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The Mechanism of Initiation of the Anionic Polymerization of Acrylonitrile with ^{14}C-Labeled Lithium Alkoxides in Dimethylformamide

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ABSTRACT

Investigations of the anionic polymerization of acrylonitrile in dimethylformamide initiated with ^{14}C-labeled lithium tertiary butoxide have shown that the tertiary butoxide group is not incorporated into the polymer chain. Comparison with the initiation behavior of other lithium alkoxides has indicated that the amount of incorporation of the alkoxyl groups from the anionic lithium alkoxide initiators depended on the basicity of the alkoxide group. A new initiation mechanism is proposed which involves as initiator an active center which consists of an electron donor-acceptor complex of the lithium alkoxide with the solvent dimethylformamide and the acrylonitrile monomer.

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INTRODUCTION

In recent years much attention has been paid to the clarification of the connection between the type and reactivity of active centers and their effectiveness in initiation, propagation, and termination in anionic polymerizations, especially in acrylonitrile (AN) polymerization. Primarily by quantum chemical and spectroscopic methods, it was shown [1-4] that in nonpolar solvents, when alkali alkyl compounds were used as initiators, intramolecular cyclization is an important side reaction of the anionic polymerization of AN; during the initiation step, oligomers were formed. Especially at the end of the polymerization another side reaction causes units to be introduced into the polymer chain which are colored; carbonyl groups are then formed by hydrolysis when the polymerization mixture is hydrolytically worked up with water. The polymers often show a broad molecular weight distribution and have a lower nitrogen content. Intermolecular attack of the counterion on a nitrile group or by proton abstraction from the tertiary carbon atom of another AN unit of the polymer chain followed by anionic propagation of AN from this new site results in branching of the polymer.

When lithium alkoxides were used as initiators for the polymerization of AN [5], an increased rate of polymerization was observed and a relatively higher molecular weight polymer was obtained; no oligomers were isolated.

Lithium alkoxides in solution form stable association products but only a small portion (less than 10%) was found to be active as initiating species for polymerization. The greater portion of the lithium alkoxide ion pairs of these associates complex the counterion:

$$ROM_nLi \cdot (ROLi)_{m-x} \qquad (1)$$

When the lithium cations are complexed with additional $(ROLi)_n$, no cyclization (which forms the oligomers) occurs. The degree of association (m-x) and the stability of the complexes depends upon the type of the lithium alkoxide, reaction medium (solvent and monomer), concentration of monomer and initiator, and temperature.

If the polymerization is not carried out in nonpolar hydrocarbon solvents but in highly polar solvents such as dimethylformamide (DMF), very high rates of polymerization are observed and the polymerization proceeds by a more complicated mechanism. No information is available in the literature about the behavior of the associates of lithium alkoxides in DMF in polymerization reactions.

It is well known that the associates of lithium alkoxides are quite stable in hydrocarbon solvents. Since lithium alkoxides in DMF showed relatively low effectivity as initiators, it was assumed that these associates existed also to some extent in this solvent [6]. The effectivity as initiators ($F_{Pol.}$) is defined as the ratio of the active part of the lithium alkoxide initiator to the total concentration of the lithium alkoxide added to initiate the polymerization:

$$F_{Pol.}\ (\%) = \frac{C_{I(Pol.)}}{C_{I_0}} \times 100 \tag{2}$$

Under the assumption that no chain transfer reaction occurs, we can write

$$F_{Pol.}\ (\%) = \frac{\overline{M}_{theor.}}{\overline{M}_n} \times 100 \tag{3}$$

$$\overline{M}_{theor.} = \frac{\chi \cdot C_M \cdot m}{C_{I_0}} \times a \tag{4}$$

where $\overline{M}_n$ = number-average molecular weight

$\overline{M}_{theor.}$ = theoretical molecular weight

χ = conversion

C_M = monomer concentration

a = number of active centers

m = molecular weight of monomer

In the specific polymerization systems of this work, the number-average molecular weight as determined is not free of error because of possible chain transfer and branching reactions.

