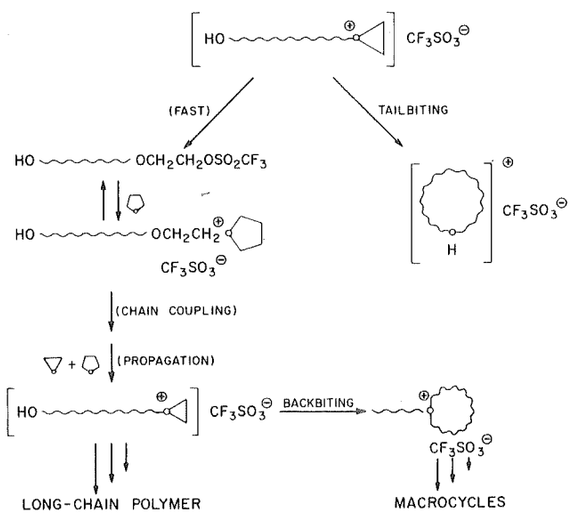
Table V
Change in Composition of EO/THF-CF_3SO_3H Reaction Products with Reaction Time[a]

cyclic product	standard GC area (% of total reaction products) 1 h[b]	5 h[b]	80 h
1,4-dioxane	2.2	6.7	
1:2	1.6	0.4	1.0
3:1	8.0	10.4	18.1
2:2	32.1	31.5	21.9
1:3	13.4	9.1	6.8
3:2	6.8	8.2	12.0
2:3	11.4	9.3	7.1
3:3	1.5	2.1	5.5
1:4	2.7	1.5	1.3
4:2	5.0	4.8	5.7
2:4	4.9	3.4	2.4
1:5	1.5	0.6	<0.4

[a] Polymerization conditions, see Table IV. [b] Total conversion to oligomer and polymer: 6.5% (1 h), 55% (5 h).

Scheme II



of the total polymer concentration, depending on the polymerization conditions. The molecular weight of copolymer isolated from this sample was relatively high, as expected with CF_3SO_3H initiation:[1] A number average molecular weight of about 9000 was found by spectroscopic end group analysis. Formation of 1,4-dioxane proceeds very slowly in these systems. From Table V it can be seen that dioxane concentration is much lower than the concentration of the larger macrocycles.

Formation of macrocycles probably occurs via tail biting and back biting, as described for the THF/CF_3SO_3H system.[1] Since no THF homocyclic oligomers were found in these mixed systems, back biting is most likely to occur when a highly strained EO oxonium ion at the chain end is attacked by a chain oxygen to relieve ring strain (Scheme II). The schematic outline illustrates some possible reaction steps in this system. For example, macrocycles which form rapidly in the initial stages of the polymerization, e.g., EO:THF crown 1:3, are probably formed by tail biting, while others, which slowly increase in concentration (Table V), may be formed by a back-biting reaction of longer chains (the wavy line ~~ represents a copolyether chain).

This rapid initial formation of macrocycles by tail biting, followed by chain formation via ring opening and coupling reactions, could be considered as a two-stage process and

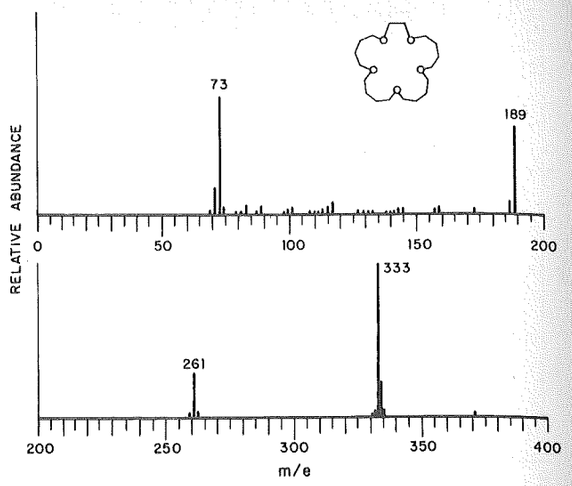


Figure 4. Chemical ionization mass spectrum of EO:THF crown 1:4 (peak H in Figure 3).

