New Activating Agents for the Anionic Polymerization of Lactams

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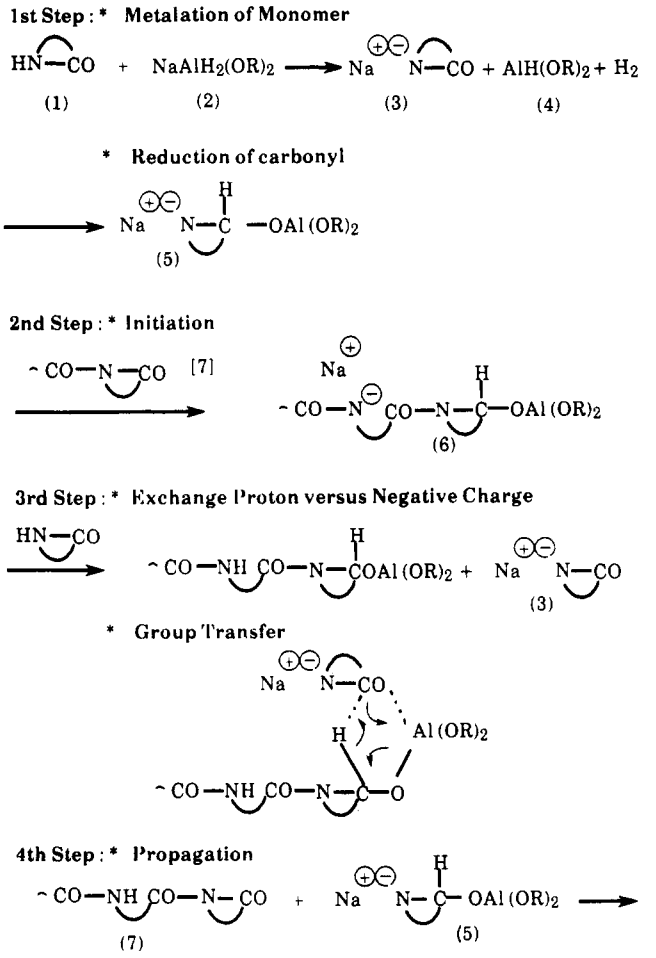
ABSTRACT: Metal dialkylaluminum hydrides and strong bases (NaH, BuLi) associated with reducing agents [$(alkyl)_2AlH$, $(alkyl)_2BH$, RMgBr] are shown to form a new class of activating agents for the anionic polymerization of lactams. Upon treating ϵ-caprolactam (ϵCL) with these new activating agents, active species of reduced nucleophilicity, as compared to the mere caprolactamate anions, are obtained. Once deprotonated, the monomer undergoes a reduction by these activating agents at its carbonyl position. These active species behave very similarly to sodium 2-(dialkoxyaluminoxy)-1-azacycloheptane, a salt obtained upon reacting ϵCL with sodium dialkoxyaluminum hydride ($NaAlH_2(OR)_2$) and whose contribution to the polymerization of lactams has been thoroughly investigated.[1] From these similarities, it is suggested that the mechanism of polymerization which occurs in the presence of these new activating agents should be very much the same as that discovered for $NaAlH_2(OR)_2$.

I. Introduction

In a recent study, Veith and Cohen[2] found that the reactive salts, obtained upon treating ϵ-caprolactam (ϵCL) with lithium dialkoxyaluminum hydride, are less nucleophilic than the classical lactamate anions generated by deprotonation of ϵCL with a strong base. Gnanou, Cohen, and their co-workers[1] described the mechanism of lactam polymerization in the presence of such activating agents, i.e., metal dialkoxyaluminum hydrides, and showed that it is quite different from the classical "activated monomer" mechanism. In the latter case, the active species is the lactamate anion and it is obtained upon deprotonation of the monomer by a strong base (NaH, $LiAlH_4$, BuLi). Initiation results from the attack of this lactamate anion onto a N-substituted lactam compound (acyllactam), intentionally introduced in the reaction medium to trigger the polymerization. A new acyllactam function is formed in this way at the chain end. Each propagation step then involves the transfer of the negative charge carried by the chain to a fresh monomer and the subsequent addition of activated monomer to the terminal acyllactam function.[3]

