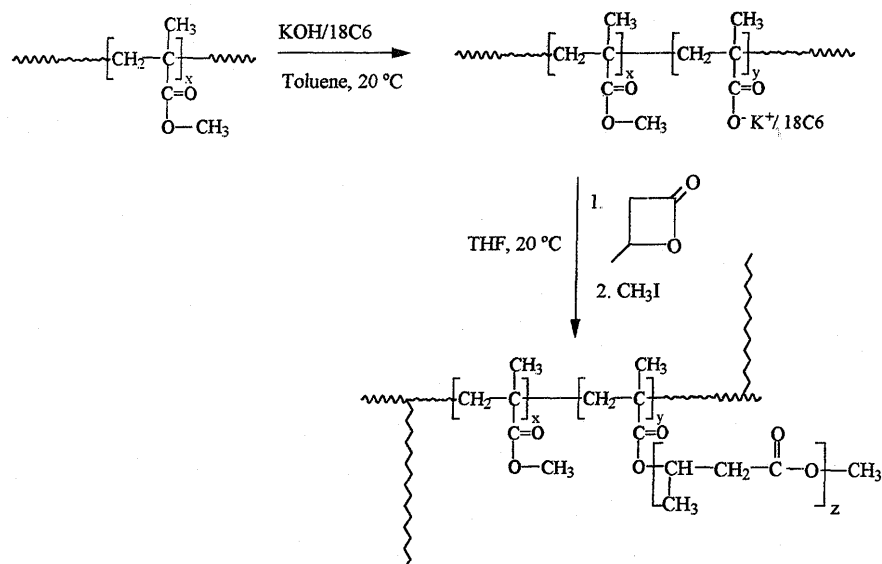
Scheme 27

Some of us [46] and Egiburu et al. [87] have studied the "macromonomer technique" as a method for producing PCL- and PLA-containing graft copolymers. Purposely* PLA and PCL macromonomers have been prepared by εCL and LA coordinative ROP as initiated by the reaction product of 2-hydroxyethyl methacrylate (HEMA) and AlEt$_3$ (see Scheme 5). These polyester macromono-mers have been copolymerized with styrene and methacrylate derivatives by using'AIBN as a free radical initiator. Nevertheless, due to the free radical process used in the copolymerization step, there was a lack of control over the formation of the main backbone. Graft copolymers polydispersed in compositions and molecular weights were accordingly obtained. In order to overcome this drawback we have examined again both metal- and nitroxyl-mediated control-led/"living" radical polymerization [88]. According to the synthetic strategies depicted in Scheme 28, a variety of graft copolymers were prepared among different styrenic and (meth)acrylic monomers and PCL and PLA grafts. The graft copolymers were characterized by controlled compositions, predetermined molecular weights for backbone and grafts, and narrow MWD (PDI=1.2-1.4). Furthermore, the radical process allowed the introduction of functional groups into the graft copolymers by copolymerization of HEMA, methacrylic acid, etc.

a)

b)
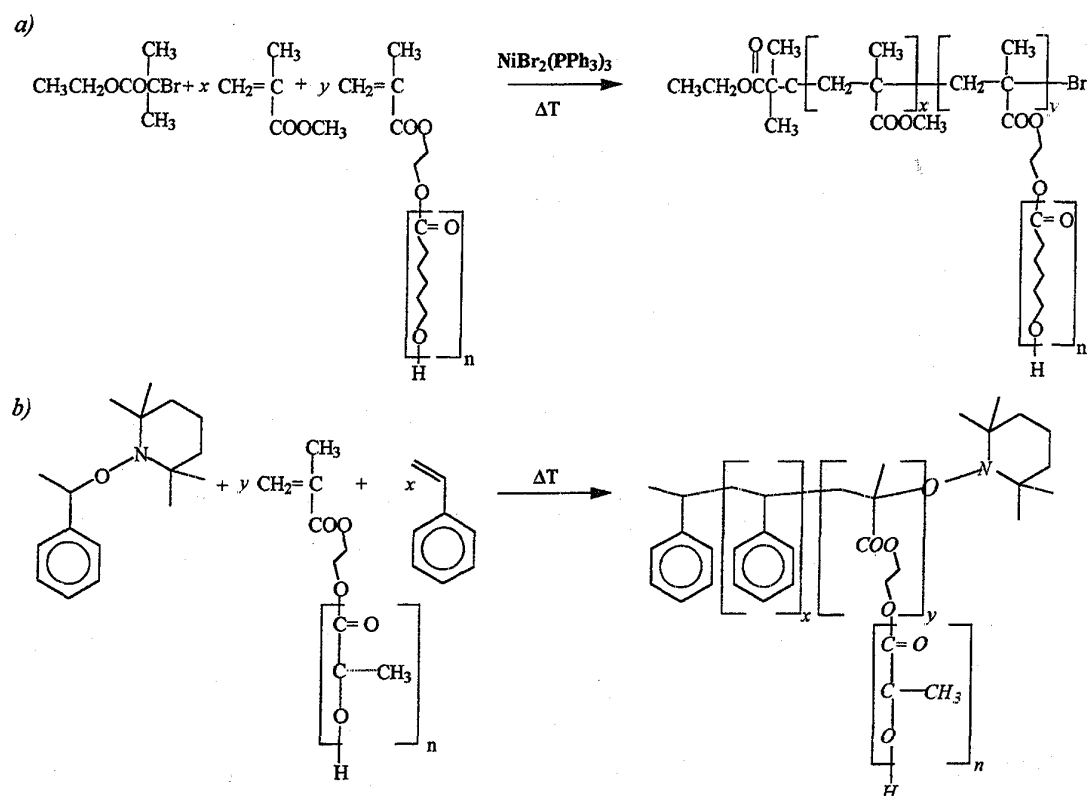
Scheme 28

3.5. Ring Opening Metathesis Polymerization

The recent developments of ring-opening polymerization (ROMP) have opened new avenues for synthesizing new polymeric materials [89]. Of particular importance is the emergence of ruthenium-based catalyst due to its versatility and compatibility with different polar functionalities and a diminished sensitivity to atmospheric oxygen and water [90]. Our laboratory has pursued the synthesis of graft copolymers by combining coordinative ROP and ROMP processes. To this end, α-norbornenyl PCL macromonomers were prepared by using a purposely functionalized aluminum monoalkoxide as initiator (see Scheme 5) [50]. Once again, the molecular parameters of the PCL macromonomers were perfectly controlled. Copolymerization of norbornene and the α-norbornenyl PCL mac-romonomers was promoted by a ruthenium based catalyst developed by Noels and Demonceau (Scheme 29) [90]. The active catalyst is generated in-situ by reaction of trimethylsilyldiazomethane (TMSD) and [RuCl$_2$(p-cymene)]$_2$ in the presence of tricyclohexylphosphine (PCy$_3$) in chlorobenzene at 60 ^{0}C. Under these experimental conditions, graft copolymers with a quite narrow MWD (PDI=I.2-1.4) were prepared at the strict condition to control kinetically the co-polymerization step. Actually, long reaction times are much more favorable to transfer side reactions with a concomitant broadening of the MWD and the formation of cyclic chains.

Very recent work has demonstrated the ability of ROMP to homopolymerize α-norbornenyl PS and PEO macromonomers in a controlled way and with high yields [91]. This new strategy has led to the preparation of PCL polymacromon-omers by homopolymerization of the above-mentioned α-norbornenyl PCL macromonomers using the same Ru based catalyst (Scheme 30) [50]. It is worth pointing out the quantitative recovering of high molecular weight polymacrom-onomers with very narrow MWDs (PDI=1.10) as observed by SEC (Fig. 4).

Scheme 29
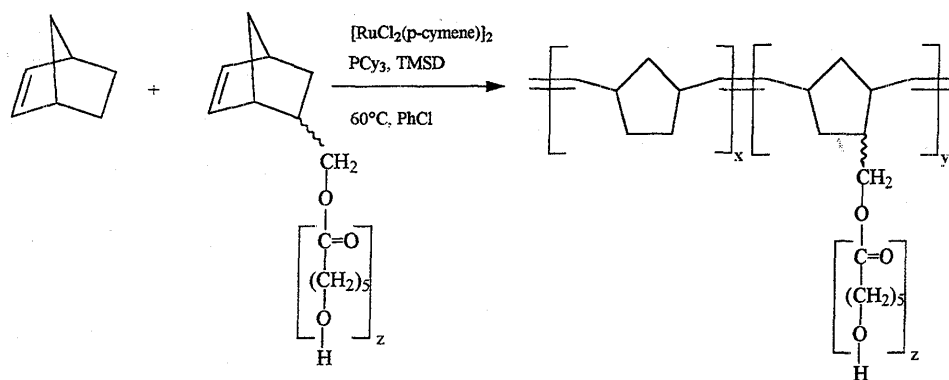
PCL polymacromonomer
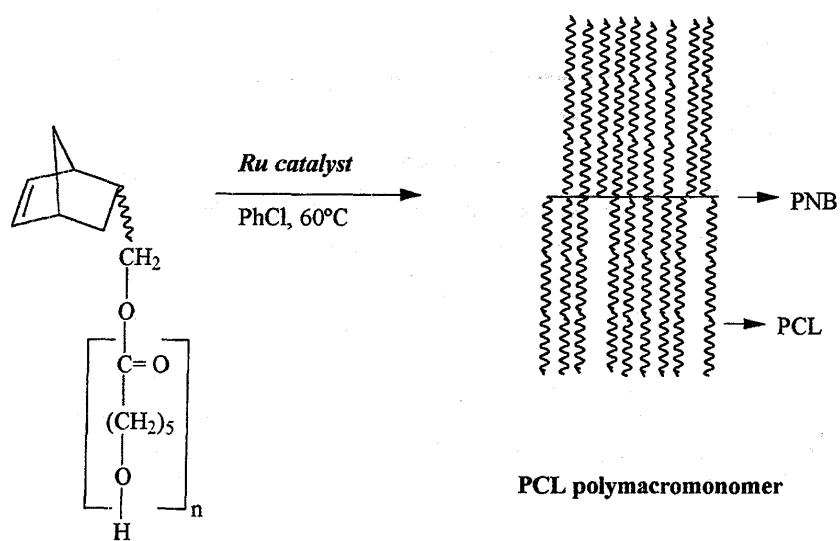
Scheme 30

