Anionic Polymerization of Lactams in the Presence of Metal Dialkoxyaluminum Hydrides: Presentation of a New Mechanism

Nathalie Mougin,† Cary A. Veith,‡ Robert E. Cohen,‡ and Yves Gnanou*,†

Institut Charles Sadron, 6 Rue Boussingault, 67083 Strasbourg Cedex, France, and Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received June 25, 1991; Revised Manuscript Received November 26, 1991

ABSTRACT: Metal dialkoxyaluminum hydrides (1) form a new class of catalysts for anionic polymerization of lactams. Propagation proceeds in their presence—as it does in the presence of conventional catalysts such as alkali metal hydrides—by successive additions of the anionically active species to the end-standing *N*-acyllactam function carried by the polymer chain. However, this is the only similarity between the two polymerization processes. The active species generated when ϵ-caprolactam (2) is treated with sodium dialkoxyaluminum hydride is the sodium salt of 2-(dialkoxyaluminoxy)-1-azacycloheptane (6) and is therefore quite different in terms of nucleophilicity from the mere activated monomer, sodium caprolactamate. The new reactive salt (6) is obtained upon deprotonation of a lactam monomer at its amide position followed by the reduction of its carbonyl function. During lactam polymerization, after each monomer addition, the active species is re-formed in two steps: first, proton exchange followed by instantaneous reduction of the lactamate formed by transfer of both hydrogen and the $Al(OR)_2$ group from the previous monomer unit added. This displacement regenerates the end-standing *N*-acyllactam and the salt of the (dialkoxyaluminoxy)-azacycloheptane (6), allowing propagation to proceed by addition of 6 to this latter function. This new mechanism still propagates by an "activated monomer" mechanism but it also involves the transfer of the dialkoxyaluminum hydride group throughout polymerization.

I. Introduction

The anionic "activated monomer" polymerization of lactams is well documented.[1] In contrast to most other anionic polymerizations, the active species is not borne in the present case by the growing chain, but it is carried by the incoming monomer. This mechanism proceeds via attack of the end-standing *N*-acyllactam by the lactamate anion and is essentially the same regardless of the catalysts; alkali metals hydrides, organometallic compounds, etc. can be used to generate the lactamate anion. Recently, Veith and Cohen[2] demonstrated the polymerization of ϵ-caprolactam in the presence of certain alkoxy-substituted lithium aluminum hydride catalysts. However, the active species involved in this type of polymerization seems quite different from the classical activated monomer generated in the presence of conventional catalysts. The anion formed, by reaction of ϵ-caprolactam (CPL) with dialkoxyaluminum hydride, is found to be less nucleophilic than its lactamate counterpart. The proof of this reduced nucleophilicity is given by the relative inertness of the new active species toward a poly(dimethylsiloxane) chain, while a mere lactam anion reacts agressively with the same polymer. The authors took advantage of this behavior to synthesize well-defined diblock polyamide (PA)–poly(dimethylsiloxane) (PDMS) copolymers, the acyllactam end-functionalized PDMS being used as the macroinitiator. However, the mechanism of lactam polymerization, when catalysts such as metal dialkoxyaluminum hydrides are employed, remained unclear. Accordingly, we decided to examine the mechanistic aspects of this polymerization, the target being to understand the entire process. We also focused on differences between the classical anionic polymerization of ϵ-caprolactam and this new method.

II. General Considerations

Lactam anions are obtained upon deprotonation of lactams by a strong base to give the activated monomer. This nucleophilic species is unable to initiate the ring-opening polymerization of lactams at moderate temperatures, unless substances such as *N*-acyllactams exhibiting enhanced electrophilicity are added.[1] The latter act as promotors for chain growth, and the polymerization proceeds through the successive attacks of activated monomer on the end-standing N-substituted lactams. This principle has been applied to the synthesis of diblock copolymers containing a polyamide sequence: Initiation and subsequent growth of the polyamide block are obtained by reaction of the activated lactam with the *N*-acyllactam function initially carried by the heterosequence. Various copolymers containing polyamide (PA) sequences which exhibit interesting properties have been synthesized in this way.[3] Attempts have also been made to prepare PDMS/PA block copolymers from a PDMS macroinitiator fitted with an *N*-acyllactam group.[4] Unfortunately, this procedure does not work out as expected, because the nucleophilicity of the activated lactam is strong enough to cleave the PDMS chain, in addition to its participation in the propagation reaction. After cleavage of the PDMS sequence, which generates siloxanolate anions, significant scrambling reactions occur, which make the resulting copolymer of little interest.

Teyssié et al.[5] and then Veith and Cohen[2a] have unambiguously evidenced this degradation process and characterized the species formed, which were identified as siloxane cycles with a molecular weight of several hundreds. In both cases, the activated monomer was prepared by action of strongly basic catalysts such as NaH or $LiAlH_4$. As a result of the siloxane degradation with conventional catalysts, Veith and Cohen[2b] employed milder catalysts, in particular those obtained upon introduction of alkoxy substituents into lithium aluminum hydride. These compounds are generally utilized whenever selective reduction of functional groups such as amides or ketones is required. Three different alkoxy derivatives of lithium aluminum hydride—from mono- to trialkoxy—have been used by Cohen and Veith as an alternate means of generating the anionically active species. The active entity,

*Author to whom correspondence should be addressed.
†Institut Charles Sadron.
‡Massachusetts Institute of Technology.

0024-9297/92/2225-2004$03.00/0

generated when each of these three catalysts was treated with monomer, was then exposed at 150 °C to an unfunctionalized PDMS to follow its behavior in the presence of the electrophilic Si sites of PDMS. Surprisingly, the best results[2b,c] in terms of inertness of the active species toward PDMS were obtained for the system CPL/$LiAlH_2$-(O*t*-Bu)$_2$, whereas CPL activated by $LiAlH(Ot\text{-}Bu)_3$ or by $LiAlH_4$ behaves more or less alike. It is believed that the greater inertness of the PDMS in the presence of CPL/$LiAlH_2(Ot\text{-}Bu)_2$ originates from the less nucleophilic character of the active species. However, the exact nature of the anionic species in the system CPL/$LiAlH_2(Ot\text{-}Bu)_2$ was unknown.

The earlier use of metallic aluminate alkylate for the anionic polymerization of lactams has to be acknowledged as well.[6] It was shown that the mechanism of polymerization in the various cases studied was not different from the classical activated monomer mechanism. On the other hand, an activating agent very similar to ours—sodium dihydrobis(2-methoxyethoxy)aluminate—has been employed by Kubanek et al.,[7] but these authors did not investigate the mechanism of propagation in the presence of such a compound.

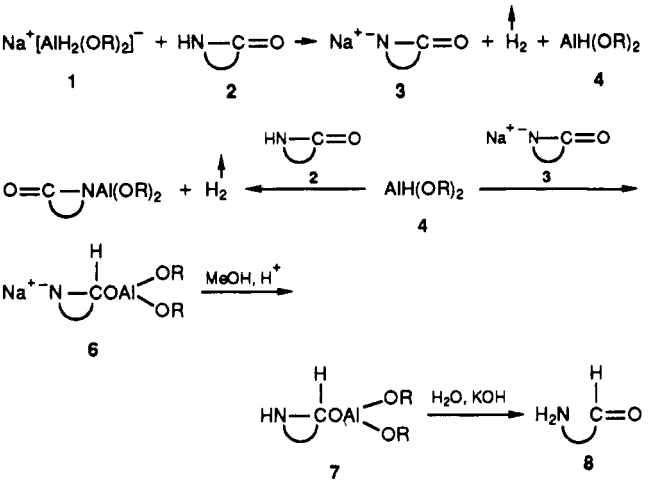
The first objective of this work is thus to identify the active entities involved in ε-caprolactam (ε-CPL) polymerization when alkali metal dialkoxyaluminum hydrides are used as catalysts. Second, emphasis will be placed more specifically on the mechanism of polymerization itself, which will include two stages: (a) understanding of the initiation process through characterization and identification of the products obtained and (b) elucidation of the propagation mechanism.

III. Results and Discussion

1. Reaction of ε-Caprolactam with $Na^+[AlH_2(OR)_2]^-$, Characterization of the Products Formed. Like most metal hydrides, $LiAlH_4$ is a versatile nucleophilic reagent generally used to reduce C=O groups.[8] It may also react with alcohols to yield less reductive and more selective compounds obtained when some of the hydrogens of $LiAlH_4$ are replaced with alkoxy groups.[9] In stark contrast to the above case, reaction of $LiAlH_4$ with the weakly acidic NH bond of cyclic amides does not give rise to the corresponding substituted lithium aluminum derivatives. The first step is certainly deprotonation of cyclic amide and formation of the lactamate anion. The resulting AlH_3 is a Lewis acid and possesses affinity for compounds with centers of high electron density. Thus, it may either deprotonate the residual hydrogenated monomer or participate in the reduction of the activated monomer, giving rise to a cyclic imine anion. Despite the side reactions,[10] the main species which is ultimately obtained is the lactamate anion. $LiAlH_4$, when used in the conditions of ε-CPL polymerization, acts essentially as another metal hydride (NaH), the entity responsible for polymerization being in both cases the "naked" lactamate anion.