It was the objective of this work to use ^{14}C-labeled lithium alkoxides as initiators to study the initiation reaction accurately. It was believed that this method of incorporation of the alkoxide group of the lithium alkoxide into the polymers could be directly determined, and this would allow us to come to a clearer understanding of the initiation reaction of AN polymerization with lithium alkoxides in DMF. The structure and basicity of the lithium alkoxides, for example, lithium tertiary butoxide (t-BuOLi) lithium isopropoxide (i-PrOLi), lithium n-propoxide (n-PrOLi), and lithium benzoxide (BeOLi), could be compared with their effectiveness as initiators, and the incorporation of the alkoxide as endgroups into AN polymers could be determined.

EXPERIMENTAL

^{14}C-Labeled lithium alkoxides were prepared by reacting pure ^{14}C-labeled alcohols gas chromatographically with lithium metal in diethyl ether or tetrahydrofuran [7-9]. For purification, the lithium alkoxides were sublimed at 0.01 mm (except BeOLi). The initiators were dissolved in dry DMF under careful exclusion of moisture and oxygen, and showed a specific activity of 8-10 R_g/mmol.

AN and DMF were purified in the usual way by distillation from calcium hydride. The concentration of the individual reagents for the polymerization reactions were as follows. Total volume of the reaction mixture: 15-20 mL with C_{AN} = mol/L and $C_{ROLi} = 2 \times 10^{-3}$ mol/L; the initial reaction temperatures were between -60 and +20°C. All operations were done at atmospheric pressure under highly purified inert gas.

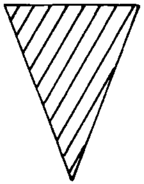
For the determination of the incorporation of ^{14}C-labeled initiators the following methods were used. (a) Gel chromatographic separation of the reaction solution into a polymer fraction containing the remaining nonpolymeric initiator fragments (Sephadex LH 20) ($E_{Pol.A}$). (b) Precipitation and reprecipitation of the polymer until the specific activity ($E_{Pol.B}$) was constant. (c) The ^{14}C activity was measured in a liquid scintillation Counter Rack beta 1215 of the LKB Wallace Co. (Sweden).

RESULTS AND DISCUSSION

The incorporation of RO endgroups from ROLi initiators into anionically prepared AN polymers has been investigated. Table 1 shows the results of experiments which indicate the amount of the RO groups of ROLi initiators introduced into the polymer chain ($E_{Pol.}$) as a function of the type of R group of the initiators. The values of $E_{Pol.B}$ are slightly lower than $E_{Pol.A}$ since small amounts of polymer were lost during the reprecipitation of the polymer. It is clear that there is a connection between the basicity of the lithium alkoxide and the degree of introduction of the RO group into the polymer. $E_{Pol.}$ for BuOLi is essentially zero. The decreased inductive effect of the alkyl group in the series from t-BuOLi to BeOLi causes an increased delocalization of the negative partial charge on the oxygen atom and consequently a decreasing basicity of the alkoxide, $RO^{\ominus}$. The result is a decreased interaction of $RO^{\ominus}$ with DMF which is also shown in the decrease of the solution and the reaction enthalpies (ΔH_R) of the ROLi's in DMF; consequently, an increased incorporation of RO at the end of the polymer chain from the initiator was observed.

These results suggest for the system ROLi/AN/DMF an initiation

TABLE 1. Incorporation of RO from Selected ROLi-Initiators into Polyacrylonitrile[a]

Initiator	Conversion (%)	$E_{Pol.A}$ (%)	$E_{Pol.B}$ (%)	RO basicity	H_R (kJ/mol)
Li t-butoxide	83	<0.3	<0.3		26.2
Li i-propoxide	65	5.6	3.6		11.7
Li n-propoxide	82	25.6	22.1		6.7
Li benzoxide	40	34.4	32.0		—

[a] Reaction temperature: 0°C.

