Anionic Polymerization of Pivalolactone Initiated by Alkali Metal Alkoxides

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Received May 26, 1995; Revised Manuscript Received July 20, 1995®

ABSTRACT: Polymerization of pivalolactone (α,α-dimethyl-β-propiolactone) initiated with alkali metal alkoxides has been studied. It has been revealed that after addition of an alkoxide anion, from the initiator, onto the carbonyl carbon atom of the monomer the selective cleavage of the acyl–oxygen bond of the monomer leads to the formation of alkoxide propagating species. Thus, it has been demonstrated that, in contrast to α-unsubstituted β-lactones and higher lactones, the anionic polymerization of pivalolactone proceeds through either alkoxide or carboxylate propagation centers, depending on the nature of initiator used, i.e. an alkoxide or a carboxylate, respectively. In the former case, however, cyclic oligomers are also formed which are unusual in the anionic polymerization of other β-lactones. This indicates that, whatever the lactone ring size (four-, six-, or seven-membered lactones), intramolecular transesterification reactions can take place if alcoholate ions are propagating species.

Introduction

During the two last decades, a growing interest has been paid to the synthesis of aliphatic polyesters and copolyesters for environmental and medical applications e.g. as biomaterials and therapeutic systems.[1–4] These polymers form indeed a very important group of bioerodable materials widely recognized for hydrolytic and enzymatic biodegradation and low toxicity for living organisms.[5]

Although aliphatic polyesters are traditionally synthesized by a step-growth mechanism from a diol and diacid mixture, or from a hydroxy acid when available, ring-opening polymerization of lactones is an alternative method which overcomes the inherent drawbacks of polycondensation.

Lactone monomers have been polymerized by various initiators and catalysts according to different mechanisms.[6–11] Among them, the anionic ring-opening polymerization has proved to offer many possibilities to control the polyester molecular parameters and to obtain *tailor-made* biodegradable materials.[12–14] It is usually believed that the mechanism for the anionic polymerization of lactones initiated by alkali metal alkoxides strongly depends on the ring size.[15] Except for γ-butyrolactone which does not polymerize for thermodynamic reasons,[16] the anionic polymerization of higher lactones, such as δ- and ε-lactones, was believed to proceed according to Scheme 1.[15,17]

However it is also well-known that competitive degradation reactions (*intra-* and *intermolecular* transesterification reactions) take place in the polymerization of the six- and seven-membered monomers, which lead to the formation of linear and cyclic oligomers with a simultaneous decrease in the apparent monomer conversion and the increase of polymolecularity of poly(δ-valerolactone) and poly(ε-caprolactone).[18]

Scheme 1

M = alkali metal

Recent investigations enable the rationalization of the old views on the anionic polymerization of β-propio- and β-butyrolactone, thus showing that the alkoxide anion attacks the carbonyl carbon atom with selective cleavage of the lactone acyl–oxygen bond and the formation of the alkali metal salt of β-hydroxy carboxylic acid ester **1**. In contrast to the anionic polymerization of higher six- and seven-membered lactones, alkoxide **1** does not propagate polymerization but it is rearranged into an unsaturated ester, e.g. acrylate or crotonate **2**, with elimination of an alkali metal hydroxide, which would be the actual initiator for the β-lactone polymerization (Scheme 2).[19,20]

This elimination reaction is quite general for α-unsubstituted-β-lactones independent of the aprotic solvent and the alkali metal alkoxide used.[21,22] The alkali metal hydroxide then reacts with the β-lactone which forms an unstable intermediate **3**, as a result of the acyl–oxygen bond scission. This intermediate is transformed into the alkali metal salt of the β-hydroxy acid **4**. Chain propagation occurs on the carboxylate group of **4** and **5**, the latter being the elimination reaction product of **4**. Indeed, the propagating chains may be end-capped by either a hydroxy or an unsaturated groups. Again in contrast to the anionic polymerization of higher lactones, formation of cyclic oligomers resulting from a *back-biting* degradation of poly(β-lactone) chains has not been observed.

