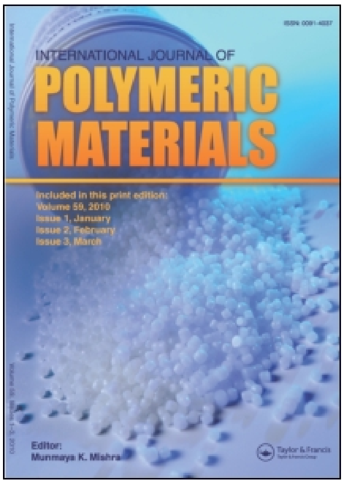

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Novel Degradable Engineering Polyesters-Synthesis and Applications

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Novel Degradable Engineering Polyesters—Synthesis and Applications

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Synthesis and applications of novel degradable engineering polyesters are presented.

KEY WORDS Biodegradable polyesters, engineering materials

INTRODUCTION

Some groups of polymers exhibiting high strength and excellent mechanical properties during long time service are considered to be high tech engineering materials. Research in this field has stimulated progress in all branches of modern technology and contributed significantly to the present state of the art.

Nowadays however, another group of polymer materials is also playing an important role. These are biodegradable polymers designed for service over a specific period of time. The importance of these materials is due to their numerous applications in medicine and biology as well as to their utility in the disposal of polymers.

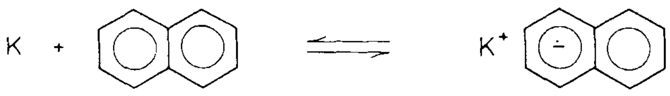
The most common biodegradable polymers are aliphatic polyesters. Many types of biodegradable polyesters are produced in nature, e.g., by some microorganisms.[1] They are made synthetically by polycondensation, i.e., step-growth polyesterification, which is the traditional method for polyester synthesis. Nowadays however, great attention is being paid to lactone polymerization aimed at syntheses of high molecular weight polyesters and specialty polymers such as biodegradable polyesters for medical applications, e.g., controlled drug release systems. The past decades have brought about an enormous growth of research into fundamental aspects of the polymerization lactones and related monomers.[2] First of all, the chemistry of β-lactone polymerization is very important because of the utility of the polymers obtained as materials for medical applications. Besides synthesis of biodegradable polymers by polymerization of β-methyl-β-propiolactone (β-butyrolactone),[3-5] the base alcoholysis of α,α-diphenyl-β-propiolactone has been studied with the expectation to prepare the corresponding analogues of tropic acid esters, which have antispasmodic activities.[6]

In this paper some new aspects of the chemistry of lactone polymerization are discussed from both mechanistic and synthetic points of view.

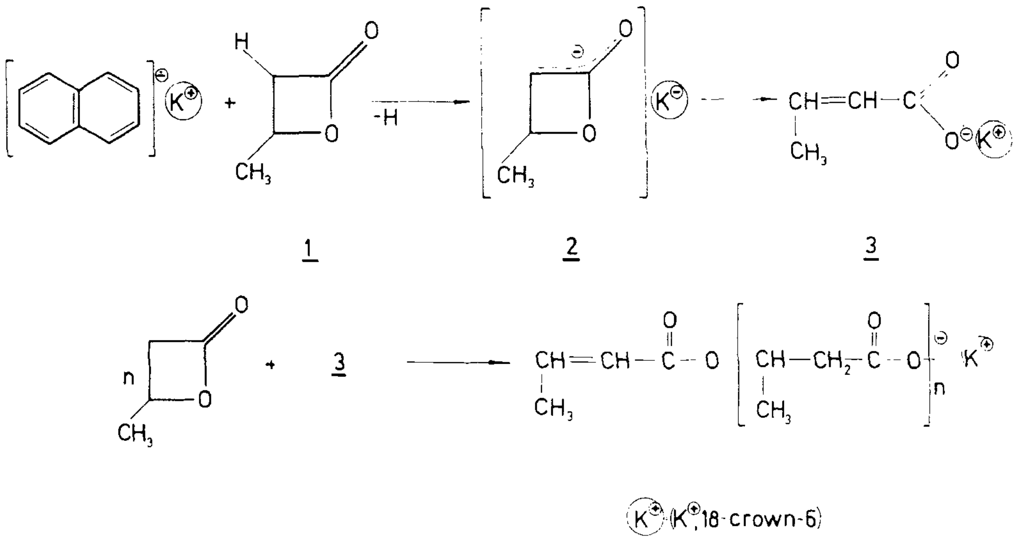
POLYMERIZATION OF LACTONES INITIATED WITH ALKALI METAL NAPHTHALENIDES

Alkali metals, such as sodium or potassium react with naphthalene (or other aromatic compounds) to form the corresponding naphthalenides by electron transfer from the outer orbital of the metal to the aromatic acceptor (Scheme I).

