Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Multiple Mechanism of NCA Polymerization: Effect of N-Acetylglycine NCA and Related Additives

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To cite this Article Amouyal, Michèle , Coutin, Bernard and Sekiguchi, Hikaru(1985) 'Multiple Mechanism of NCA Polymerization: Effect of N-Acetylglycine NCA and Related Additives', Journal of Macromolecular Science, Part A, 22: 4, 451 — 471
To link to this Article: DOI: 10.1080/00222338508056613
URL: http://dx.doi.org/10.1080/00222338508056613

J. MACROMOL. SCI.–CHEM., A23(4), pp. 451-471 (1986)

Multiple Mechanism of NCA Polymerization: Effect of N-Acetylglycine NCA and Related Additives

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ABSTRACT

Polymerization of α-aminoisobutyric acid NCA by alkaline salts of various basicity as well as amines has been investigated. The study was focused on the effect on the initial polymerization rate of additives such as N-acetylglycine NCA and some other less electrophilic additives (1-acetyl-2-pyrrolidone, 3-acetyl-2-oxazolidone, 1-acetyl-3-methylhydantoin) which are all models of the growing chain end produced by the NCA anion pathway. The acetyl endgroup was detected by 250 MHz ^{1}H-NMR in all the polymers of α-aminoisobutyric acid NCA obtained in the presence of 1-acetyl-3-methylhydantoin and triethyl amine or sodium methoxide initiators, whereas the additives influenced variously the kinetics of polymerization according to the nature of the initiator used. The results were interpreted in the light of a multiple mechanism supposing the simultaneous presence of the initiator anion, its conjugate acid, and NCA anion for basic salt initiation. Thus, the observed effect has to be considered as the sum of an elementary acceleration due to NCA anion and of an elementary deceleration due to the initiator anion. Predominance of the pathways involving NCA anion could be shown this way. This

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conclusion could be extended to γ-benzyl-L-glutamate NCA which is a more reactive NCA. However, the deceleration observed with some additives led us to believe that a nonnegligible participation of initiator anion during initiation cannot be excluded.

INTRODUCTION

A previous study [1] related to the polymerization of α-aminoisobutyric acid NCA (AIB-NCA) by various basic salts (alkaline hydroxides, lactamates, and alcoholates) for which the mechanism was not totally elucidated. It stressed the effect of some additives, expecially protic ones, on the polymerization of this NCA. The present work is more focused on the use of N-acylated NCAs as additives. The utilization of such compounds has been suggested by Shalitin [2] as a model of the growing chain end produced by an NCA anion mechanism. It is worth noting that similar compounds, N-acylated lactams, are commonly used in the polymerization of lactams that proceeds by an activated monomer mechanism [3]. Until now, several N-acyl derivatives of glycine or alanine NCA have been reported [4], among which N-acetyl glycine NCA is the most accurate copy of the growing chain end according to an NCA anion mechanism. Kricheldorf has used it to confirm the existence of this mechanism in the polymerization of various N-unsubstituted NCAs by tertiary amines such as triethylamine [4] and to reject the same mechanism in the case of polymerization of L-phenylalanine and glycine NCAs by secondary amines with small substituents [5]. We report here the effects of N-acylated compounds (NAG-NCA and related compounds) on the polymerization of AIB-NCA by various initiators. Polymerization of γ-benzyl-L-glutamate NCA (γ-BLG-NCA) in similar conditions has also been examined.

EXPERIMENTAL PART

Monomers

AIB-NCA and γ-BLG-NCA were synthesized as previously described [1, 6].

Initiators

Sodium methoxide was prepared as in Ref 1. Commercial triethylamine and n-hexylamine were dried over calcium hydride and distilled before use. 9-Fluorenylpotassium was prepared according to the method described in Ref. 7. Anhydrous sodium acetate was dried by fusion of the commercial hydrate. Neutralization of benzoic

acid by sodium methoxide dissolved in methanol gave sodium benzoate as a precipitate. It was dried at 100°C in vacuo. Sodium 5,5-dimethyl-3-hydantoin isobutyrate was also prepared this way from the corresponding acid synthesized according to Ref. 8. These three salts were stored in vacuo over phosphorus pentoxide. In the following part of the paper, initiator concentrations are given in fractions of the monomer concentration.

Solvents

Pure grade dioxane, tetrahydrofuran, hexamethylphosphoramide, N,N-dimethylacetamide, and dimethylsulfoxide were refluxed over calcium hydride and distilled just before use. Acetonitrile was first distilled over calcium hydride, then over phosphorus pentoxide. Distillation was repeated when the water content was above 30 ppm (Karl Fischer method, "Automate Bizot et Constant," Société Prolabo). The water content of dimethylsulfoxide could not be determined because of inadequacy of the Karl Fischer method for this solvent. The solvents were handled with the precautions described in Ref. 1.

Additives

N-Acetylglycine NCA was prepared according to Ref. 4. 1-Acetyl-3-methylhydantoin, 1-acetyl-2-pyrrolidone, and 3-acetyl-2-oxazolidone were prepared according to Ref. 9. The concentrations of additives indicated in this paper are expressed as fractions of the monomer concentration.

POLYMERIZATION

Conversion was followed by gasometry under constant pressure (atmospheric pressure) at 20.0 ± 0.5°C. The apparatus and the technique used in gasometric measurements have been previously described [1].

DETECTION OF THE ACETYL RESIDUE IN POLY-α-ISOBUTYRAMIDE OBTAINED IN THE PRESENCE OF 1-ACETYL-3-METHYLHYDANTOIN

250 MHz ^{1}H-NMR measurements were performed on a Bruker 250 apparatus with the sodium salt of trimethylsilylpropanoic acid (purchased from "Spectrometrie, Spin et Techniques") as an internal standard. Poly-α-isobutyramide was dissolved in deuterated sulfuric acid, 96-98% in D_2O (Fluka).

Poly-α-isobutyramide (A) was prepared by polymerizing AIB-NCA (4 mol/L in acetonitrile) with triethylamine (5 mol% with respect to monomer) in the presence of 1-acetyl-3-methylhydantoin (10 mol% with respect to monomer). The polymer that precipitated was filtered and washed several times with acetonitrile and ethyl ether (gravimetric conversion: 45%). Poly-α-isobutyramide (B) was similarly prepared using sodium methoxide in place of triethylamine (AIB-NCA, 4 mol/L in acetonitrile, sodium methoxide 5%, and 1-acetyl-3-methyl hydantoin 10%).

To identify the acetyl signal, the following model compounds were prepared.