(b) PCL polymacromonomer
Mn = 88000
Mw/Mn = 1.10

(a) PCL macromonomer
Mn = 2800
Mw/Mn = 1.10

Elution time (min)
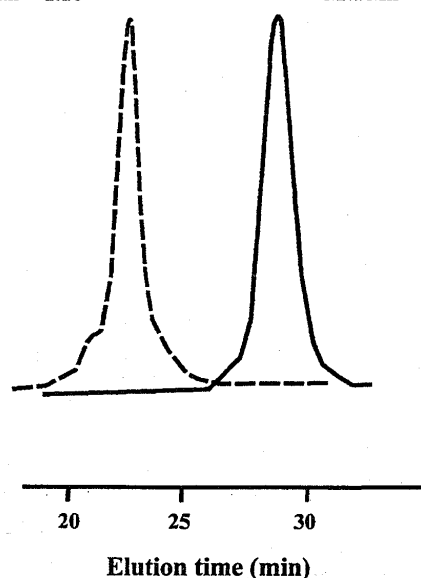
Fig. 4. *SEC traces for PCL macromonomer (curve a) and PCL polymacromonomer (curve b) For synthetic conditions, see Scheme 30.*

Moreover, alcohol functionalities have been introduced into the polynor-bornene (PNB) backbone by copolymerization of norbornene with a few percent of 5-acetate norbornene and subsequent acetate reduction. After transformation of the pendant hydroxyl functions into diethyl aluminum alkoxides, εCL has been ring opening polymerized (Scheme 31). Owing to the controlled/"liv-ing" character of both polymerization processes the isolated poly(NB-g-CL) graft copolymers were characterized by well-defined composition, controlled molecular weight and branching density, and narrow MWD (PDI= 1.2-1.4) [92].
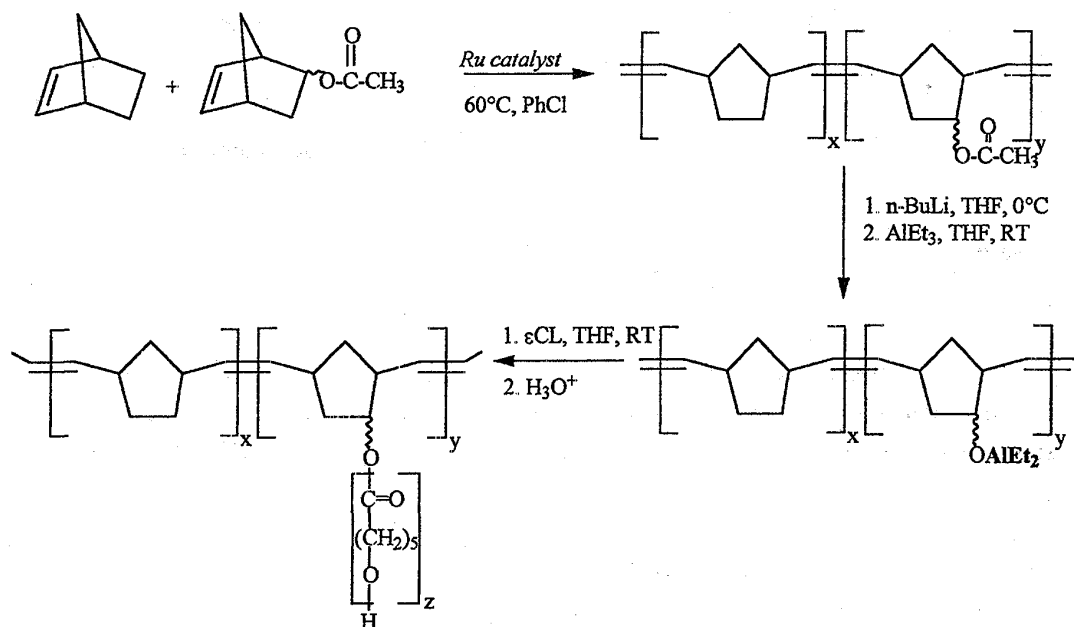
Scheme 31

3.6.Polycondensation

Although polycondensation does not lead to well-defined polymers with precisely controlled molecular weight and narrow MWD, it offers easy access to polymer families and structures difficult or impossible to be obtained through a polyaddition process. For instance, the synthesis of multiblock copolymers is readily achieved by the step-growth process. Despite their commercial interest, only a few examples of the introduction of aliphatic polyester oligomers as building blocks in polycondensates have been reported in the scientific literature. As an example, Maglio et al. used hydroxy-terminated PL-LA oligomers, coded as HO-(PLA)-OH, together with sebacoyl dichloride and 1,6-hexanedi-amine in the synthesis of random multiblock PL-LA-polyamide copolymers by means of a two-step polycondensation (Scheme 32) [93].

with R = -(CH$_2$)$_8$-

R'= -(CH$_2$)$_6$-
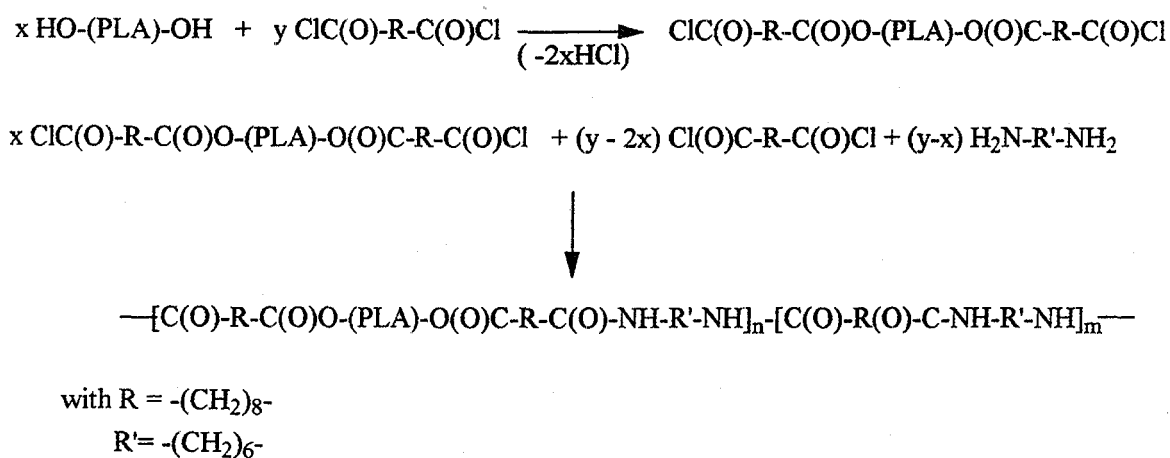
Scheme 32

Another approach was attempted by Seppala and Kylma who reported the synthesis of poly(ester-urethane)s by condensation of hydroxyl terminated tel-echelic poly(CL-co-LA) oligomers with 1,6-hexamethylene diisocyanate (Scheme 33) [94]. The diisocyanate acts as chain extender producing an increase in molecular weight of the preformed oligomers. The authors claim that some of the copolymers present elastomeric properties. Using a similar method, Storey described the synthesis of polyurethane networks based on D,L-LA, GA, ϵCL, and TMC (Scheme 33b) [95]. The condensation of preformed trifunctional oligomers with tolylene-2,6-diisocyanate triggered the network formation.

