Polymerization of Propylene Oxide by Diethylzinc-α,β-Unsaturated Ketone Systems

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SUMMARY

Propylene oxide was polymerized by a catalyst consisting of diethylzinc and α,β-unsaturated ketones. Ten α,β-unsaturated ketones and some other related compounds were examined. All methyl ketones were effective. α,β-Unsaturated phenyl ketones were effective except for a β,β-disubstituted derivative. α,β-Unsaturated carbonyl compounds other than ketones were practically ineffective. The initial step of the catalyst formation is considered to be the reaction of diethylzinc and α,β-unsaturated ketone which is either the conjugate addition to the α,β-unsaturated group or the hydrogen abstraction from the methyl group next to the carbonyl group. The conjugate addition gives the catalyst having larger activity and better stability at high temperature.

INTRODUCTION

Polymerization of epoxides by dialkylzinc-ketone systems was first reported by Garty et al. [1]. The relation of the structure of saturated ketones and the catalytic reactivity was investigated by the present authors [2] and the abstraction of hydrogen at the α-carbon by a four-centered mechanism was proposed as a necessary step in catalyst formation. The methyl vinyl

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ketone-diethylzinc system was found to be another effective catalyst in propylene oxide polymerization by Tsuruta and one of the present authors [3]. They investigated the copolymerization of methyl vinyl ketone and propylene oxide with diethylzinc as catalyst [4] and, when relatively small amounts of methyl vinyl ketone were used, polypropylene oxide of very high molecular weight was found to be formed. In the present study, the relation of the structure and cocatalytic reactivity of α,β-unsaturated ketones is investigated and reactions involved in the catalyst formation are discussed.

EXPERIMENTAL

Materials

Commercial methyl vinyl ketone was dried with Molecular Sieves 4A, distilled twice in the presence of hydroquinone, and kept over Molecular Sieves. Methyl isopropenyl ketone was prepared by dehydration (with phosphoric acid) of β-methyl-γ-ketobutanol which was prepared from methyl ethyl ketone and paraformaldehyde according to Landau et al. [5]; bp 97-99°C; yield 49% based on β-methyl-γ-ketobutanol. Mesityl oxide and benzalacetone were obtained commercially, distilled, and dried. Commercial β-phenylacrylophenone (chalcone) was recrystallized from ethanol and dried.

Furfurylideneacetone was prepared from acetone and furfural according to Leuck et al. [6]; bp 94°C/5 mm Hg; yield 64%. Acrylophenone was prepared by decomposition of a Mannich's base which was prepared from acetophenone, paraformaldehyde, and dimethylaniline hydrochloride [7]; bp 48-49°C/0.47 mm Hg; yield 17% based on Mannich's base. α-Phenyl-acrylophenone was prepared by dehydration (by distillation over potassium bisulfate) of α-methylbenzoin which was prepared by the reaction of benzil and methylmagnesium bromide [8]; yield of α-methylbenzoin 37.2%; yield of α-phenylacrylophenone 48.8% based on α-methylbenzoin; bp 168°C/8.4 mm Hg.

β,β-Dimethylacrylophenone was prepared by the following steps: β,β-dimethylacrylic acid was prepared by oxidation of mesityl oxide with hypochlorous acid [9]. The product was converted into the corresponding acid chloride by the reaction with thionyl chloride [10]. The acid chloride was added to a solution of diphenylcadmium which was prepared from the Grignard reagent and cadmium chloride [11]. The yield of β,β-dimethyl-acrylophenone was 1% based on mesityl oxide; bp 65°C/0.3 mm Hg.

Divinyl ketone was prepared by decomposition of a Mannich's base which was prepared from acetone, 35% aq formaldehyde and diethylamine hydrochloride [12]. The Mannich's base was decomposed at 200°C under 60 mm Hg and the distillate was directly trapped into toluene containing a small amount of hydroquinone to prevent polymerization. Yield of divinyl ketone was 8.5%.

Other carbonyl compounds were obtained commercially and purified by the conventional methods.

Propylene oxide was refluxed over potassium hydroxide, distilled, and dried over calcium hydride. Diethylzinc was distilled and diluted with toluene. Toluene was distilled and dried by Molecular Sieves.

Procedure

Pressure bottles (ca. 100 ml) were used for the polymerization. The solvent, the monomer, a ketone, and diethylzinc were added successively to a bottle under nitrogen atmosphere. The bottle was capped and tumbled in a water bath of the desired temperature. After the reaction was stopped by adding methanol into the bottle, volatile components were removed in vacuo.

Intrinsic viscosity and specific viscosity were measured in benzene at 30°C.