Naphthalenides have been previously employed as efficient initiators of styrene polymerization.[7,8] The initiation proceeds via electron transfer from the naphthalenide to a styrene molecule involving formation of the styrene radical anion.[9] Ring opening polymerization of oxiranes,[10] thiiranes[11] and thiethane[12] have also been accomplished using this initiator. However, sodium naphthalenide has been claimed not to polymerize β-lactones at room temperature.[13] After addition of a crown ether (18C6) or a cryptand (C222), which is able to complex sodium or potassium anions, the equilibrium depicted in Scheme II is obviously shifted to the right and this modified initiator is able to polymerize β-propiolactones, yielding "living polymers" with a narrow molecular weight distribution. The ^{1}H NMR spectrum of the polymer obtained, Figure 1, indicates the presence of unsaturated double bonds, but the absence of any naphthalene moieties from the initiator (Figure 1). However, hydrogenated naphthalene was found in the reaction mixture. According to these experimental results the following polymerization mechanism may be proposed (Scheme II):



SCHEME I



SCHEME II

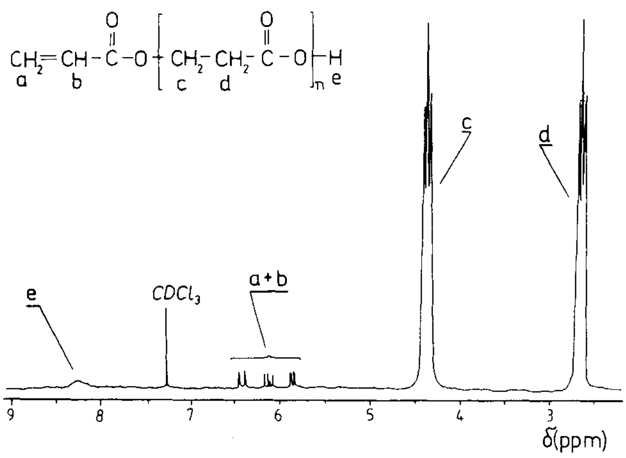


FIGURE 1 ^1H NMR spectrum of poly(β-propiolactone) obtained with potassium naphthalenide/18C6 complex as initiator.

TABLE 1

Results of anionic polymerization of β-lactones initiated by potassium naphthalenide (at the temperature of 20°C)

Monomer	Cation complexing agent	$[M]_0/[I]_0$	Time, h	Yield, %	M_n[a]	M_w/M_n[b]
β-Propiolactone	non	50[c]	20	10	—	—
β-Propiolactone	18-crown-6	40[c]	5	92	2500	—
β-Propiolactone	cryptand [2,2,2]	200[d]	10	90	13600	—
β-Propiolactone	cryptand [2,2,2]	2000[d]	24	89	120500[e]	—
β-Butyrolactone	non	50[c]	200	8	—	—
β-Butyrolactone	18-crown-6	40[c]	96	90	2800	1.28
β-Butyrolactone	cryptand [2,2,2]	40[c]	96	98	2950	1.22
β-Butyrolactone	cryptand [2,2,2]	75[d]	110	97	6200	1.25
β-Butyrolactone	cryptand [2,2,2]	150[d]	200	95	11000	1.29

[a] Number-average molecule masses were determined by the VPO technique in $CHCl_3$ using Knauer vapor pressure osmometer.

[b] Determined by GPC according to polystyrene standards with a low polydispersity.

[c] Conducted in THF M_0 = 2.0 mol/L.

[d] Conducted in THF M_0 = 3.0 mol/L.

[e] Estimated from viscosimetric measurement.

During the initiation step a lactone enolate is formed due to α-proton abstraction from the β-lactone molecule and hydronaphthalene is formed as a side product. The rearrangement of the lactone enolate leads to potassium crotonate (or acrylate). The latter, in the presence of a metal complexing agent (cryptand or crown ether) is capable of acting as an initiator. The polymerization proceeds via alkyl-oxygen bond scission, carboxylate anions being the propagating species. Another evidence for the proposed mechanism was provided by the outcome of a model reaction (monomer naphthalenide molar ratio = 1:1). The observation that polymerization of β-butyrolactone and β-propiolactone initiated with potassium naphthalenide proceeds only after the addition of a complexing agent, e.g., 18-

crown-6, indicates that the propagation is operating by means of loose ion pairs or free anions, producing telechelic polymers with a narrow molecular weight distribution (Table I).