The use of an alkoxy-substituted alkali metal aluminum derivative as the catalyst of ε-caprolactam polymerization apparently yields a different type of species, as demonstrated by its inertness toward PDMS. To determine the actual nature of the species formed, we have first treated the monomer with $Na^+[AlH_2(OR)_2]^-$ at 60 °C for several hours and neutralized the medium with an excess of methanol. The catalyst (in dry toluene solution) is introduced dropwise into an anhydrous solution of ε-caprolactam until the strong H_2 evolution witnessed at the beginning of $NaH_2(OR)_2$ addition ceases. The hydrogen

Scheme I



(H_2) produced arises from the deprotonation and hence from the activation of ε-caprolactam. Addition of $NaAlH_2(OR)_2$ is stopped at approximately a ratio of [catalyst]/[ε-CPL] = 0.5, which is well before stoichiometry is reached. Concomitant with the formation of lactamate anion, $AlH(OR)_2$ (dialkoxyaluminum hydride) is generated. This latter compound is a weak Lewis acid and may either deprotonate the residual monomer or reduce the activated monomer through an attack at the high electron density carbonyl oxygen. The final outcome should be quite different depending on whether $AlH(OR)_2$ reacts with the remaining monomer or with the activated monomer. If the first hypothesis were to happen, the reaction would produce two entities, the lactamate anion and the amidoaluminum dialkoxy derivative $O{=}C(CH_2)_5NAl(OR)_2$ (Scheme I). Upon aqueous workup the N–Al bond should be easily hydrolyzed, which should merely give back the initial amount of protonated monomer (lactam). In this case, the reaction medium would only contain as the active species the conventional lactamate anion, which would be in contradiction with the reduced nucleophilicity observed.

It was checked independently whether $AlH(OR)_2$ can deprotonate ε-caprolactam and form a dialkoxyamidoaluminum derivative. Upon addition of $AlH(OR)_2$ to a solution of ε-caprolactam in THF, the evolution of H_2—which can be taken as an indication of the deprotonation of monomer—was not witnessed. By contrast, introduction of some methanol gave rise to a strong hydrogen bubbling, which means that the hydride was still present as such in the reaction medium. $AlH(OR)_2$ being inert toward ε-caprolactam, deprotonation of the latter compound or its reduction by $AlH(OR)_2$ can therefore be ruled out.

The inertness of $AlH(OR)_2$ toward ε-CPL implies that during formation of the active species—when $Na^+[Al(OR)_2H_2]^-$ is added to ε-CPL to give the lactamate anion and $AlH(OR)_2$—the only product able to react with $AlH(OR)_2$ is the activated monomer. Indeed, in the lactamate form, the carbon of the carbonyl function may be prone to sustain an attack by the aluminum hydride and undergo a reduction. The results obtained speak for themselves. Upon neutralization of the reaction medium by MeOH/HCl, only 50% of the lactam initially introduced was recovered in its hydrogenated form. The rest of the monomer is therefore part of the voluminous aluminum hydroxide precipitate, in the reduced aluminoxyimine form. The balance between the aluminum residue and the protonated monomer recovered can thus be considered as proof of the reduction of activated monomer.

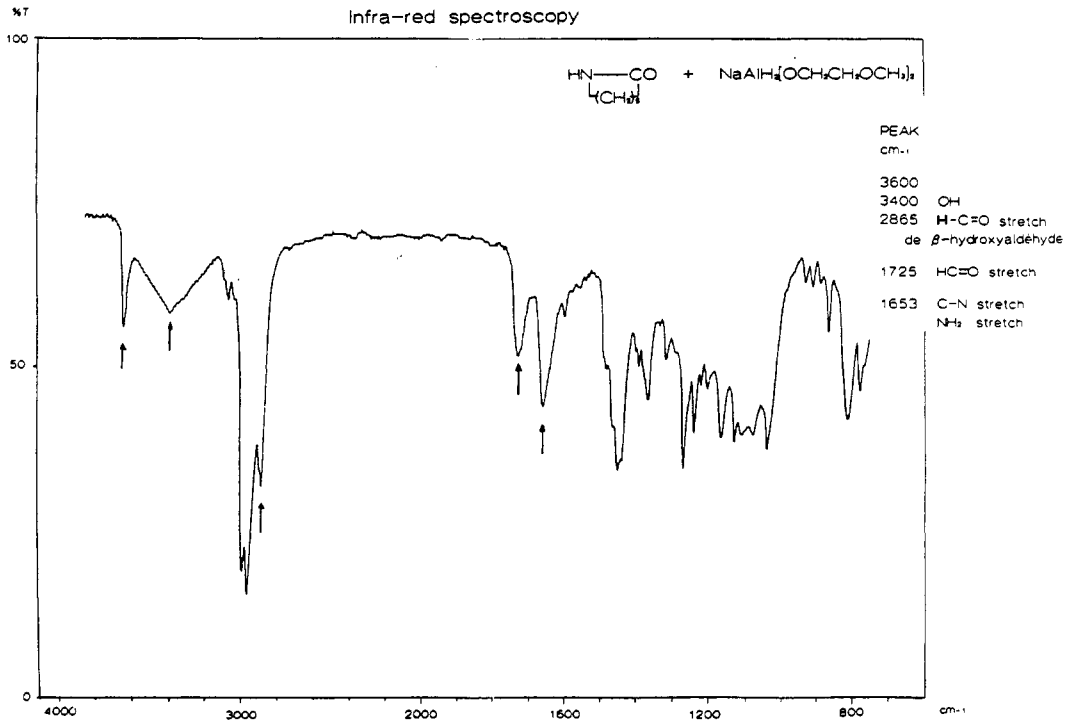


Figure 1. IR spectrum of the product obtained after hydrolysis of dialkoxyaluminum–1-oxo-hexamethyleneimine.

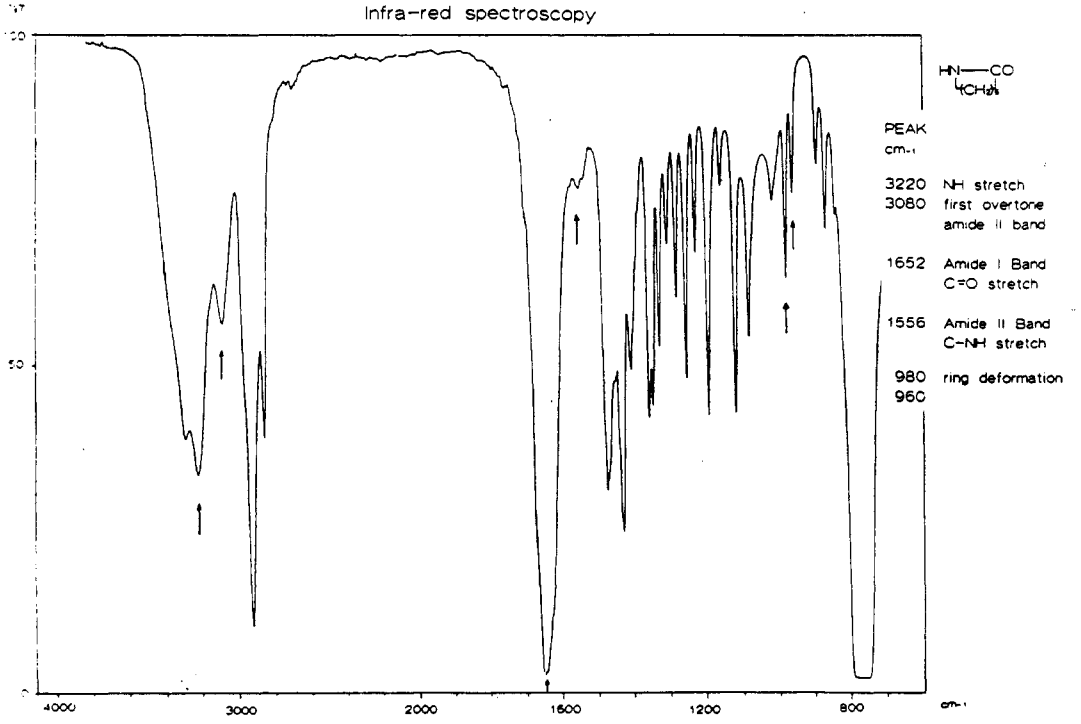


Figure 2. IR spectrum of **2**.

The hydrolysis of the dialkoxyaluminoxy derivative (**7**) was purposely carried out in aqueous basic medium. Acidic conditions were indeed avoided since they are favorable to the condensation between the amine and the aldehyde functions formed upon hydrolysis. Attempts to quantitatively isolate the 6-aminocaproaldehyde in basic medium were, however, not successful, because the condensation between the two functional groups still occurs.

The product isolated after repeated extractions with ether was first characterized by IR. Its spectrum (Figure 1) shows a distinct band at 1730 cm^{-1}, which corresponds to the absorbance of the carbonyl aldehyde and two bands (3400 and 1650 cm^{-1}) characteristic respectively of the primary amine group (NH_2) and of the azomethine double bond (N=C). When compared to the spectrum of ϵ-caprolactam (Figure 2), another striking difference can be noted: the two bands at 950–900 cm^{-1} characteristic of the cyclic structure of ϵ-CPL have disappeared from the IR spectrum of the reduced and hydrolyzed derivative (**8**).

Besides the condensation reactions mentioned above, 6-aminocaproaldehyde may have undergone aldol condensation made possible by the treatment in highly basic medium. The shape of the band at 3600 cm^{-1} could be indicative of the presence of an alcohol function; in addition, the absorption characteristic of the hydrogen of