In an original way, hyperbranched aliphatic polyesters (PCL) have been prepared by condensation OfAB$_2$ macromonomers (Scheme 34) [96]. The PCL mac-romonomers were prepared by living JlOP of ϵCL coupled with a sequence of protection-deprotection reactions. The AB$_2$ macromonomers were self-polymerized in the presence of dicyclohexylcarbodiimide (DCC) producing the expected hyperbranched polyesters. Other AB$_2$ macromonomers have also been synthesized by copolymerization of ϵCL and a few molar percent of TOSUO. After self-polycondensation, the hyperbranched polyesters so obtained have been treated successively with $(C_6H_5)_3CBF_4$ and $NaBH_4$ in order to remove the ethylene ketal protection and to reduce the resulting ketone functions, respectively. Pendant hydroxyl groups are therefore made available along the PCL branches and can initiate further polymerizations of ϵCL catalyzed by $Sn(OCt)_2$, for instance. Highly branched polycaprolactones, i.e., dendri-graft PCL, with significant additional functionalities have been accordingly synthesized [121].
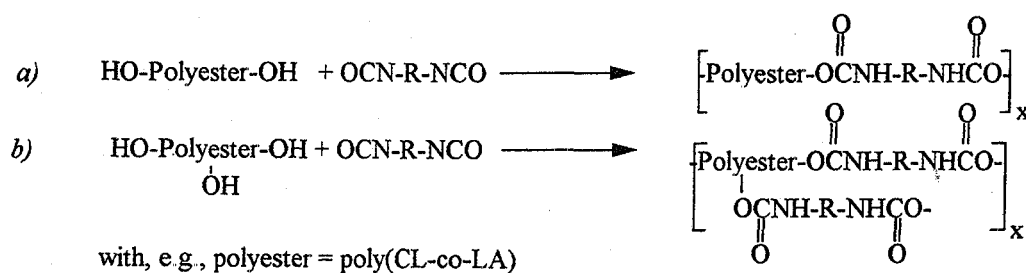
Scheme 33
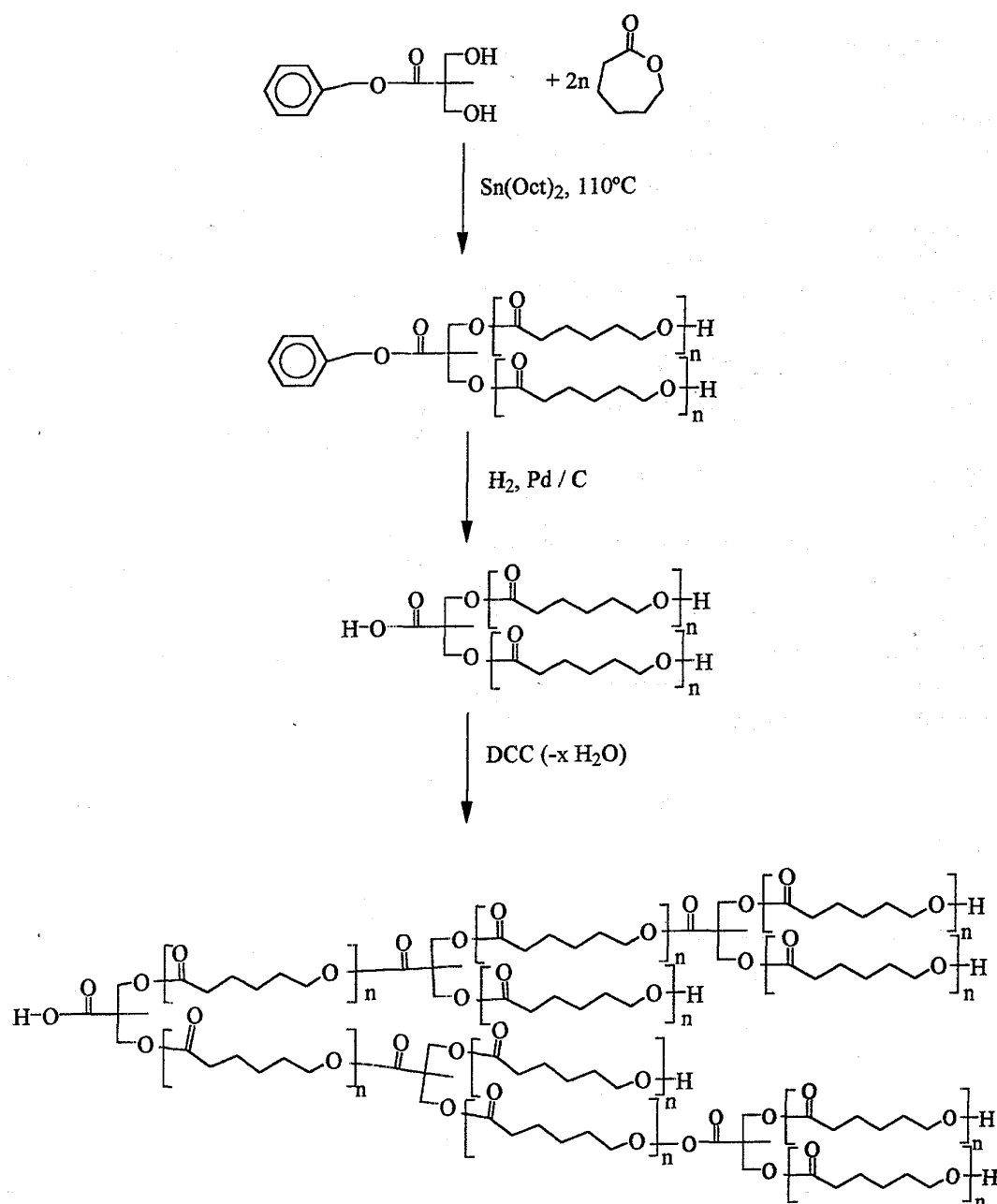
Scheme 34

Last but not least, some of us have recently synthesized polyimide-aliphatic polyester triblock and graft copolymers in collaboration with Hedrick and his coworkers [97,98]. Well-defined aminophenyl or diaminophenyl end-functional polyester oligomers have been synthesized on purpose and used as end-cappers or macromonomers leading to the aforementioned triblock or graft copolymers, respectively. The polyimide-polyester copolymers so obtained proved to be highly efficient promoters of polyimide nanofoams (for more details see Sect. 4.2).

3.7. Dendritic Construction

Pioneer works by Frèchet and coworkers have reported on the synthesis of polymers with hybrid linear-globular architectures [99]. Generally, the synthesis has been accomplished by end-capping a preformed linear polymer with a complementary monofunctionalized dendrimer. An alternative approach consists of using convergent dendrimers with a single reactive group at their focal point, as macroinitiator. For instance, poly(aromatic ether) dendrimers bearing a potassium alcoholate at the focal point appeared to be able to initiate the polymerization of εCL and to offer a better kinetic control by comparison to anionic ROP as initiated by simple low molecular weight potassium alkoxides [100]. The authors explain that the bulky dendritic moiety is able to screen, at least temporarily, the active anionic centers and to delay the occurrence of inter- and intramolecular transesterification

reactions. Nevertheless, prolonged reaction times again proved to be favorable for promoting the formation of cyclic oligomers. More recently, we have examined the use of similar polyether dendrons bearing a diethylaluminum alkoxide at their focal point, as macroinitiators for the coor-dinative ROP of εCL and LA in toluene at 25^0C and 70^0C, respectively (Scheme 35; shown for εCL ROP) [101]. Hybrid linear-globular AB-type block copolymers with well tailored substructures and narrow MWD have been synthesized with high yields under mild conditions.

