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

Activated Monomers and Nucleophilic Reagents in Addition and Polymerization Reactions

T. Tsuruta[a]
[a] Department of Synthetic Chemistry Faculty of Engineering, University of Tokyo, Tokyo, Japan

To cite this Article Tsuruta, T.(1975) 'Activated Monomers and Nucleophilic Reagents in Addition and Polymerization Reactions', Journal of Macromolecular Science, Part A, 9: 5, 687 — 702
To link to this Article: DOI: 10.1080/00222337508065889
URL: http://dx.doi.org/10.1080/00222337508065889

J. MACROMOL. SCI.—CHEM., A9(5), pp. 687-702 (1975)

Activated Monomers and Nucleophilic Reagents in Addition and Polymerization Reactions

T. TSURUTA

Department of Synthetic Chemistry
Faculty of Engineering
University of Tokyo
Hongo 7-3-1, Bunkyo-ku, Tokyo, Japan

ABSTRACT

A number of examples of addition and polymerization reactions is presented with special emphasis on the chemical behaviors of activated monomers and/or activated nucleophilic reagents. Lithium alkoxyethanolate forms a complex with lithium alkyl. Spectroscopic studies showed this complex to possess agent-separated ion pairs. The nature of the complex is characterized by the enhanced reactivity of styrene in the copolymerization reaction with butadiene initiated by the complex. Magnesium alkyl can be sufficiently activated by magnesium alkoxyethanolate to polymerize styrene and diene. Aluminum alkyl and zinc alkyl are able to induce the anionic polymerization of vinyl ketones, but not of unsaturated esters or nitriles. Aluminum or zinc alkoxyethanolates fail to activate their corresponding metal alkyls. Bipyridyl, sparteine, triphenylphosphine, HMPT, and related Lewis bases, however, activate aluminum alkyl enough to react with carbon-carbon double bonds of the unsaturated esters and nitriles. Crotononitrile can be polymerized by the

AlR_3-HMPT system to form a colorless polymer, where possible side reactions between CN and AlR_3 are prevented by HMPT. Mutual activation through complex formation is confirmed by a model system of a vinyl ketone with organozinc compounds. AlR_3-HMPT does not polymerize vinyl ketones because of a lack of complex formation. N-Carboxy-α-alanine anhydride (NCA) can be polymerized with zinc alkyl as initiator. The formation of activated NCA by proton abstraction from the NH group is shown to be the essential stage for polymerization. Zinc alkyl is also activated by conventional acid anhydrides. The propylene oxide ring can be cleaved with the ZnR_2-phthalic anhydride system, which is the initiation step in the alternate copolymerization between propylene oxide and the acid anhydride. The propagation mechanism of the CO_2-epoxide copolymerization is also discussed.

INTRODUCTION

Since the brilliant success of the Ziegler-Natta polymerization, a variety of research on polymerization reaction has been carried out with various types of organometallic compounds or nucleophilic reagents as initiator. We compiled a large collection of experimental results in early 1960s, but there were few studies directed to systematizing the structure-reactivity relationship of vinyl monomers and initiators in anionic polymerization. In 1961 the author proposed a correlation diagram which systematizes the reactivities of nucleophilic initiators in terms of their ability to effectuate anionic polymerizations of a group of vinyl monomers [1]. For instance, magnesium alkyl was ranked as an initiator possessing a smaller reactivity than lithium alkyl because a group of hydrocarbon monomers such as styrene and butadiene were polymerized by lithium alkyl but not by magnesium alkyl. The reactivity of aluminum alkyl was still smaller because a group of acrylic esters such as methyl methacrylate and methyl acrylate were polymerized by magnesium alkyl but not by aluminum alkyl.

Significant changes in the reactivity of organometallic compounds have recently been observed when an appropriate complexing agent is coupled with the organometallic compounds. Magnesium alkyl, for example, could be sufficiently activated by magnesium alkoxyethanolate to polymerize styrene and diene. A part of the results of studies on the activated nucleophilic reagents was discussed briefly in another review article [2].

In addition to the activated nucleophilic reagents, the formation of activated monomers was confirmed in some reactions. Vinyl ketone, for instance, must be activated by the coordination of aluminum alkyl (or zinc alkyl) to accept the nucleophiles at the conjugated double bond.

Examples of activated nucleophilic reagents and for activated monomers have also been found in the polymerization reactions of ring compounds. This paper reviews the recent results of the author's studies with special reference to the chemical behaviors of activated nucleophilic reagents and activated monomers in the elementary reactions of the polymerization of vinyl and ring compounds.