When metal dialkoxyaluminum hydrides are employed as activating agents, the nucleophilic species produced is no longer the classical lactamate anion and a new mechanism of polymerization has been proposed[1] to account for the results obtained (Scheme I). We showed that the reaction of ϵ-caprolactam (ϵCL; **1**) with sodium dialkoxyaluminum hydride (**2**) gives rise to the sodium salt of 2-(dialkoxyaluminoxy)-1-azacycloheptane (**5**). The formation of the latter compound occurs in two steps: first, deprotonation of ϵCL at its amide position and, second, reduction of its carbonyl function by the dialkoxyaluminum hydride formed during the previous step. For the initiation to occur, the presence of N-acylated lactam is required, as in the classical case. The attack and the addition of the nucleophilic species (**5**) results in the formation of a 2-(dialkoxyaluminoxy)-1-azacycloheptane group (**6**) at the chain end. The activation process of a fresh monomer, which follows the previous addition, is more complex than in the classical scheme. After the transfer of the negative charge carried by the penultimate unit to the monomer, the reduction of the lactamate anion immediately ensues by displacement of both the hydride and dialkoxyaluminum groups from the terminal function

Scheme I



(**6**). Upon this process the active species (**5**), identified above as resulting from the reaction of $NaAlH_2(OR)_2$ with ϵCL, is restored, while an acyllactam function is re-formed at the chain end. The way is thus paved for a new propagation step which will occur by addition of **5** onto the electrophilic acyllactam function. Such a concerted transfer of a group as large as dialkoxyaluminum and of hydride resembles the Meerwein–Ponndorf reduction, which also involves the displacement of both hydride and aluminum derivatives.

From the mechanism outlined above, it can be seen that the monomer has to be activated before each propagation step. It therefore shares with the classical mechanism the

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Table I
Characteristics of PDMS Chains after a Contact Period of 2 h with Various Lactam Salts at 80 °C

active species	initial PDMS	PDMS after a given period of contact with the active species: t = 2 h	t = 2 h + 1 h[b]	convn of εCL
$Na^{+-}N$-CO	M_n = 5037, M_ω = 6000, I = 1.18	M_n = 700, M_ω = 4800, I = 6.9		less than 10%
HN-CO + $LiAlH_2(O\text{-}t\text{-}Bu)_2$	M_n = 3800, M_ω = 4200, I = 1.1	M_n = 3600, M_ω = 4600, I = 1.27, small shoulder is the small MW domain		80%
HN-CO + $NaAlH_2(OCH_2CH_2OCH_3)_2$	M_n = 3400, M_ω = 3800, I = 1.10	M_n = 3100, M_ω = 3550, I = 1.17		80%
HN-CO + $LiAlH[OCH(CH_3)_2]_3$[a]	M_n = 5000, M_ω = 5900, I = 1.18	M_n = 2400, M_ω = 3600, I = 1.53		no polymn
HN-CO + $NaAlH_2Et_2$	M_n = 3850, M_ω = 4400, I = 1.14	M_n = 3500, M_ω = 4200, I = 1.2		80%
NaN-CO + $HAl[CH_2CH(CH_3)_2]_2$	M_n = 5030, M_ω = 6000, I = 1.18	M_n = 4830, M_ω = 5600, I = 1.16		25%
NaN-CO + $HB[CH(CH_3)CH(CH_3)_2]_2$ (stoichiometry)	M_n = 3800, M_ω = 4400, I = 1.14	M_n = 1800, M_ω = 4000, I = 2.11		58%
NaN-CO + $HB[CH(CH_3)CH(CH_3)_2]_2$ (excess)	M_n = 4800, M_ω = 5400, I = 1.12	M_n = 4600, M_ω = 4900, I = 1.3	M_n = 5150, M_ω = 5800, I = 1.12	85%
LiN-CO + $(CH_3)_2CHCH_2MgBr$	M_n = 3400, M_ω = 3770, I = 1.10	M_n = 3500, M_ω = 3900, I = 1.11	M_n = 3200, M_ω = 3600, I = 1.10	84%
BrMgN-CO	M_n = 3400, M_ω = 3800, I = 1.10	M_n = 3430, M_ω = 3800, I = 1.1		79%