It is interesting to notice that the mechanism of β-lactone ring opening reactions with alkali metal naphthalenides differs from that operating during styrene polymerization. In the polymerization of styrene the transfer of an electron occurs from the initiator to the styrene monomer. In the polymerization of β-lactone, however, there is a proton transfer from the monomer to the naphthalene radical anion, resulting in protonation of the naphthalene. Polymerization of γ-lactones with sodium or potassium naphthalenide does not take place, because of the thermodynamic stability of 5-membered lactones.[14] However 6-membered δ-valerolactone polymerizes easily yielding living polyesters, the α-proton abstraction from the monomer being the first step of initiation process.[15]

POLYMERIZATION OF LACTONES WITH AN ALKALI METAL SUPRAMOLECULAR COMPLEX AS THE ELECTRON TRANSFER CATALYST

Discovery of crown ethers, cryptands and other organic ligands, capable of complexing metal cations, by Pedersen[16] and Lehn[17] have opened new perspectives in the chemical research. In the early seventies it was revealed that alkali metals such as sodium, potassium, rubidium, and cesium can easily be dissolved in etheral

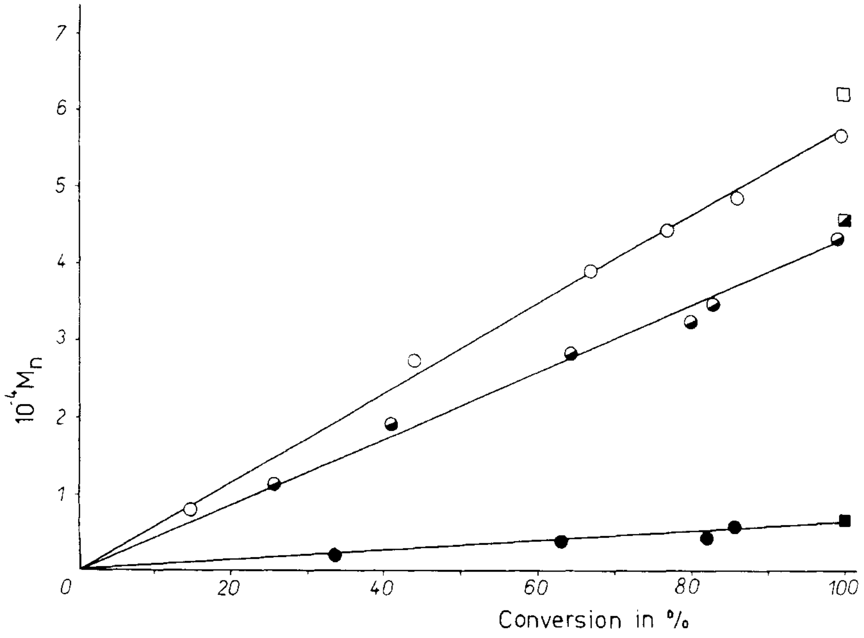


FIGURE 2 Dependence of M_n/conversion for poly(β-lactones) obtained in the presence of potassium solution: (◒) β-propiolactone (◪) M_n(calc) = 46,000; (○) α.α-methylethyl-β-propiolactone (□) M_n(calc) = 62,900; (●) β-butyrolactone (■) M_n(calc) = 6700.