(a) N-Acetyl-α-aminoisobutyric acid. α-Aminoisobutyric acid was acylated by acetic anhydride in glacial acetic acid. The solution was evaporated in vacuo to a syrup, from which N-acetyl-α-aminoisobutyric acid (C) precipitated when treated with water. The compound was washed several times with water, then with ethyl ether, and dried in vacuo at room temperature. $C_6H_{11}NO_3$ (145.16): Calculated: C, 49.60; H, 7.60; N, 9.66; O, 33.10%. Found: C, 48.95; H, 7.70; N, 9.50; O, 32.90%.

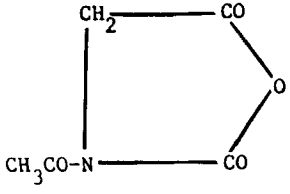
(b) Acetylated poly-α-isobutyramide. AIB-NCA (2 mol/L) was polymerized in acetonitrile with n-hexylamine (3%). The polymer thus obtained (D) was acetylated in boiling acetic anhydride for about 10 h and then washed and dried.

RESULTS

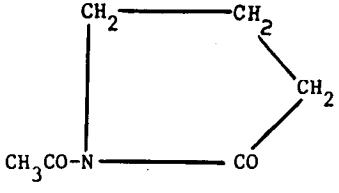
Sodium Methoxide

We have examined the effect of NAG-NCA and related compounds on the polymerization of AIB-NCA (2 mol/L) by sodium methoxide (3 mol% with respect to NCA) in acetonitrile (Fig. 1).

Polymerization is accelerated in the presence of NAG-NCA (I) (3 mol%), whereas it is slowed down by 3% of other compounds: 1-acetyl-2-pyrrolidone (II), 3-acetyl-2-oxazolidone (III), 1-acetyl-2-pyrrolidone (II), 3-acetyl-2-oxazolidone (III), 1-acetyl-3-methylhydantoin (IV):



(I)



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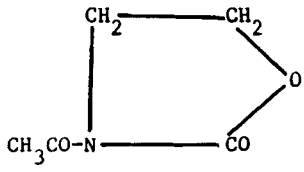

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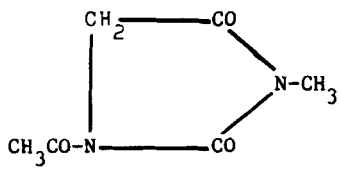

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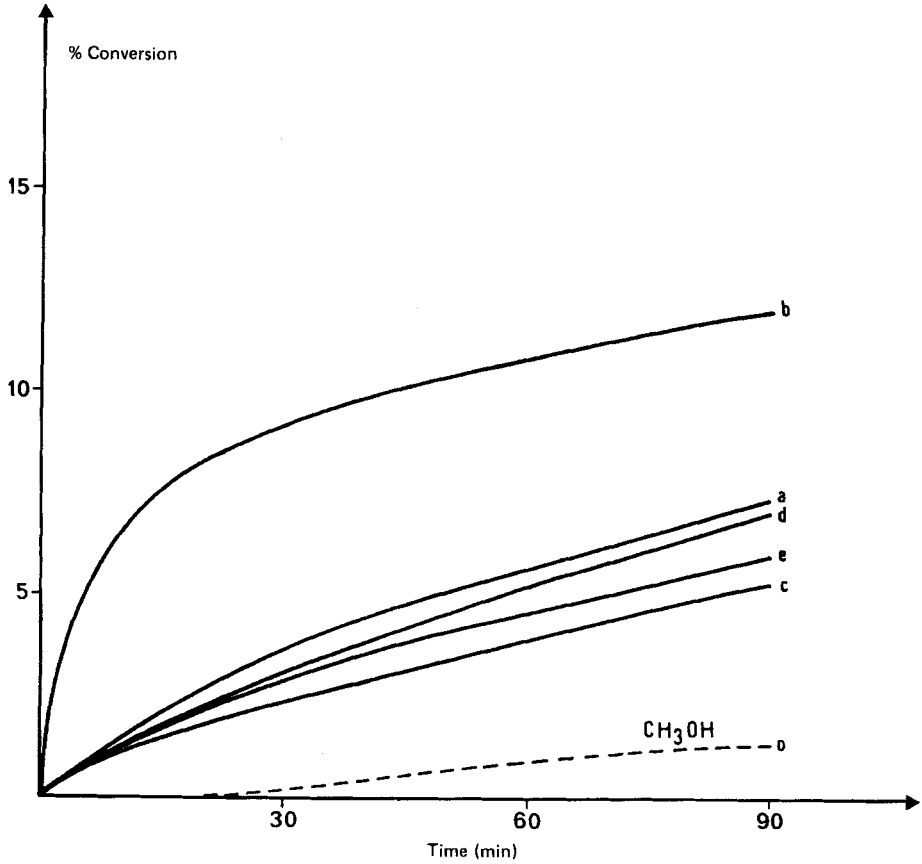


FIG. 1. Effect of NAG-NCA and related additives on polymerization of AIB-NCA (2 mol/L) in acetonitrile by CH_3 ONa. (a) CH_3ONa (3%), (b) CH_3ONa (3%) + NAG-NCA (3%), (c) CH_3 ONa (3%) + 1-acetyl-2-pyrrolidone (3%), (d) CH_3ONa (3%) + 1-acetyl-2-oxazolidone (3%), (e) CH_3ONa (3%) + 1-acetyl-3-methylhydantoin (3%), (o) CH_3OH (3%).