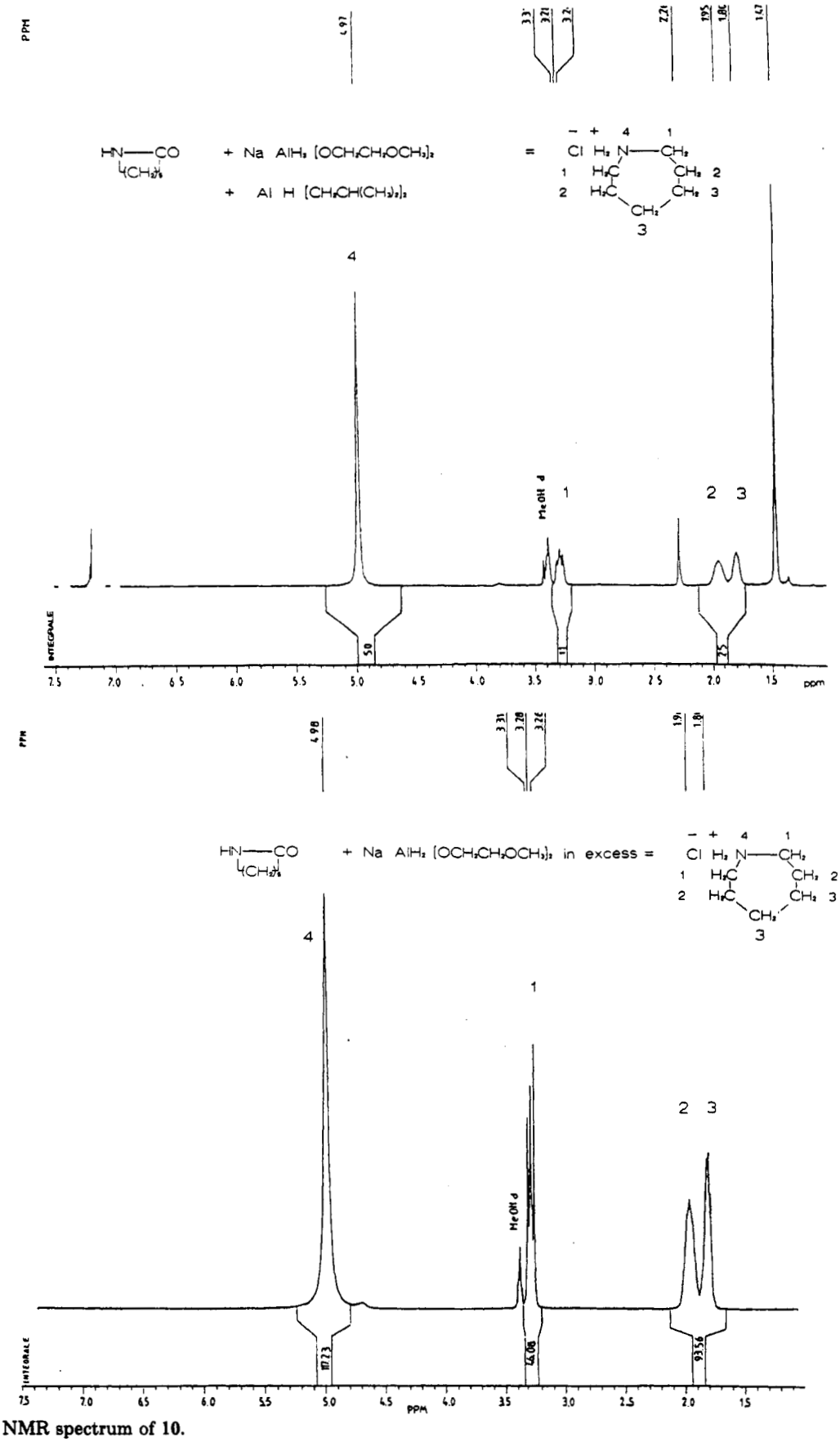


Figure 3. ^{1}H NMR spectrum of **10**.

a β-hydroxyaldehyde is seen at 2854 cm^{-1}. The extracted material is thus a mixture of 6-aminocaproaldehyde and various products resulting from side reactions induced by hydrolysis.

To demonstrate that the activated monomer effectively undergoes reduction, when $Na^+[AlH_2(OR)_2]^-$ is used as catalyst, we have undertaken the following experiment (Scheme II). Monomer and catalyst are mixed in a

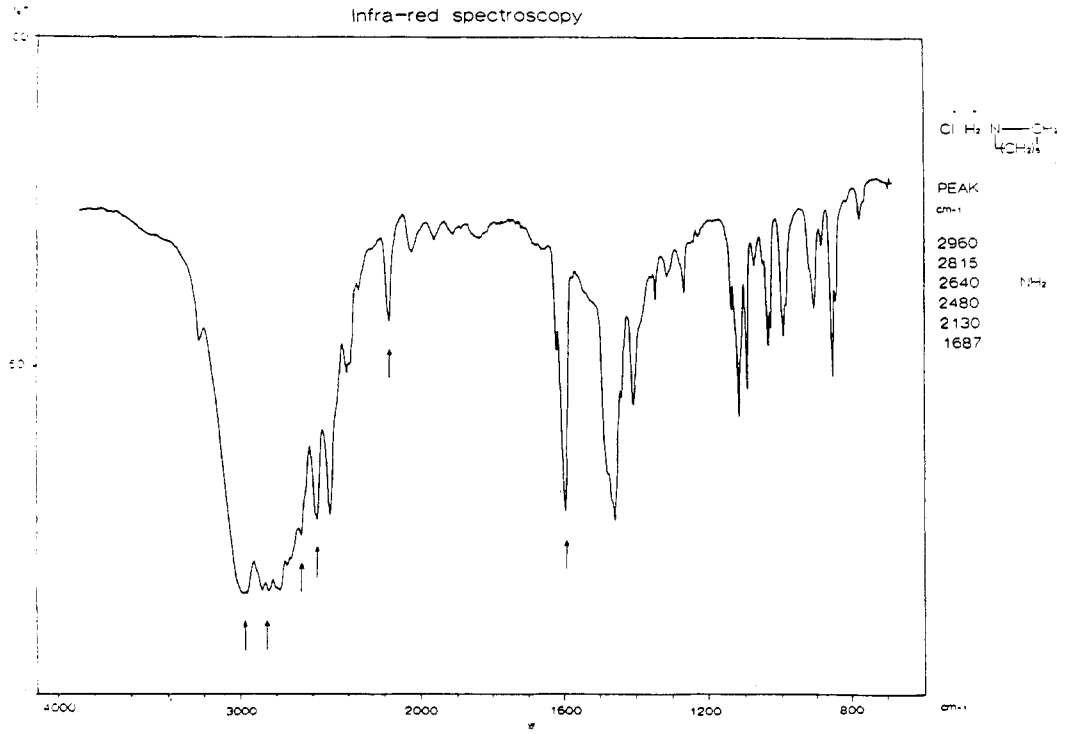
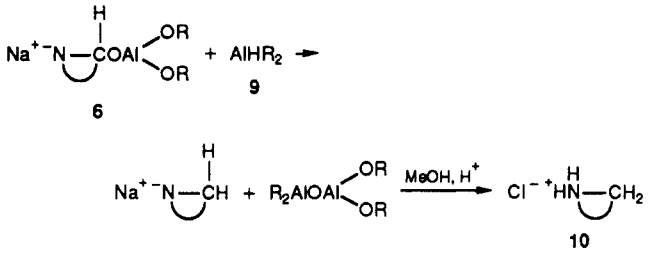
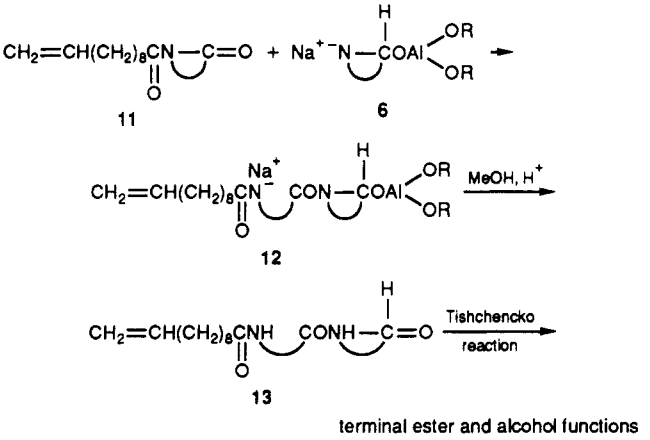


Figure 4. IR spectrum of 10.

Scheme II



Scheme III



proportion roughly equal to 2/1. After deprotonation of the monomer, which is instantaneous, the reaction medium is heated at 60 °C for 3 h to allow a thorough reduction of the activated monomer. Then another reducing agent, dialkylaluminum hydride ($AlHR_2$) (**9**), known elsewhere for its selectivity in the reduction of tertiary amides,[11] is introduced into the medium. A further reduction of the already reduced lactam (**6**) is desired, which should yield hexamethyleneimine (**10**) after neutralization. Although $AlHR_2$ is also known to deprotonate the monomer, it is anticipated that it will preferentially participate in the second reduction of lactamate. A slight excess of $AlHR_2$, as compared to the amount of activated monomer, was used, to achieve complete reduction. Stirring is continued for an additional 2 h at 60 °C after introduction of $AlHR_2$. The reaction mixture is then neutralized with MeOH and acidified to allow the formation of the hexamethyleneimine hydrochloride (**10**), which precipitates in THF. After filtration of the hydrochlorinated imine (see characterizations, Figures 3 and 4), the medium is worked up to isolate the 50% of the initial monomer which did not participate in the activation and in the subsequent reduction process. The molar amount of imine ultimately obtained is consistent with the molar amount of catalyst introduced at the beginning, which shows that, once activated, the monomer undergoes a reduction by $AlH(OR)_2$. The above experiment was carried out for the resulting imine is much easier to isolate than 6-aminocaproaldehyde (**8**). Since the second reduction can only occur once the first one—by the catalyst—has taken place, the amount of imine separated is additional proof of the validity of Scheme I suggested (see above).

Moreover, the fact that the activated monomer is reduced by $AlH(OR)_2$ to a metal salt of 2-(dialkoxyaluminoxy)-1-azacycloheptane (**6**) can account for the weaker nucleophilicity of this new active species. In conventional activated caprolactam, the positive charge of the cation is considered to be spread over a large area, due to the bidendate character of this active species. Once in the reduced form, the carbonyl oxygen is involved in a covalent bond with aluminum, leading to a tighter ionic bond between amide anion and cation. This accounts for the reduced nucleophilicity observed.

2. Characterization of the Initiation Step: Reactions of 6 with *N*-Acyllactam (Scheme III). Having clearly identified the nature of the active species obtained upon treating ϵ-caprolactam with $Na^+[AlH_2(OR)_2]^-$, we will now focus on the initiation step and attempt to identify the product formed upon reacting **6** with undecylenoylcaprolactam (**11**). The synthesis of the latter compound is described under Experimental Section and its characterization displayed in Figures 6 (IR) and 9 (NMR).