In a different approach, Hedrick et al. have studied multifunctional dendritic initiators for the synthesis of multiarm star-shaped copolymers [102]. Several dendritic initiators with hydroxyl functionality ranging from 2 to 48 have been prepared according to the method developed by HuIt et al. [120]. The bulk polymerization of εCL initiated by these multifunctional macroinitiators and activated by either $Sn(Oct)_2$ or $Al(OfPr)_3$ as catalyst (see Sect. 3.3) yielded star-shaped copolymers with unimodal and narrow MWD (PDI= 1.1-1.3) (Scheme 36, shown for a 6-arm star). Whatever the hydroxyl functionality of the starting dendritic initiator the initiation efficiency evaluated by ^{13}C NMR analysis was very high (>90%). Furthermore, the resulting hydroxy end-functionality of the star-shaped copolymers was explored to prepare novel radial block copolymers. Reaction of every hydroxyl end-group with 2-bromo-2-methyl pro-panoyl bromide provided a multifunctional macroinitiator very efficient in MMA ATRP (see Sect. 3.4). Following this strategy, an ω-bromo 6-arm PCL star as ATRP macroinitiator was quantitatively converted into a 6-arm radial po-ly(CL-b-MMA) block copolymer with controlled molecular weights for each block and narrow apparent MWD (PDI= 1.16) (Scheme 36).
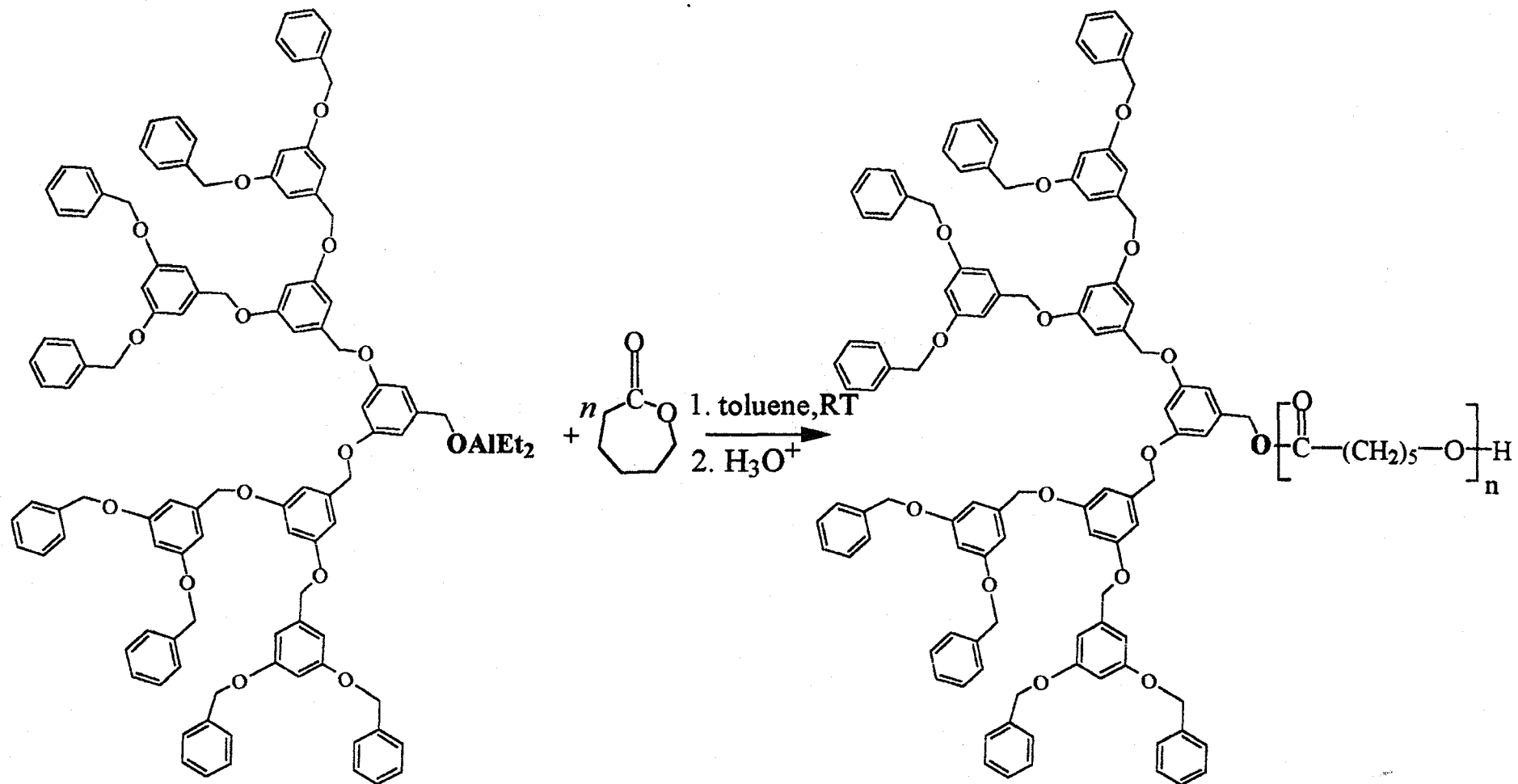
Scheme 35
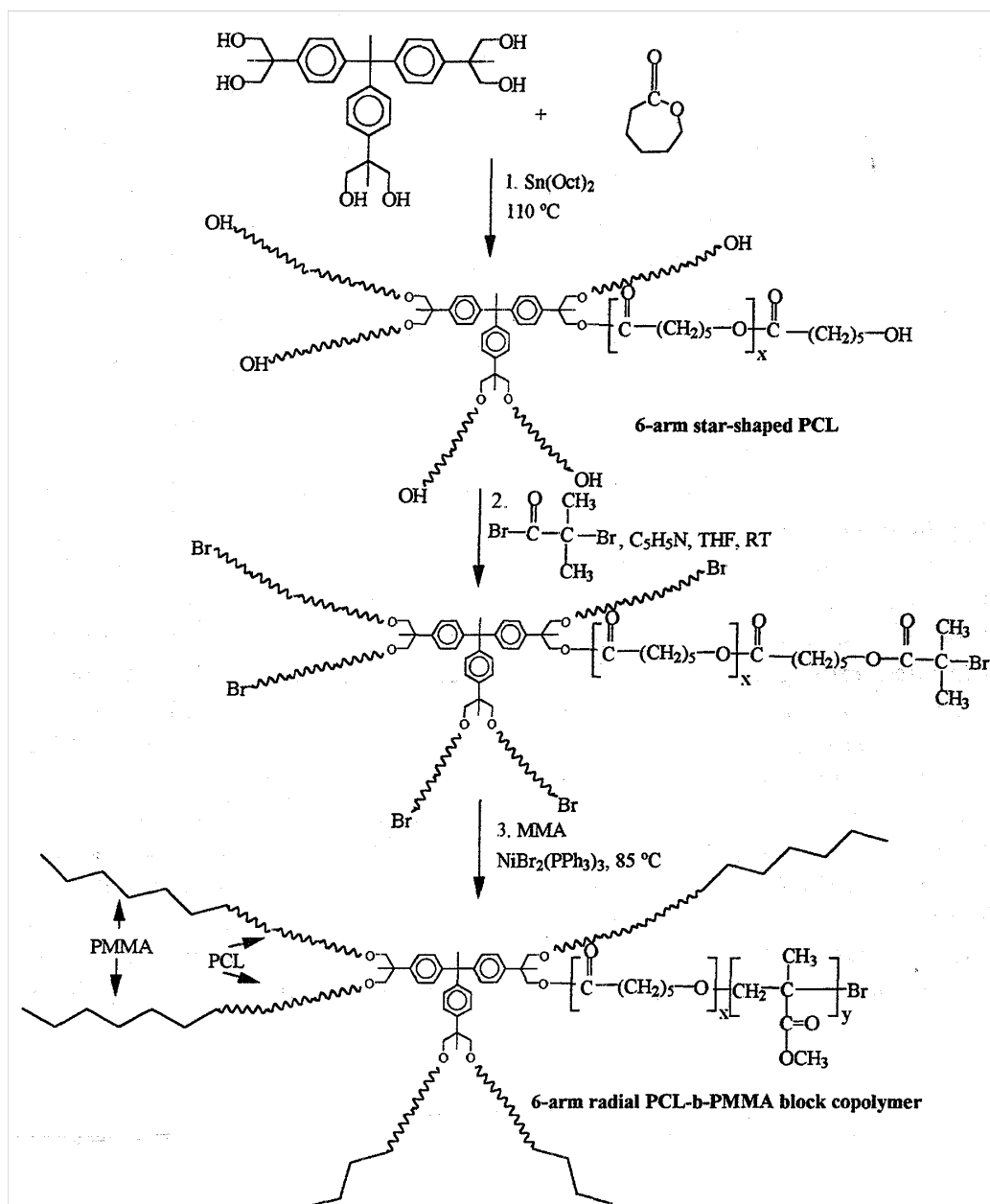
Scheme 36

3.8. Coordination Polymerization

Recent advances in the development of well-defined homogeneous metallocene-type catalysts have facilitated mechanistic studies of the processes involved in initiation, propagation, and chain transfer reactions occurring in olefins coordi-native polyaddition. As a result, end-functional polyolefin chains have been made available [103].For instance, Waymouth et al. have reported about the formation of hydroxy-terminated poly(methylene-l,3-cyclopentane) (PMCP-OH) via selective chain transfer to the aluminum atoms of methylaluminoxane (MAO) in the cyclopolymerization of 1,5-hexadiene catalyzed by di(pentameth-ylcyclopentadienyl) zirconium dichloride (Scheme 37). Subsequent equimolar reaction of the hydroxyl extremity with AlEt$_3$ afforded an aluminum alkoxide macroinitiator for the coordinative ROP of εCL and consecutively a novel poly(MCP-*b*-CL) block copolymer [104]. The diblock structure of the copolymer has been confirmed by selective fractionation and ^{1}H NMR; however the MWD was quite broad as a result of the lack of control in the first 1,5-hexadiene polymerization (PDI=2-5).

Finally, interesting research work has recently been published on the ability of organolanthanide complexes to promote the polymerization of monomers such as (meth)acrylates, lactones, and epoxides in a "living" manner, and olefins but with rather poor control [103]. Accordingly, Yasuda has synthesized block copolymers of MMA and lactones, e.g., εCL and δVL, by sequential addition of the two comonomers [103]. When MMA was added