ALKOXYETHANOLATE AS A COMPLEXING AGENT

The reactivity of n-BuLi—$CH_3OCH_2CH_2OLi$ in toluene is characterized by the enormous enhancement of reactivity of styrene in the copolymerization reaction with butadiene [3]. Neither $CH_3OCH_2CH_2OCH_3$ nor $LiOCH_2CH_2OLi$ exhibits such an enormous enhancement of styrene reactivity as the complexing agent. An aminoethanolate showed a similar reactivity to $CH_3OCH_2CH_2OLi$ as the complexing agent [4].

Measurements [5] of the electronic spectra of 1,1-diphenyl-n-hexyllithium (DPHLi) in cyclohexane in the presence of varying quantity of $CH_3OCH_2CH_2OLi$ showed a considerable bathochromic shift (from 413 to 490 nm) in the absorption maximum as the [OLi]/[CLi] ratio increased from 0 to 2. No pronounced shift, however, was observed in the range of the [OLi]/[CLi] ratio higher than 2. The results suggest the formation of a one to two complex between DPHLi and $CH_3OCH_2CH_2OLi$.

It was also found in the electronic spectrum of one to two system of 9-fluorenyllithium—$CH_3OCH_2CH_2OLi$ that the peak assignable to the contact ion pairs has virtually disappeared, the only peak observed at 373 nm being in agreement with that expected for the solvent (or coordination agent)-separated ion pairs.

With the use of the lithium methoxyethanolate complex in a catalytic amount, diphenylmethane was easily butenylated on reacting with butadiene to form predominantly 5,5-diphenyl-cis-2-pentene (DPPE) [6]:

Metallation: $Ph_2CH_2 + n\text{-}BuLi{\cdot}D \longrightarrow Ph_2CHLi{\cdot}D + nBuH$ (1)

Butenylation: $Ph_2CHLi{\cdot}D + C_4H_6 \longrightarrow Ph_2CH(C_4H_6)Li{\cdot}D$ (2)

Transmetallation: (recycle)

$Ph_2CH(C_4H_6)Li{\cdot}D + Ph_2CH_2 \longrightarrow Ph_2CH(C_4H_6)H + Ph_2CHLi{\cdot}D$ (3)

where D is a complexing agent such as $CH_3OCH_2CH_2OLi$.

Table 1 shows the main feature of reactivity of the lithium methoxyethanolate complex in comparison with two other complex systems. A high yield of DPPE, despite of the low matallation yield, was characteristic with n-BuLi—$CH_3OCH_2CH_2OLi$ as the catalyst.

Magnesium alkyl can also be activated by magnesium alkoxyethanolate [7]. For instance, an equimolar mixture of n-Bu_2Mg with $CH_3OCH_2CH_2OH$ is capable of initiating styrene polymerization, in contrast with the lack of the ability of n-Bu_2Mg alone. According to a study on the influence of the added amount of $CH_3OCH_2CH_2OH$ on the extent of styrene polymerization while keeping the feed concentration of n-Bu_2Mg constant, the conversion to polystyrene was increased enormously under the condition of [O-Mg]/[C-Mg] = 3.

TABLE 1. Comparison of Reactivity of Three Types of Activated BuLi System[a] [6]

Complexing agent	Molar[b] ratio	Metallation yield (%)	DPPE yield (%)
$CH_3OCH_2CH_2OLi$	2	16	62
TMEDA	2	100	31
HMPT	2	37	80

[a] Reaction between diphenylmethane and butadiene.

[b] Molar ratio = [complexing agent]/[BuLi].

Colorless precipitates were formed from a mixture of n-Bu_2Mg and 2-methoxyethanol. The precipitates were recrystallized to colorless prisms, the analysis of which showed the composition Mg:n-Bu:$CH_3OCH_2CH_2O$:dioxane = 2.0:1.06:3.05:1.0, in agreement with the formula of n-$BuMgO\text{-}CH_2CH_2OCH_3 \cdot Mg(OCH_2CH_2OCH_3)_2 \cdot$ dioxane. Tetrafurfuryl alcoholate (THFA) was an excellent complexing agent for magnesium alkyl [8]. For instance, 100% conversion was obtained at -70°C within 1 min in the polymerization of styrene with $[C_6H_5CH_2Mg(THFA)][(THFA)_2Mg]$ as initiator, contrary to the very poor reactivity of $[C_6H_5CH_2MgOCH_2CH_2OCH_3]\text{-}[(CH_3OCH_2CH_2O)_2Mg]$. The THFA complex also induced the rapid polymerization of butadiene at -70°C to form a polymer consisting of more than 90% of 1,2-enchainment. With the magnesium methoxyethanolate complex, on the other hand, practically no polymer was obtained after a 4-day reaction at temperatures as high as 50°C. An electronic spectrum of the $[C_6H_5CH_2Mg(THFA)][(THFA)_2Mg]$ system showed λ_{max} at 458 nm, suggesting the formation of a coordination agent separated ion pairs.