[a] $LiAlH_4$ + $LiAl[OCH(CH_3)_2]_4$. [b] Contact period = 2 h + 1 h of εCL polymerization.

same basic feature. However, the two mechanisms differ on two crucial points, namely, on the type of active species formed and on the activation process of fresh monomers throughout the polymerization. In addition to these specificities, Veith and Cohen[2] found that the two kinds of active species behave quite differently toward the electrophilic Si–O bonds of poly(dimethylsiloxane) (PDMS) chains. The mere lactamate anion aggressively reacts with siloxane bonds, giving rise to silanolate anions, which were found to be detrimental to lactam polymerization (see run 1 in Table I). In contrast, the sodium salt of 2-(dialkoxyaluminoxy)-1-azacycloheptane formed upon using sodium dialkoxyaluminum hydride is totally inert toward PDMS and yet able to bring about the polymerization of lactams[1,2] (see runs 2 and 3 in Table I).

This unique feature prompted us to develop new activating agents which could function toward εCL as metal dialkoxyaluminum hydrides and exhibit the same selectivity. The key idea upon which the current investigation is based is to utilize compounds able first to deprotonate εCL and then to reduce its carbonyl function.

We did not undertake a mechanistic study similar to our recent investigation on the behavior of **5**, nor did we endeavor to identify the active species formed upon treating each of the activating agents with εCL. Instead, we have merely exposed the various active species to PDMS chains and examined their subsequent ability to induce lactam polymerization. Upon checking the integrity of the PDMS and determining the conversion of εCL, we should be able to establish which of the new activating agents would work as metal dialkoxyaluminum hydrides. The PDMS merely serves to assess the nucleophilicity of the active species formed. If a given nucleophilic species, obtained upon using one of the new activating agents, is found inert toward PDMS and yet able to bring about polymerization of lactams, one could conclude that it presumably possesses a structure similar to **5**, a salt of 2-(dialkoxyaluminoxy)-1-azacycloheptane. The mechanism of polymerization would be in this event much the same as that found for **5**.

II. Selection of New Activating Agents for the Anionic Polymerization of Lactams

We have evidenced the selectivity of sodium bis(2-methoxyethoxy)dihydroaluminate in its reaction with εCL and stressed the role of the two hydrides.[1] As a nucleophilic reagent, $NaAlH_2(OR)_2$ attacks the weakly acidic N–H bond of εCL and generates both a caprolactamate anion and dialkoxyaluminum hydride. The latter compound, as an electrophile (Lewis acid), preferentially reacts with centers exhibiting high electron density and therefore serves to reduce the carbonyl function of the activated monomer. With metal aluminum derivatives containing either more or less Al–H bonds ($LiAlH_4$ or $LiAlH(OR)_3$, respectively) than the dialkoxydihydroaluminates mentioned above, it was shown that the product obtained upon reaction with εCL is the lactamate anion.[2]

While examining the various compounds which could function toward εCL as did **2**, we came to consider two possible approaches:

(a) To make use of alkali-metal aluminate or borane complexes possessing two metal hydrogen bonds. Besides metal dialkoxyaluminum hydrides, whose behavior is known, dialkoxy- or dialkyl-substituted metal borohydrides and dialkyl-substituted metal aluminohydrides fall in these two families of reducing agents. Unfortunately,

neither metal dialkoxydihydroborane nor the dialkoxy derivative was commercially available at the time of our investigation. Sodium dialkyldihydroaluminate was thus the only activating agent of this category to be investigated.

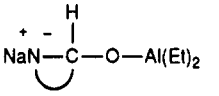
(b) To associate a strong base with a compound capable of reducing the carbonyl function of lactams. The role of the base (BuLi or NaH) is merely to deprotonate the lactam, while the function of the reducing agent is to give rise to a structure similar to 5. Dialkylaluminum hydride, disiamylborane—known for its selectivity toward substituted amides—and Grignard reagents possessing a hydrogen on their β carbon atom are the three reagents used to reduce the activated monomer.