first the copolymerization proceeded smoothly and gave copolymers with narrow MWD (PDI=I.1-1.3). Upon reversed addition of the respective monomers, the copolymerization did not proceed at all, i.e., the polylactone active end-species were totally unable to add an MMA unit. Similarly, original poly(ethylene-*b*-caprolactone) block copolymers have been prepared by sequential addition of ethylene and εCL (Scheme 38). Again, ethylene needs to be added first. Even though the block copolymer structure has been confirmed by GPC-FTIR, the MWD so obtained was relatively broad and one may not exclude the formation of homopolymers (PDI=I.5-2).
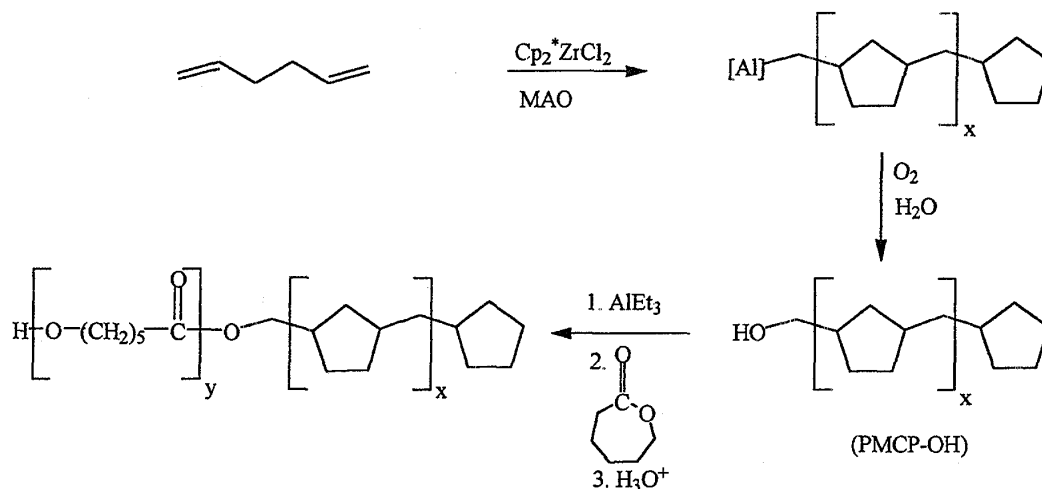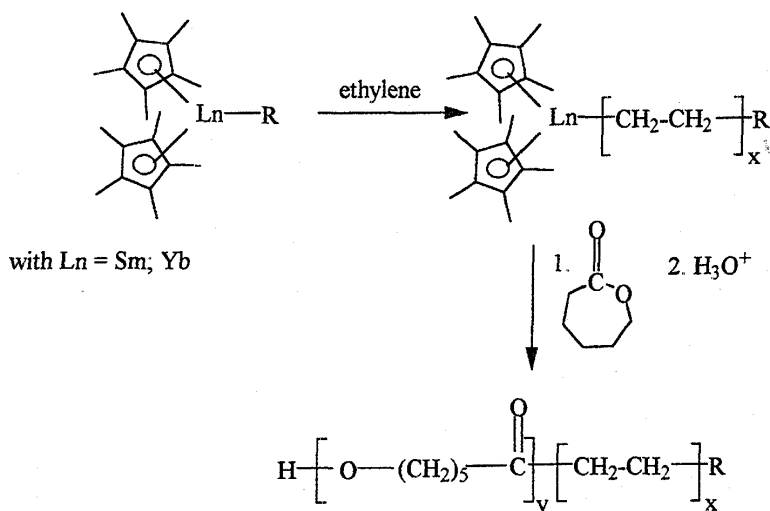
Scheme 37

Scheme 38

4. Aliphatic Polyesters as Building Blocks for New Materials

4.1. Biodegradable and Biocompatible Thermoplastic Elastomers

Since their commercial introduction by Shell in 1965, the poly(styrene-*b-(*buta-diene or isoprene*)-b*-styrene) triblock copolymers (SBS or SIS) have attracted a lot of attention regarding their elastomeric properties. The unique thermome-chanical properties of these SBS or SIS thermoplastic elastomers relies upon the microphase separation of the PS hard blocks into glassy microdomains dispersed in a continuous rubbery polydiene matrix. Such a phase morphology provides a physical network of flexible chains cross-linked by thermoreversible glassy microdomains. Clearly, these materials combine the mechanical performances of vulcanized rubbers and the straightforward processing of thermoplastics. SBS and SIS triblock copolymers are currently synthesized by a three-step anionic living copolymerization, typically using butyllithium as initiator. • Albertsson and some of us have investigated the synthesis of all aliphatic polyester based ABA triblock copolymers and characterized their performances as original biodegradable and biocompatible thermoplastic elastomers. In fact, po-ly(CL-*b*-DXO-*b*-CL) symmetrical triblock copolymers with high molecular weights and narrow MWD (PDI=1.20) have been synthesized by sequential co-ordinative ROP of the monomers, i.e., εCL and DXO, as initiated by Al(OfPr)$_3$ in

toluene at RT (Scheme 39) [26,106]. For low PCL contents, the PCL teleblocks form separate semi-crystalline microdomains dispersed in a continuous PDXO rubbery matrix, the glass transition temperature of which is well below RT (T_g= -36 ^{0}C, see Table 1). A temperature increase above 60 °C, which is the melting temperature of the PCL physical cross-linking points of the three-dimensional network, allows for an easy melt material processing.

Of prime interest are the tensile properties summarized in Table 4, and typical of stress-strain curves exhibited by thermoplastic elastomers. The elongation and strength at break were measured above 1000% and 50 MPA, respectively. Both the tensile modulus and the stress at yield increased by increasing the PCL relative content whereas, as expected, the ultimate elongation at break slightly decreased.

Table 4. *Tensile properties of the poly(CL-b-DX-b-CL) ABA triblock copolymers (see Scheme 39)*

Block lengths A/B/A	15K/50K/15K	15 K/70 K/15 K
Tensile modulus (MPA)	31	21
Stress at yield (MPA)	3.0	2.1
Elongation at yield (%)	15	18
Strength at break (MPA)	52	53
Elongation at break (%)	1070	1210
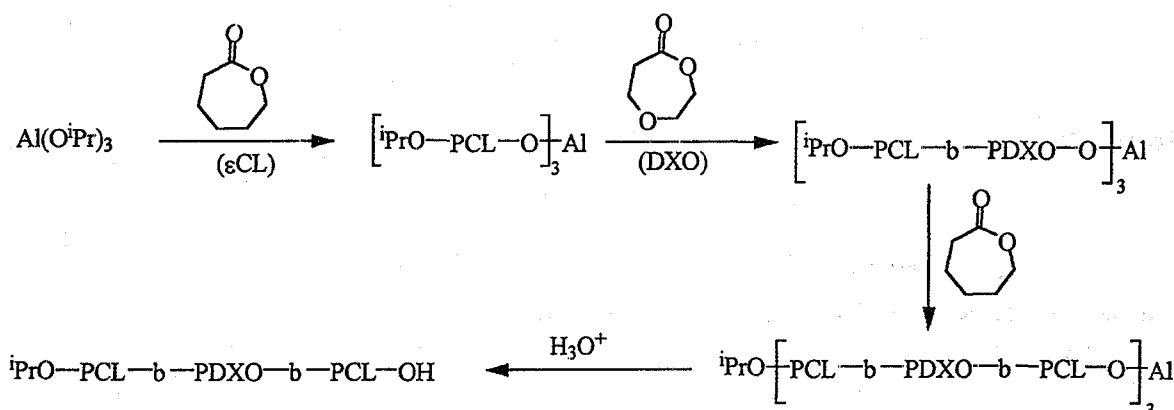
Scheme 39

To sum up, the "living" character of the aluminum alkoxide mediated ROP of lactones has permitted the synthesis of novel ABA triblock copolymers, the composition and molecular weight of which can purposely be tuned up for displaying excellent elastomeric properties. Interestingly, the inherent biodegrad-ability of each partner, PCL and PDXO, would open up new applications for these novel thermoplastic elastomers.

4.2.Polyimide Nanofoams

Polyimides are currently used as interlayer dielectrics in *microelectronic packaging,* since they have the requisite properties to survive the thermal, chemical, and mechanical stress of manufacturing and operation. The main advantage realized by the use of polyimides over inorganic alternatives is the lower dielectric constant. A reduction in the dielectric constant of the medium reduces pulse propagation delay, allowing for faster machine time, and minimizes the noise between lines. The most common approach for modifying the dielectric properties of polyimides has been via the incorporation of fluorinated substituents, such as hexafluoroisopropylidene linkages or pendant trifluoromethyl groups. While this approach reduces water absorption and the dielectric constant significantly, the mechanical and thermal properties are often compromised. Another means of reducing the dielectric constant while maintaining the desired thermal and mechanical properties is by the generation of a foam. The reduction in the dielectric constant is simply achieved by replacing the polymer with air, which has a dielectric constant of 1. However, it is obvious that the pore size must be much smaller than the film thickness or any microelectronic features. In order to meet the last statement, a new method of generating a polyimide foam with pore sizes in the nanometer regime has been developed by Hedrick and his coworkers at IBM [107]. This approach involves the use of phase separated block or graft copolymers comprised of a high thermally stable