LITHIUM AMIDE-SECONDARY AMINE COMPLEXES

A stereospecific addition reaction was found to take place when lithium diethylamide was reacted with butadiene in cyclohexane [9]. It was noted in this reaction that at least 2 moles of free amine should be present in the reaction system to activate 1 mole of the lithium amide to add to the butadiene double bonds. The formation of the two to one complex, $2R_2NH.R_2NLi$, was indicated by the results of IR and NMR spectra. The overall reaction scheme of the addition reaction is depicted as

$$Et_2NLi + 2Et_2NH \longrightarrow Et_2NLi \cdot 2Et_2NH \tag{4}$$

$$\begin{tikzcd}[column sep=small]
Et_2NLi \cdot 2Et_2NH + C_4H_6 \arrow[r, "k"] & Et_2NC_4H_6Li \cdot 2Et_2NH \\
Et_2NC_4H_6Li \cdot 2Et_2NH + Et_2NH \arrow[r] & Et_2NCH_2{-}CH{=}CH{-}CH_3 + Et_2NLi \cdot 2Et_2NH \arrow[ul, bend left, "\text{(recycle)}"']
\end{tikzcd}$$

(5), (6)

(cis 98 to 99%)

Kinetic studies revealed that the rate (v) of the addition reaction was expressed as

$$v = k[A][\text{butadiene}] \tag{7}$$

where [A] is the concentration of the one to two complex. For diethylamine, k was 8.5×10^{-4} [liter/(mole)(sec)]; for diisobutylamine k was 2.4×10^{-3} [liter/(mole)(sec)].

Kinetics similar to Eq. (7) was obtained in the addition reaction of diethylamine to styrene [10]. In order to compare the reactivity of lithium diethylamide with that of lithium alkyl, the reactivity of styrene toward the lithium amide was examined in the presence of butadiene. It is seen in Table 2 that the presence of butadiene has no effect on the reactivity of styrene in contrast to the reaction with lithium alkyl. The mechanism of the stereospecific addition reaction of the lithium diethylamide complex to butadiene seems to be different from the usual stereospecific addition of lithium alkyl in hydrocarbon solvents.

ACTIVATION OF ALUMINUM ALKYL WITH LEWIS BASES

Contrary to lithium and magnesium alkyls, aluminum or zinc alkyl was not activated by the corresponding alkoxyethanolates. Bipyridyl (Bipy), triphenylphosphine (PPh_3), sparteine (Spar), HMPT, and some other Lewis bases activated aluminum (or zinc) alkyl enough to react with carbon-carbon double bonds of unsaturated esters and nitriles [11]. Among several $AlEt_3$-Lewis base complexes investigated, the $AlEt_3$ complex with bidentate ligand or with monodentate ligand of sufficiently high basicity showed high catalytic activity for the polymerization of AN and MMA. $AlEt_3$ and rigid bidentate Lewis bases such as Bipy and Spar form an unstable equimolar five-coordinated complex, and the complex is stabilized to assume a six-coordinated structure by the coordination of another complex or solvent to its sixth coordinate site. When monomers are present along with the aluminum complex, some of the ligands at the sixth coordination site are replaced with monomer molecules, which is the preliminary stage for the initiation reaction of polymerization [12].

The electronegativity, χ, of Al and Zn in $AlEt_3$ and $ZnEt_2$ was estimated, respectively, from the differences between the chemical

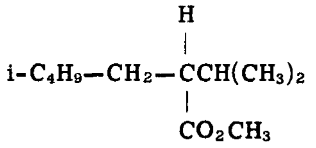
TABLE 2. Second-Order Rate Constants of Addition Reaction of $Et_2NLi.2Et_2NH$ Complex with Styrene and Butadiene[a] [10]

$\frac{[Et_2NH]_0}{[Et_2NLi]_0}$	Styrene, $k_s \times 10^3$ [liter/(mole)(sec)]	Butadiene, $k_b \times 10^3$ [liter/(mole)(sec)]	Styrene, $k_s \times 10^3$ [liter/(mole)(sec)]	Butadiene, $k_b \times 10^3$ [liter/(mole)(sec)]
3.0	-	0.85	-	-
10	1.6	1.4	1.5	1.6
15	2.0	-	-	-
28	2.6	-	-	-

[a] In cyclohexane at 50°C.

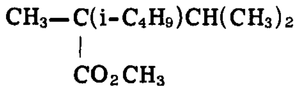
shifts of their methyl and methylene protons, $\Delta CH_3{-}CH_2$, in NMR spectra. The coordination of Bipy or PPh_3 to $AlEt_3$ makes the electronegativity of Al decrease. The coordination of Bipy to $ZnEt_2$ causes the electronegativity of Zn in the complex to increase, which may suggest a possible role of the back donation from the Zn d-orbital to the Bipy π-orbital. Compared to the Al complexes, the zinc complexes showed a much smaller activity as initiators for MMA polymerization.