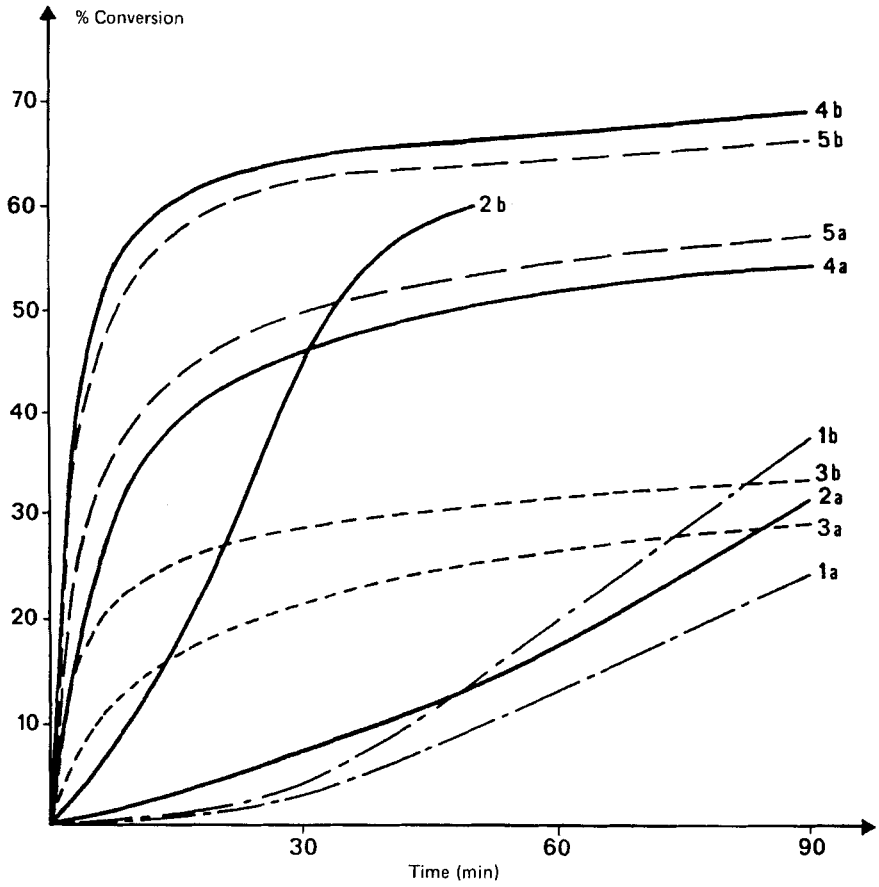


FIG. 2. Effect of NAG-NCA on polymerization of γ-BLG-NCA (0.08 mol/L) by CH_3 ONa in various solvents: dioxane (Curves 1), tetrahydrofuran (Curves 2), hexamethylphosphoramide (Curves 3), N,N-dimethylacetamide (Curves 4), dimethylsulfoxide (Curves 5). Curves a: catalyst alone (8%). Curves b: catalyst (8%) + NAG-NCA (8%).

We still observe this acceleration in the presence of NAG-NCA when γ-BLG-NCA, a more common and more reactive NCA than AIB-NCA, is polymerized by sodium methoxide in various solvents (Fig. 2) such as dioxane (dielectric constant ϵ = 2.2. [10]), tetrahydrofuran (ϵ = 7.58 [10]), hexamethylphosphoramide (ϵ = 30 [10]), N,N-dimethylacetamide (ϵ = 37.78 [10], comparable to acetonitrile ϵ = 37.5 [10]), and dimethylsulfoxide (ϵ = 46.68 [10]). In these solvents, polymerization is homogeneous from the beginning. Aceto-

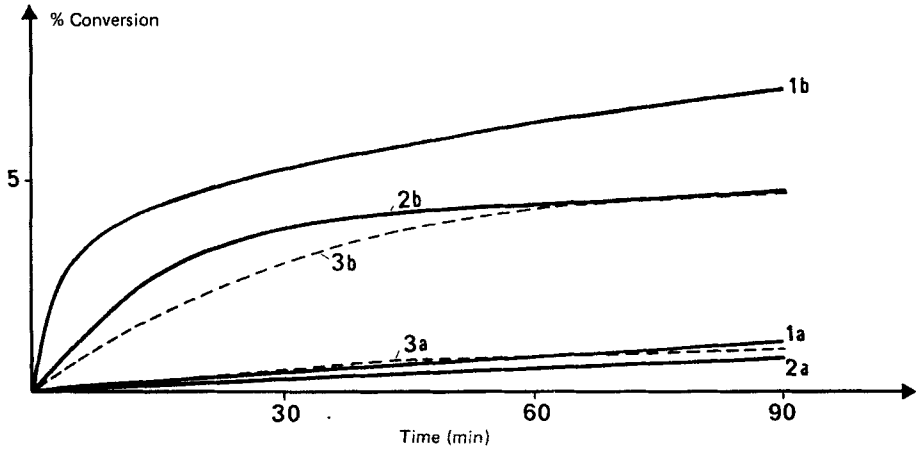


FIG. 3. Effect of NAG-NCA on polymerization of AIB-NCA (2 mol/L) by sodium carboxylates in acetonitrile. Curves 1: sodium acetate; Curves 2: sodium benzoate; Curves 3: sodium dimethyl-5,5-hydantoin-3-isobutyrate. Curves a: catalyst alone (25%). Curves b: catalyst (25%) + NAG-NCA (5%).

nitrile could not be used since the polymer precipitates immediately in this solvent.

Sodium Carboxylates

Figure 3 displays the results obtained with some carboxylates: AIB-NCA (2-mol/L) was polymerized with sodium acetate (25%), sodium benzoate (25%), and sodium dimethyl-5,5-hydantoin-3-isobutyrate (25%) in acetonitrile, with or without NAG-NCA (5%).

Polymerization is weak with all three initiators, and NAG-NCA enhances their reactivity considerably. The increment of acceleration due to NAG-NCA (Fig. 4) is in the following order: acetate > benzoate > hydantoin derivative. NAG-NCA is still efficient in the polymerization of γ-BLG-NCA by sodium acetate in N,N-dimethylacetamide (Fig. 5).

9-Fluorenylpotassium

The effect of NAG-NCA addition on the kinetics of γ-BLG-NCA polymerization (0.08 mol/L in dioxane) was examined for the case of 9-fluorenylpotassium initiation (4%).

NAG-NCA (4%) is no more efficient when it is added at the same

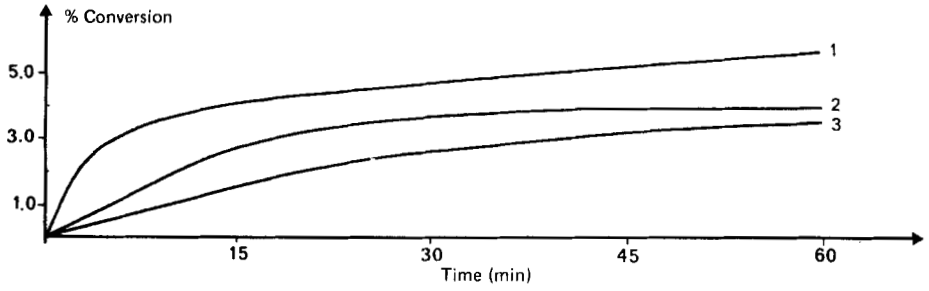


FIG. 4. Increment of conversion due to NAG-NCA additive. Curve 1: 1b (Fig. 3) minus 1a (Fig. 3); Curve 2: 2b (Fig. 3) minus 2a (Fig. 3); Curve 3: (Fig. 3) minus 3a (Fig. 3).