polymer and a second component, which can undergo clean thermal decomposition with the evolution of volatile by-products to form a closed-cell, porous structure. Block copolymers are well known for presenting different morphologies, interestingly on the nanometer scale and which depend on their nature and composition. By designing the block copolymers such that the matrix material is a thermally stable polymer with a high T_g and the dispersed phase is a labile polymer that undergoes thermolysis at a temperature below the T_g of the matrix, one can prepare foams with pores in the nanometer dimensional regime. The foam formation takes place by thermal degradation of the labile block, leaving behind pores the size and shape of which depend on the initial block copolymer morphology (Fig. 5).
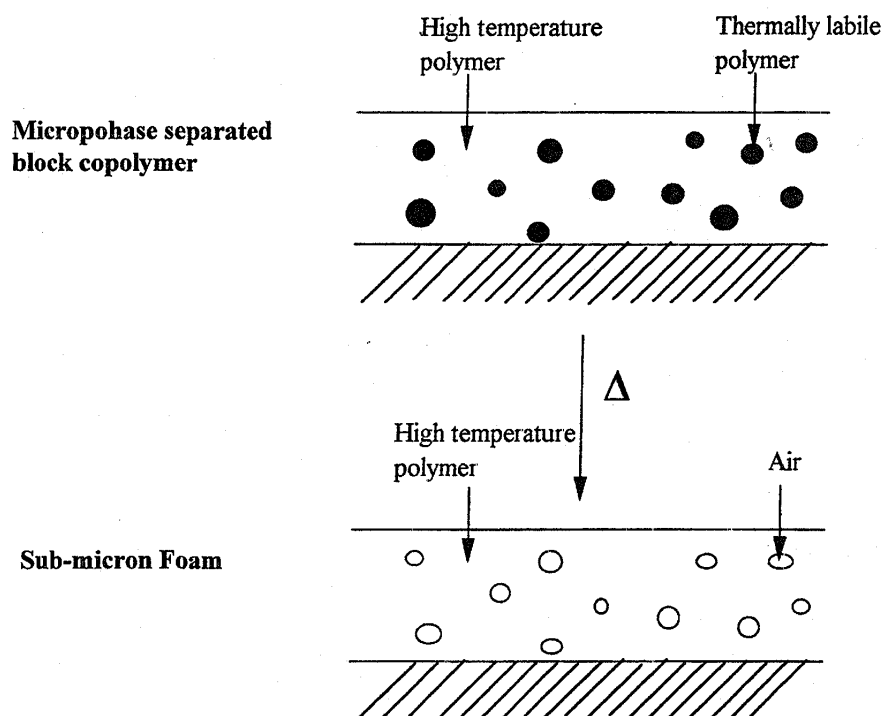
Fig. 5. Illustration of the block copolymer approach to nanofoam formation
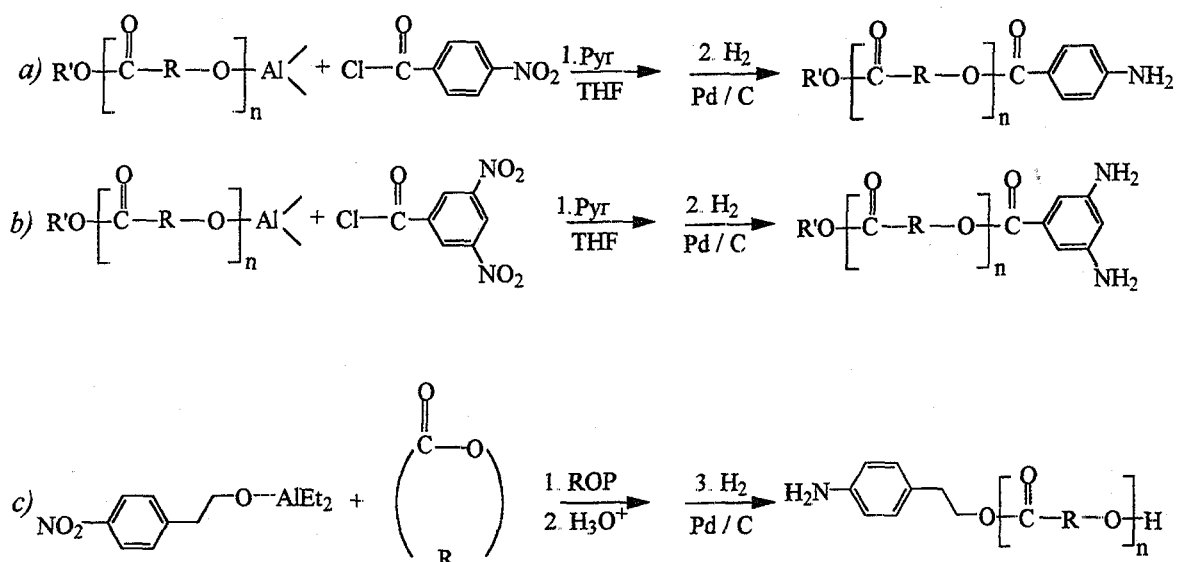
Scheme 40

Nanofoams have been prepared first by using poly(propylene oxide) as the labile coblock with different polyimides for the continuous matrix [108]. The degradation of the poly(propylene oxide) component can be achieved at 300 ^{0}C in an oxygen or air environment via a thermooxidative degradative mechanism which is, however, unacceptable in microelectronic fabrication. In order to overcome this difficulty, aliphatic polyesters have been studied as labile coblocks [97, 98]. Aliphatic polyesters degrade quantitatively in an inert atmosphere

into cyclic monomers and other products of low molecular weight. In addition, the decomposition temperature is much lower than the T_g of many polyimides. Concerning the synthetic requirements, the first important step was the availability of preparing well-defined oligomers having controlled molecular weight and functionality. Like the previously studied polyether blocks, polyesters end-capped with a single or double aryl-amine functionality were needed to be amenable towards polyimide copolymerization. The synthesis of such ω-functional polyesters has been accomplished by reacting monofunctional living aluminum alkoxide terminated oligomers with 4-nitrophenyl chloride or 3,5-dinitrophe-nylchloride in the presence of pyridine (Pyr) and further modification by hydro-genation over Pearlman's catalyst, giving the corresponding and desired (di)amine (Scheme 40a,b). Alternatively, the single aryl-amine functionality has been incorporated by using diethyl aluminum 2-p-nitrophenyl-ethoxide as initiator of the lactone ROP (Scheme 40c). It is worth remembering that the nitro protecting group was required instead of the primary amine due to its ability to co-initiate the coordinative ROP (see Sect. 2.3).

The next step concerned the synthesis of the polyester-polyimide copolymers. Triblock copolymers have been prepared by a step-growth copolymeriza-tion of stoichiometric amounts of an aromatic diamine and dianhydride (e.g., PMDA and 3FDA, as depicted in Scheme 41a) added with the single ω-amino polyesters as chain end-cappers. Graft copolymers can be prepared as well. In this case, the diamine end-functionalized oligomeric macromonomers are co-polymerized with the polyimide condensation comonomers (Scheme 41b).
Block and graft copolymers based on PMDA-3FDA polyimide and either PVL, PCL or PD-L-LA have been accordingly prepared. The copolymers were characterized by ^{1}H NMR, DSC, TGA, SAXS, and DMTA. Microphase separation was observed in all the studied copolymers and the polylactone blocks were not able to crystallize. Films of the polycondensates were prepared by solution casting from N-methyl pyrrolidone followed by a slow heating increase up to 300 [0]C. This thermal treatment removed the residual solvent and imidized the prepoly-mer without degrading the labile block [97]. Then different cure treatments were applied in order to degrade efficiently the labile polyester coblocks. The use of PCL as the thermally labile coblock was a successful route to polyimide nano-foams, although the PVL and PD,L-LA based copolymers did not show the expected nanopore formation. The explanation was found in the plasticization of the polyimide matrix by the PVL and PD$_1$L-LA degradation products which produce the collapse of the porous structure. Although some collapse was also observed in the case of PCL-based copolymers, the foam efficiency was high specially for cross-linked polyimide matrix. The nanofoams were characterized by a variety of experiments including TEM, SAXS, density, and refractive index measurements. Thin organic film with pores of 10-20 nm and volume fraction of voids 10-20% were obtained by this method and were characterized by dielectric constants as low as 2.4.

a) Synthesis of ABA triblock copolymers

Polyester   Polyimide   Polyester

A   B   A

b) Synthesis of graft copolymers
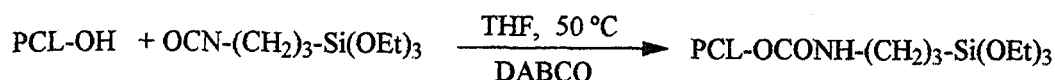

Polyimide backbone

Polyester
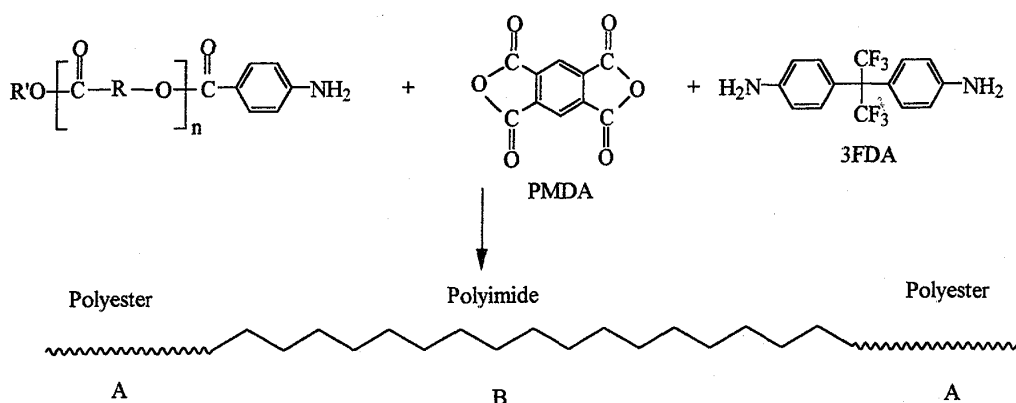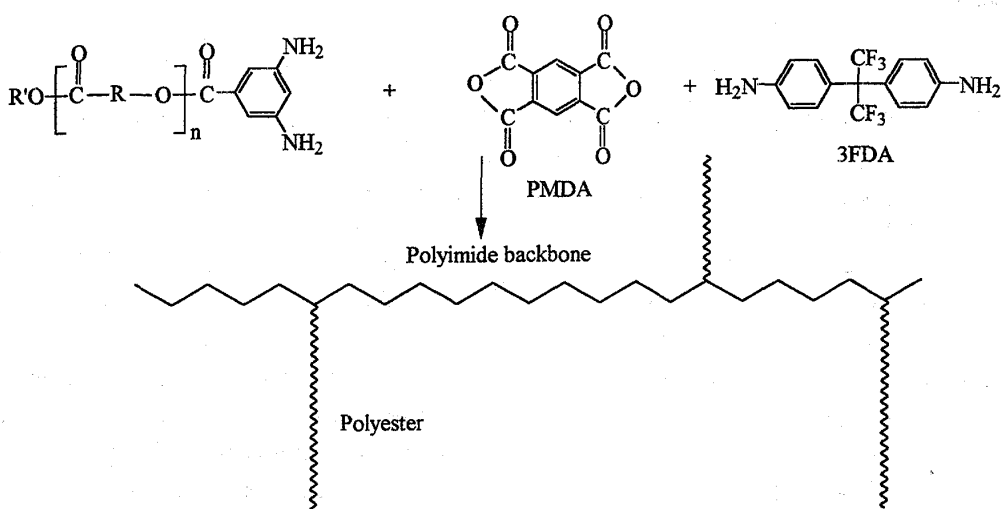
Scheme 41