Model reactions were studied with methyl α-isopropylacrylate to elucidate the initiation mechanism, because the α-isopropylacrylate has been shown to be nonpolymerizable. Two addition products, I and II, were isolated from a reaction mixture of α-isopropylacrylate and $(i\text{-}C_4H_9)_3Al$-Bipy. It was also confirmed that only one isobutyl group of $(i\text{-}C_4H_9)_3Al$ has entered the addition reaction, even in the presence of excess (20 times) methyl α-isopropylacrylate [12].



$$i\text{-}C_4H_9{-}CH_2{-}\underset{\displaystyle CO_2CH_3}{\overset{\displaystyle H}{C}}CH(CH_3)_2$$

I



$$CH_3{-}\underset{\displaystyle CO_2CH_3}{C}(i\text{-}C_4H_9)CH(CH_3)_2$$

II

Methyl crotonate undergoes an isomerized dimerization in the presence of a catalytic amount of the AlR_3-Spar complex [13]. With the aid of an α-deuterated methyl crotonate, it was confirmed that the reaction starts with proton abstraction from the β-methyl group of the crotonate. From the facts that AlR_3 by itself did not dimerize methyl crotonate and that the dimer of methyl crotonate obtained by the AlR_3-Spar complex showed optical activity, it is concluded that the coordination of Spar to AlR_3 not only activates the Al—C bond but also affords a chiral structure to the environment around the aluminum species [14].

From the results stated above, it was concluded that AlR_3-Lewis base complexes are capable of abstracting hydrogen from monomer molecules. Thus, in the polymerization of AN and methyl acrylate by an AlR_3-Lewis base complex, the initiation reaction and the chain transfer reaction may also occur partially through the abstraction of the somewhat acidic α-hydrogen of the monomer [14].

Equilibrium constants for the complex formation between $AlEt_3$ and several Lewis bases were estimated from the IR data of these systems. A parallel correlation was found between the equilibrium constants and the anionic reactivity of the binary systems [15]. HMPT exhibited a very unique behavior. Crotononitrile can be polymerized by $AlEt_3$ in HMPT to form a colorless polymer. The formation of the colorless polycrotononitrile indicates that possible side reactions between nitrile group and aluminum alkyl have been excluded because all of the coordination sites of aluminum are occupied by the strong coordination of HMPT. The behavior of the double bond of crotononitrile toward the AlR_3-HMPT system can reasonably be understood in terms of the concept proposed by Tsuruta [16].

Methyl isopropenyl ketone was not polymerized with the AlR_3-HMPT system. Since methyl isopropenyl ketone is easily polymerized with AiR_3 alone, HMPT seems to deactivate the aluminum alkyl in contrast to the case of crotononitrile. As stated in the next section, vinyl ketone must be activated by the coordination of AlR_3 (or ZnR_2) to accept nucleophilic reagents at the conjugated double bond.

MUTUAL ACTIVATION IN VINYL KETONE-ORGANOZINC COMPOUND SYSTEM

Anionic polymerization of phenyl vinyl ketone (PVK) was carried out in toluene at 0°C by the use of an initiator, enthylzinc 1,3-diphenyl-1-pentene-1-olate (ZC), which possesses the same structure as the growing chain end of PVK in $ZnEt_2$-initiated polymerization [17, 18]. Gas volumetric analysis confirmed that the ethyl-zinc bond in ZC, $C_6H_5(C_2H_5)CHCH{=}C(C_6H_5){-}OZnC_2H_5$, was kept intact during the polymerization process.

A unimodal molecular weight distribution was found in the polymer obtained. The polymerization system exhibited a "living characteristic" with an initiator efficiency being 1.0. The reactions between ZC and PVK were kinetically traced under various conditions. Rate analysis showed a second-order dependence with respect to the concentration of ZC. The second-order dependence of zinc alkyl was previously observed in the reaction between vinyl ketone and dibutylzinc [19]. Tsuruta suggested a concerted mechanism for this addition reaction. The facts that ZC exhibits the highest reactivity in toluene and that its reactivity decreases in polar solvents or by the addition of Lewis bases seem to support the above mechanism.