The aim of this work is to establish the mechanism of polymerization of α,α-dialkyl-substituted-β-lactones initiated by alkali metal alkoxides. These monomers do not bear acidic protons in the α-position, thus they

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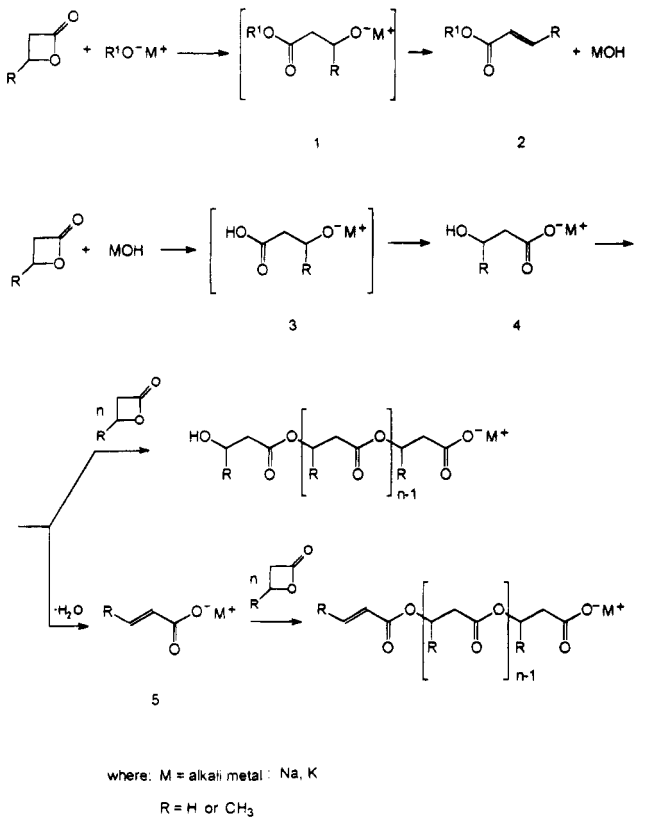
® Abstract published in *Advance ACS Abstracts,* September 1, 1995.

0024-9297/95/2228-7276$09.00/0

Scheme 2



are unable to undergo the elimination reaction reported in Scheme 2. The knowledge of their polymerization mechanism may contribute to the general chemistry of β-lactones and their reactions with alkoxides in particular. α,α-Dimethyl-β-propiolactone (pivalolactone) has been selected as a model monomer and alkali metal alkoxides (methoxide and *tert*-butoxide) have been used along with potassium acetate (reference) as initiators.

Experimental Part

Materials. Pivalolactone (3,3-dimethyl-2-oxetanone) was dried over calcium hydride and distilled under reduced pressure. The fraction boiling at 48–49 °C (9 mm g) was collected. Potassium methoxide was obtained as described in ref 19. Potassium *tert*-butoxide (from Aldrich) and lithium *tert*-butoxide (from Fluka) were used as received. Potassium acetate (Aldrich) was dried for 60 h at 40 °C under vacuum. THF was purified as described in ref 23.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ + TFA (trifluoroacetic acid) with TMS as the internal standard by using a Varian VXR-300 spectrometer. The number average molecular weight of polypivalolactone was determined from ^{1}H NMR spectroscopy on the basis of intensity of the signals of the CH_3 substituents at δ = 1.22 ppm and of the end groups at δ = 3.78 ppm (CH_3O in the case of methoxide initiator) or 1.50 ppm ($(CH_3)_3CO$ in the case of *tert*-butoxide initiator), respectively, on the assumption that one alkoxide residue is attached at each polymer chain. GC–MS analyses were run either on a 30-m-long DB-5 fused silica capillary column, by using a Varian 3400 chromatograph connected to an SSQ-700 Finnigan MAT mass spectrometer, or on a 30-m-long fused silica capillary column DB-1701, by using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800AT ion trap detector. FTIR spectra were recorded with a FTS 40A Bio-RAD spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer.