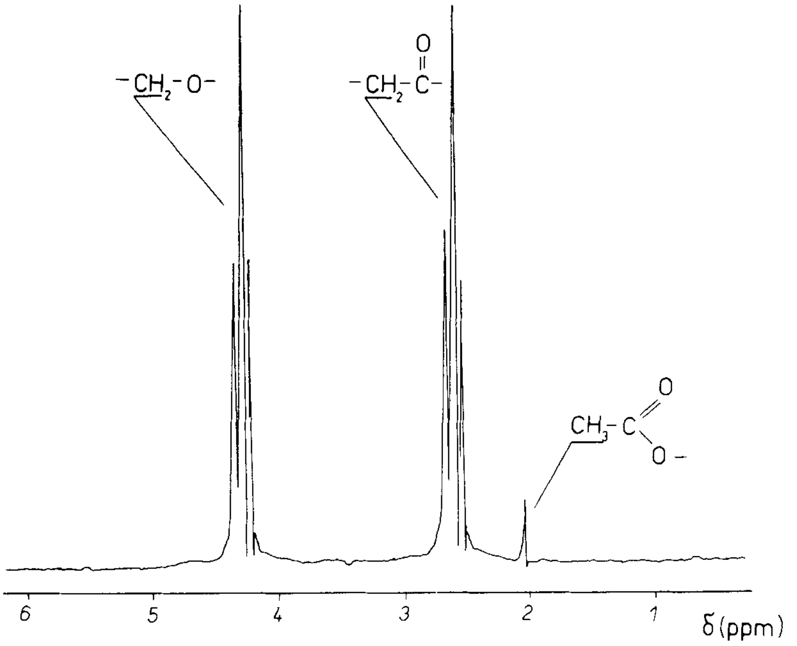


FIGURE 3 ^{1}H NMR spectrum of poly(β-propiolactone) obtained with potassium solution as initiator.

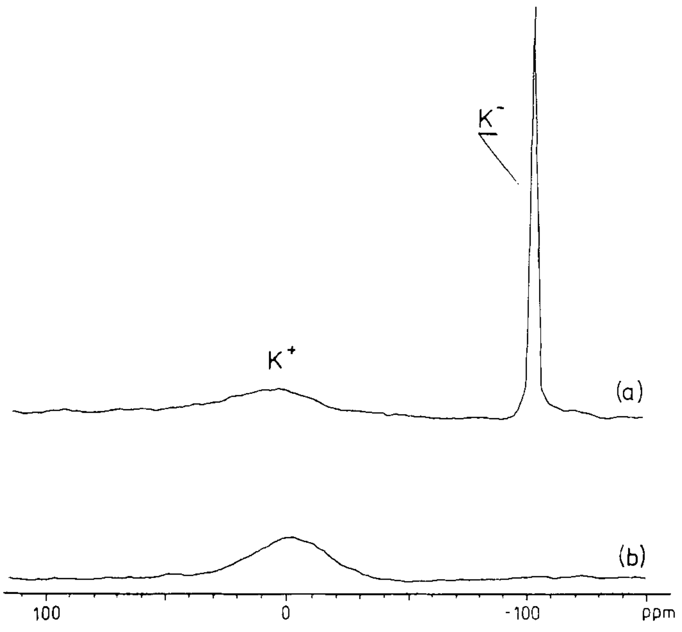
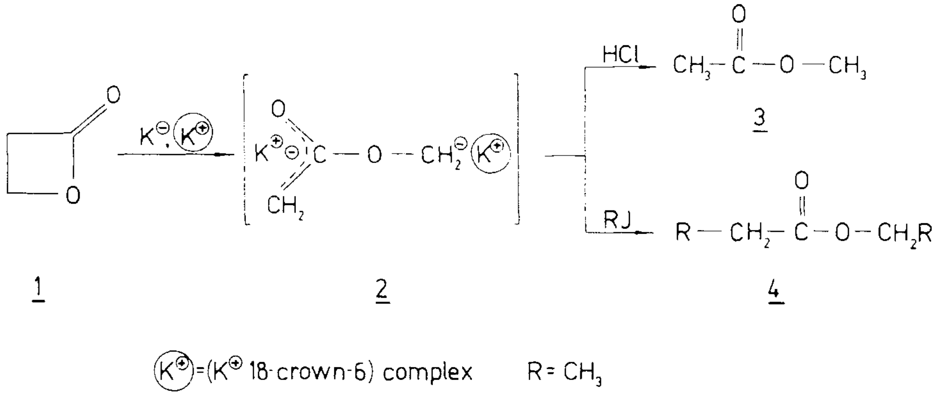


FIGURE 4 ^{39}K NMR spectra of: (a) the potassium solution obtained by complexation of K with 18C6 in THF, (b) the mixture after treatment with β-propiolactone.