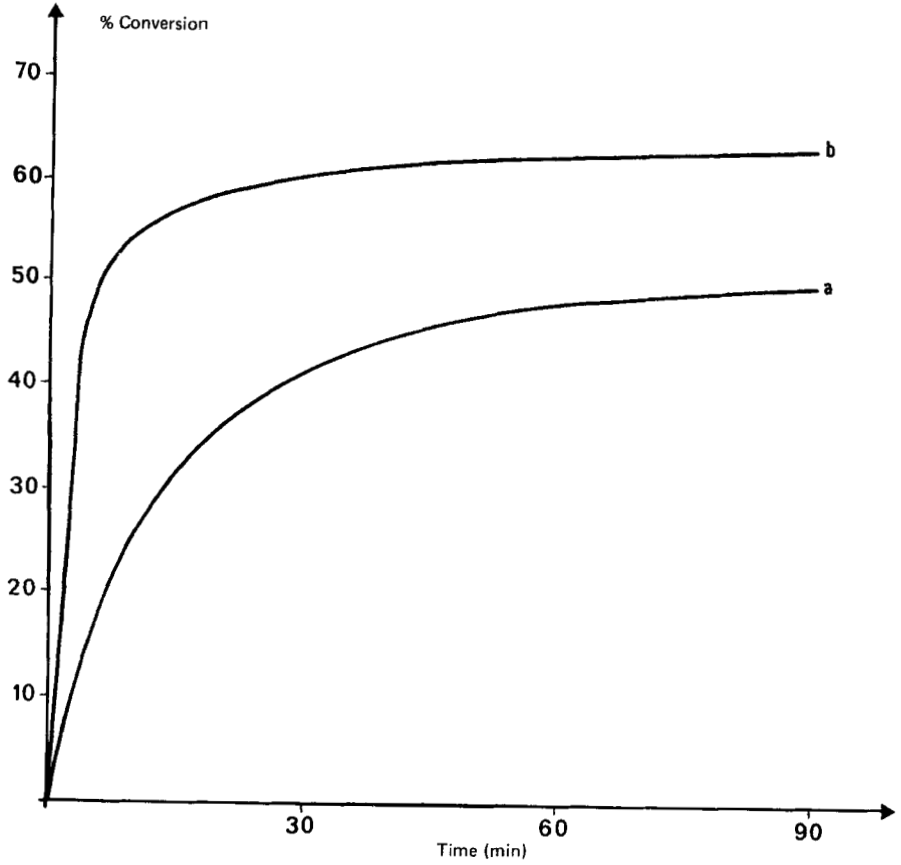


FIG. 5. Effect of NAG-NCA on polymerization of γ-BLG-NCA (0.08 mol/L) by sodium acetate in N,N-dimethylacetamide. (a) Sodium acetate (8%), (b) sodium acetate (8%) + NAG-NCA (8%).

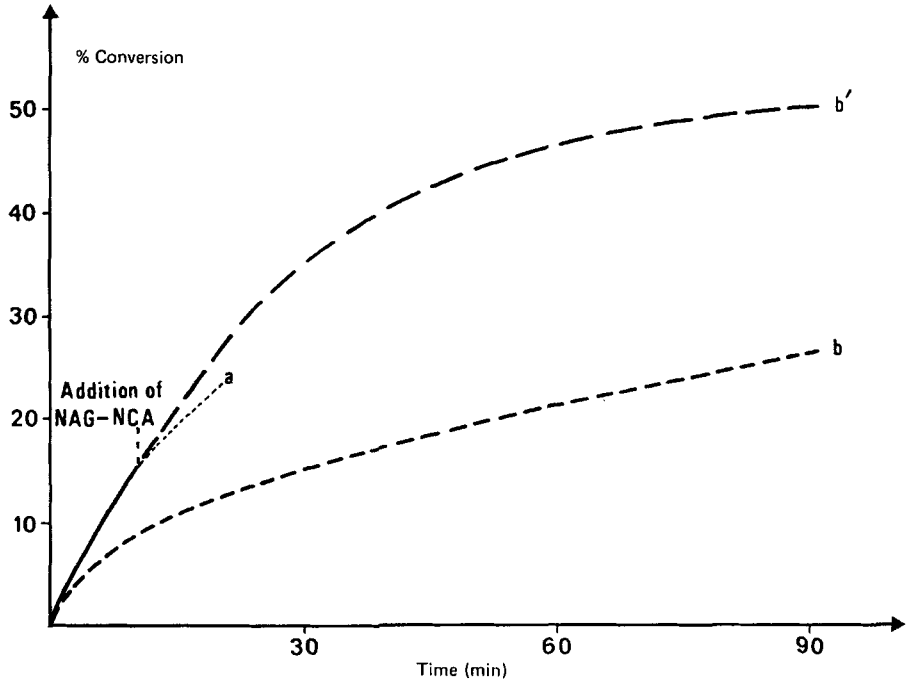


FIG. 6. Effect of NAG-NCA on polymerization of γ-BLG-NCA (0.08 mol/L) by 9-fluorenylpotassium in dioxane. (a) 9-Fluorenylpotassium (4%), (b) 9-fluorenyl potassium (4%) + NAG-NCA (4%), (simultaneous addition), (b') 9-fluorenylpotassium (4%) + NAG-NCA (4%) (addition at t = 10 min).

time as the initiator. On the contrary, it is still efficient when it is added 10 min after the beginning of the reaction (Fig. 6).

Triethylamine and n-Hexylamine

We observe an acceleration when AIB-NCA (2 mol/L in acetonitrile) is polymerized with triethylamine (3%) in the presence of NAG-NCA (3%) (Fig. 7). On the contrary, NAG-NCA slows down the polymerization when AIB-NCA (2 mol/L) is polymerized with n-hexylamine (3%), (Fig. 7).

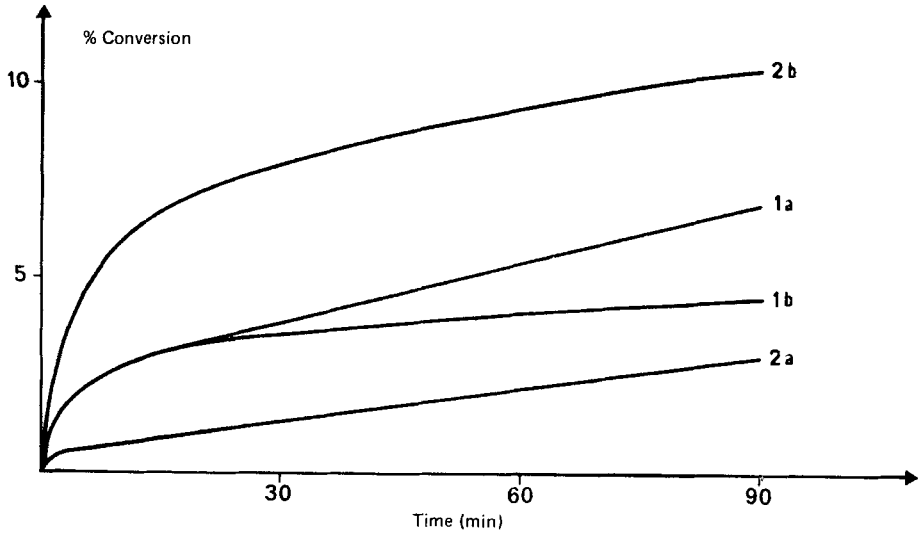


FIG. 7. Effect of NAG-NCA on polymerization of AIB-NCA (2 mol/L) by n-hexylamine (Curves 1) and triethylamine (Curves 2) in acetonitrile. (a) Triethylamine or n-hexylamine (3%), (b) triethylamine or n-hexylamine (3%) + NAG-NCA (3%).