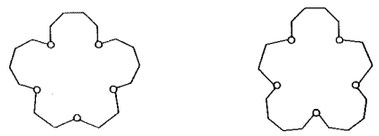
Table VI
Chemical Ionization Fragmentation Pattern of EO/THF Crown Ethers[a]

1:2	2:2	1:3	3:2	2:3	1:4	2:4	1:5	MAJOR FRAGMENTS OBSERVED (EO:THF)
							404	(1:5)
						376		(2:4)
					332		332	(1:4)
				304		304		(2:3)
			276		260		260	(3:2)
		260		232		232		(1:3)
	232		(188)		188		188	(2:2)
188		188		188				(1:2)
88								(2:0)
(72)	72	72	72	72	(72)	72	72	(0:1)

[a] Molecular weights and composition of parent compounds are underlined; major fragments observed (m/e − 1) are shown in vertical columns.

might be similar to the two-stage processes observed in the polymerization of cyclic acetals.[9]

The crown ether nomeclature[10] cannot be easily adapted to mixed macrocycles without leading to ambiguities. We have found it convenient to use trivial names such as "EO:THF crown 2:3", with the smaller monomer always preceding. Such a name does not distinguish between possible isomers, e.g., 1,4,7,12,17-pentaoxacycloheneicosane (I) and the 1,4,9,12,17-pentaoxaisomer II. However, no



EO : THF - CROWN 2:3

isomers have been found so far with the analytical techniques employed. The following EO:THF crown ethers have been identified by chemical ionization/mass spectroscopy: 1:2, 1:3, 1:4, 1:5; 2:2, 2:3, 2:4; 3:1, 3:2, 3:3, 3:4; 4:1, 4:2, 4:3; 5:1. The largest rings identified are the 28-membered ring EO:THF crown 1:5 and the 29-membered EO:THF crown 3:4. Larger rings are also present, as evidenced by GC peaks at longer retention times, but these have not yet been unambiguously assigned.

Fragmentation patterns show an interesting regularity (Figure 4). Under the mild conditions of chemical ionization, the macrocycles lose single or multiple THF units, and m/e signals appear at (M + 1) − 72n, where n = 1, 2, 3,. . ., etc. (Table VI). This is similar to the fragmentation pattern observed earlier with tetrahydrofuran crown ethers.[1,2]

Conclusion

Macrocyclic oligomer formation is common to EO, THF, and EO/THF polymerization systems, initiated by nonhydrolyzable, strong, protonic acids. Formation of high molecular weight linear polymers by oxonium ion ring opening and chain coupling steps is accompained by formation of macrocycles via a tail biting–back biting mechanism. In systems in which the less reactive covalent ester end group is stabilized, some linear oligomers are also found. There is a preference for certain ring sizes and compositions in THF/EO polymerizations, depending on polymerization conditions and monomer concentrations.

Acknowledgment. We would like to thank Drs. G. E. Heinsohn and T. K. Wu for a critical review of the manuscript.

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Block Copolymerization of 3,3-Dimethyl-2-oxetanone. 1. About the Mechanism of α,α-Disubstituted β-Propiolactones Block Copolymerization

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ABSTRACT: Block copolymerization of 3,3-dimethyl-2-oxetanone (or pivalolactone, PVL) has been reported by different authors by applying an anionic process initiated by carboxylate salt end groups. A living (co)polymerization of PVL is observed, and the mechanism could be assume as being of wide application. However, in every successful block PVL copolymerization described, a polarizable group is present in the vicinity of the initiating carboxylate salt. From our observations, it is concluded that the absence of such a structural feature is responsible for PVL homopolymerization. Accordingly, the initiating carboxylate end group cannot be free but must be interacting with a neighboring polarizable group to avoid this unexpectedly drastic limitation. The extension of this requirement to the PVL grafting processes has not been ascertained.

The interest of the thermoplastic elastomers has been dramatically demonstrated by the discovery and applications of the (styrene-*b*-diene-*b*-styrene) copolymers. The range of service of these materials is however limited by the relatively low softening point of the rigid polystyrene sequences (70–80 °C). Accordingly, many attempts have been made to find out new combinations of very soft and extremely cohesive sequences in order to extend considerably this service temperature range.