RESULTS AND DISCUSSION

It has been reported that the methyl vinyl ketone-diethylzinc system polymerizes propylene oxide to form polymers of very high molecular weight [3]. The active catalyst can be considered to be formed through reaction of methyl vinyl ketone with diethylzinc. Major reactions between an α,β-unsaturated ketone and an organometallic compound are carbonyl addition, conjugate addition, and hydrogen abstraction. These reactions were investigated by Kawakami, Yasuda, and Tsuruta [13], and the conjugate addition and the hydrogen abstraction were shown to be the major reactions in the reactions involving dialkylzinc. The relation between the structure of α,β-unsaturated ketones and the cocatalytic reactivity for the propylene oxide polymerization is investigated on the basis of this knowledge.

Phenyl Ketones

Methyl vinyl ketone has two reactive groups toward dialkylzinc: α,β-unsaturated group and methyl group next to the carbonyl group. Reaction

Table 1. Cocatalytic Reactivity of α,β-Unsaturated Phenyl Ketones[a]

Ketone	$\dfrac{\text{Ketone}}{(C_2H_5)_2Zn}$ (mole ratio)	Polymerization time (hr)	Conversion (%)	$[\eta]$[b]
None	–	96	3	–
$CH_2=CHCOC_6H_5$	0.7	96	88	2.56
"	1.5	"	74	1.41
"	2.2	"	100	1.55
"	3.0	"	100	1.04
"	4.0	"	100	–
$CH_2=C(C_6H_5)COC_6H_5$[c]	0.5	7	Small	–
"	1.0	"	8	0.43*(0.21)
"	1.5	"	13	0.33*(0.21)
"	2.0	"	16	0.16*(0.20)
"	2.5	"	20	0.33*(0.19)
"	3.0	"	25	0.16*(0.23)
"	4.0	"	33	0.13*(0.24)

$C_6H_5CH{=}CHCOC_6H_5$	0.7	96	15	—
"	1.5	"	25	—
"	2.2	"	46	0.50*(0.12)
"	3.0	"	37	—
"	4.0	"	32	—
$(CH_3)_2{=}CHCOC_6H_5$	0.5-4.0	>5^d	0	—
$(CH_2{=}CH)_2CO^e$	0.75	7	7	8.59
	1.5	"	61.5	8.60
	3.0	"	11.8	1.37

[a]Conditions of polymerization: diethylzinc, 3 mole % based on propylene oxide; toluene as the solvent; solvent/monomer, 1 by volume; temperature, 50°C.
[b]Values with asterisk are reduced viscosities at concentration (g/100 ml) in parenthesis.
[c]Monomer concentration, 2.0 mole/1; diethylzinc, 1.5 mole % based on propylene oxide; temperature, 100°C.
[d]Five hours at 100°C and overnight above the room temperature.
[e]Solvent/monomer, 3 by volume; temperature, 100°C.

at the methyl group will be eliminated by replacing the methyl group with the phenyl group. Cocatalytic reactivities of a series of phenyl ketones were examined. The results are listed in Table 1. The ketones examined were: acrylophenone (phenyl vinyl ketone) $CH_2=CHCOC_6H_5$, α-phenyl-acrylophenone $CH_2=C(C_6H_5)COC_6H_5$, β-phenylacrylophenone (chalcone) $C_6H_5CH=CHCOC_6H_5$, β,β-dimethylacrylophenone $(CH_3)_2C=CHCOC_6H_5$, and divinyl ketone $(CH_2=CH)_2CO$.

Since acrylophenone is a very effective cocatalyst, it is clear that the structure $CH_2=CHCO-$ is effective for the formation of the active catalyst. The α-phenyl and β-phenyl derivatives of acrylophenone are also effective though the activity is lower than with acrylophenone. It is remarkable that the dimethyl derivative is entirely inactive. This shows that the structure $(CH_3)_2C=CHCO-$ is not effective. Thus, it may be concluded that the structure $-CH=\overset{|}{C}-CO-$ is effective for the formation of the active catalyst.

Though divinyl ketone is not a phenyl ketone, it is also lacking in functional groups other than the $CH_2=CHCO-$ group. The result that it is also an effective cocatalyst is in accordance with the above conclusion.

Methyl Ketones

Now that the cocatalytic reactivity of the unsaturated ketone group has been examined, derivatives of methyl vinyl ketone having methyl ketone structure are another group of unsaturated ketones to be examined. Cocatalytic reactivities of the following ketones were examined: methyl vinyl ketone $CH_2=CHCOCH_3$, methyl isopropenyl ketone $CH_2=C(CH_3)COCH_3$, mesityl oxide $(CH_3)_2C=CHCOCH_3$, benzalacetone $C_6H_5CH=CHCOCH_3$, and furfurylideneacetone . The results are shown in Table 2.