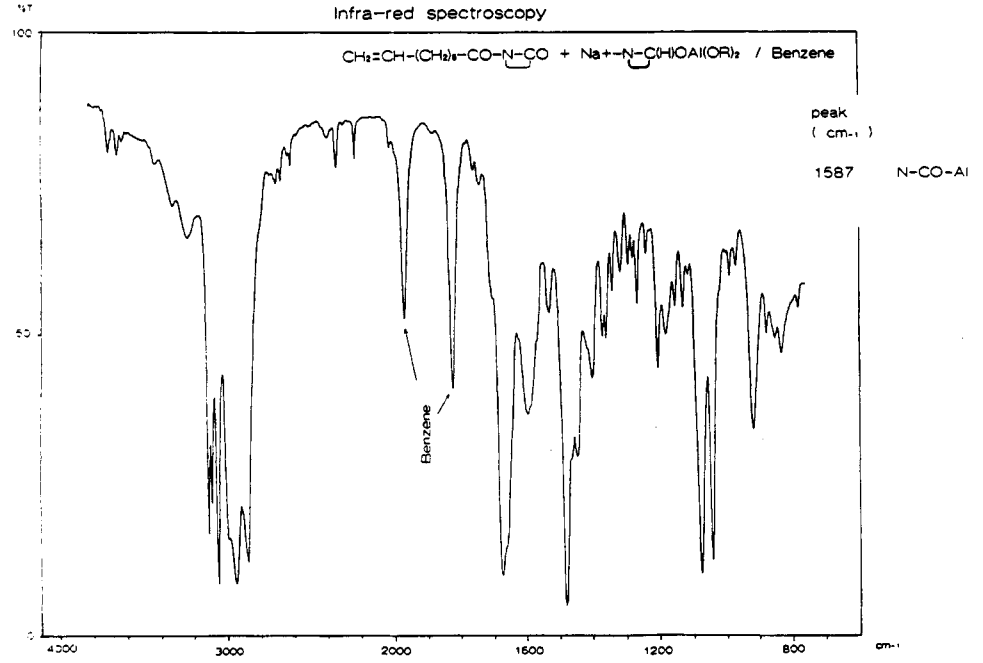


Figure 5. IR spectrum of 12.

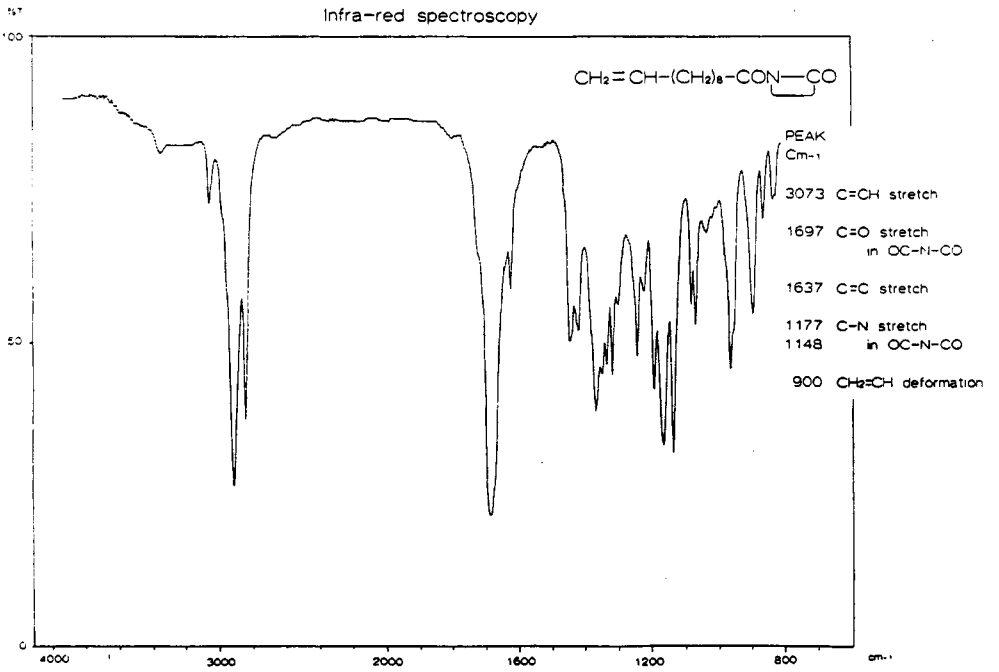


Figure 6. IR spectrum of 11.

a. Characterization of the Medium before Hydrolysis. To the reaction medium maintained at 60 °C and containing (6)—prepared as previously described—was introduced an equimolar amount of undecylenoylcaprolactam (11). The product resulting from this addition was immediately characterized by IR. From a comparison of the spectrum (Figure 5) of the latter adduct (12) to that obtained after reaction of 11 with the naked lactamate salt (Figure 7), two main differences can be stressed: (1) The band at 1700 cm^{-1} characteristic of the *N*-acyllactam function is clearly seen in Figure 7 (classical case) but has completely disappeared from Figure 5. (2) The occurrence in Figure 5 of an absorption at 1580 cm^{-1}, which can be attributed to the stretch vibration of the dialkoxyaluminum oxygen group (NCOAl), is easily discerned. Such a band is absent in Figure 7.

We have not characterized further the adduct 12. It can, however, be suggested from these qualitative analyses that the end-standing function obtained after completion of the initiation step is nothing but the (dialkoxyaluminoxy)azacycloheptane group, in contrast to the "classical" case for which an acyllactam function is obtained.

b. Characterization of the Medium after Hydrolysis. To further confirm the presence of the above group 12 at chain end, we decided to characterize the hydrolyzed form of structure 12. When the reaction medium is treated with slightly acidic methanol, ring opening of structure 12 and subsequent formation of an end-standing aldehyde function are expected. The same acidic treatment on the adduct formed when 3 is reacted with 11 merely gives an acyllactam as end-standing function.

The solution containing the hydrolyzed product (13) was first separated from the white precipitate formed upon hydrolysis and was thoroughly dried before characterization by IR and ^1H NMR. Its IR spectrum (Figure 8) reveals several interesting features: (1) The band at 1580 cm^{-1}

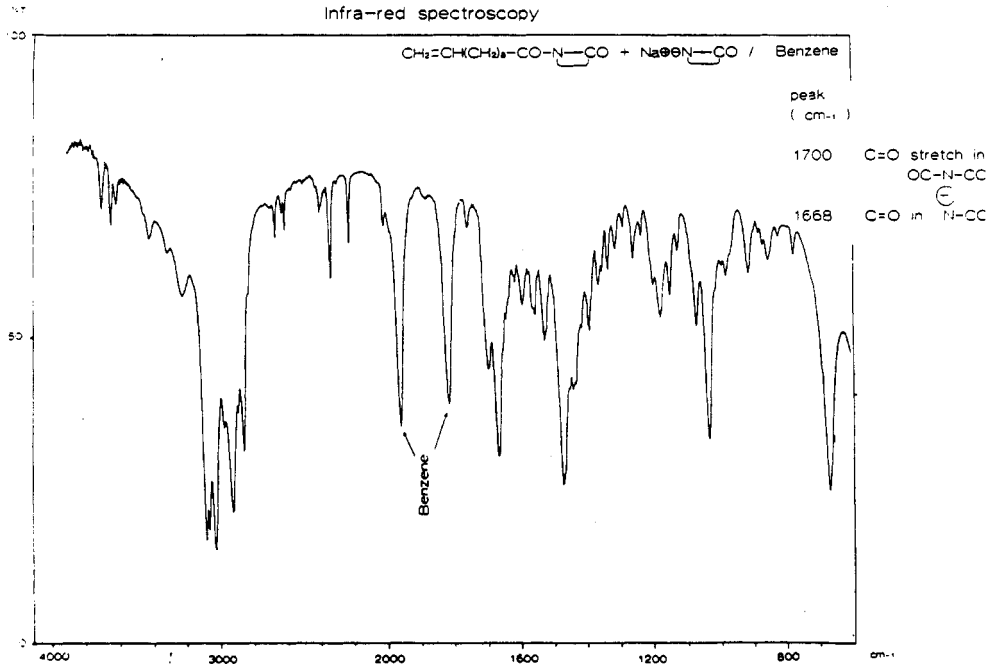


Figure 7. Reaction of sodium lactamate (3) with undecylenoylcaprolactam (11); IR spectrum of an aliquot.

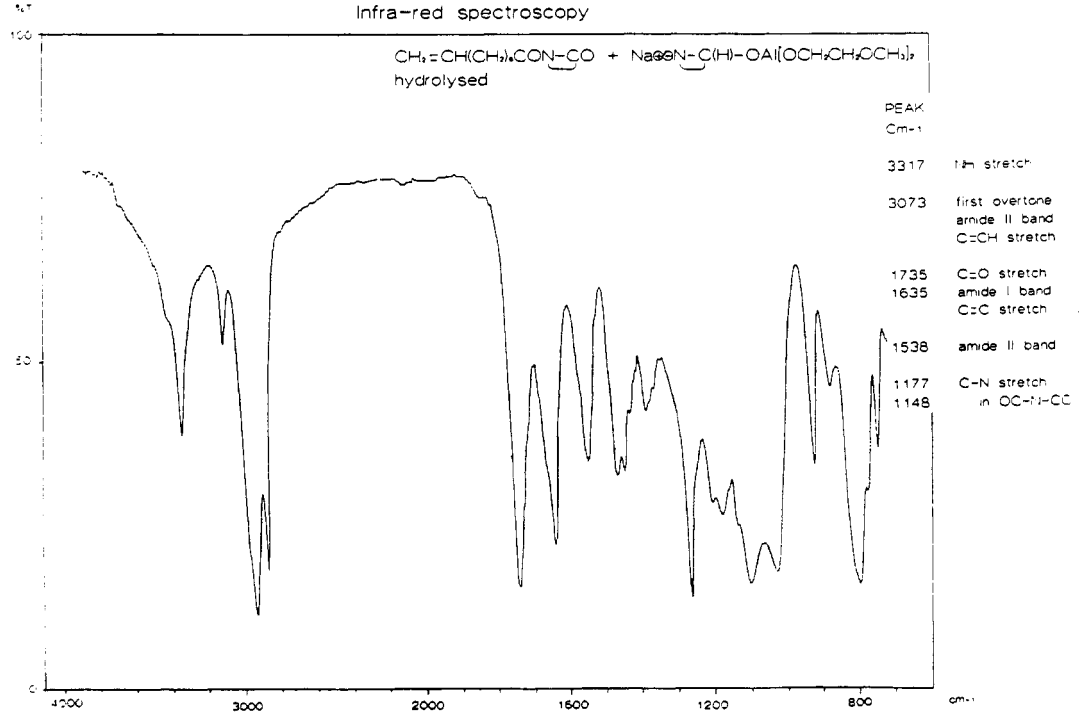


Figure 8. IR spectrum of the product obtained after hydrolysis of 12.

characteristic of the alkoxyaluminum residue—which was very strong in Figure 5—has completely disappeared from Figure 8. (2) Two bands respectively at 1540 (NHC(=O)O) and 1640 cm^{-1} (NHC=O) show up. This means that the addition reaction has actually occurred. (3) The absence of any absorption at 1700 cm^{-1} indicates that there is no residual acyllactam function left. (4) A distinct band at 1730 cm^{-1} is observed.