III. Results and Discussion

It is important that the reduction of activated monomer be complete before introducing PDMS. Otherwise, some lactamate anions may be left in the reaction medium and could induce the degradation of PDMS chains. It is equally essential that this reduction be selective—no further reduction—and occurred according to a scheme similar to that established for metal dialkoxyaluminum hydrides. For these various reasons, the experimental conditions chosen to generate the active species differ from one activating agent to another. On the other hand, the procedure followed afterward is essentially the same, regardless of the active species obtained. Then, fresh monomer and a PDMS sample of sharp and known molecular weight distribution are introduced into the reaction medium. After a 2-h stirring at 80 °C, an aliquot is sampled out and washed with MeOH; the PDMS isolated in this way is analyzed by GPC. Subsequently, undecylenoyl caprolactam, whose concentration is the same for all runs, is introduced in the reaction medium to trigger lactam propagation. The polymerization is systematically stopped after 1 h of reaction at 80 °C and the conversion of ϵCL determined. The PDMS which has experienced this additional 1 h of lactam polymerization is isolated and characterized by GPC.

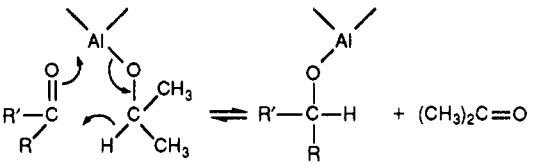
(a) Sodium Diethyldihydroaluminate as Activating Agent ($NaAlH_2R_2$). Addition of sodium diethyldihydroaluminate (2 M solution in toluene) into the flask containing pure molten ϵ-caprolactam is carried out at 80 °C and stopped as soon as the H_2 evolution, characteristic of monomer deprotonation, ceases. Continuing the addition may provoke a second reduction of the activated monomer. The amount of activating agent introduced (4×10^{-3} mol, 2 mL), per mole of ϵCL present (6.7×10^{-3} mol, 0.75 g), does not exceed 60%. The reaction is stirred for several hours at 80 °C before 9.3×10^{-2} mol of fresh monomer (10.5 g) and 6 g of a PDMS sample are introduced.

The PDMS isolated after a 2-h exposure to the active species is intact and did not experience any degradation (MWD is unchanged). Then, 4×10^{-4} mol of undecylenoyl caprolactam (0.11 g) is introduced. Conversion of ϵ-caprolactam amounts to a value as high as 80% after 1 h of polymerization, which is a remarkable result (Table I). These two features, nondegradation of PDMS and high ϵCL conversion, do indicate that the active species generated upon reacting ϵCL with $NaAlH_2(Et)_2$ behaves very similarly to 5. These results suggest that the lactamate anion is indeed reduced by the $AlHR_2$ formed upon monomer deprotonation. Active species of reduced nucleophilicity, as compared to the mere lactamate anion, are obtained. Their structure could be



(b) Lithium Triisopropylhydroaluminate as Activating Agent ($LiAlH(OCH(CH_3)_2)_3$). Veith and Cohen[2] have shown that trialkoxy-substituted lithium aluminum hydrides are unable to give rise, upon reaction with ϵCL, to a species similar to 5. It was inferred from this observation that two Al–H bonds are needed in the activating agent to generate a structure equivalent to 5.

Yet, the reduction of carbonyl functions does not necessarily require the use of a true hydride, such as aluminum or boron hydride. This reduction can for instance be obtained upon reacting the carbonyl function with aluminum triisopropoxide; such a reaction occurs by hydrogen transfer from the carbinol carbon to the carbonyl and is called Meerwein–Ponndorf reduction.[4]



We thought of applying this reaction to the reduction of the activated lactam. This could be theoretically possible upon using an activating agent such as $LiAlH[OCH(CH_3)_2]_3$. After deprotonation of ϵCL (0.75 g, 6.7×10^{-3} mol) by the hydride (4×10^{-3} mol, 5 mL of a 1 M THF solution), we expected the reduction of its carbonyl function by the triisopropoxide aluminum group formed during the previous step. The medium is stirred for 5 h at 80 °C, before fresh monomer (9.3×10^{-2} mol, 10.5 g) and PDMS (6 g) are added.