Detection of the Acetyl Residue in the Poly-α-isobutyramide Obtained in the Presence of 1-Acetyl-3-methylhydantoin

Poly-α-aminoisobutyrate (A), prepared in the presence of triethylamine and 1-acetyl-3-methylhydantoin, gave Spectrum a, Fig. 8. Chemical shift $\delta(CH_3)_2C<$ = 1.34 ppm.

N-Acetyl-α-aminoisobutyric acid (C) gave Spectrum c, Fig. 8: $\delta(CH_3CO-)$ = 2.25 ppm; $\delta((CH_3)_2C<)$ = 1.27 ppm. This model compound did not allow detection of any acetyl residue in the polymer.

Acetylated poly-α-isobutyramide (D), which is a closer model, gave Spectrum d, Fig. 8. Three signals were absent in the original polymer: 2 (δ = 2.46 ppm) 6 (δ = 2.09 ppm), and 7 (δ = 2.21 ppm). Numbers 6 and 7 were assigned to acetic acid and the excess acetic anhydride remaining adsorbed on the polymer, respectively, while Number 2 was attributed to the acetyl end of the polymer. Note that Number 2 was also absent in a polymer prepared with triethylamine alone (data not shown in Fig. 8). Moreover, Kricheldorf [4] found the acetyl end signal at this same place (δ = 2.46 ppm) for the tertiary amine-initiated N-acetylglycylpolyglycine, N-acetylglycylpolyal-

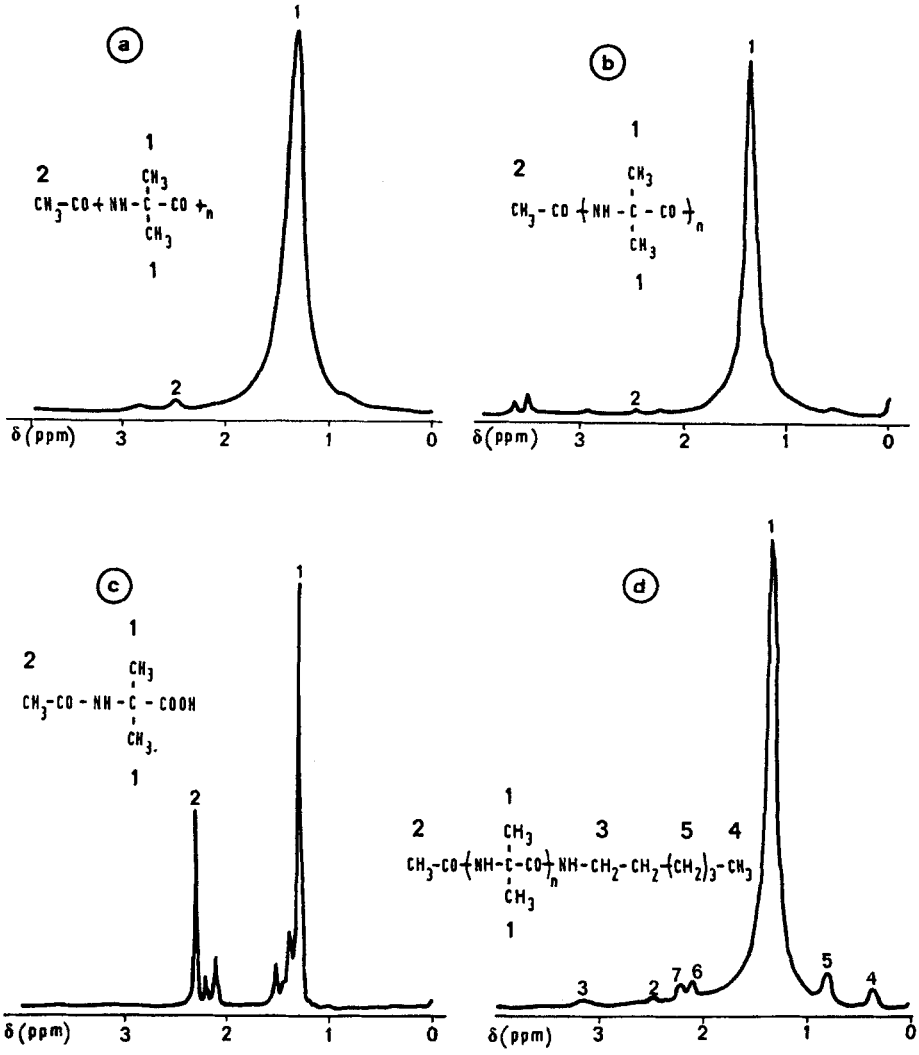


FIG. 8. ^{1}H-NMR spectra (250 MHz). Spectrum a: Poly-α-isobutyramide; initiator, triethylamine; additive, 1-acetyl-3-methylhydantoin. Spectrum b: Poly-α-isobutyramide; initiator, sodium methoxide; additive, 1-acetyl-3-methylhydantoin. Spectrum c: N-acetyl-α-aminoisobutyric acid (reference). Spectrum d: Poly-α-isobutyramide; initiator, n-hexylamine; polymer acetylated by acetic anhydride (reference).

anine, and N-acetylglycylpolyphenylalanine in trifluoroacetic acid (with TMS as an internal standard).

The acetyl signal was also detected in Spectrum a, proving that some, if not all, transacetylation takes place during polymerization of AIB-NCA with triethylamine and 1-acetyl-3-methylhydantoin. Note that even though the isolated polymer still contains some 1-acetyl-3-methylhylhydantoin ($\delta(CH_3CO)$ = 2.79 ppm, $\delta(CH_3{-}N)$ = 2.23 ppm, $\delta(CH_2)$ = 4.08 ppm for 1-acetyl-3-methylhydantoin (spectrum not shown in Fig. 8)), the corresponding acetyl signal is distinct from that of the acetyl residue in the polymer.

The acetyl residue was also found in poly-α-isobutyramide (B) similarly prepared with sodium methoxide in the place of triethylamine, Fig. 8, Spectrum b.