At first glance we can attribute this absorption to the presence of the expected aldehyde. However, the absence of any band at 2740 cm^{-1}—specific to the aldehyde hydrogen—does not allow us to conclude in favor of terminal aldehyde functions.

The same conclusion can be drawn from an examination of the ^1H NMR spectrum (Figure 10) of the hydrolyzed product. Indeed, no signal due to the hydrogen of an aldehyde—occurring at δ 10—is seen. Instead, methylene signals at δ 4.2, 3.5–3.6, 2.4, and 1.4 arising respectively from $CH_2(=O)CO$, $CH_2OC=O$, $CH_2(=O)COH$, and CH_2OH are exhibited. The presence in the hydrolyzed product of functional groups such as ester and alcohol and the absence of any aldehyde function may result from unexpected reactions occurring during hydrolysis. The aldehyde formed upon hydrolysis may have reacted either with alkoxyaluminum derivatives or with residual (12) to give in turn the terminal ester and alcohol functions found. Indeed, it is well-known that aldehydes easily react with alkoxyaluminum residue (Tishchencko reaction) and ultimately produce ester and alcohol functions, whose

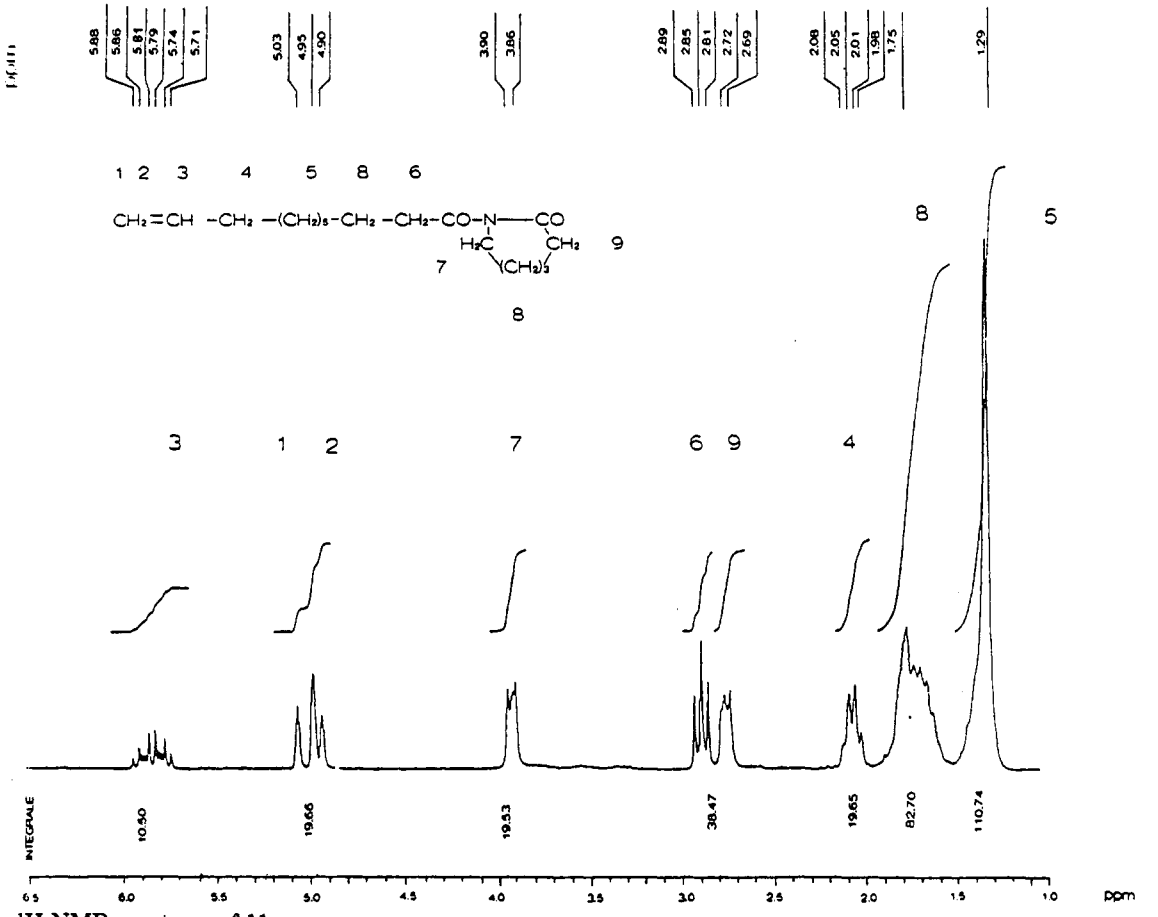


Figure 9. ^{1}H NMR spectrum of 11.

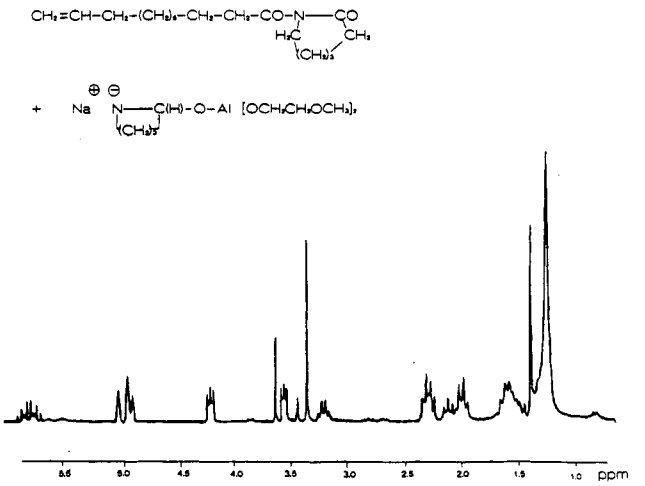


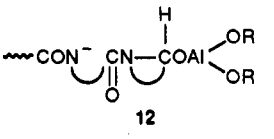
Figure 10. ^{1}H NMR spectrum of the product obtained after hydrolysis of 12.

relative proportions depend upon experimental conditions.[9a,b]

The band at 1730 cm^{-1} in the IR spectrum (Figure 8) can now be assigned to the ester group. Like the IR analysis (Figure 8), ^{1}H NMR (Figure 10) also shows the presence of amide functions δ 2.2 (CH_2(=O)CNH) and 3.3 (CH_2-NHC(=O)). The fact that amide functions are formed as well as end-standing ester or alcohol functions is convincing evidence that addition of 6 to 11 has effectively occurred. We did not try to pursue further characterizations, given the complexity of the reactions involved during hydrolysis. The outcome of this investigation on the initiation reaction indicates that the end-standing function obtained, after the first step of polymerization, in the presence of $Na^+[AlH_2(OR)_2]^-$ is 2-oxy-1-azacycloheptane, in contrast to the conventional *N*-acyllactam function found in the classical case.

3. Characterization of the Propagation Step. We have identified so far the active species formed upon mixing ϵ-caprolactam and $Na^+[AlH_2(OR)_2]^-$ and established the nature of the functional group fitting the chain end after the first reaction step. It remains now to understand how the propagation proceeds.

After the initiation step, the structure of the site can be represented as



12

The nitrogen atom of the initial *N*-acyllactam (11) has experienced the attack of 6 and carries now a negative charge. In the presence of ϵ-caprolactam, the proton of which is more acidic than that of the chain, the charge is transferred to the monomer, causing the formation of the amide function on the chain.