The results obtained are disappointing (Table I). The PDMS exposed for 2 h to the active species is noticeably degraded; as to the polymerization of lactam, triggered after introduction of undecylenoylcaprolactam (4×10^{-4} mol, 0.11 g), it resulted in a negligible ϵCL conversion.

The reduction of the activated monomer by $AlOCH(CH_3)_2$, which was envisaged, has not occurred. This unexpected result may be due to the peculiar behavior of $LiAlH(O\text{-}i\text{-}Pr)_3$.[5] Indeed, it was shown to disproportionate, as soon as it is formed into lithium aluminum tetraisopropoxide—which precipitates out of the solution—and lithium aluminum hydride ($LiAlH_4$).

$$4LiAlH(O\text{-}i\text{-}Pr)_3 \rightarrow 3LiAl(O\text{-}i\text{-}Pr)_4 + LiAlH_4$$

The latter reagent, which is known to mainly generate lactamate anions upon reacting with ϵCL, might have played the role of the activating agent in lieu of $LiAlH(O\text{-}i\text{-}Pr)_3$. This could therefore explain the behavior observed.

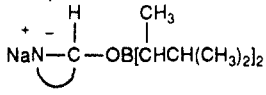
(c) Association of a Strong Base (NaH) with a Reducing Agent (Lewis Acid). Two types of Lewis acids have been tried in association with sodium hydride as deprotonating agent.

Bis(1,2-dimethylpropyl)borane (Disiamylborane). Only 60% of the ϵCL introduced (0.75 g, 6.7×10^{-3} mol) can be deprotonated in the experimental conditions chosen, T = 80 °C and in the bulk, with sodium hydride as the activating agent. Further addition of NaH does not give rise to hydrogen evolution. The reaction medium is thus constituted of 4×10^{-3} mol of sodium lactamate (60% of initial ϵCL) and of 2.7×10^{-3} mol of ϵCL (40% of initial ϵCL) when disiamylborane is introduced. Addition of the latter compound is carried out at 0 °C; the

medium is then stirred overnight at room temperature. Fresh monomer (9.3×10^{-2} mol) and PDMS (6 g) are then added. The amount of reducing agent to be used in the first step was found to be of paramount importance. We envisaged two possibilities:

(1) To add 1 equiv of lactamate salt, assuming that the reducing agent (4×10^{-3} mol, 8 mL of a 0.5 M THF solution) will react exclusively with the carbonyl function of the latter reactive species and stay inert toward the 40% of nonactivated ϵCL still present. The results obtained clearly indicate that this is not the case. The PDMS (6 g) in contact with the nucleophilic species is indeed slightly degraded; the conversion of ϵCL (58%), determined after introduction of undecylenoylcaprolactam (4×10^{-4} mol, 0.11 g) and 1 h of heating at 80 °C, is noticeably lower than a would-be active species inert toward PDMS (Table I). It is reasonable to infer from these results that some disiamylborane hydride has been consumed in the deprotonation of ϵCL, preventing the expected complete reduction of lactamate anion. The residual lactamate anion (2) should be responsible for the degradation of PDMS.

(2) Increasing the quantity of disiamylborane (6.7×10^{-3} mol, 13.4 mL of a 0.5 M THF solution) brought about dramatic changes. In this second attempt, we did not refer to the concentration of a lactamate salt as previously but to the total amount of lactam. We thus added 1 equiv disiamylborane/1 mol of the initial caprolactam. The PDMS exposed to the active species formed in these conditions is intact, and at the same time the ϵCL conversion determined as above is quite high (85%) (Table I). These results bring an undisputed confirmation to our above statement: due to the loss of some $HB(alkyl)_2$ in the deprotonation of the monomer present in the reaction medium, it was not possible to achieve a quantitative reduction of lactamate anion. Upon augmenting the amount of $HB(alkyl)_2$ the reduction of the residual lactamate anion became possible, leading to the quantitative formation of the expected active species whose structure should be



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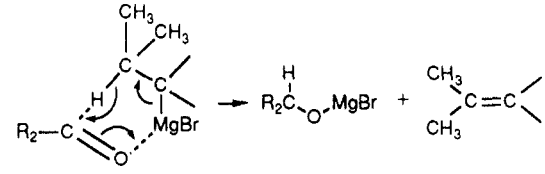
This active species of reduced nucleophilicity behaves very similarly to 5 and fully meets our objectives: nondegradation of PDMS and high conversion obtained for ϵCL.