Polymerization of PVL Initiated by Alkali Metal Alkoxides. General Procedure. The polymerization experiments were conducted at 20 °C, in THF. The monomer concentration was changed from 0.50 to 1.53 mol/L, and the concentration of alkali metal alkoxide was varied from 0.1 to 0.01 mol/L. The polymers were precipitated in acidic methanol or in hexane. Then polymers were washed and dried under vacuum. The hexane filtrates were analyzed by GC–MS.

Polymerization of PVL Initiated by Potassium Acetate. The polymerization experiments were conducted at 20 °C, in THF. The monomer concentration was either 1.20 or 0.51 mol /L, and the concentrations of potassium acetate were 0.09 and 0.03 mol/L, respectively. Polymers were precipitated and purified as described above. The PPVL yields were almost quantitative, and no cyclic oligomers were detected in the hexane filtrate by GC–MS spectroscopy.

Supercritical Fluid Extraction (SFE). Oligomers present in the crude polymerization products were isolated by supercritical fluid extraction (SFE).[24–26] A ISCO SFX 220 extractor was used with supercritical CO_2 as the mobile phase at 150–500 bar and 40 °C. Under these conditions, PPVL oligomers were dissolved in the supercritical fluid and extracted from the crude polymer. The restrictor allowed for CO_2 expansion, and oligomers were trapped in CH_2Cl_2. Oligomeric fractions were analyzed by GC–MS, and polymer residue was analyzed by ^{1}H NMR and FTIR spectroscopies.

Analysis of Cyclic Oligomers by GC–MS and Fractional Crystallization. Cyclic oligomers, i.e. trimer, tetramer, and pentamer, were analyzed by GC–MS in the hexane filtrates received after the PPVL separation. Trimer: MS m/z 301 ($M^+ + 1$), 282 ($M^+ - H_2O$), 270 ($M^+ - CH_2O$), 242 (270 – CO), 201 (301 – $C_5H_8O_2$), 182 (282 – $C_5H_8O_2$), 170 (270 – $C_5H_8O_2$), 142 (242 – C_5HO_2), 101 (201 – $C_5H_8O_2$), 82 (182 – $C_5H_8O_2$), 70 (170 – $C_5H_8O_2$), 42 (142 – $C_5H_8O_2$) (where $C_5H_8O_2$ is the unit of the same molecular weight as the pivalolactone monomer: MW = 100).

Tetramer: MS m/z 401 ($M^+ + 1$), 382 ($M^+ - H_2O$), 370 ($M^+ - CH_2O$), 342 (370 – CO), 301 (401 – $C_5H_8O_2$), 282 (382 – $C_5H_8O_2$), 270 (370 – $C_5H_8O_2$), 242 (342 – $C_5H_8O_2$), 201 (301 – $C_5H_8O_2$), 182 (282 – $C_5H_8O_2$), 170 (270 – $C_5H_8O_2$), 142 (242 – $C_5H_8O_2$), 101 (201 – $C_5H_8O_2$), 82 (182 – $C_5H_8O_2$), 70 (170 – $C_5H_8O_2$), 42 (142 – $C_5H_8O_2$).

Pentamer: MS m/z 501 ($M^+ + 1$), 482 ($M^+ - H_2O$), 470 ($M^+ - CH_2O$), 442 (470 – CO), 401 (501 – $C_5H_8O_2$), 382 (482 – $C_5H_8O_2$), 370 (470 – $C_5H_8O_2$), 342 (370 – $C_5H_8O_2$), 301 (401 – $C_5H_8O_2$), 282 (382 – $C_5H_8O_2$), 270 (370 – $C_5H_8O_2$), 242 (342 – $C_5H_8O_2$), 201 (301 – $C_5H_8O_2$), 182 (282 – $C_5H_8O_2$), 170 (270 – $C_5H_8O_2$), 142 (242 – $C_5H_8O_2$), 101 (201 – $C_5H_8O_2$), 82 (182 – $C_5H_8O_2$), 70 (170 – $C_5H_8O_2$), 42 (142 – $C_5H_8O_2$).

The recorded mass spectra were in full agreement with those published in the scientific literature[27–29] for the cyclic oligomers formed upon the thermal degradation of polypivalolactone.