4.3. Organic-Inorganic Nanocomposites

During the last few years, special attention has been paid to the design and characterization of inorganic-organic hybrid materials prepared by the sol-gel process. This interest has been driven by the opportunity offered by this method to combine in a quite controlled way the most remarkable properties of inorganic glasses and organic polymers. In order to obtain a successful incorporation and a nanoscopic dispersion of the organic polymers into the hybrid materials, a prerequisite is needed - the existence of strong interactions between the inorganic and organic components. Therefore, polymers prone to hydrogen bonding with residual protic moieties, e.g., Si-OH, have been successfully incorporated into silicon oxide networks. Another method consists of attaching covalently the organic component to the inorganic material by using tailored-functionalized polymers, which can participate in the sol-gel process via a condensation with the in-situ generated Si-OH groups, for instance. Aliphatic polyesters are ideally suited for being incorporated into hybrid materials because they can be readily end-capped with functional groups and their ester carbonyl functions can interact strongly and form hydrogen bonds with the inorganic component. On that basis, the preparation of biodegradable and biocompatible inorganic-organic hybrid materials by sol-gel process between tetraethoxysilane (TEOS) and PCL oligomers has been investigated in our laboratory [109-112]. Depending on the coordinative ROP conditions (nature of the aluminum alkoxide initiator, type of termination reaction, copolymerization of εCL with TOSUO, etc.), PCL can be end-capped with hydroxyl groups at one end, at both ends, or with pendant hy-droxyl functions along the chain. Reaction of those hydroxyl groups with 3-iso-cyanatopropyltriethoxysilane has proved to be an easy and direct access to the introduction of inorganic functionalization into the PCL (Scheme 42). The oversimplified reaction pathway of the sol-gel process for the synthesis of PCL containing ceramers is also schematized. The network formation is a complex process where hydrolysis and condensation interplay depending on the reaction conditions. The extent of the PCL incorporation into the silica network depends on the PCL relative content and

molecular weight, and the number and reactivity of the PCL functional groups, e.g., HO- or $(EtO)_3Si$- functions. Totally transparent hybrid materials incorporating up to 50 wt% PCL into TEOS-based silica networks have been prepared [HO]. PCL is so intimately incorporated into the polymer that it remains completely amorphous as confirmed by DSC and DMA analysis. TEM and image analysis achieved on thin films of ceramer containing 46 wt% PCL shows a co-continuous two-phase morphology with microdomains ca. 5 nm in size. These materials have a number of potential applications in the biomedical field. For example, the hybrid ceramers containing ca. 50 wt% PCL may be envisaged as a novel type of degradable bi-oglass. They could also be used as coating films for bone implants and prosthetic devices and, due to an unexpectedly high scratch resistance, they would be a valuable coating for organic polymers as well, particularly for polymers compatible with PCL, such as polycarbonate and PVC. On the other hand, bioglass can serve as support for enzyme immobilization and culture. To confirm their biocompat-ibility, fibroblast cultures were attempted to evaluate the cytotoxicity of the new hybrid materials. It has been observed that the extent of the cellular attachment depends on the PCL content of ceramers; the density of cells attached to the ceramer surface actually decreases when the PCL content is increased. In other words, the fibroblast adherence decreases with decrease of hydrophilicity of the substrate. As presumed, "in-vitro" biodegradation studies have clearly shown that the inherent biodegradability of PCL is preserved while incorporated in the nanocomposites [111].

Hedrick et al. have investigated the preparation of nanoporous inorganic oxides by sol-gel process carried out on hyperbranched polyesters (see Sect. 3.6) and polysilesquioxanes [96]. Interestingly, the organic species are used to template the inorganic counterpart and, after the completion of the polycondensa-tion reaction, they can be selectively removed through thermolysis, leaving behind a nanoporous inorganic oxide. Similar investigations have been carried out by Chujo et al. using "starburst" dendrimers to generate porosity in silica gel [124]. Hyperbranched polyesters are again ideally suited for this study since they are capable of significant interaction with the inorganic alkoxides and they thermally decompose quantitatively into non-reactive species via an unzipping mechanism. Nanoporous silica films have great potential as low dielectric materials for semiconductor applications [113].
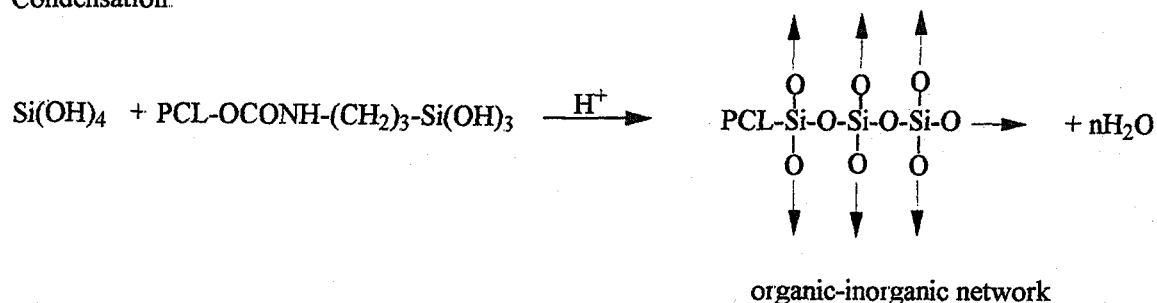
PCL functionalization

$$PCL\text{-}OH \ + OCN\text{-}(CH_2)_3\text{-}Si(OEt)_3 \ \xrightarrow[\text{DABCO}]{\text{THF, 50 °C}} PCL\text{-}OCONH\text{-}(CH_2)_3\text{-}Si(OEt)_3$$

Preparation of tetraethylorthosilicate / PCL networks (sol-gel process)

Hydrolysis:

$$Si(OEt)_4 \ + \ 4H_2O \ \xrightarrow{H^+} \ Si(OH)_4 \ + \ 4\,CH_3CH_2OH$$

$$PCL\text{-}OCONH\text{-}(CH_2)_3\text{-}Si(OEt)_3 \ + 3\,H_2O \xrightarrow{H^+} PCL\text{-}OCONH\text{-}(CH_2)_3\text{-}Si(OH)_3 + 3CH_3CH_2OH$$

Condensation:

$$Si(OH)_4 \ + PCL\text{-}OCONH\text{-}(CH_2)_3\text{-}Si(OH)_3 \ \xrightarrow{H^+} \ PCL\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O \ \longrightarrow \ + nH_2O$$

organic-inorganic network
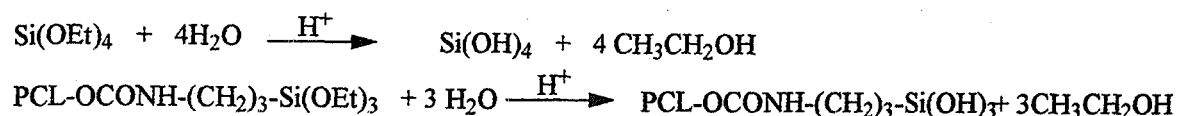
Scheme 42

4.4.Biodegradable Amphiphilic Networks

Biodegradable amphiphilic networks have been synthesized by free radical co-polymerization of PCL or PD_1L-LA dimacromonomers with a hydrophilic comonomer, i.e., 2-hydroxyethylmethacrylate (HEMA) [45, 46, 114]. Well-defined α,co-methacryloyl PCL and PD_3L-LA oligomers were synthesized by the living ROP of the parent

monomers initiated by diethyl aluminum 2-hydroxyethyl-methacrylate and then terminated by a controlled reaction of the propagating aluminum alkoxide groups with methacryloyl chloride (Scheme 43). The free radical copolymerization of those dimacromonomers with HEMA was performed in bulk at 65 ^{0}C using benzoyl peroxide and yielded homogeneous networks with high comonomer conversions (ca. 90%).

The amphophilic nature of the polyester/PHEMA networks provides gels able to swell in both organic and aqueous media, which prompted us to study them as controlled drug delivery systems [114]. The most valuable characteristic feature of these amphiphilic networks is their potential to sustain the drug delivery of both hydrophilic and hydrophobic drugs. First, the swelling characteristics of the binary networks have been studied in relation to the network composition, the length, and the nature of the dimacromonomers. Further, dexamethasone was chosen as a drug model, since it can be handled as either a hydrophilic (sodium phosphate salt) or a lipophilic (acetate) compound. The drug was incorporated into the network directly during the free radical synthesis and cross-linking step or by swelling of the preformed network in water or in CHCl$_3$, depending on the drug formulation. It has been concluded that the kinetics of the drug release were mainly governed by the network swelling rate.