SCHEME III

solvents, e.g., tetrahydrofuran after the addition of a macrocyclic ligand. The metal "blue" solutions contain complexed metal cations associated with metal anions and solvated electrons.[18] These alkali metal organic solutions have been employed as organic reagents[19,20] and initiators for the polymerization of butadiene, vinyl monomers and some sulfur containing monomers.[21-24] As a result of kinetic studies on metal solubilization we were able to rationalize the process of metal dissolution, thus showing that under proper conditions (time, temperature) metal solutions containing metal ions but only small, negligible amounts of electrons could be produced.[25] Novel initiators with a well defined concentration of metal ions, controlled by metal NMR measurements[26,27] were prepared in a simple manner by dissolution of solid metal, e.g., potassium mirror or sodium-potassium alloy (1:1) in an organic solvent, such as THF or tetraglyme, containing an organic ligand. The latter attracts cations, forming supramolecular metal complexes with following formulae:

$$K^+/15C5/,K^-$$

$$K^+/18C6/,K^-$$

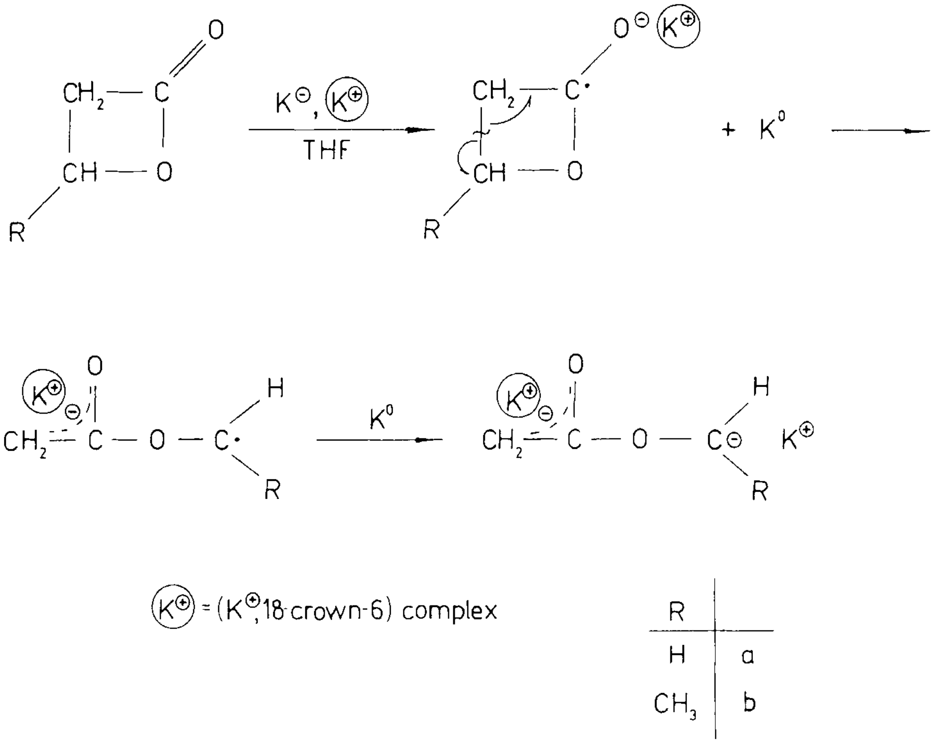
$$K^+/glyme/,K^-$$

$$K^+/15C5/,Na^-$$

where: 18C6 = 18-crown-6, 15C5 = 15-crown-5.

It turned out that in the polymerization of substituted and unsubstituted β-lactones, as well as lactides the initiation is very fast and "living" polymers are produced, as evidenced by GPC and kinetic measurements[28] (Figure 2).

Due to the "living character" of this polymerization the use of novel initiators enables the preparation of block polymers, e.g., diester blocks of β-propiolactone and β-butyrolactone, styrene-lactone[29] and acrylate-lactone blocks. These block polymers are degradable in suitable environmental conditions or that can be hy-