The cyclic trimer and tetramer, formed in the studied polymerization, were separated by fractional crystallization from a hexane–THF (4/1) mixture. Trimer (purity 99.8% GC): IR (KBr) ν = 2984, 2938, 2878, 1729, 1477, 1394, 1370, 1307, 1253, 1232, 1159, 1032, 1008, 985, 971, 939, 920, 797, 763, 610, 594, 556 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.24 (s, 6H, CH_3), 4.07 (s, 2H, CH_2). Anal. Calcd for $C_{15}H_{24}O_6$: C, 33.3; H, 53.3. Found: C, 33.2; H, 53.1. Tetramer (purity 98.3% GC): IR (KBr) ν = 2982, 2938, 2877, 1733, 1482, 1457, 1397, 1365, 1313, 1237, 1166, 1018, 980, 954, 940, 908, 790, 765, 626, 598, 547 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.21 (s, 6H, CH_3), 3.97 (s, 2H, CH_2). Anal. Calcd for $C_{20}H_{32}O_8$: C, 33.3; H, 53.3. Found: C, 33.1; H, 53.3.

Results and Discussion

Polymerization. Polymerization of pivalolactone (PVL) has been initiated with potassium methoxide and potassium *tert*-butoxide, respectively, in THF at 20 °C. The ^{1}H NMR spectra of low molecular weight polypivalolactone (PPVL) show, in addition to the signals characteristic of the polymer chain (δ = 1.22 ppm, CH_3, and 4.28 ppm, CH_2), two signals assigned to protons of the CH_2OH end group at δ = 3.72 ppm and alkyl ester end groups at δ = 1.49 or 3.78 ppm, depending on the

Table 1. Results of Anionic Polymerization of Pivalolactone Initiated with Alkali Metal Alkoxides and Potassium Acetate in THF at 20 °C

initiator	$[M]_0$ (mol/L)	$[I]_0$ (mol/L)	time (min)	yield (%)	M_n (calcd)[a]	$M_{n\ NMR}$
MeOK	1.27	0.07	15	86	1600	1800
MeOK	1.00	0.10	15	74	740	1900
MeOK	0.53	0.03	30	30	530	1000
MeOK	1.23	0.01	120	43	5300	1700
t-BuOK	1.37	0.08	15	87	1500	1700
t-BuOK	1.00	0.06	15	68	1100	2100
t-BuOK	0.50	0.03	30	31	500	800
t-BuOLi	1.30	0.09	15	89	1300	1500
t-BuOLi	0.70	0.07	30	70	700	900
AcOK	1.20	0.09	120	95	1100	1500
AcOK	0.51	0.03	180	94	1600	1700

[a] Calculated from $M_{n(calcd)} = [M]_0/[I]_0 \cdot (yield/100) \cdot M(PVL) = [M]_0/[I]_0 \cdot yield$.

initiator used (*tert*-butyl or methyl ester, respectively) (Figure 1a,b). Additional evidence for the assignment of the peak at 3.72 ppm has been obtained by reacting the polymer solution with trichloroacetyl isocyanate according to ref 30. The downfield shift of this signal to 4.25 ppm (≅0.5 ppm), characteristic for a CH_2OH group, was observed. The intensity ratios of signals ascribed to the CH_2OH and alkyl ester end groups were 2:3 and 2:9, respectively, in the case of methoxide and *tert*-butoxide initiator.

The above results show that the ring-opening polymerization takes place *via* the selective cleavage of the acyl–oxygen bond of PVL. Table 1, however, shows that there is no direct relationship between the polymer molecular weight (determined by ^1H NMR spectroscopy)[31] and the initial monomer-to-initiator molar ratio.