In a separate experiment to further confirm the deprotonation of ϵCL by $HB[CH(CH_3)CH(CH_3)_2)]_2$, we have separately examined the behavior of disiamylborane hydride toward pure ϵCL. Upon adding the Lewis acid to melted ϵCL, a strong H_2 evolution, characteristic of monomer deprotonation, is seen, but the reduction of the carbonyl function does not seem to occur. We then checked the ability of disiamylborane to induce the polymerization of ϵCL in the presence of acyllactam. Disiamylboron lactamate is found totally inactive, and no polymerization occurs in its presence. It can thus be concluded that the dialkylboron lactam that is formed simultaneously to the reduced amide salt (8) does not harm the polymerization process.

Diisobutylaluminum Hydride [(i-Bu)$_2$AlH]. This Lewis acid behaves essentially as disiamylborane. The reduction of the lactamate anion carbonyl should be quantitative, provided no residual ϵCL is present in the reaction medium. Upon adding an appropriate amount of diisobutylaluminum hydride (4×10^{-3} mol of $HAl(alkyl)_2$ for 4×10^{-3} of ϵCL), an active species of reduced nucleophilicity is obtained, upon stirring the reaction medium for 5 h at 80 °C. Indeed, it behaves similarly to 5 as far as the inertness toward PDMS is concerned: the latter polymer (6 g) which is introduced, in a second step, along with fresh monomer (9.6×10^{-2} mol, 10.85 g) remains undamaged. Addition of undecylenoylcaprolactam (4×10^{-3} mol) results, however, in an unexplained rather low ϵCL conversion.

(d) Strong Base Associated with Organomagnesium Compounds. The reduction of amide carbonyls and more generally of ketones by organomagnesium compounds is well-known.[6] It should therefore be possible to use these reactants to reduce the carbonyl function of lactamate anion, in order to generate a structure equivalent to 5.

Attention must, however, be given to the selection of the appropriate Grignard reagents. To obtain a structure similar to 5, which implies the reduction of the carbonyl, we must choose a Grignard reagent possessing a single β hydrogen such as isobutylmagnesium bromide.[7] With such a compound, the reduction of the carbonyl function occurs by hydride transfer, according to the following six-membered transition state:

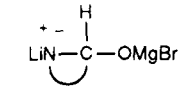


A mere alkylmagnesium bromide would give 1,2 addition, which we do not want.

On the other hand, it should be borne in mind that organomagnesium compounds, as nucleophilic reagents, can deprotonate the cyclic lactam and give rise to "caprolactam magnesium bromide". The latter species is known to induce lactam polymerization in the presence of an initiator (acyllactam).[8] We show (see Table I) that it actually brings about the polymerization of ϵCL. If one wants to strictly use Grignard reagents as reducing agents, it is therefore of importance that the monomer be first entirely deprotonated by a base. Otherwise, one could have two types of propagation upon polymerizing ϵCL.

The monomer (4×10^{-3} mol, 0.45 g) is reacted first with a stoichiometric amount of BuLi (2.5 mL of a 1.6 M solution in hexane), in THF solution at −40 °C for 2 h. Under these conditions only can we be sure that deprotonation of ϵCL is complete. The solvent is then evaporated and the temperature raised to 80 °C. A stoichiometric amount of isobutyl magnesium bromide (4×10^{-3} mol, 2 mL of a 2 M solution in diethyl ether) is introduced, and the reduction of the lactamate anion carbonyl is carried out. The reaction medium is stirred at 80 °C for 8 h, before a further amount of ϵCL (9.6×10^{-2} mol, 10.85 g) and 6 g of a PDMS sample are added.