Two entities are now present, the conventional activated monomer and the end-standing (dialkoxyaluminoxy)azacycloheptane group. It should be kept in mind that the active species responsible for PA polymerization (with $NaAlH_2(OR)_2$ as catalyst) is less nucleophilic than in the conventional case. This means that when the lactamate anion is formed, it only exists as a short-lived intermediate. We have thus tried to clarify this apparent contradiction: formation at a given stage of reaction of a lactamate anion and, despite this, occurrence of an active species exhibiting a reduced nucleophilicity. We have particularly examined the reaction of the end-standing 2-(dialkoxyaluminoxy)-

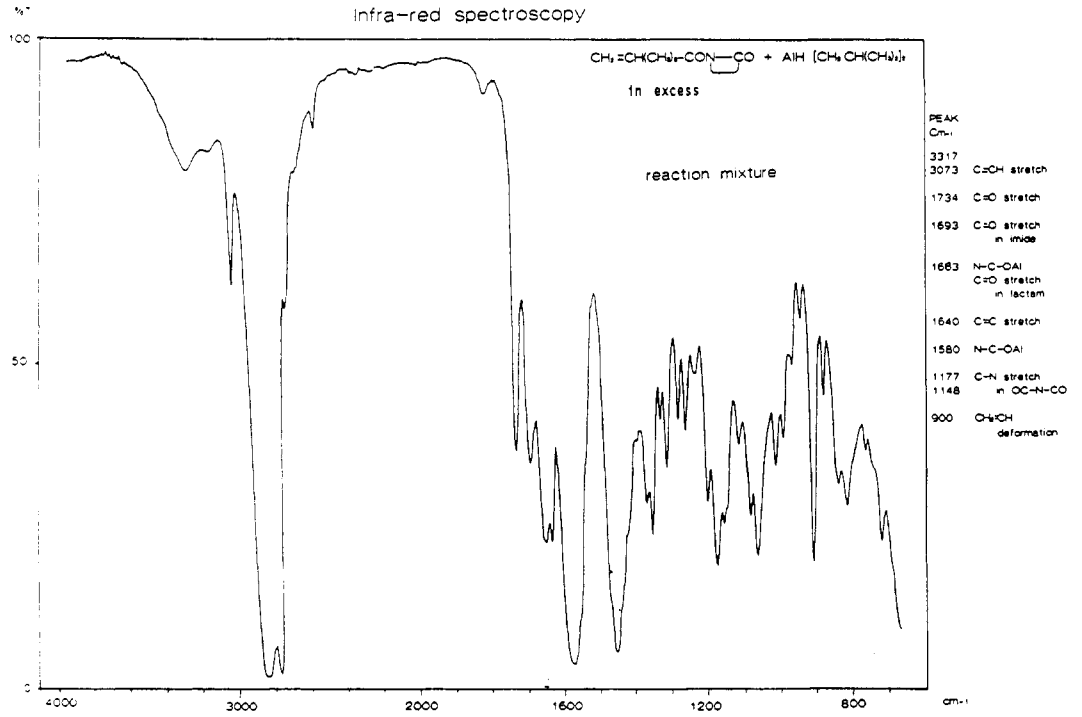


Figure 11. IR spectrum of 15.

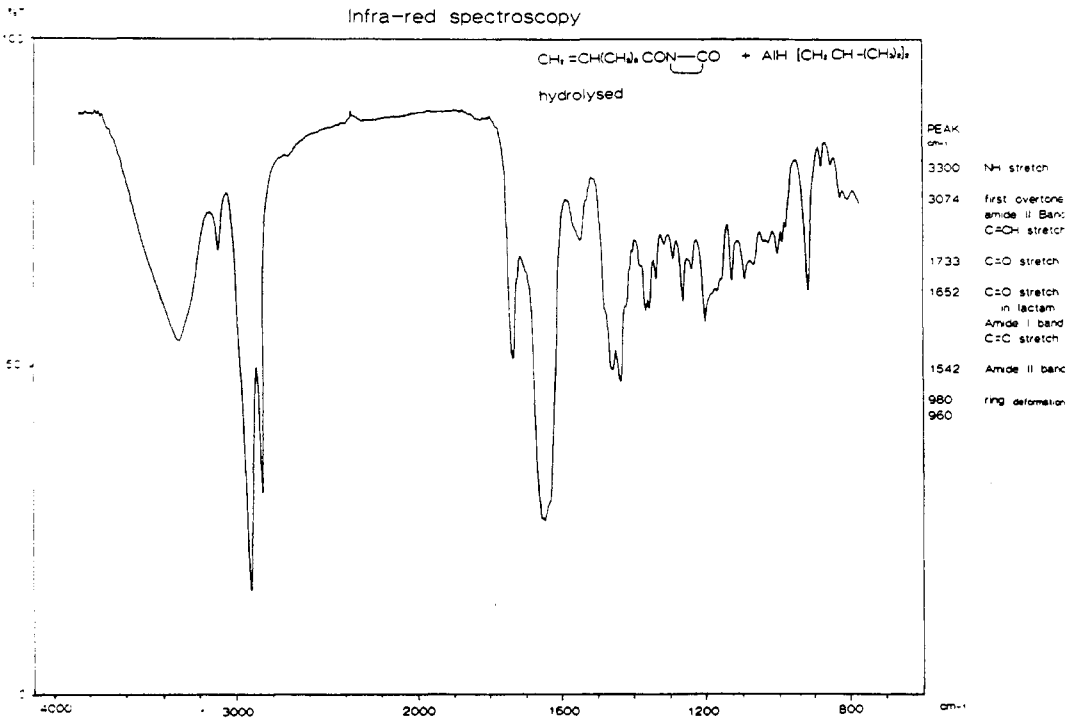


Figure 12. Hydrolysis of 15; IR spectrum of the product isolated.

azacycloheptane group with the sodium salt of ϵ-caprolactam, the two products identified after the first step of polymerization.

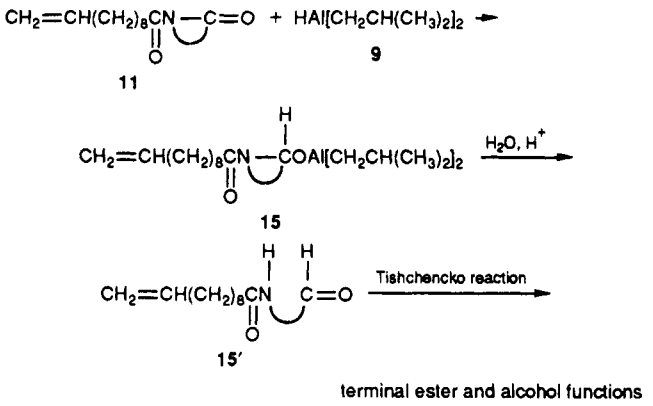
The aluminum derivative has been synthesized independently in benzene solution by reduction of undecylenoylcaprolactam with dialkylaluminum hydride (9). The choice of the latter compound as reducing agent in lieu of a dialkoxyaluminum hydride derivative ($AlH(OR)_2$) was motivated by the two following reasons: (a) 9 is commercially available, which is not the case for $AlH(OR)_2$. (b) Dialkylaluminum hydrides are known as selective reducing agents of tertiary amides.[12]

The introduction of a dialkyl substituent in 12 in place of the dialkoxy group should not affect the subsequent behavior of the (aluminoxy)azacycloheptane function toward sodium lactamate salt.

The reduction of undecylenoylcaprolactam is followed by IR; the band at 1700 cm^{-1} characteristic of the lactam carbonyl ($OCN(CH_2)_5C{=}O$) in the IR spectrum (Figure 11) slowly decreases as reduction proceeds, whereas a distinct band at 1580 cm^{-1} specific to the aluminoxy derivative steadily increases. This latter structure can be easily hydrolyzed in a slightly acidic medium, whereupon formation of an aldehyde function is expected (Figure 12). However, when the latter functional group undergoes a Tishchencko reaction in the presence of alkoxyaluminum derivative, ester (1730 cm^{-1}) and alcohol (3400 cm^{-1}) functions are ultimately obtained. When the reduction is

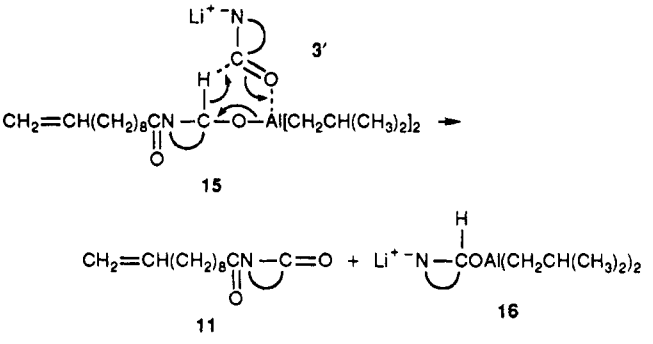
completed, a stoichiometric amount of lactamate anion is introduced (Scheme IV). The reaction medium is intentionally kept at low temperature to properly follow the various sequences of propagation. Aliquots are taken from the reaction mixture and neutralized with an excess of slightly acidic water. Upon this treatment, the residual dialkylaluminoxy function of **15** is cleaved, giving rise to the structures described above. The insoluble part, which is the aliphatic undecylenic residue, is isolated, dried, and characterized by IR.

a. Reduction of 11.



b. Transfer of Hydrogen and of the Dialkylaluminum Group from 15 to the Lactam Anion (3′). As

Scheme IV



the reaction proceeds, the absorption band at 1700 cm^{-1} (Figure 13), which is specific to the *N*-acyllactam function, increases with time at the expense of the peaks at 1730 and 1540 cm^{-1}, assigned respectively to ester and amide functions.

This remarkable finding points to the fact that the hydride and dialkylaluminoxy groups are transferred from **15** to the activated monomer. The aliquot taken from the medium after 10 min of reaction and characterized by IR and ^1H NMR turns out to be pure undecylenoylcaprolactam (Figure 14). The rate of reduction is quite fast at room temperature and is complete in about 10 min; in the conditions of polymerization (at elevated temperatures), it should occur even more rapidly than the propagation itself, known to be slower.

It was separately checked from elemental analysis on the isolated product, i.e., the recovered *N*-acyllactam, that the addition of activated lactam to the intermediately formed reduced acyllactam (**15**) does not interfere with the transfer reaction shown. The transfer of a group as large as dialkylaluminoxy, together with the displacement of hydride, may remind one of the Meerwein–Ponndorf–Verley reduction,[13] which also involves transfer of both hydride and aluminum derivative. However, the two reactions are of quite different nature. The Meerwein–

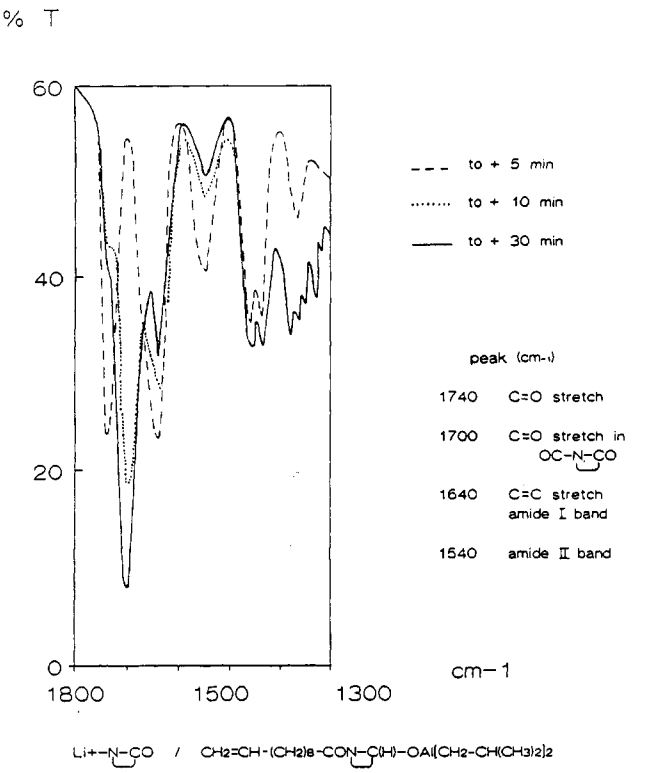


Figure 13. IR absorption diagrams showing the progressive reduction of lactamate anion (3′) by **15** obtained via the transfer of both hydrogen and dialkoxyaluminum group.