In our laboratory, we have considered the combination of either polydienes or polysiloxanes on the one hand with Nylon 6 (T_m 220 °C)[1] or poly(pivalolactone) (T_m 240 °C) on the other hand.[2] At the same time, similar researches were developed in other laboratories. As far as polypivalolactone is concerned, the contributions of Yamashita[3,4] and of the Du Pont Co.[5–8] must be mentioned, the block copolymerization always being based on the anionic polymerization of pivalolactone by a polymeric carboxylate salt.

We intend to report in this paper some limitations of this apparently general procedure and to clarify the mechanism of pivalolactone block polymerization by polymeric carboxylate salts. Our work has not been extended to PVL grafting onto polymeric backbone-carrying carboxylate pendant groups whose distribution along the trunk is more often hardly controlled except for some alternating copolymers.[7]

Experimental Section

Preparation of Carboxyl-Terminated Prepolymers. Carboxyl-terminated prepolymers were prepared by three different methods in accordance with the needed structure of the carboxylate end group.

The first aim of this work was to prepare a pivalate-terminated polystyrene as a model initiator for the PVL block copolymerization. This prepolymer was prepared by reacting the lithio salt of 2-isopropyl-4,4-dimethyl-2-oxazoline with 1-bromobutane-terminated polystyrene, followed by the hydrolysis of the oxazoline. The details of the whole synthesis have been published elsewhere.[9]

The hydroxyl-terminated polymers poly(ethylene oxide) (PEO) and poly(caprolactone) (PCL) were converted to carboxyl-terminated polymers by reaction with a twofold molar excess of

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succinic anhydride in toluene. The reaction solution was heated under reflux for several days after which carboxyl-terminated polymers were isolated by precipitation into either ethanol (PCL) or hexane (PEO). The PCL polymer was purified by three reprecipitations into ethanol and finally reprecipitation into hexane. PEO was purified by three reprecipitations from benzene into hexane. Hydroxyl-terminated PEO's were commercial products (HOECHST AG), while hydroxyl-terminated PCL was easily obtained by ϵ-caprolactone polymerization with soluble μ-oxoalkoxides.[10]

A hydroxyl-terminated PCL was reacted in toluene with a twofold molar excess of sebacoyl, adipoyl, and succinyl chloride, respectively. The reaction solution was refluxed overnight, and after water addition, the reflux was continued for 1 h. The aqueous phase was separated, and the carboxyl-terminated PCL was isolated by precipitation into hexane; three successive reprecipitations into hexane were undertaken to purify the polymer.

The so-purified carboxyl-terminated polymers were neutralized with an excess of tetrabutylammonium hydroxide in THF up to pH 11. After centrifugation of the solution, the polymer was twice precipitated. All of these precautions were taken to eliminate completely any residue of low molecular weight acid salt.

PVL Block Copolymerization. The macromolecular initiators were dried through three azeotropic distillations of benzene: once the polymer was dissolved in benzene, the solvent was distilled off under reduced pressure.

β-Lactones were dried over calcium hydride and distilled under reduced pressure before use.

The copolymerizations took place under argon for 48 h at room temperature (RT) in a 5% THF solution of the carboxyl-terminated polymer, the reaction medium becoming more and more cloudy and gellified.

The crude product obtained was extracted with THF, either in a Soxhlet device or by suspension in THF followed by centrifugation at 3000 rpm for 1 h until no more PCL or PEO was extracted. The insoluble part was then analyzed by ^{1}H NMR in trifluoroacetic acid as solvent.

The gel permeation chromatograms were obtained at 25 °C, using THF as solvent (Waters 200).

A (pivalolactone-*b*-caprolactone) copolymer, whose molecular weight of the PCL sequence was 2000, was fractionated (Table V). The copolymer was dissolved in THF (5%), and an insoluble part was isolated (fraction 6). Five other fractions were precipitated successively by addition of hexane to the copolymer solution at RT. Each fraction was recovered by centrifugation.