Moreover, the polymerization yield strongly depends on the reaction conditions and decreases with the increase of the reaction time and decrease of initial monomer concentration, respectively (see Table 1). The substitution of the lithium counterion for potassium increases the reaction yield. These observations have prompted us to know whether the transesterification reactions, which are commonly observed in the anionic polymerization of higher lactones, do occur or not in this process. Accordingly, the residues of the hexane filtrates received after the PPVL separation have been analyzed by ^1H NMR and GC–MS analysis. The ^1H NMR spectrum recorded in $CDCl_3$ + TFA (Figure 2) shows not only the signals characteristic of the low molecular weight open chain PPVL but also additional singlets at δ = 1.28 and 4.18 ppm. These additional signals, that are actually of a very low intensity in Figure 1, might be assigned to cyclic oligomers.

The filtrates have also been analyzed by GC–MS. The total ion current (TIC) chromatograms show two series of chromatographic peaks, i.e. peaks for the linear oligomers,[32] the retention times of which depend on the initiator used, and several peaks with a retention time which is independent of the alkoxide used. The second series of peaks has been accordingly assigned to cyclic oligomers (Figure 3).

The MS spectra of the expected cyclic oligomers (see Experimental Part) show the following sequence of fragmentation: $M^+ - H_2O - nC_5H_8O_2$, $M^+ - CH_2O - nC_5H_8O_2$, and $M^+ - CH_2O - CO - nC_5H_8O_2$, where $C_5H_8O_2 = 100$, i.e. the molecular weight of the PVL unit and $0 \leq n < m$ for the *m*-mers. These spectra are consistent with those previously reported for cyclic oligomers formed as a result of the thermal degradation of PPVL.[27–29] Actually, the cyclic trimer, tetramer, and

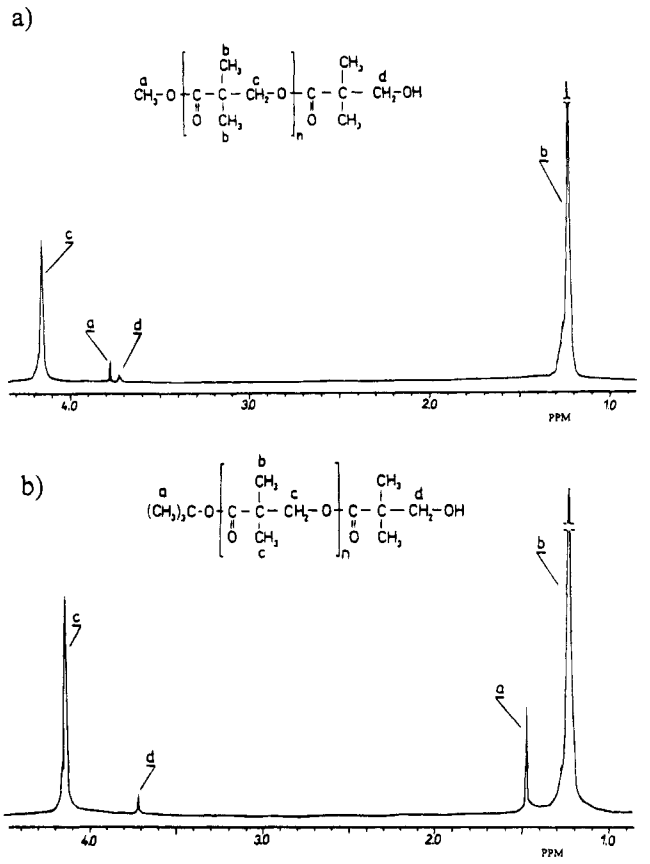


Figure 1. ^1H NMR spectrum of PPVL obtained in the presence of (a) potassium methoxide and (b) potassium *tert*-butoxide as initiator.

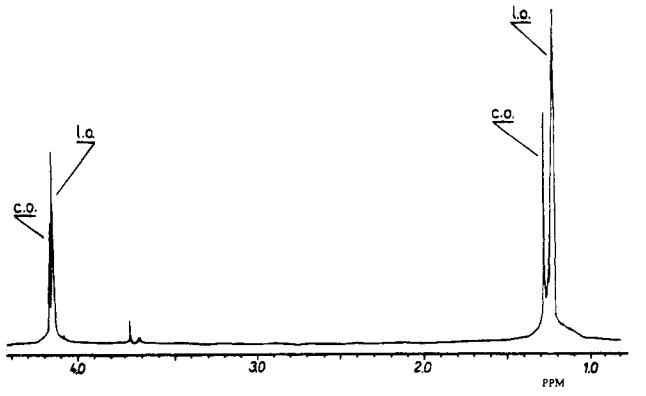


Figure 2. ^1H NMR spectrum of residue after hexane evaporation from filtrate obtained after precipitation of PPVL formed in the presence of potassium methoxide: c.o. = cyclic oligomers; l.o. = linear oligomers and open chain polymer.

pentamer are observed in the polymerization medium. The cyclic dimer was not detected.