DISCUSSION

Three mechanisms are usually put forth for the polymerization of NCAs depending on the initiator: the mechanism of "normal" polymerization by primary amines, the activated monomer mechanism, and the carbamate anion mechanism. The multiple mechanism hypothesis [11] presumes the existence of an acido-basic Equilibrium (1) between the acidic monomer and the basic initiator (A^-Q^+),

$$NCA + A^-Q^+ \rightleftharpoons NCA^-Q^+ + AH, \qquad (1)$$

before the polymerization starts and consequently involves in the first stage three nucleophilic species capable of initiating the polymerization, i.e., the initiator anion (A^-), the NCA anion (NCA^-), and the conjugate acid of the initiator anion (AH), and later two others, i.e., carbamate anion and amino endgroup of the polymer. When the initiator used is an amine, Equilibrium (1) is replaced by

$$NCA + B \rightleftharpoons NCA^-BH^+ \qquad (2)$$

with one or two nucleophilic species, i.e., NCA anion (NCA^-) and, when protic, amine (B) (tertiary amines are not initiating species from the mechanistic point of view). Carbamate anion and amino endgroups of the resulting polymer must also be taken into account in later stages, as above. In Reactions (1) and (2), NCA anion, originally consumed by initiation and propagation, is regenerated by ionization of residual monomer to a concentration defined by the basicity of the reaction mixture of the moment, whereas the other initiating species (protic amine or initiator anion and its conjugate acid) are consumed as initiation progresses by their action. It then

follows that the three former classical mechanisms are just extremes of the multiple mechanism under the designation of "aminolytic mechanism," "NCA anion mechanism," and "initiator and carbamate anion mechanism of initiation and propagation," and that they coexist and interpenetrate to various degrees during polymerization, whichever initiator is used.

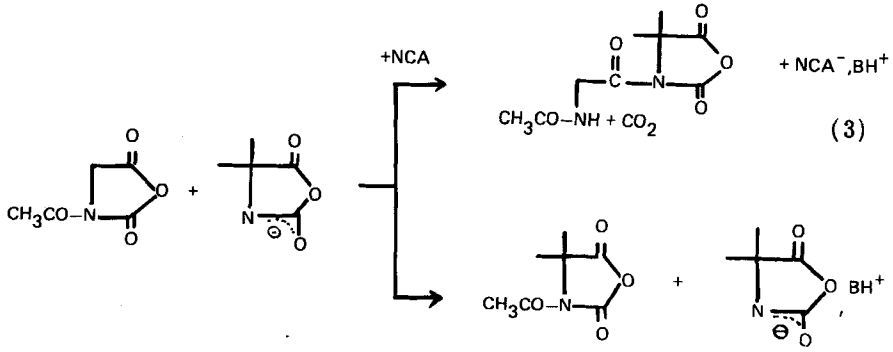
Thus, we are going to examine our experimental results, especially those related to basic salts, from the point of view of the multiple mechanism hypothesis.

Effect of N-Acetylglycine NCA Addition

A basic salt A^-Q^+ gives rise to three initiating species: A^-, AH, and NCA^-Q^+. When NAG-NCA, which is a stronger nucleophile acceptor than the monomer, is added, these three nucleophilic species attack it in preference to the monomer, and the result observed is the sum of these attacks. For tertiary amine initiation, the sole initiating species is NCA^-BH^+, while for primary amine initiation the salt NCA^-BH^+, if formed, would be in such a small amount that B can be considered as the main initiating species [7]. In this sense, primary and tertiary amine initiation can be regarded as extreme, though not ideal, models for basic salt initiation. Thus, the experiments with hexylamine and triethylamine reported here must be considered as tests and references for our basic salt study.

Triethylamine Initiation

When NCA^-BH^+ is the sole attacking species, two reactions are expected to take place according to the carbonyl (exocyclic or 5-positioned) of NAG-NCA that reacts:



Reaction (3) is a model reaction for the propagation by NCA^-. In other words, addition of NAG-NCA allows bypassing of the difficult step of initiation by NCA^-, producing an elementary acceleration. A similar process is well known for the anionic polymerization of lactams [3].

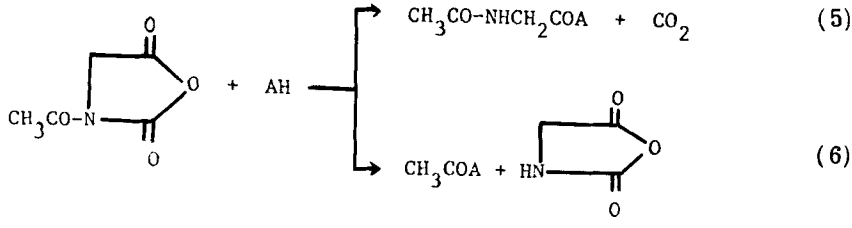
Reaction (4) is a simple transacetylation between glycine NCA and AIB-NCA, consuming NCA^-. Therefore it should normally slow down the polymerization. However, NCA^- is regenerated, and the resulting N-acetyl AIB-NCA, with a slightly different activity, can again take part in reactions similar to (3) and (4), producing in its turn an elementary acceleration as described above.

The various causes of deceleration (essentially reaction 4) are not significant since an acceleration is universally observed (Fig. 7). A similar acceleration as a result of NAG-NCA addition was indicated by Kricheldorf for the polymerization of N-unsubstituted NCAs by tertiary amines [4].

Reactions (3) and (4) should result in the incorporation of acetyl groups into the polymer. Kricheldorf [4] showed that this actually happens in the polymerizations cited above. However, initiation with the help of NAG-NCA does not prevent normal initiation through attack of the monomer by NCA anion at the same time. Thus, chains terminated by a carbamate anion or an amino endgroup should also appear [7]. Since these nucleophilic species are theoretically able to react with NAG-NCA or N-acetyl AIB-NCA, the resulting polymer chain would also carry an acetyl group on the N-end and could not be differentiated from the one formed by Reaction (3) by any method of characterization. Thus the detection of an acetyl group in the polymer obtained in the presence of NAG-NCA can be clearly related to initiation by NCA anion only when it is coupled with the observation of acceleration.

N-Hexylamine Initiation

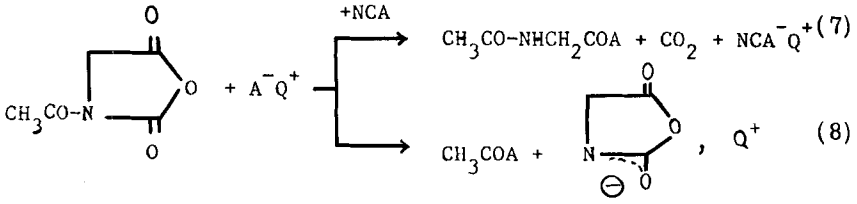
When attack of the monomer by B (n-hexylamine in the present case) is by far predominant over that by NCA anion, the acceleration effect of NAG-NCA due to this anion, if any, should be insignificant. Besides, since NAG-NCA is a stronger nucleophile acceptor than the monomer, it should be preferentially attacked by the nucleophilic initiator, Reactions (5) and (6), consuming the latter without regenerating it. The polymerization is consequently slowed down, as is shown in Fig. 7. In Reactions (5) and (6) the protic amine is represented by AH:



Sodium Methoxide Initiation

As previously said, we assume the coexistence in the initial reaction mixture of initiator anion ($A^- = CH_3O^-$), of NCA anion, and of the conjugate acid of the initiator ($AH = CH_3OH$).