PVL Polymerization by Low Molecular Weight Carboxylate Initiators. 11-Bromoundecanoic acid, 6-bromohexanoic acid, chloroacetic acid, and mercaptoacetic acid were dissolved in toluene and neutralized by a solution of tetramethylammonium hydroxide in methanol. The carboxylate salts precipitated as they were formed; after the salts were filtered, washed, and dried under vacuum, they were dissolved in the polymerization solvent (propylene carbonate or 4/1 THF–methanol mixture, Table IV), and PVL (5%) was added.

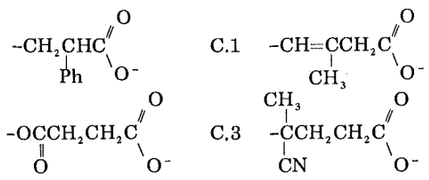
The polymerizations took place under argon for 48 h at room temperature. Once the insoluble polyester formed was recovered by centrifugation, it was suspended in a 1/1 THF–methanol mixture to dissolve any residue of free initiator, and it was isolated again by centrifugation. This purification treatment was repeated five times and completed with the extraction of the polyester by THF in a Soxhlet device.

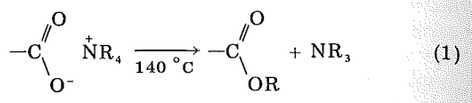
The ^{1}H NMR spectra of the poly(pivalolactone) were measured in trifluoroacetic acid; they were unmodified by further polyester purification. The average number molecular weight ($\bar{M}_n$) was calculated from the relative intensity of the signal of the CH_2 (4.3 ppm) or CH_3 (1.2 ppm) polyester group to the signal due to the CH_3 (3.2 ppm) counterion group. The mean number of halogen or sulfur atoms present per chain was determined thanks to the comparison of the signal of the counterion CH_3 group to the signal of the carbon in the α position of the halogen or sulfur atom. These latter signals were observed at 3.7, 3.75, and 2.3 ppm respectively for $Br(CH_2)_5COO$-, $ClCH_2COO$-, and $HSCH_2COO$-terminated polyesters.

Results and Discussion

Pivalolactone (PVL) is easily ring-opening polymerized by a wide variety of nucleophiles,[11] but a living and easily-controlled polymerization is obtained only when using carboxylate salts;[4] tetraalkylammonium salts are selected for their higher reactivity and their contribution to the thermal stability of the polymer so obtained.

Table I
Structure of the Carboxylates Used in PVL Block Copolymerization





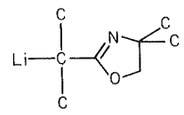
(1)

Hall[14] and Yamashita[3,4] also outlined the influence of the basicity of the initiator on the propagation-over-initiation rate constants ratio (k_p/k_i), as well as that on the initiation efficiency.

In the block copolymerization described, the carboxylate end groups are obtained by various methods: deactivation of living anionic polymers (polystyrene or polyisoprene) with CO_2,[3,6] reaction of a hydroxyl-terminated polymer with succinic anhydride,[3] and radical polymerization initiated with 4,4′-azobis(4-cyanovaleric acid).[4] The structures of these different carboxylates are summarized in Table I.

Since the poly(pivalolactone) segments have very low solubility in common solvents, it is very difficult to determine the molecular characteristics of the corresponding block copolymers. However, well-controlled and homogeneous block copolymers should be obtained by polymerizing the second monomer with a macromolecular initiator identical with the propagating species ($k_p/k_i = 1$) or promoting a k_p/k_i ratio higher than 1.

To prepare well-defined block copolymers of pivalolactone, we have selected as a model a pivalate-terminated polystyrene; this pivalate functionalization was obtained by reacting the lithio salt of 2-isopropyl-4,4-dimethyl-2-oxazoline



with 1-bromobutane-terminated polystyrene.[9] The end oxazoline group was then hydrolyzed, and the resulting carboxylic acid was neutralized with tetrabutylammonium hydroxide $-(CH_2)_4C(CH_3)_2(COO^-)$ (I). PVL was quantitatively polymerized at 25 °C, but the fractionation of the crude product showed that no block copolymer was formed.