The cyclic trimer and tetramer have further been separated by fractional crystallization from a solution in a hexane–THF mixture. Their characterization by ^1H NMR, FTIR, MS, and elemental analysis are reported in the Experimental Part.

The supercritical fluid extraction (SFE) technique has been used in order to isolate higher cyclic oligomers from the PPVL linear chains.[24–26] The oligomeric fractions extracted from the crude PPVL by supercritical CO_2 were analyzed using the GC–MS technique. The GC–MS analysis of the separated fractions confirmed the presence of both cyclic and linear oligomers although in a ratio different from that observed for the hexane filtrate (Figure 3a, Figure 4).

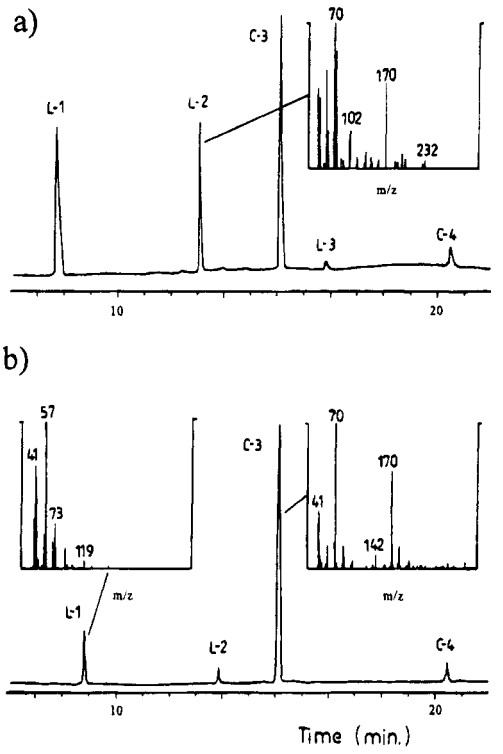


Figure 3. GC–MS (ITD) TIC chromatograms of filtrates obtained after polymer separation from a polymerization of PVL initiated with (a) potassium methoxide: **L-1** (retention time t_r = 8.09 min), $CH_3OC(O)C(CH_3)_2CH_2OH$; **L-2** (t_r = 12.39), $CH_3[OC(O)C(CH_3)_2CH_2]_2OH$; **C-3** ($t_r$ = 15.08), cyclic trimer; **L-3** (t_r = 16.33), $CH_3[OC(O)C(CH_3)_2CH_2]_3OH$; **C-4** ($t_r$ = 20.25), cyclic tetramer. (b) Same as in (a) but initiated with potassium *tert*-butoxide. **L-1** (t_r = 9.08), $(CH_3)_3COC(O)C(CH_3)_2CH_2OH$; **L-2** ($t_r$ = 13.13), $(CH_3)_3C[OC(O)C(CH_3)_2CH_2]_2OH$; **C-3** ($t_r$ = 15.06), cyclic trimer; **C-4** (t_r = 20.23), cyclic tetramer.