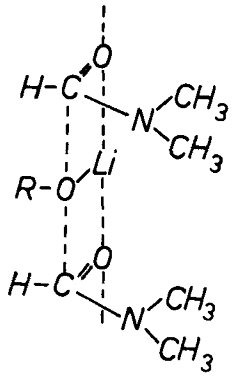
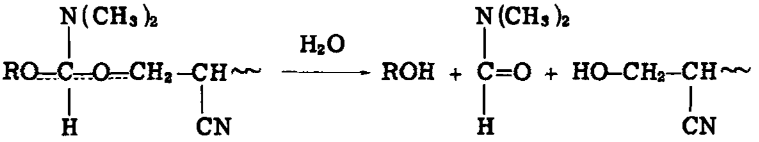


FIG. 1. Proposed complex of ROLi with DMF.

mechanism which is significantly different from previous proposals of anionic initiations of polymerization, especially of AN polymerization. The basis of this interpretation is the existence of an equilibrium between free but also associated lithium alkoxide molecules with DMF; these interactions of ROLi and DMF play a significant role in the complex formation shown in Fig. 1.

In the first case, the direct initiation of AN by RO$^{\ominus}$ proceeds by a nucleophilic addition of RO$^{\ominus}$ to the methylene group of AN and leads to incorporation of RO$^{\ominus}$ as endgroups but initially to the formation of active centers AC_1 in accordance to the established proposals of initiation observed in nonpolar solvents (Fig. 2). This mechanism for t-BuOLi initiation has been shown by NMR investigation and ^{14}C-labeled studies using t-BuOLi as initiator to be valid for the initiation of the anionic polymerization of chloral [10-12]; this mechanism in its ionic form has been discussed by us in a previous communication [13].

In the second case, the initiation seems to occur by an electron donor acceptor complex (EDA) with the direct interaction of ROLi with the solvent. The values n and x of the complex (ROLi)$_n$·DMF$_x$ depend on the basicity of the alkoxide ROLi. Favorable conditions for the coordination of the lithium counterion of the ROLi with DMF are given if the initial product of interaction is assumed to be a sandwichlike structure of the complex (Fig. 1). After synchronous rearrangements of bonds, an active center, AC_2 (Fig. 2) is formed. The EDA complex at the chain end is not stable and is ultimately hydrolyzed (Eq. 5) during the work-up with water. Consequently, no RO endgroup could be detected as no RO group incorporated into the polymer.



$$\mathrm{RO{\cdots}\underset{H}{\overset{N(CH_3)_2}{C}}{\cdots}O{\cdots}CH_2{-}\underset{CN}{CH}{\sim\sim}} \xrightarrow{\mathrm{H_2O}} \mathrm{ROH} + \mathrm{\underset{H}{\overset{N(CH_3)_2}{C}}{=}O} + \mathrm{HO{-}CH_2{-}\underset{CN}{CH}{\sim\sim}} \qquad (5)$$

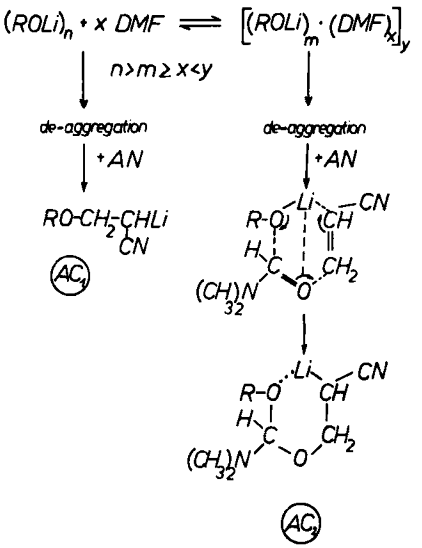


FIG. 2. Reaction mechanism of the initiation of anionic polymerization in the system ROLi/AN/DMF.

The position of the equilibrium in Fig. 2 depends on the type of R group of initiator ROLi and the reaction conditions. If t-BuOLi was used as the initiator, the initiation occurred completely through the DMF complex. With decreasing basicity of the initiator, the $RO^{\ominus}$ of ROLi was increasingly more effective for direct reaction with the AN monomer, and an increased value for $E_{Pol.}$ was the result.