Experimental evidences for complex formation have recently been obtained by use of a model system consisting of benzalacetophenone

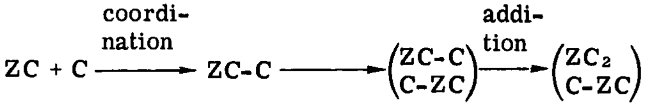
(C) and ZC. Benzalacetophenone is sparingly soluble in cyclohexane, whereas a mixture of C and ZC is easily soluble in the same solvent, suggesting a significant interaction to be operative between C and ZC. The complex formation was also suggested by the UV absorbance at 302 nm of the binary system of C and ZC in cyclohexane. When the ratio [C]/[ZC] was changed, a break of linearity in the UV absorbance was observed at a one to one mole ratio. In the light of the results of cryoscopic measurements in cyclohexane, it is plausible to assume that the ZC-C species were present as a dimeric form [20].

In the range of larger concentrations, ZC could undergo an addition reaction with benzalacetophenone to form ZC_2:

$$ZC + C_6H_5CH{=}CHCOC_6H_5 \longrightarrow$$

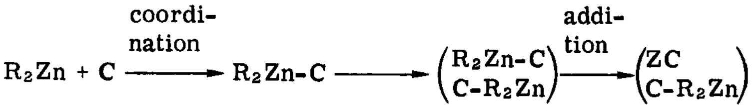
$$C_6H_5CH(Et){-}CH(COC_6H_5){-}CH(C_6H_5){-}CH{=}C(C_6H_5)OZnEt \qquad [ZC_2]$$

A series of studies on the addition reaction were carried out by changing the C/ZC ratio and other conditions. The results obtained are 1) the maximum percent conversion of reaction did not exceed 50% with respect to the minor component C or ZC, and 2) the reaction proceeded according to the second order of ZC concentration. These results can be interpreted in terms of the formation of dimeric ZC-C or ZnR_2-C species [20].



$$ZC + C \xrightarrow{\text{coordination}} ZC\text{-}C \longrightarrow \begin{pmatrix} ZC\text{-}C \\ C\text{-}ZC \end{pmatrix} \xrightarrow{\text{addition}} \begin{pmatrix} ZC_2 \\ C\text{-}ZC \end{pmatrix}$$

III IV V



$$R_2Zn + C \xrightarrow{\text{coordination}} R_2Zn\text{-}C \longrightarrow \begin{pmatrix} R_2Zn\text{-}C \\ C\text{-}R_2Zn \end{pmatrix} \xrightarrow{\text{addition}} \begin{pmatrix} ZC \\ C\text{-}R_2Zn \end{pmatrix}$$

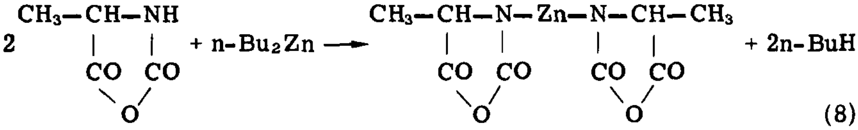
VII VIII IX

The mutual activation of vinyl ketone and the organozinc compound in IV or VIII should be the essential step for the coordination-addition type reaction.

The ^{13}C shieldings of β-carbon atom in olefinic double bonds of butadiene-type monomers were measured in 10% cyclohexane solution; δ_C values (ppm from TMS) are $CH_2{=}CH{-}CH{=}CH_2$ (119.16), $CH_2{=}CHCOCH_3$ (129.05), $CH_2{=}CHCOOCH_3$ (131.66), and $CH_2{=}CHCN$ (138.21). These NMR data are nicely correlated with the Hammett substituent constants, but they are not compatible with the reactivity of these monomers toward organozinc compounds. The reactivity of chemical species operative in the coordination-addition type reaction should not be directly correlated with spectroscopic data on the "free" monomers or "free" nucleophilic reagents.

MODE OF ACTIVATION IN SOME RING-OPENING POLYMERIZATIONS

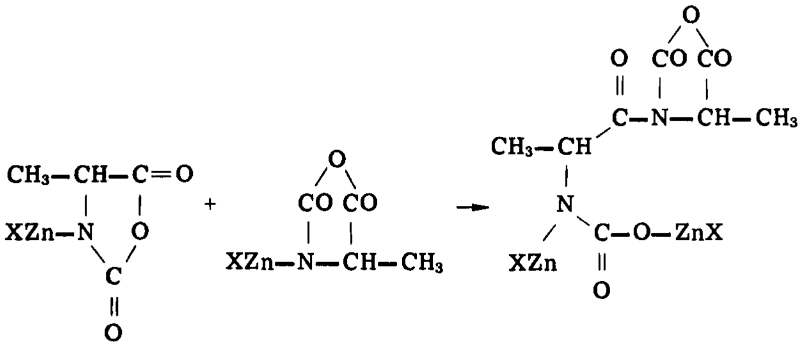
The ring-opening polymerization of N-carboxy-α-amino acid anhydride (NCA) initiated by zinc alkyl affords us another example of the activated monomers [21]. In the reaction between n-Bu$_2$Zn and DL-alanine NCA, it was confirmed that the proton abstraction reaction took place rapidly and quantitatively, no sign of the occurrence of the carbonyl addition being detected:



XI

(8)

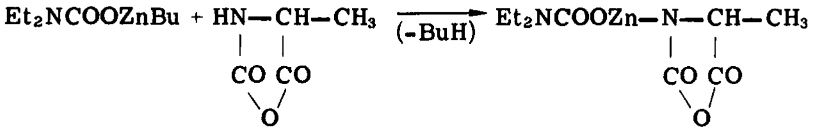
When n-Bu$_2$Zn was mixed with an equimolar mixture of DL-alanine NCA and sarcosine NCA in a 3 to 10 mole ratio, the proton abstraction reaction from the alanine NCA took place rapidly in the first stage. The IR spectra of the reaction mixture showed that the concentration of DL-alanine NCA decreased gradually with time in contrast with the unchanged concentration of sarcosine NCA. This result suggested that XI was not able to add directly to the carbonyl group of free DL-alanine NCA as well as to sarcosine NCA. An interpretation was made in terms of a reaction between the activated NCA's themselves:



(9)

XII

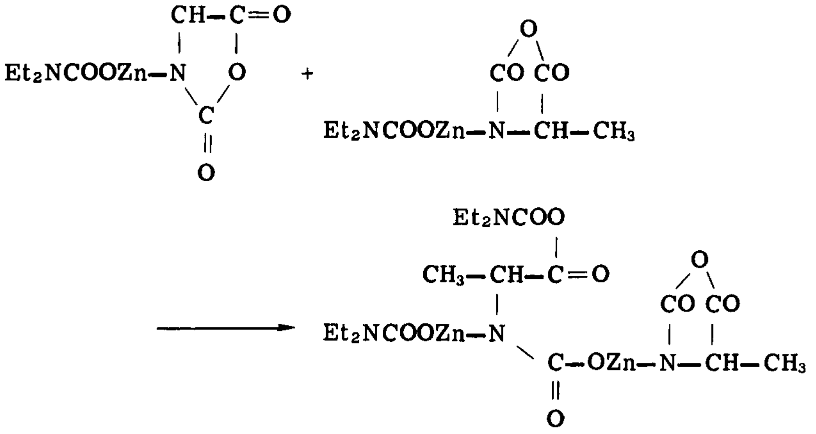
n-Butylzinc-N,N-diethylcarbamide (BZC), a model compound for the growing chain end of the NCA polymerization, exhibited no reactivity toward sarcosine NCA. The first stage of the reaction of BZC with DL-alanine NCA was shown to be a proton abstraction (or metallation) reaction:



(10)

XIII

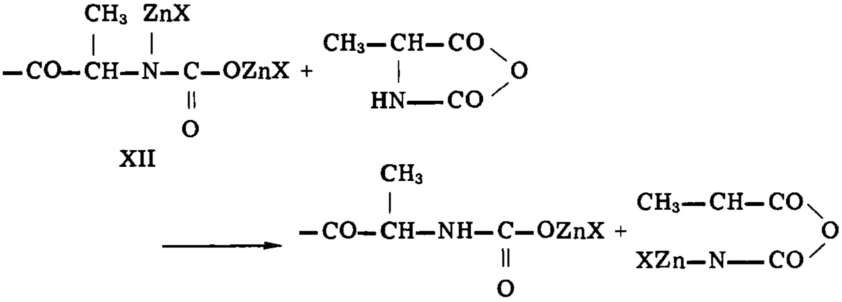
XIII was activated enough to accept the nucleophilic attack at the carbonyl-carbon in the 5-position.



(11)

XIV

In the reaction system of polymerization initiated by R_2Zn or BZC, the activated monomer molecules should be regenerated from XII or XIV:



XII

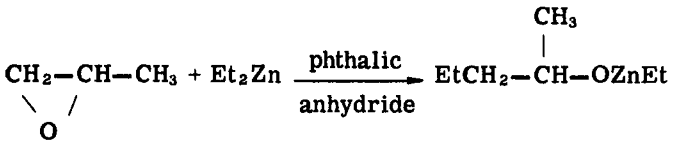
(12)

The acidity of the —NH—COOZnX group in XII is expected to be lower than that of NH in NCA owing to the electropositive nature of the Zn atom in the carbamate group.