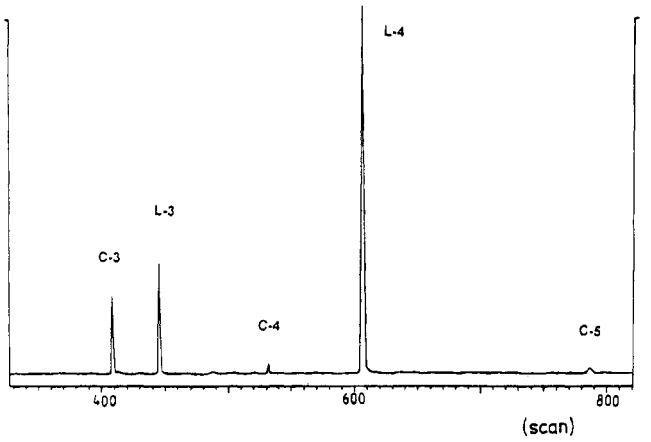
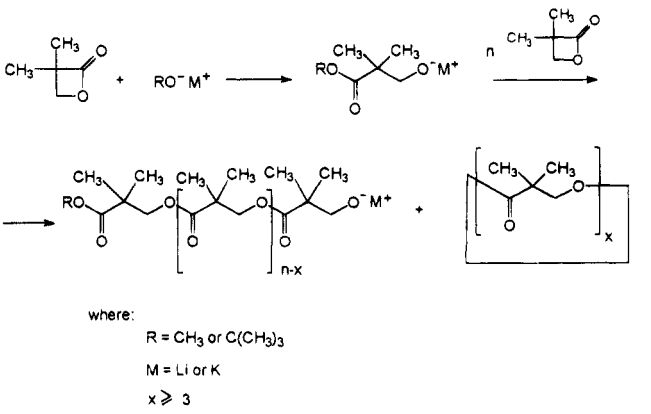


Figure 4. GC–MS (SSQ 700) TIC chromatogram of oligomers separated by SFE from crude PPVL obtained in the presence of potassium methoxide: **C-3**, cyclic trimer; **L-3**, $CH_3[OC(O)C(CH_3)_2CH_2]_3OH$; **C-4**, cyclic tetramer; **L-4**, $CH_3[OC(O)C(CH_3)_2CH_2]_4OH$; **C-5**, cyclic pentamer.

It is worth pointing out that the relative content of cyclic tetramer is not increased in the series of cyclic oligomers in contrast to what happens for the higher species in the series of linear oligomers. Whatever the separation technique, i.e. selective precipitation in hexane or SFE, no trace of cyclic dimer was detected, but cyclic trimer is preferentially formed in the PVL polymerization. In this respect, a similar distribution of the cyclic oligomers has been reported by Garozzo and Montaudo[33] in the case of the thermal degradation of PPVL.

Scheme 3



The material insoluble in supercritical CO_2 has been analyzed by ^1H NMR and FTIR. The ^1H NMR spectrum of the polymer residue left by SFE does not show any signal for the cyclic oligomers.

Mechanism of the Polymerization. All the experimental data confirm that alkoxide anions are the active species in both the initiation and the propagation of the α,α-disubstituted-β-lactones polymerization initiated with lithium and potassium alkoxides. Thus, the ring opening takes place *via* the cleavage of an acyl–oxygen bond. However, during the chain growth, transesterification reactions also occur, i.e. intramolecular *back-biting* reactions that lead to the formation of cyclic oligomers and intermolecular reactions responsible for linear oligomers soluble in the solvent used for the PPVL precipitation and/or the supercritical CO_2. The mechanism accordingly proposed for the PVL polymerization is shown in Scheme 3.

The alkoxide initiator is attached to the growing chains as an ester end group and an alkoxide anion is the propagating species, similar to the anionic polymerization of higher lactones with these initiators (Scheme 1). Formation of cyclic oligomers by the *back-biting* reaction, indicated in this polymerization, has not previously been observed in polymerization of α-unsubstituted-β-lactones initiated by alkali metal alkoxides and propagated by carboxylate centers.[19–21] Similarly, no cyclic oligomers are formed when the PVL polymerization is initiated by potassium acetate and propagated by carboxylate species. This statement has been supported by the GC–MS analysis of the hexane filtrate after the PPVL precipitation. In the polymerization initiated by potassium acetate the ^{1} H NMR spectrum of the crude PPVL (Figure 5) shows only the signal for the acetoxy end group, at δ = 2.06 ppm, associated with the initiator residue, in addition to the signals for the polymer CH_3 and CH_2 groups. According to these results, the PVL polymerization initiated by potassium carboxylate proceeds as in Scheme 4.