The influence of the reaction temperature on the position of the equilibrium was observed when the incorporation of RO into the polymer was determined at different reaction temperatures (Fig. 3). With decreasing temperature the incorporation of the initiator increased because the initiation reaction required only a relatively small activation energy, e.g., direct initiation was favored.

As the reaction temperature was increased, the incorporation of the RO-portion of the initiator decreased and the competitive reaction which required a higher activation energy occurred at a faster rate, e.g., initiation occurred increasingly via the DMF complex.

A number of additional arguments can be made for the pathway of initiation via the DMF complex proposed in this article.

(a) After the work-up of the polymerization reaction mixture from the aqueous medium where hydrolysis can occur, OH groups were found in the polymer (Eq. 5). These endgroups have been observed in AN polymers in the order of magnitude that was expected and could be shown by their ^{14}C-labeled esterification products (reaction with ^{14}C benzoyl chloride in the presence of pyridine).

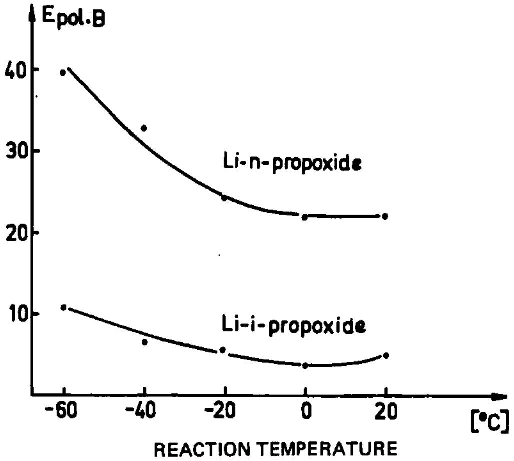


FIG. 3. Temperature dependence of the incorporation of RO groups from the ROLi initiator ($E_{Pol.}$): C_{AN} = 1 mol/L, C_{ROLi} = 2 × 10^{-3} mol/L. Time: 5 min. Conversion: 80 to 100%.

(b) According to Eq. (1), after hydrolysis of the remaining $RO^{\ominus}$ of the unused ROLi initiator, the free ^{14}C-labeled alcohol could be isolated and identified. The amount of alcohol in the solution was determined by the isotope dilution technique and separated as 3,5-dinitrobenzoate after esterification with 3,5-dinitrobenzoyl chloride. As previously shown [8, 9], the total of the amount of RO– groups incorporated into the polymer and the amount of RO– groups of the alcohol from the initiator which were not incorporated, in other words, the total amount of ^{14}C-labeled *RO– identified, was nearly 100%. According to this method, more than 99% of the t-BuOLi used for the initiation of AN polymerization and subsequent hydrolysis was found and identified at ^{14}C-labeled t-butanol.

(c) From saturated solutions of t-BuOLi in DMF, crystals could be obtained with a t-BuOLi to DMF ratio of 1:1. This complex could be purified by recrystallization from n-hexane.

(d) While NMR spectra in solution showed no indication for the existence of the postulated complex, IR spectroscopic investigation clearly showed such a complex formation. After the addition of t-BuOLi to DMF, a shift of the carbonyl band ($\nu_{C=O}$) of 20-30 cm^{-1} was found; on the other hand, upon addition of DMF to a solution of t-BuOLi in Nujol, the –O... Li–O– association band at 580 cm^{-1} disappeared.

In conclusion, using ^{14}C-labeling techniques, it was possible to clarify the reaction of ROLi addition to AN and presumably the initiation of this anionic polymerization of AN in polar solvents, e.g., DMF.

An anionic initiation mechanism can be postulated for the AN polymerization initiated by ROLi in DMF which can best be explained by a complex of ROLi/DMF/AN as the actual initiating species. This mechanism is substantially different from previous mechanisms of initiation of AN polymerization with ROLi in nonpolar hydrocarbon medium. The use of ROLi initiators of various degrees of basicities of the $RO^{\ominus}$ group confirmed the general validity of this proposal for the initiation of AN with $RO^{\ominus}$. This mechanism may be of very general value for the initiation of other monomers with $RO^{\ominus}$ in highly polar solvents, particularly carbonyl-containing solvents such as DMF.

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