When NAG-NCA chain initiator is added, NCA anion will react according to Reactions (3) and (4), and the conjugate acid of the initiator AH according to reactions (5) and (6). Similar reactions will take place with A^-:



The significance of Reactions (3) to (8) will depend on both the nucleophilicity of the respective attacking species and of the electron efficiency of the various carbonyl groups of NAG-NCA. Therefore, the significance of Reactions (3) to (8) varies with the nature of NCA and alkoxide anion A^- (methoxide anion in the present example). The kinetic contribution of AH, Reactions (5) and (6), is weak in the presence of A^- and NCA^- anions (cf. Fig. 1) and can be neglected.

Reactions (5) to (8) reduce the concentration of initiator and should therefore depress polymerization. The acceleration observed in the present case of sodium methoxide initiation indicates that the pathways involving NCA anion, Reactions (3) and (4), are favored to the detriment of that involving the initiator anion A^-.

A similar conclusion can be drawn from the results obtained in the polymerization of γ-BLG-NCA by sodium methoxide in a variety of solvents (Fig. 2).

Sodium Carboxylate Initiation

Polymerization with sodium carboxylates requires a high concentration of the salt because of its low activity.

The acceleration observed (Fig. 3) upon addition of NAG-NCA shows that the NCA anion pathway is predominant in the polymerization of AIB-NCA. Besides, the acceleration observed in the presence of NAG-NCA (Figs. 3 and 4) increases with increasing basicity of the salt (acetic acid, $pK_a = 4.75$ [10]; benzoic acid, $pK_a = 4.19$; 5,5-dimethylhydantoin-3-isobutyric acid, $pK_a = 3$ when titrated with sodium hydroxide), as expected from the NCA anion mechanism.

However, basicity of these salts is weak compared to that of triethylamine (pK_{BH^+} = 10.7 [10]) or that of sodium methoxide (methanol, pK_a = 15.5 [10]). Thus, formation of NCA anion should be less important with sodium carboxylates, leading us to assume that the acceleration observed upon addition of NAG-NCA is the consequence of a relatively weak participation of initiator anion rather than an important participation of NCA anion [11]. This would also explain the low reactivity of the three initiators, NAG-NCA exacerbating the small differences among them because of its high efficiency as a chain initiator.

The results obtained in the polymerization of γ-BLG-NCA with sodium acetate in N,N-dimethylacetamide (Fig. 5) also show that NCA anion is mainly responsible for this polymerization.

9-Fluorenylpotassium Initiator

This initiator is usually included with other basic salts, and its reactions have been examined on the same basis as those with alkoxides or carboxylates [7, 12]. For us, this is not entirely justified because of its basicity, which is much higher than that of alkoxides or carboxylates (fluorene, pK_a = 25 [13]). In its presence the corresponding part of NCA should be immediately converted into NCA anion:

$$NCA + C_{13}H_9^-K^+ \longrightarrow NCA^-K^+ + C_{13}H_{10} \qquad (9)$$

One thus expects that NAG-NCA will accelerate polymerization. Experimentally, we observe that it does so only if added after the beginning of polymerization, while it depresses the polymerization when added at the same time as the initiator (Fig. 6). It seems that 9-fluorenylpotassium reacts with NAG-NCA at the same time as with the NCA, probably with the "acidic" protons at the C-4 of the NCA ring [7] or the acetyl CH_3 group [14] to yield various kinds of condensation products (presumably of β-diketone, β-diketoamide, or β-ketoimide structure) in a way similar to the secondary reactions called "Claisen type condensation reactions" in the anionic polymerization of lactams [15]. In all cases these secondary reactions decrease the concentration of NCA anion, hence the deceleration. These secondary reactions are absent when NAG-NCA is added to the reaction mixture of fluorenylpotassium and NCA after Reaction (9).

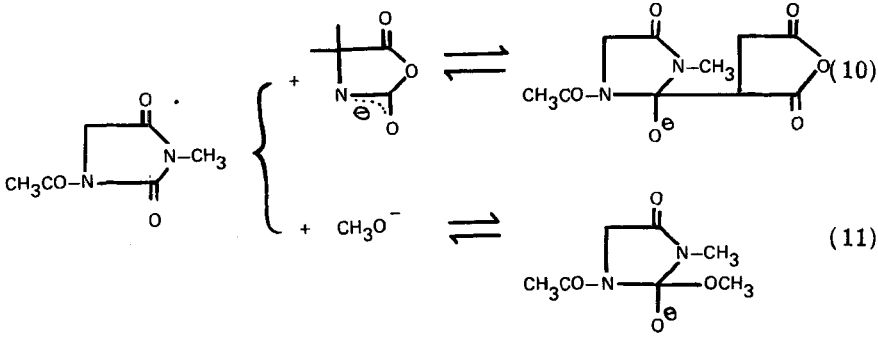
Effect of 1-Acetyl-3-methylhydantoin, 3-Acetyl-2-oxazolidone, and 1-Acetyl-2-pyrrolidone Addition

Sodium Methoxide Initiation

First, one must note that 1-acetyl-3-methylhydantoin (IV), 3-acetyl-2-oxazolidone (III), and 1-acetyl-2-pyrrolidone (II) have, respectively,

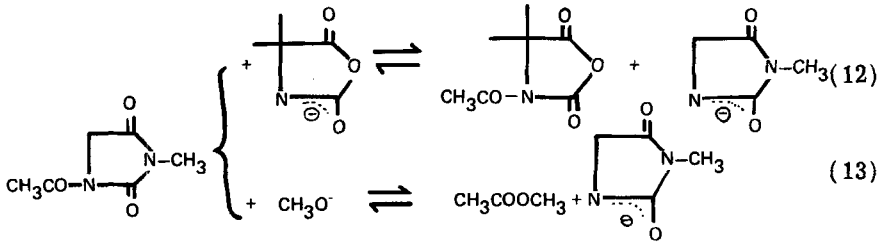
a N–CH_3 group in place of the 1-O atom in NAG-NCA (I), a CH_2 group in place of the 5-CO group, and two CH_2 groups instead of the 5-CO group and the 1-O atom, and are all less active as nucleophile acceptors, with their carbonyl groups less polarized than NAG-NCA. Moreover, unlike the NCA ring, which is easily polymerizable, polymerization of oxazolidone [16], N-methylhydantoin [17], and of their acetyl derivatives is unknown. Pyrrolidone polymerizes anionically in the presence of alkaline catalysts, but not by tertiary amines [3]. In short, their cyclic part is more stable against ring-opening (except, perhaps, for pyrrolidone) than the corresponding part of NAG-NCA. In the following discussion, we use 1-acetyl-3-methylhydantoin as an example.