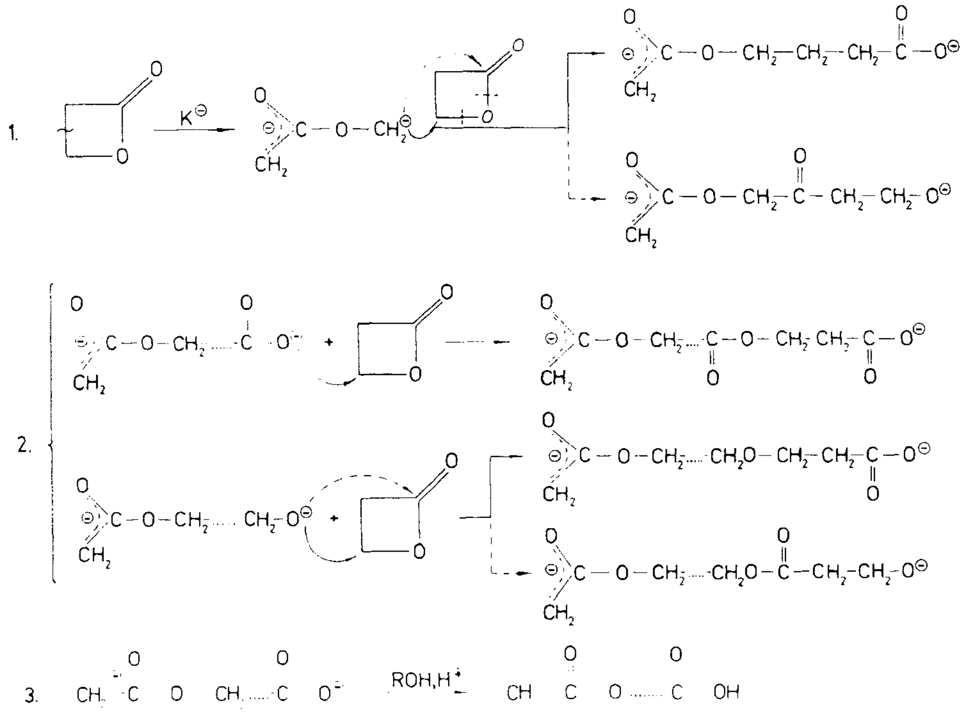
SCHEME IV

drolyzed, which is important in recycling processes. On the other hand polymers of β-methyl-β-propiolactone (β-butyrolactone) can serve as models of natural poly-β-hydroxybutyrates produced by some bacteria as storage materials in their cells.[1] These polymers are biodegradable and bioresorbable and may be used for medical applications, e.g., for controlled drug release, etc.

The question arises what was the mechanism of this unusual polymerization? End group analysis revealed that acetoxy end groups are present in the polymers (or oligomers) formed and carboxylate anions are the propagating species, as indicated by ^{1}H NMR spectroscopy (Figure 3).

The results of model reactions, carried out in an NMR instrument tube and followed by ^{39}K NMR spectroscopy, suggested that two electrons are transferred from the metal anion to a monomer molecule at the initiation step of polymerization, as evidenced by the signal of potassium anion, which vanished completely after addition of the monomer, the signal of potassium cation being broadened (Figure 4).

The model reactions between β-lactone monomer and potassium anion (molar ratio 1:1) have revealed that uncommon α-carbon to β-carbon bond scission takes place and enolate carbanion is formed as the initial product of the ring cleavage of a monomer as evidenced by analysis of the final products of this reaction after protonation or methylation (Scheme III).



SCHEME V

The mechanism of this reaction is a general one, valid for substituted and unsubstituted β-lactone monomers.[30] As proven by ESR measurements, the reaction at first involves a single electron transfer from the metal anion to the β-lactone molecule, resulting in the formation of lactone radical anion (Scheme IV).

The latter, being unstable, undergoes β-elimination to form an enolate radical, which was observed in the ESR spectra (Scheme IV). This radical reacts with potassium, forming the corresponding enolate carbanion which exists in mezomeric forms stabilized by resonance.[31] It may be assumed that the driving force for this reaction is a stabilization effect, guiding the reaction along the thermodynamically most convenient route. Under common polymerization conditions, when a monomer is available in excess, the enolate carbanion initially formed attacks the monomer to produce growing polymer chains. The propagation proceeds via alkoxide (Scheme V) and carboxylate active centers, formed due to acyl-oxygen and alkyl-oxygen bond scission of the monomer. At higher conversions the alkyl-oxygen bond cleavage prevails and polymers having carboxylate active centers are eventually produced[28] (Scheme V).

The proposed mechanism is very complex, involving the scission of α-carbon to β-carbon bonds of a β-lactone monomer (in the initiation step) and cleavage of both heterobonds, i.e., acyl-oxygen and alkyl-oxygen in the propagation step. In spite of the complexity of this polymerization, properties of the final polymers can be strictly controlled due to the living character of this process.

CONCLUSIONS

The ring-opening polymerization of simple lactones constitutes a convenient method for the synthesis of aliphatic polyesters. Some of the polyesters produced by ring-opening polymerization exhibit such unique properties as biodegradability, bioresorbability, and nonimmunogenicity, and therefore are considered to be very interesting materials for medical applications. On the other hand vinyl-ester block polymers offer novel applications as materials for the packing industry, being convenient for recycling. Novel catalysts and initiators as well as novel chemistry of polymerization of lactones has been reviewed in this paper.

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