The concept of "an activated monomer" has been advanced for the elucidation of the mechanism of NCA polymerization initiated by strong bases, in which "an activated NCA" was assumed to add to the carbonyl group of free NCA molecules [22-24]. Seeney and Harwood [24a], however, have recently shown that both weak and strong base initiated polymerizations of NCA proceed through the attack of carbamate ion as the propagating species onto free NCA molecules. It should be noted that copolymerization between sarcosine NCA and DL-alanine NCA was caused with tertiary amines or alkali metal alkoxide, but not with dialkylzinc. The different behaviors of the strong bases and zinc alkyl in the copolymerization are also interpreted in terms of the postulated mechanism discussed above.

N-Carboxyl-α-amino acid anhydride (NCA) could be copolymerized with propylene oxide by means of dialkylzinc or trialkylaluminum as initiator [25]. The copolymers formed seem to contain many kinds of linkages such as amide, ester, ether, and urethane in the polymer chain. There were, however, significant differences between the structures of Copolymers XV and XVI formed with R_2Zn and R_3Al, respectively, as initiator. The IR spectrum of Copolymer XV indicated the presence of a considerable amount of peptide block. On the other hand, Copolymer XVI seemed to contain urethane linkages. It was also confirmed that strong bases such as sodium methoxide caused only homopolymerization of NCA even in the presence of propylene oxide.

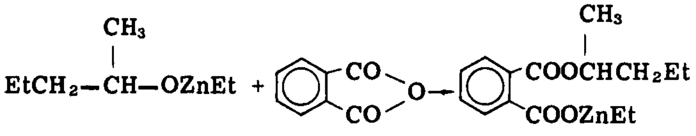
A previous study showed that dialkylzinc could induce alternating copolymerization of phthalic anhydride and propylene oxide at room temperature [26]. This result is to be noted because homopolymerization of either of these monomers is not effectuated by dialkylzinc alone in hydrocarbon or in ether. Later studies revealed that ZnR_2 is activated by the complexation with phthalic anhydride [27]. The activated R_2Zn cleaved the $O-CH_2$ bond of propylene oxide to form 2-pentanolate (XVII). The nature of the complex of phthalic anhydride is presumably very similar to $[ZnR_2-C]$ as stated above.



$$\underset{\diagdown\;O\;\diagup}{CH_2-CH}-CH_3 + Et_2Zn \xrightarrow[\text{anhydride}]{\text{phthalic}} EtCH_2-\overset{\overset{CH_3}{|}}{CH}-OZnEt \qquad (13)$$

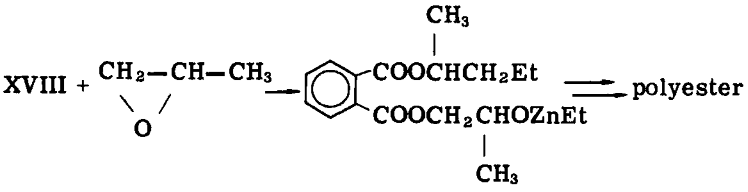
XVII

XVII reacts selectively with phthalic anhydride to form XVIII, which reacts in turn with propylene oxide to form IX. Since carbon dioxide is one of the acid anhydrides, it was expected that there would be a series of reactions similar to Eqs. (14) and (15) when CO_2 was used as the comonomer. An alternating copolymerization between CO_2 and epoxides was found possible with the use of the ZnR_2-H_2O system as initiator [28]. Contrary to phthalic anhydride, CO_2 could



(14)

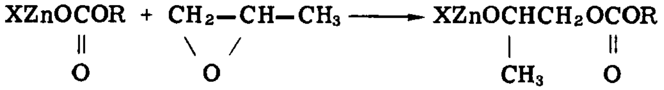
XVII XVIII



(15)

IX

not activate ZnR_2 enough to cleave the epoxide ring. According to later studies, binary systems involving primary amine, dihydric phenol, aromatic dicarboxylic acid, or aromatic oxycarboxylic acid as the partner component with ZnR_2 formed the most effective initiators for copolymerization [29]. These initiator systems are characterized by the repetition of ZnO (or ZnN) linkages [30]. The ZnR_2-methanol system has no activity, though the methanol system was one of the most excellent initiators for homopolymerization of propylene oxide [30]. The difference in the catalytic behaviors of the various types of zinc compounds can be interpreted in terms of changes of reactivity in the Zn—OCOOR bond toward epoxide in response to variation of the structure of X [31].



$$XZnO\underset{\underset{O}{\|}}{C}OR + \underset{\diagdown\, O\, \diagup}{CH_2{-}CH}{-}CH_3 \longrightarrow XZnO\underset{\underset{CH_3}{|}}{C}HCH_2O\underset{\underset{O}{\|}}{C}R \qquad (16)$$

This reaction should be the "key step" for the copolymerization with epoxide, the ZnR_2-methanol system having been confirmed as reacting readily with CO_2 in a way similar to the ZnR_2-water system. The repetition of ZnO linkages in X seems to favor the "key" reaction, though the mechanism of activation has not been detailed.