The active species formed are proven to be inert toward PDMS. The sample which has experienced a 2-h contact with the active species is not degraded as shown by its unaltered MWD. This means that reduction of lithium caprolactamate has occurred as expected, leading to the presumed following structure:



The new active species does cause ϵCL polymerization in the presence of undecylenoylcaprolactam (4×10^{-4} mol, 0.11 g). The conversion of ϵCL (84%) is indeed fairly high after 1 h of polymerization.

IV. Conclusions

In the classical anionic polymerization of lactams, the active species responsible for chain growth is the lactamate anion. The latter species is generated upon deprotonation of the monomer by a strong base such as NaH or BuLi.

We introduce in this paper a series of new activating agents which do not function as the above-mentioned bases when they are reacted with lactams. The active species generated upon treating these reagents with lactams are less nucleophilic than the mere lactamate anions, yet they are able to bring about the polymerization of lactams. The behavior of these activating agents toward lactams reminds us of that exhibited by $NaAlH_2(OR)_2$,[1,2] which gives rise to sodium 2-(dialkoxyaluminoxy)-1-azacycloheptane by reaction with ϵCL.

Although the structure of the various active species formed has not been characterized, the similarities found between $NaAlH_2(OR)_2$ and some of the activating agents presented herein suggest that the latter reagents reduce the carbonyl function of activated monomer. The reduced nucleophilicity of some active species may be explained using this argument.

V. Experimental Part

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

Reagents. Sodium hydride, sodium diethyldihydroaluminate, diisobutylaluminum hydride, and isobutylmagnesium bromide were purchased from Aldrich and used without further purification.

Isopropyl alcohol is purified according to the well-known Lund and Bjeruum procedure.

The synthesis of undecylenoylcaprolactam is described elsewhere.[1]

Synthesis of Bis(1,2-dimethylpropyl)borane (Disiamylborane). Bis(1,2-dimethylpropyl)borane (disiamylborane) is prepared by hydroboration of 2-methylene-2-butene with borane in the ratio of 1:2.[9] The reaction is carried out in THF at 0 °C.

Synthesis of Lithium Triisopropoxide Aluminum Hydride. To a solution of $LiAlH_4$ (10^{-2} mol) in THF (10 mL) are added 3×10^{-2} mol of isopropyl alcohol slowly at 0 °C. The medium becomes turbid soon after the beginning of isopropyl alcohol addition, and a precipitate is formed.

Synthesis of a α,ω-Bis(trimethyl)poly(dimethylsiloxane) Exhibiting a Narrow Distribution. The best way to obtain such a sample is to resort to the anionic polymerization of hexamethylcyclotrisiloxane (D_3). The polymerization of D_3 is initiated with BuLi, in benzene solution; propagation occurs upon adding some THF (THF/C_6H_6 = 1). The polymerization is terminated with trimethylchlorosilane (see ref 10 for more details).

Procedure Used To Assess the Nucleophilicity of the Active Species Formed. The synthesis of the various active species is described in the text. We systematically worked with the same molar amount of active species (4×10^{-3} mol). Once the active species is formed, fresh monomer (generally 9.6×10^{-2} mol, 10.85 g), whose amount is calculated to make a ratio [active species] to [ϵCL] of 4:100, and the above-mentioned PDMS (6 g) are introduced. In all cases, the reaction medium is "macroscopically" homogeneous. After a 2-h exposure to the active species at 80 °C, an aliquot is taken off and analyzed by GPC with toluene as eluent. The activator, undecylenoylcaprolactam, is added next; its molar amount was chosen equal to that of the active species. In the majority of cases, whenever ϵCL polymerization occurs, the polyamide precipitates out of the medium at low conversion, because of its tendency to crystallize. Polymerization then proceeds in a heterogeneous medium, stirred at 80 °C for an additional 1 h. PDMS and the polyamide formed are separated upon washing the medium with THF. Residual monomer can be removed in this way as well. After a thorough drying of the polyamide, the conversion of ϵCL is obtained. In some cases, the PDMS, which has experienced the 1-h lactam polymerization, has been characterized by GPC.

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