The refusal of the cyclic part to open does not, however, mean the absence of interaction of the nucleophilic reagent with the electron-poor sites of the ring. Thus, 1-acetyl-3-methylhydantoin should interact with NCA anion and initiator anion at the 2-CO (and in a similar way at the 4-CO (Reactions 10 and 11).



These reactions would simply immobilize a part of the nucleophiles. As a result, polymerization would be decelerated.

Besides, as in the case of NAG-NCA, reactions of NCA anion and initiator anion with the exocyclic carbonyl group (transacetylation) must also be considered.



Equilibria (12) and (13) would occur at a point which depends on the concentration and nucleophilicity of the two anions and of the nucleophile accepting power of their acetyl derivatives (especially at the acetyl site).

Transacetylation by NCA anion (Reaction 12), if it occurs, consumes NCA anion. However, it yields an N-acetylated NCA capable of starting propagation. Besides, NCA anion should be regenerated by Equilibrium (1), in which AH represents both methanol and 3-methylhydantoin, 3-methylhydantoin having an acidity close to (and slightly lower than) that of the NCA [9]. Therefore, the kinetic effect is expected to be positive and the polymer acetylated.

On the contrary, transacetylation by CH_3O^-, Reaction (13), would uselessly consume the initiator anion and should slow down polymerization without giving an acetylated polymer. Overall, among the four reactions considered (10-13), only Reaction (12) can lead to an acceleration of polymerization, and this is the only one that proceeds via incorporation of acetyl group into the polymer.

We have verified (Fig. 8) that the polymer was acetylated when AIB-NCA was polymerized with sodium methoxide in the presence of 1-acetyl-3-methylhydantoin (see under Results), although it is difficult to say to what extent. On the other hand, we have observed (Fig. 1) a general deceleration of polymerization in the presence of our additives (except NAG-NCA).

Acetylation of the polymer is not proof in itself of transacetylation by NCA anion (Reaction 12) as indicated above. Nor can we affirm which ones among Reactions (10), (11), and (13) are responsible for the observed deceleration. However, we can say that NCA anion (from the results obtained with NAG-NCA) is present in the polymerization mixture and that the presence of methoxide anion cannot be rejected although it cannot be proved. Since the same acetylation is observed in triethylamine-initiated polymerization, and since it is accompanied by acceleration instead of deceleration (see next paragraph), we can reasonably admit that Reactions (10) to (13) actually take place on our additives, the acceleration caused by Reaction (12) being canceled by the other ones.

Triethylamine Initiation

In the polymerization of AIB-NCA with triethylamine, Sekiguchi and Froyer [9] observed that the addition of 1-acetyl-3-methylhydantoin gives rise to acceleration, contrary to sodium methoxide-initiated polymerization. A significant effect was obtained with nearly 2 mol% of the additive for 3 mol% of triethylamine, a great excess of the former being harmful to polymerization. Still, a small acceleration was observed for the addition of 10% 1-acetyl-3-methylhydantoin [18].

Triethylamine is probably not nucleophilic enough to react with 1-acetyl-3-methylhydantoin, which would explain the absence of depression due to reactions similar to Reactions (11) and (13); on the other hand, triethylamine is basic enough to ionize NCA and to give NCA^--

$N(Et)_3H^+$ in small concentration [19]. As in the case of sodium methoxide initiation, this allows transacetylation (Reaction 12) to take place as well as immobilization of NCA anion (Reaction 10). Actually, because acceleration is observed, transacetylation seems to predominate.

Detection of acetyl groups in the polymer obtained with triethylamine in the presence of 1-acetyl-3-methylhydantoin (see under Results) allowed us to verify that transacetylation by NCA anion (Reaction 12) actually took place, at least partially. It is scarcely probable that acetylation of the polymer totally results from acetylation of carbamate anion or amino endgroups of the polymer. If this were the case, the growth of these chains would be stopped and one would observe deceleration, or at least no sensible change, instead of acceleration (see above, the reaction of NAG-NCA with n-hexylamine).

Diversity of the Behavior of NAG-NCA and Related Additives

The above results as a whole are difficult to explain if one does not assume the coexistence of more than one active species, namely initiator anion, its conjugate acid, and NCA anion, in sodium methoxide-initiated polymerization, in contrast to the tertiary amine-initiated one in which NCA anion is the only active species, at least initially. According to the multiple mechanism hypothesis, the observed acceleration or deceleration has to be considered as the sum of elementary accelerations and of elementary decelerations due to the simultaneous attack of the additives by these active species.

Thus, NAG-NCA gives rise to an overall acceleration in both polymerizations (and to a deceleration in n-hexylamine-initiated polymerization), whereas 1-acetyl-3-methylhydantoin accelerates the triethylamine-initiated polymerization and decelerates the sodium methoxide-initiated one. Thus, not only does 1-acetyl-3-methylhydantoin behave differently than NAG-NCA when sodium methoxide is used, but the same compound behaves differently with sodium methoxide and triethylamine. On the precise point of the polymerization of AIB-NCA with triethylamine, it turns out that Kricheldorf [20] wrongly questioned the occurrence of transacetylation by NCA anion as well as formation of a polymer.

NAG-NCA addition did not allow the observation of any difference between triethylamine and sodium methoxide initiation. Thus, there are strong presumptions to consider that participation of methoxide anion can be observed with 1-acetyl-3-methylhydantoin precisely because it is a less appropriate model of the propagating species than NAG-NCA.

CONCLUSIONS

The results of polymerization of AIB-NCA and γ-BLG-NCA in the presence of NAG-NCA and related additives were interpreted in the

light of the multiple mechanism hypothesis. It was shown that NCA anion was mainly responsible for polymerization of these NCAs by salts of various basicity. However, direct initiation to a lesser extent by the basic salt as well as its conjugate acid cannot be wholly excluded, at least in the polymerization of AIB-NCA by sodium methoxide, in conformity with the multiple mechanism hypothesis.

ACKNOWLEDGMENTS

The authors are grateful to Professor H. R. Kricheldorf, University of Hamburg, as well as Professor J. P. Vairon and Dr M. Moreau, from this laboratory, for help and advice on the NMR work.

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Received February 26, 1985
Revision received June 22, 1985