The same disappointing results were observed when operating similarly with the lithio salt 2,4,4-trimethyloxazoline, i.e., with a less hindered carboxylate group $(CH_2)_4CH_2COO^-$ (II). Although the initiator (I) has the same structure as the propagating group $-CH_2C(CH_3)_2(COO^-)$, the PVL polymerization surprisingly takes place with release of the growing chain; accordingly, the basicity of the initiator is surely not the only parameter governing the initiation of PVL polymerization. In this respect, we think that it is more correct to consider the nucleophilicity of the carboxylate instead of its basicity. In a homologous

Table II
Pivalolactone Block Copolymerizations

expt no.	prepolymer ($\bar{M}_n$)	a	b	prepolym extracted g	prepolym extracted %
1	PEO (2000) difunct	2.00	2.00	0.20	10
2	PEO (6000) difunct	5.00	5.00	0.25	5
3	PCL (2000) difunct	1.00	5.00	0.04	4
4	PEO (8500) monofunct	2.00	2.00	0.06	3

[a] Initial amount of prepolymer, g. [b] Initial amount of PVL, g.

series, nucleophilicity and basicity are similarly modified, but in the present case the propagating carboxylates are in the β position of an ester group while the carboxylates I and II are at the end of a longer hydrocarbon chain (six C atoms); this structural difference must influence the respective electronic characteristics of these two kinds of active sites.

In fact, a literature screening of the PVL block copolymerization reveals that every efficient macromolecular initiator (Table I) presents a polarizable group in the α, β, or at least γ position of the carboxylate. This observation is in favor of a not completely free initiating species and might imply that the catalytic sites have to present a peculiar electronic environment to ring-opening polymerize PVL without secondary reactions.

To assess this hypothesis, different hydroxyl-terminated polymers (PEO, PCL) were reacted with an excess of succinic anhydride and capped with a carboxylate end group in the β position of an "inverse" ester (structure C.3, Table I). Yamashita[3] had previously described such a functionalization method in the case of poly(tetrahydrofuran) (2000), but he used a Na counterion, and he attributed a very low block efficiency (20%) to a slow PVL initiation rate. Our results, summarized in Table II, are in accordance with the published data and correlate the efficiency of the PVL block copolymerization to the presence of a polarizable group next to the catalytic site. Furthermore, the yields of the block copolymerization are never less than 90%, i.e., much higher than the results obtained by Yamashita with the same carboxylate initiator except for the counterion. In experiment 1, the molecular weight of the PPVL sequence must be low (10^3 theoretically), and some block copolymer can be mixed with the PEO extracted; the 90% yield would be a minimum value. Experiment 4, based on a monofunctional initiator, clearly shows that practically every carboxylate site is highly efficient in the PVL block copolymerization; in the case of a bifunctional initiator, an 80% efficiency per carboxylate would indeed be sufficient to explain mixed copolymer yields as high as 96%.

In a second series of PVL block copolymerizations, the distance between the carboxylate end group and the same adjacent polarizable group has been modified. To this purpose, a ω-hydroxyl-terminated poly(caprolactone) ($\bar{M}_n$ 4200) has been reacted with an excess of sebacoyl, adipoyl, and succinyl chloride, respectively. After a treatment described in the Experimental Section, PCL samples carrying the three different end groups mentioned in Table III have been obtained. PVL has been polymerized by these polymeric initiators, and the results reported in Table III are very clear; once the distance between the initiating carboxylate and the adjacent "inverse" ester exceeds three methylene units, the modified PCL is no longer able to initiate copolymerization of PVL and is recovered as homopolymer. These observations, which agree with the two first unsuccessful block polymerizations

Table III
Pivalolactone Block Copolymerizations

expt no.	nature of the carboxylate end group	b	c	prepolymer (PCL) extracted g	prepolymer (PCL) extracted %
1	$-OC(O)(CH_2)_8COO^-$	2.00	2.00	2.03	100
2	$-OC(O)(CH_2)_4COO^-$	2.00	2.00	1.96	98
3	$-OC(O)(CH_2)_2COO^-$	2.00	2.00	0.34	17[a]

[a] The PCL extracted has been titrated by a tetramethylammonium hydroxide solution; accordingly, its equivalent molecular weight would be as high as 5×10^4. The three original polymers have the same equivalent molecular weight, 5000 ± 100. [b] Initial amount of PCL, g. [c] Initial amount of PVL, g.