REFERENCES

[1] T. Tsuruta, *Kobunshi no Gosei (Synthesis of Macromolecules)*, Kagaku-Dojin, Kyoto, 1961, p. 54; T. Tsuruta and K. F. O'Driscoll, *Structure and Mechanism in Vinyl Polymerization*, Dekker, New York, 1969, p. 31.

[2] T. Tsuruta, *Progr. Polym. Sci., Japan*, **3**, 2 (1972).

[3] T. Narita and T. Tsuruta, *Kogyo Kagaku Zasshi*, **72**, 994 (1969); T. Narita, A. Masaki, and T. Tsuruta, *J. Macromol. Sci.—Chem.*, **A4**, 277 (1970).

[4] T. Narita, M. Kazato, and T. Tsuruta, *Ibid.*, **A4**, 885 (1970).

[5] T. Narita and T. Tsuruta, *J. Organometal. Chem.*, **30**, 289 (1971).

[6] T. Yamaguchi, T. Narita, and T. Tsuruta, *Polym. J.*, **3**, 573 (1972).

[7] T. Narita, T. Yasumura, and T. Tsuruta, *Ibid.*, **4**, 421 (1973).

[8] T. Narita, Y. Kunitake, and T. Tsuruta, *To Be Published*.

[9] N. Imai, T. Narita, and T. Tsuruta, *Tetrahedron Lett.*, **38**, 3517 (1971); *Bull. Chem. Soc. Japan*, **46**, 1242 (1973).

[10] T. Narita, T. Yamaguchi, and T. Tsuruta, Bull. Chem. Soc. Japan, 46, 3825 (1973).

[11] M. Ikeda, T. Hirano, and T. Tsuruta, Makromol. Chem., 150, 127 (1971).

[12] M. Ikeda, T. Hirano, S. Nakayama, and T. Tsuruta, Ibid., 175, 2775 (1974).

[13] M. Ikeda, T. Hirano, and T. Tsuruta, Tetrahedron Lett., 43, 4477 (1972).

[14] M. Ikeda, T. Hirano, and T. Tsuruta, Tetrahedron, 30, 2217 (1974).

[15] M. Ikeda, T. Hirano, and T. Tsuruta, To Be Published.

[16] T. Tsuruta and Y. Yasuda, J. Macromol. Sci.—Chem., A2, 943 (1968); T. Tsuruta, Progr. Polym. Sci. Japan, 3, 39 (1972).

[17] R. Tsushima and T. Tsuruta, Makromol. Chem., 166, 325 (1973).

[18] R. Tsushima and T. Tsuruta, J. Polym. Sci., Polym. Chem. Ed., 12, 183 (1974).

[19] Y. Kawakami, Y. Yasuda, and T. Tsuruta, J. Macromol. Sci.—Chem., A3, 205 (1969).

[20] R. Tsushima and T. Tsuruta, To Be Published.

[21] T. Makino, S. Inoue, and T. Tsuruta, Makromol. Chem., 131, 147 (1970).

[22] C. H. Bamford, H. Block, and A. C. P. Pugh, J. Chem. Soc., 1961, 2057, 4989.

[23] M. Goodman, J. Hutchison and U. Arnon, J. Amer. Chem. Soc., 86, 3384 (1964); 87, 3524 (1965); 88, 3627 (1966).

[24] M. Szwarc, Carbanions, Living Polymers, and Electron-Transfer Processes, Wiley-Interscience, New York, 1968, p. 592.

[24a] C. E. Seeney and H. J. Harwood, Japan-U.S. Seminar on Unsolved Problems in Ionic Polymerization, 1974.

[25] T. Tsuruta, S. Inoue, and K. Matsuura, J. Polym. Sci., Part C, 22, 981 (1969).

[26] T. Tsuruta, K. Matsuura, and S. Inoue, Makromol. Chem., 75, 211 (1964).

[27] S. Inoue, K. Kitamura, and T. Tsuruta, Ibid., 126, 250 (1969).

[28] S. Inoue, H. Koenuma, and T. Tsuruta, J. Polym. Sci., Part B, 7, 287 (1969); Makromol. Chem., 130, 210 (1969).

[29] M. Kobayashi, S. Inoue, and T. Tsuruta, Macromolecules, 4, 658 (1971); J. Polym. Sci., Polym. Chem. Ed., 11, 2383 (1973).

[30] M. Ishimori, O. Nakasugi, N. Takeda, and T. Tsuruta, Makromol. Chem., 115, 103 (1968); 128, 52 (1969).

[31] M. Kobayashi, Yang-Lik Tang, T. Tsuruta, and S. Inoue, Ibid., 169, 69 (1973).