Ponndorf–Verley reduction is a reversible equilibrium reaction, whereas the reduction of the activated monomer carbonyl function is rapid and irreversible. It was checked that a protonated ϵ-caprolactam is unable to undergo a similar reduction. Whether this transfer occurs via a six-membered cyclic transition state—as suggested in Scheme V—or through a more complex mechanism is still open to debate. Only a kinetic study can settle this question. Yet the experimental results presented herein teach us that reduction of the activated monomer and concomitant formation of the end-standing *N*-acyllactam precede the propagation step itself. In the conditions of polymerization, more precisely at elevated temperatures, this double phenomenon of rapid reduction of the lactamate anion and slower addition to the *N*-acyllactam fully accounts for the observed reduced nucleophilicity of the active species.

Propagation involves therefore three stages:

(1) After each chain-growth step, a (dialkoxyaluminoxy)-azacycloheptane group is formed at chain end, whereas the negative charge is carried by the main-chain amide nitrogen of the penultimate unit. Owing to the more acidic character of the amide hydrogen of ϵ-caprolactam, a rapid proton exchange ensues to give the lactamate and the main-chain amide.

(2) The lactamate is immediately reduced by transfer of a dialkoxyaluminum group and displacement of a hydride, both from the chain end to the neighboring activated monomer. This regenerates the active species, the sodium salt of (dialkoxyaluminoxy)azacycloheptane (**6**).

(3) The propagation step—addition of a unit to the chain end—then takes place, upon reaction of the end-standing *N*-acyllactam with **6**. Since this is by far the slowest process, the overall rate of propagation will be determined by this last reaction.

The polymerization of ϵ-CPL was then attempted in the presence of $NaAlH_2(OR)_2$ as activating agent. ϵ-CPL

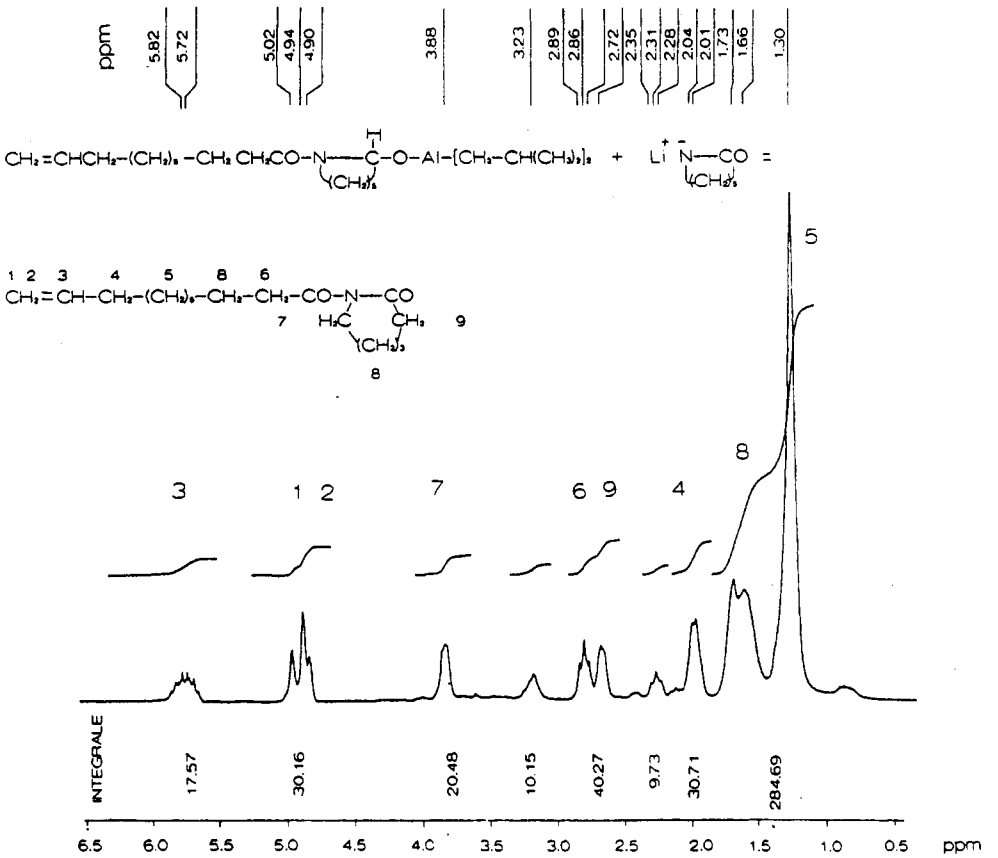
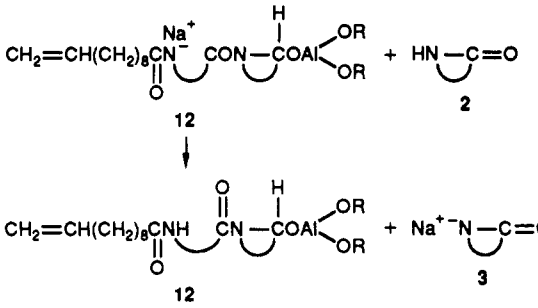


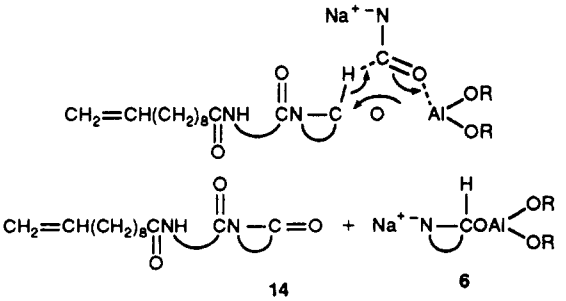
Figure 14. ^1H NMR spectrum of 11 obtained after total reduction of (3′).

Scheme V

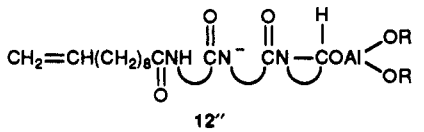
first step: transfer of the charge



second step: transfer of hydrogen and dialkyoxy aluminum group



third step: propagation



(3 g, 2.7×10^{-2} mol) and $NaAlH_2(OR)_2$ (2.7×10^{-4} mol) are first mixed and stirred for 3 h. Undecylenoyl caprolactam (2.7×10^{-4} mol) is subsequently introduced. The medium is further heated for 1 h and neutralized by adding acidic water. Unreacted ϵ-CPL is extracted by repeated washings with MeOH. A conversion of 85% in monomer is obtained after 1 h of polymerization. A slightly higher conversion (90%) is observed when using NaH as activating agent in similar experimental conditions.

Conclusion. A new mechanism of polymerization of lactams, catalyzed by alkali metal dialkoxyaluminum hydrides, is described and mechanistically explained step by step. Three reactions, corresponding to the three main stages of polymerization, have been investigated: the formation of the active species, the initiation reaction, and the propagation step.

Unlike the conventional anionic polymerization of lactams, the active species obtained in the present case is not the simple lactamate anion. A less nucleophilic species is generated when ϵ-caprolactam is treated with $Na^+[AlH_2(OR)_2]^-$. The classical activation of ϵ-caprolactam is followed by the reduction of its carbonyl function by $AlH_2(OR)_2$ to yield the structure **6**, the sodium salt of 2-(dialkoxyaluminoxy)-1-azacycloheptane.

The second step consists in the addition of this newly formed alkali metal salt (**6**) to the promoting function, namely undecylenoylcaprolactam. Thus, after the initiation step, the functional group fitting the chain end is the (dialkoxyaluminoxy)azacycloheptane entity (**12**).

The propagation comprises three phases. The negative charge carried on the penultimate unit is first transferred to the monomer, whereupon reduction of lactamate anion instantaneously ensues. This latter reaction involves rapid transfer of both hydride and dialkoxyaluminum group from the end-standing function (**12**) to the activated monomer (**3**). The above-mentioned active species (**6**) is restored as well as the end-standing *N*-acyllactam function. The chain growth actually occurs upon addition of **6** to the electrophilic *N*-acyllactam function.

This type of polymerization shares with the classical activated monomer mechanism the same basic features but differs from the latter by the nature of active species involved. Each propagation step is preceded by the reduction of the lactamate anion by means of a group transfer, and this occurs throughout the polymerization.

Experimental Section

Solvents. Tetrahydrofuran (THF) and benzene, used in the various reactions described below, were carefully purified and made free of protonic impurities, following classical procedures.

tert-Butyl alcohol was purified according to the well-known Lund and Bjerrum method.

Monomer. ε-Caprolactam was distilled twice under vacuum in the presence of CaH_2. The monomer was then freeze-dried prior to its use.

Catalysts. Lithium aluminum hydride, diisobutylaluminum hydride, and sodium bis(2-methoxyethoxy)aluminum hydride were purchased from Aldrich and Lancaster and used without purification.

All reaction vessels were flamed in a dry argon atmosphere and cooled in the same atmosphere prior to use. All reactions were carried out under anhydrous argon atmosphere.