Table IV
Pivalolactone Polymerizations by Low Molecular Weight Carboxylate Salts

carboxylate salt	solvent	$\bar{M}_n$	a
I_1, $Br(CH_2)_{10}COO^-$	THF–methanol (4/1)	3600	0
I_2, $Br(CH_2)_5COO^-$	propylene carbonate	4500	0.95
I_3, $ClCH_2COO^-$	propylene carbonate	2800	0.95
I_4, $HSCH_2COO^-$	THF–methanol (4/1)	1600	0.90

[a] Mean number of halogen or sulfur atoms per chain.

hereabove mentioned, are significant since all the experiments summarized in Table III have been done in the same experimental conditions. Furthermore, the longer the aliphatic chain of the acid dichloride is, the higher is its solubility in hexane; the elimination of the excess of the acid dichloride by PCL precipitation into hexane (see the Experimental Section) is accordingly more efficient, and the presence of nonpolymeric initiator in the polymerization medium is less probable. The extraction of non-carboxyl-terminated prepolymer (experiment 3, Table III) perhaps indicates that acid chloride (samples of Table III) would be less suitable than anhydride (samples of Table II) to carboxylate the hydroxyl-terminated polymers.

To complete the hereto described experiments, PVL has been polymerized by low molecular weight initiators (linear aliphatic carboxylates carrying an end-halogen atom as polarizable adjacent group I_1, I_2, and I_3 (Table IV)). If the initiation takes place without transfer, the halogen atom of the initiator must be linked to the polyester formed, and significant mechanistic information can be so obtained.

Propylene carbonate, a nonprotic solvent, was used except for the undecanoic initiator, which was insoluble. In this case, polymerization was carried out in a 4/1 THF–methanol mixture (Table IV). This was the only case in which an initiator residue was not attached to the polyester. To show that the protic medium was not the cause of this result, we polymerized PVL in the same 4/1 THF–methanol solvent with the I_4 protic initiator (Table IV) carrying its polarizable or thiol group in the α position of the carboxylate salt. The thiol is detected on the polyester recovered after careful purification, and the results obtained with the I_1 initiator are accordingly supported.

The behavior of polymeric and low molecular weight initiators is thus in good agreement. From the results so obtained (Tables III and IV), it appears that the chemical nature of the polarizable group adjacent to the carboxylate initiator could exert a marked influence; this parameter would effectively control the distance between these two

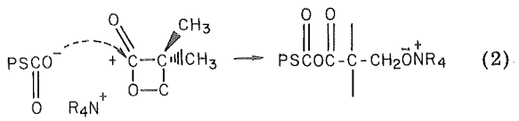
Table V
Fractionation of a PPVL-PCL (2000) Block Copolymer

fraction no.	wt, g	%	$\bar{M}_{PPVL}$ (calcd)
1	1.94	22	810
2	1.38	15	790
3	1.18	13	800
4	1.32	14	830
5	1.24	14	1170
6	1.84	21	1380

groups beyond which the PVL polymerization takes place with release of the growing chain.