Synthesis of the polyester dimacromonomers:
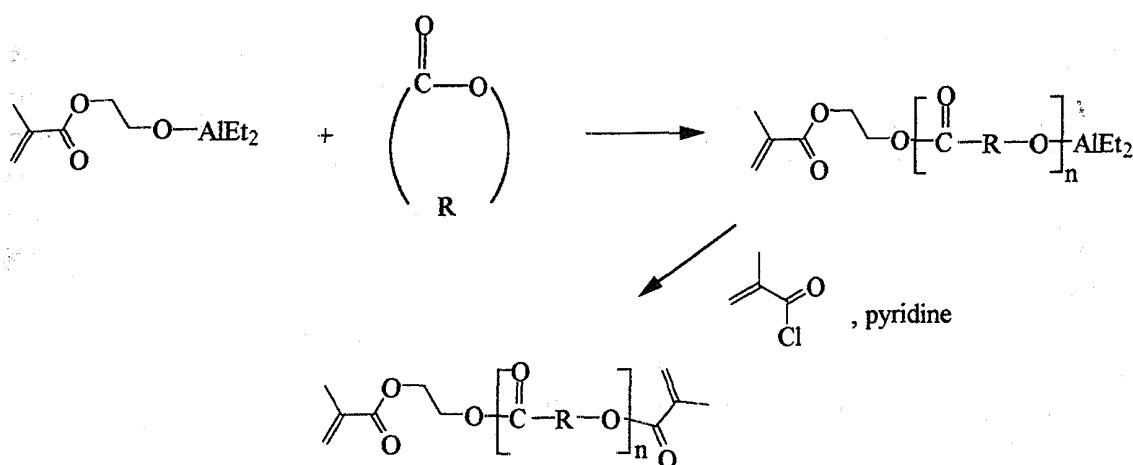
Synthesis of the amphiphilic networks:
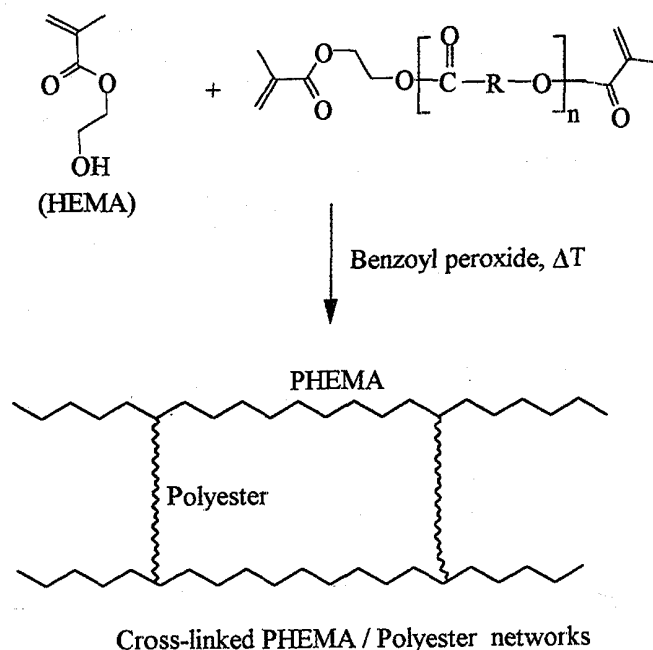
Scheme 43

4.5. Nano- and Microspheres for Biomedical Applications

Biodegradable and biocompatible microspheres of PCL, PLA, PGA, and blends thereof have currently been prepared by different methods, such as emulsion/evaporation, precipitation processes, and dispersion polymerization, and have found applications as carriers for sustaining the release of bioactive molecules. In this section our attention will be exclusively focused on the advantages offered by new molecular architectures available from the macromolecular engineering of aliphatic polyesters in micro- but also nanocarriers. For instance, Slomkowski et al. have prepared microspheres by the straightforward dispersion polymerization of L-LA and εCL in a solvent mixture in which the generated polyesters are poorly soluble. The polymerizations were carried out in a 1,4-diox-ane/heptane solvent mixture and were promoted by either $Sn(C^1Ct)_2$ catalyst or aluminum alkoxide initiators [115]. The dispersion of the growing polyester particles was actually stabilized by poly(dodecylacrylate-g-caprolactone) graft copolymers. The graft copolymers were prepared by the macromonomer technique, as reported previously (see Sect. 3.3). The appropriate selection of these polymeric surfactants allows one to obtain, in a one-step dispersion polymerization, PLA and PCL microspheres with controlled mean particle size and narrow size polydispersity. In a different approach, Egiburu et al. have prepared microspheres of preformed PL-LA grafted copolymers by the emulsion/evapora-tion method [116]. Three types of copolymers were reported: poly(MMA-g-LA), poly(MA-g-LA), and poly(VP-g-LA). The authors monitored by UV spectroscopy the encapsulation loading level and release kinetics of ibuprofen, an anti-inflammatory drug, from small microspheres (mean size= 1-5 μm) in buffered water solution. Interestingly, by varying the composition and thus the hydrophilic character of the copolymers, good control over the release rate was reached.

Biodegradable polyester-based nanoparticles have also been studied, especially in the biomedical domain. Like microelectronics, biomedical research follows the rule: "smaller is better". A typical example of nanoparticles based on the aliphatic polyester engineering by living ROP is provided by the poly(CL-*b*-GA) copolymers which form stable colloidal dispersions in organic solvents such as toluene and THF without the need of any additional surfactant *[27]*. The poly(CL-*b*-GA) particles form a new class of stable non-aqueous dispersions in which a PGA core is stabilized by a PCL shell [122]. The copolymer micelles were characterized by TEM and PCS that show a bimodal distribution. The smallest particles usually dominate the size distribution curve. Their average size is in the range 10-40 nm when the diblocks are dispersed in toluene at a 0.1 wt% concentration. The average size increases as the concentration of the dispersion increases, which might be due to the aggregation of the smallest particles. These colloidal particles of diblocks consisting of two biocompatible polyesters with drastically different physical properties, such as melting temperatures and bio-degradability, are very attractive for biomedical applications. Our group also studied the use of poly(HEMA-g-(D,L-LA)) graft copolymers (for their synthesis, see Sect. 3.3) in nanoparticles formulation [123]. In a DMSO/H_2O (10/90 v/v) solvent mixture, these graft copolymers formed stable micelles as observed by PCS, the average size of which was in the range 40-70 nm, depending on the copolymer composition, molecular weight, and concentration. It is worth noting the high efficiency of these copolymers for immobilizing soma-totrophine without losing protein activity. Finally, as already discussed in Sect. 2.5, the PoIy(SCL-CO-TOSUO) copolymers were able to form stable aqueous dispersions with a mean particle size below 100 nm. Surprisingly enough, even though the functional comonomer was incorporated on a statistical basis at quite a low content (12 mol%), the copolymer was able to stabilize the hydrophobic PCL segment in water. The size of the colloidal dispersions decreases from 213 nm in the case of ethylene acetal pendant groups to 72 nm and 74 nm upon successive deprotection and reduction steps which lead to more polar ketone and hydroxyl groups, respectively. A decrease in the dispersion concentration from 0.10% to 0.01% results in smaller colloidal particles (from 213 to 72 nm). The suspensions are stable for more than 48 h at room temperature as checked by PCS [74]. This novel family of copolymers has potential for biomedical applications, particularly as tailored drug colloidal vectors with a core-shell-like structure. Reactive groups on the surface of the nanoparticles are indeed available to the binding of species selected for molecular recognition and drug targeting.

5. Conclusions

In conclusion, a quite complete macromolecular engineering of aliphatic polyesters, recognized as biocompatible and biodegradable materials, has been reached. The perfectly well controlled "coordination-insertion" ROP of cyclic (di)esters as initiated by aluminum alkoxides, functionalized or not, has proved to be essential to this end. The related (co)polyesters can be designed in such a way that α-, or α,ω- functional telechelic polymers, block, graft, comb-like, and star-like copolymers, hyperbranched and dendri-graft (co)polymers, and one-or two-component polymer networks are now readily available. Along with the above topologies, macrocyclic (block) polylactones have been very recently synthesized by using 2,2-dibutyl-2-stanna-l,3-dioacyclalkanes as cyclic initiators

[125]. This method exclusively yields macrocyclic polyesters without any competition with linear polymers. Furthermore, the "coordination-insertion" ROP process can take part in a more global construction set, ultimately leading to the development of new polymeric materials with versatile and original properties. Note that other types of efficient "coordination" initiators, i.e., rare earth and yttrium alkoxides, are more and more studied in the framework of the controlled ROP of lactones and (di)lactones [126-129]. These polymerizations are usually characterized by very fast kinetics so as one can expect to (co)polymerize monomers known for their poor reactivity with more conventional systems. Those initiators should extend the control that chemists have already got over the structure of aliphatic polyesters and should therefore allow us to reach again new molecular architectures. It is also important to insist on the very promising enzyme-catalyzed ROP of (di)lactones which will more likely pave the way to a new kind of macromolecular control [6,130-132].

Acknowledgments

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