The addition of the acetate anion to PVL is thus responsible for the selective scission of the alkyl–oxygen bond. Propagation selectively proceeds through carboxylate active species. Thus, this mechanism is the same as that proposed previously for other β-lactones, independent of the substitution at the β-lactone ring.[6] The carboxylate anion is, however, not strong enough as a nucleophile to initiate transesterification reactions, and no cyclic oligomers are formed.

These results clearly indicate that formation of cyclic oligomers is also possible in the β-lactone polymerization but can only occur when propagation proceeds *via* alkoxide active species.

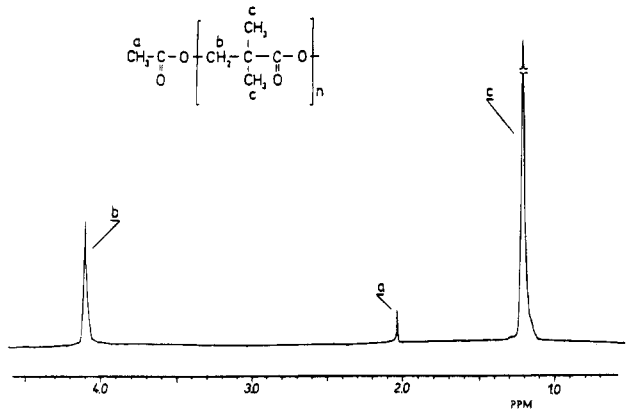
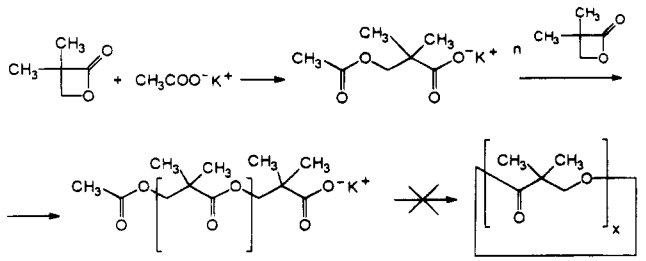


Figure 5. ^{1}H NMR spectrum of PPVL obtained in the presence of potassium acetate as initiator.

Scheme 4



Conclusions

The anionic polymerization of pivalolactone can proceed on either alkoxide or carboxylate propagation centers, depending on the anionic initiator used, i.e. an alkoxide or a carboxylate in contrast to other β-lactones, which polymerize only exclusively on carboxylate centers, independent of the initiator used (Scheme 2). It can be concluded that alkali metal alkoxides initiate the polymerization of pivalolactone (α,α-dimethyl-β-propiolactone) by the nucleophilic attack on the carbonyl carbon atom followed by the cleavage of the acyl–oxygen bond of PVL and formation of alkoxide propagating species. It turns out that *back-biting* reactions occur in the polymerization of PVL initiated with alkali metal alkoxides. Formation of PVL cyclic oligomers in the course of anionic polymerization, which to our best knowledge is reported herein for the first time in the literature, indicates that in the anionic polymerization of lactones the intramolecular transesterification reactions can take place regardless of the lactone size (four-, six-, or seven-membered lactones). However, cyclic oligomers are formed in the anionic polymerization of β-lactones only when chain propagation proceeds *via* alkoxide active species, as observed in the case of PVL polymerization. Thus, when α-unsubstituted-β-lactones are polymerized with an alkali metal alkoxide, the *back-biting* reaction does not occur because the chain growth proceeds *via* carboxylate species which are formed at the initiation step[20,21] and are not nucleophilic enough to initiate the transesterification reactions.[6-8]

Acknowledgment. The authors are very grateful to Dr. G. Ghitti for helpful assistance in the supercritical fluid extraction techniques. R.J. and Ph.D. would like to thank the Belgian FNRS and the Polish Academy of Sciences for a grant to visit the Institute of Polymer Chemistry, PASci., in Zabrze, as well as to thank the Service de la Programmation de la Politique Scientifique for financial support.

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MA950727L