To evaluate the polydispersity of the polyester sequence as well as the amount of eventual homopolyester, a block copolymer has been prepared from PEO 6000 (Table II) and from a soluble polyester derived from 3-ethyl-3-methyl-2-oxetanone. The gel-permeation chromatography of the crude product (58% PEO) in THF shows a rather narrow and symmetrical peak; except for a very low shoulder at higher elution volumes attributed to the homo-PEO (ca. 5%), the heterogeneity index μ is evaluated at 0.2, only ca. 10% higher than the PEO 6000 one. On the other hand, experiment 3 (Table II) was repeated with a lower amount of PVL (4 g of PVL for 5 g of PCL 2000), and the crude product separated into six fractions (Table V); except for the last fraction 6, all of the other ones are soluble in THF. The composition of the fractions has been determinated by ^{1}H NMR in trifluoroacetic acid, and the molecular weights of the PPVL sequences are calculated assuming a constant molecular weight (2000) for the PCL block (Table V). On such an ideal basis, the polydispersity index of the PPVL sequence is very low, 1.05. The results of Table V clearly show the very satisfying homogeneity of the copolymer obtained and the low amount of homo-PPVL and PCL if any; the initiation rate is evidently not lower than the propagation one, as is often reported.[3] In other words, the basicity of the carboxylates could have a lower influence than expected on the block copolymerization efficiency and would not be the determining parameter.

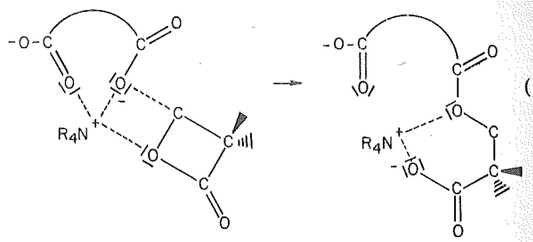
From this work, it is concluded that the mechanism of the initiation step of the PVL ring-opening polymerization by a carboxylate salt depends on the electronic environment of the initiator. The absence of a polarizable group in the vicinity of a ω-carboxylate salt end group could perhaps confer a sufficient freedom to this initiator and explain its attack on the most electron-deficient site of the lactone and the cleavage of the acyl–oxygen bonding.



(2)

Along this pathway, a rather unstable link (anhydride) would be formed between the growing polyester and the starting chain PS; the attack of this anhydride by carboxylates and anions present in the reaction medium, or its hydrolysis during the recovery of the crude product, would lead ultimately to a mixture of homopolymers.

On the contrary, the carboxylate salt could be intramolecularly solvated by an adjacent polarizable group. If the counterion is fixed to the chain end in a chelate-like solvation complex, as is schematized by eq 3 for the C.3 initiator (Table I), the approach of the lactone ought to be favorable to the expected alkyl–oxygen ring opening. A simple electronic rearrangement can thus explain the addition of a lactone unit with the restitution of a new



(3)

carboxylate site. Even though an interaction between the carbonyl oxygen of the lactone and the counterion takes place, the attack of this carbonyl group should be sterically impeded.

The high solvating power of the ester group has been described in the literature. In particular, Bovey et al.[12] and Schulz et al.[13] assume that the counterions of the carbonionic species are solvated intramolecularly by the penultimate or the antepenultimate ester group of the poly(methyl methacrylate) (PMMA) in the systems PMMA–Li/THF, PMMA–Cs and Na/THF, respectively. A similar situation could be invoked in the initiation step of the PVL polymerization by a carboxylate salt. Additional solvation of the initiation site by solvent molecules and an equilibrium between both solvation structures are to be considered, the initiation rate constant being of course controlled by the most stable of both complexes. The same arguments can be applied to the propagation step and explain the strong solvent effects reported in the literature.[14,15] In particular, Eisenbach and Lenz[15] observe that the rate of polymerization of 3-methyl-3-propyl- (or butyl) -2-oxetanone is much higher in THF (ϵ 7.35) than in solvents with a high dielectric constant such as Me_2SO (ϵ 35.0) and acetonitrile (ϵ 38.0). These results are unexpected on the sole basis of the relative dielectric constants of the solvents, but they indicate that probably the active species are not free ions but are most likely solvated ion pairs. Similar conclusions can be drawn from (EO-*b*-PVL) copolymerization experiments we have done in THF and propylene carbonate (PC). The rate of PVL block copolymerization initiated by carboxylate-ended PEO is four times higher in THF than in PC. The higher the dipole moment of the solvent is (PC, 4.98 D; Me_2SO, 3.9; THF, 1.75 D at room temperature), the stronger is the interaction between the solvent and the counterion and the less frequent is the approach of the lactone.