Synthesis of Undecylenoylcaprolactam. ε-Caprolactam (1×10^{-2} mol) was first treated with Na (0.75×10^{-2} mol) in benzene solution at 70 °C for 3 h. The reaction medium was then cooled down with an ice bath, and 10-undecenoyl chloride (1×10^{-2} mol) was dropwise introduced at 10 °C. The mixture was allowed to stand overnight. Afterward, the medium was washed twice with water to remove the free ε-caprolactam and evaporated to dryness. Undecylenoyl-*N*-acyllactam was isolated by distillation (T_{eb} = 150 °C, 6×10^{-3} mmHg, yield 80%) and characterized by IR, NMR, and elemental analysis. Found: C, 72.4; O, 12.4; H, 10.55; N, 4.75. Calcd: C, 73.1; O, 11.5; H, 10.4; N, 5.

Reaction of ε-Caprolactam with $Na^+[AlH_2(OCH_2CH_2OMe)_2]^-$. To a solution of ε-caprolactam (1×10^{-2} mol) in benzene (1.13 g of ε-CPL on 8 mL of benzene) was slowly introduced $Na^+[AlH_2(OCH_2CH_2OMe)_2]^-$ at room temperature. Its addition was discontinued immediately after hydrogen had stopped evolving. The molar quantity of catalyst (5×10^{-3} mol) was approximately 50–60% of the monomer present in the medium. The reaction mixture was stirred for 3 h at 60 °C and subsequently neutralized with a methanolic solution of HCl (%). A bulky precipitate of aluminum hydroxide formed, which was readily filtrated off. The soluble part was evaporated to dryness. The residue (70% of the monomer introduced at the beginning) was shown as being ε-caprolactam. The previous aluminum precipitate was then treated in a highly basic aqueous medium (1 g of KOH in 30 mL of water). Upon stirring, a clear solution containing the aminoaldehyde (8) was obtained. The extraction of this product was tedious; only a small amount of 8 was isolated after two washings with ether. Data from IR and NMR and values from elemental analysis indicate the presence of some byproducts in addition to the expected structure 8.

Reduction of the Sodium Salt of 2-(Dialkoxyaluminoxy)-1-azacycloheptane (6) by Diisobutylaluminum Hydride (9). The synthesis of the sodium salt of 2-(dialkoxyaluminoxy)azacycloheptane is described above. The further reduction of ε-caprolactam was achieved by adding diisobutylaluminum hydride (6×10^{-3} mol). The reaction mixture was stirred for an additional 2 h at 60 °C and acidified. Hexamethyleneimine was easily isolated (yield 60% vs the initial ε-caprolactam) as it precipitated out from the THF solution in the hydrochlorinated form. Characterizations by IR, NMR, and elemental analysis all confirm the proposed structure. Found: C, 52.6; H, 10.4; N, 10; Cl, 25.1. Calcd C, 53.7; H, 9.7; N, 10.4; Cl, 26.2. The rest of the solution contained 40% of unreacted ε-caprolactam.

Reaction of 6 with Undecylenoylcaprolactam (11). Undecylenic *N*-acyllactam (6×10^{-3} mol) was added to a benzene solution containing 6 (6×10^{-3} mol of 1×10^{-2} mol of ε-caprolactam). The reaction was stirred for about 20 min at 60 °C. Aliquots were taken off at 5, 10, and 20 min and washed with water to extract unreacted ε-caprolactam. After a thorough drying, the residues were characterized by IR. The IR spectrum of the aliquot sampled after 20 min did not display any absorption at 1700 cm^{-1}, attesting to the addition of 6 to 11 and the formation of 12. Several bands specific to aluminum alkoxy functions were observed, in addition to two thin bands respectively at 1730 (aldehydes) and 1540 cm^{-1} (NH of amide), which arose from a partial hydrolysis. Treating the above residue in slightly acidic methanol allowed the total hydrolysis of 12. The product isolated after neutralization of the acidic medium by KOH, filtration of the salt formed, and solvent removal was characterized. The IR spectrum of the residue did show strong bands at 1730 and 1540 cm^{-1}—characteristic of ester and amide (NH) functions. The absence of any aldehyde function was ascribed to the occurrence of side reactions during hydrolysis, between aldehyde and alkoxyaluminum derivatives present in the reaction medium (Tishchencko reaction). The NMR spectrum and elemental analysis satisfactorily agreed with the conclusions drawn from the IR analysis.

Reduction of Lactamate Anion (3′) by 15 via Transfer of both Hydrogen and Dialkoxyaluminum Group. 3′ was prepared by action of BuLi on ε-caprolactam (2). The activation of 2 was carried out in THF at low temperature (−40 °C) by slowly adding BuLi (0.7 M, 14 mL) to 2 (1.5 g). A complete deprotonation of 2 can never be achieved, and the addition of BuLi was stopped after 75% conversion.

15 (9.3×10^{-3} mol) was synthesized by treating 11 with a stoichiometric amount of 9 (9.3×10^{-3} mol) at room temperature in benzene medium. The reaction was complete after 45 min of stirring as proven by the disappearance of the *N*-acyllactam band at 1700 cm^{-1} in the IR spectrum of the last aliquot.

The third step investigated the mutual behavior of 15 and 3′. In a reaction vessel filled with 3′ (9.8×10^{-3} mol) and fitted with an argon inlet, 15 (9.3×10^{-3} mol) was introduced at room temperature. The kinetics of reduction (Scheme IV) was followed by IR. Each aliquot was washed with slightly acidic water to remove water-soluble material—namely ε-caprolactam and its derivative—and extensively dried. The reduction was shown to be complete after 10 min. The isolated residue was undecylenoylcaprolactam (11) as confirmed by the perfect concordance between the IR spectra of 11 (Figure 6) and of the product of reaction (Figure 13, see also Figure 14).

Synthesis of Bis(*tert*-butoxy)aluminum Hydride ($HAl(OR)_2$). Bis(*tert*-butoxy)aluminum hydride was obtained from reaction of *tert*-butyl alcohol with aluminum hydride (AlH_3). The latter product was prepared according to a recipe[13] recommending the use of aluminum chloride ($AlCl_3$) and lithium aluminum hydride ($LiAlH_4$) as reactants. The reaction was carried out at low temperature (0 °C).

A THF solution of aluminum hydride (0.01 mol) was placed in a tight three-neck flask equipped with an argon inlet to produce a small overpressure. Dry *tert*-butyl alcohol (0.020 mol) was added dropwise with stirring at low temperature (0 °C). The solution became slightly turbid during the addition.

Bis(*tert*-butoxy)aluminum hydride (0.020 mol) was then slowly added to an anhydrous solution of ε-caprolactam (1.4×10^{-1} mol in 25 mL of THF). No H_2 evolved during the addition, and the overpressure was kept constant in the meantime. Introduction of a small quantity of methanol was characterized by a strong evolution of H_2 and the increase of the overpressure. This showed that dialkoxyaluminum hydrides are unable to deprotonate secondary amides such as ε-caprolactam, while the same products easily react with primary alcohols.

Acknowledgment. Authors N. Mougin and Y. Gnanou gratefully acknowledge Rhône-Poulenc (RP) Company for financial support. One of us (N. Mougin) is very much indebted to RP for a fellowship. We are also grateful to Drs. P. Rempp, J. E. Herz and F. Leising for their valuable comments and contributions.

References and Notes

(1) Sebenda, J. *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1988; Vol. 3, p 511.
(2) (a) Veith, C. A.; Cohen, R. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 42. (b) Veith, C. A.; Cohen, R. E. *Makromol. Chem.* **1992**, in press. (c) Veith, C. A.; Argon, A. S.; Cohen, R. E. *Polymer* **1991**, in press.

(3) (a) Schmitt, M.; Franta, E.; Rempp, P.; Froelich, D. *Makromol. Chem.* **1981**, *182*, 1695. (b) Nitadori, Y.; Franta, E.; Rempp, P. *Makromol. Chem.* **1978**, *179*, 927.
(4) Owen, M. J.; Thompson, J. *Br. Polym. J.* **1972**, *24*, 297.
(5) Lefèbvre, P. M.; Jérome, R.; Teyssié, P. *Makromol. Chem.* **1982**, *18*, 2453.
(6) (a) Tani, H.; Konomi, T. *J. Polym. Sci. Part A-1* **1966**, *4*, 301. (b) Konomi, T.; Tani, H. *J. Polym. Sci., Part A-1* **1971**, *9*, 2247. (c) Solomon, O.; Oprescu, Cr. *Makromol. Chem.* **1969**, *126*, 197. (d) Pufr, R.; Sebenda, J. *Eur. Polym. J.* **1972**, *8*, 1037.
(7) Kubanek, V.; Marik, J.; Mrkackova, Z.; Kralicek, J. *Proceedings*, Conference "Polyamidy 75", Chrudim, 1975; p 70.
(8) Finholt, A. E.; Bond, A. C., Jr.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 1199.
(9) Brown, H.; McFarlin, R. F. *J. Am. Chem. Soc.* **1958**, *80*, 5372.
(10) Ruzicka, L.; Kobelt, M.; Hafliger, O.; Prelog, V. *Helv. Chim. Acta* **1949**, *32*, 544.
(11) (a) Ogata, Y.; Kawasaki, A.; Kishi, I. *Tetrahedron* **1967**, *23*, 825. (b) Ogata, Y.; Kawasaki, A. *Tetrahedron* **1969**, *25*, 929.
(12) Zackarhin, L. I.; Khorkina, I. M. *Izv. Akad. Nauk SSSR, Otd. Chim. Nauk* **1959**, 2146.
(13) (a) Shriver, V. J.; Whitaker, D.; *J. Am. Chem. Soc.* **1963**, *85*, 2337. (b) Warnhoff, E. W.; Reynolds-Warnhoff, P.; Wong, M. *J. Am. Chem. Soc.* **1980**, *102*, 5956.

Registry No. 2, 105-60-2; 11, 36363-27-6; $Na^+[AlH_2(OCH_2CH_2OMe)_2]$, 22722-98-1; 10-undecenoyl chloride, 38460-95-6.