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Syndiotactic Specific Polymerization of Propene: Some Evidence for Insertion of the Monomer on the Metal–Carbon Bond

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ABSTRACT: ^{13}C NMR analysis of selectively enriched polypropylene seems to support, at least for syndiotactic polymerization, the traditional mechanism involving insertion of the monomer on the σ metal–carbon bond vs. the more recently proposed mechanism involving carbene intermediate, in analogy with olefin metathesis.

In previous papers we devoted considerable effort to the interpretation of the stereochemistry of polymerization of α-olefins in the presence of Ziegler–Natta catalytic systems.[1–11]

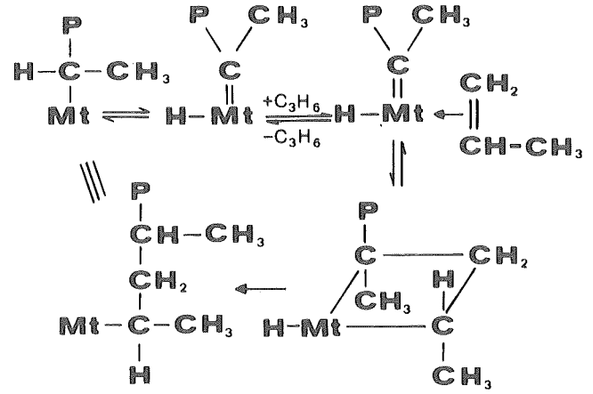
In our reasoning concerning the reaction mechanism, we assumed that polymerization involved insertion of the monomer on σ metal–carbon bonds. Actually, this belief was generally accepted in the literature.[12]

More recently, Ivin and co-workers[13] suggested a different picture of the insertion reaction involving α-hydrogen reversible shift, carbene, and metallocyclobutane intermediates (Scheme I).

The stereospecificity should depend on the relative configuration of the substituted carbons of the metallocyclobutane ring, and the H transfer from the metal to the more substituted carbon should exclude branching.[13] The evidence put forward by these authors are: (i) there are no unambiguous examples where a characterized metal–alkylolefin compound may be induced to react, giving the expected insertion product; and, (ii) there is a close identity between catalysts which cause Ziegler–Natta polymerization and those which give rise to olefin metathesis. On the other hand, it is generally accepted that metathesis involves metallocyclobutane and metal–olefin–carbene interconversion as the key steps in breaking and forming carbon–carbon bonds, and there is also evidence that transition metal alkyls can give rise to the reversible elimination of α-hydrogen.

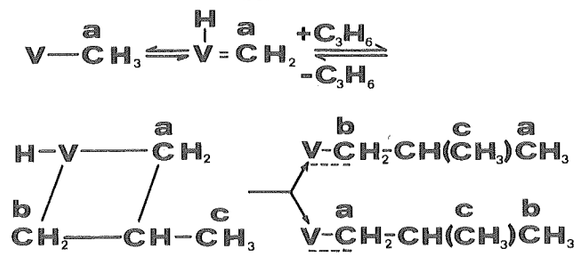
The mechanism proposed by these authors is oversimplified[13a] because it ignores the experimentally observed regiospecificity of propene polymerization,[4,6,10,14] in spite of the fact that it cannot be disregarded. On the contrary, when the correct regiospecificity of the monomer is accounted for by the isotactic and syndiotactic propagation steps, the different energies of the steric control could be qualitatively explained by the Ivin mechanism by simply considering the different distances between the substituted carbons of the cyclobutane ring depending on the regiospecificity (Figure 1). This fact prompted us to look for more direct evidence on the matter. In this paper, only syndiotactic polymerization of propene is considered, while the study of isotactic polymerization is still in progress.

Scheme I[a]



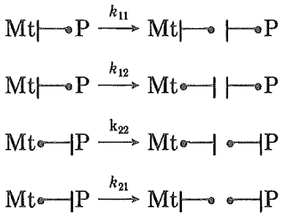
[a] P = polymer; Mt = metal atom of the catalytic complex.

Scheme II



Results

Syndiotactic polymerization of propene is only partially regiospecific.[6,7,15,16] Consequently, four propagation steps are possible:



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