All the ketones examined are effective. Reactivity of mesityl oxide is attributed to the methyl ketone structure, CH_3CO-, because the unsaturated ketone structure, $\overset{\backslash}{\underset{/}{C}}=CHCO-$, in this ketone should be ineffective.

The higher reactivity of benzalacetone than that of β-phenylacrylophenone may be related to the presence of methyl ketone structure in this compound. Substitution of the phenyl group in benzalacetone by the furyl group does not make any difference. Thus, it is confirmed that the methyl ketone structure is also effective for the formation of the active catalyst.

Possible Reactions Involved in the Catalyst Formation

The conclusion so far is that either the $-CH{=}\overset{|}{C}-CO-$ or the $-COCH_3$ structure in an unsaturated ketone is effective for the formation of the active catalyst. Since none of the unsaturated ketones or the dialkylzinc is effective by itself, the reaction between the ketone and the dialkylzinc must take place first. The effective structures are considered to be related in their reactivity toward the dialkylzinc. The major possible reactions are conjugate addition and hydrogen abstraction, as mentioned before. It is likely that the former reaction is related to the structure $-CH{=}\overset{|}{C}-CO-$ and the latter reaction to the structure $-COCH_3$.

To look into this point closer, a part of the results reported by Kawakami et al. [13] is cited in Table 3. It is shown that conjugate addition takes place exclusively with acrylophenone and hydrogen abstraction exclusively with mesityl oxide and benzalacetone. Mixed reactions are found to take place with methyl vinyl ketone, methyl isopropenyl ketone, and β-phenylacrylophenone. The typical compounds showing the cocatalytic effect of the structures $-CH{=}\overset{|}{C}-CO-$ and $-COCH_3$ (acrylophenone and mesityl oxide, respectively) correspond to the typical ones related with conjugate addition and hydrogen abstraction, respectively. Most of the other compounds fall between these two compounds.

Thus, it may be concluded that either conjugate addition to the unsaturated ketone structure or hydrogen abstraction from the methyl ketone structure is sufficient as the initial step in the formation of the active catalyst. Both reactions appear to take place simultaneously in many cases.

Disubstitution at the β-carbon of the unsaturated group results in the loss of reactivity. Substitution at the α-position keeps the group reactive even when the substituent is the bulky phenyl group. Since a number of nucleophillic addition reactions are known to take place at the β-carbon of mesityl oxide [14], the present result does not appear to be explained as a simple nucleophillic addition reaction. Steric effects may be considered.

It has been reported that the reaction of dibutylzinc toward α,β-unsaturated ketones in nonpolar media is the most homolytic among similar reactions of organometallic compounds and also that more homolytic reactions tend to produce more stereospecific polymers of methyl methacrylate [15]. Based on these results and also on the

Table 2. Cocatalytic Reactivity of α,β-Unsaturated Methyl Ketones[a]

Ketone	$\dfrac{\text{Ketone}}{(C_2H_5)_2Zn}$ (mole ratio)	Polymerization time (hr)	Conversion (%)	$[\eta]$[b]
$CH_2{=}CHCOCH_3$	1.3	50	40	14.0
$CH_2{=}C(CH_3)COCH_3$	0.7	96	98	4.36
"	1.5	"	77	4.59
"	2.2	"	26	1.82
"	3.0	"	26	–
"	4.0	"	19	–
$(CH_3)_2C{=}CHCOCH_3$	0.7	96	91	1.59
"	1.5	"	100	1.09
"	2.2	"	62	0.7

"	3.0	"	59	0.5
"	4.0	"	43	—
$C_6H_5CH=CHCOCH_3$	0.7	96	26	—
"	1.5	"	100	1.11*(0.22)
"	2.2	"	90	—
"	3.0	"	57	—
"	4.0	"	35	—
⬠—CH=CHCOCH₃	0.7	144	99	13.9*(0.50)
"	1.5	"	100	3.2*(1.44)
"	2.2	"	87	—
"	3.0	"	83	—
"	4.0	"	38	—

a,b See footnotes a and b of Table 1.

Table 3. Mode of Reaction of Dialkylzinc and
Unsaturated Ketones[a]

| Ketone	Conjugate addition, % / Hydrogen abstraction, %
$CH_2=CHCOCH_3$	86/14
$CH_2=C(CH_3)COCH_3$	96/4
$CH_2=CHCOC_6H_5$	100/0
$(CH_3)_2C=CHCOCH_3$	0/100
$C_6H_5CH=CHCOCH_3$	0/100
$C_6H_5CH=CHCOC_6H_5$	78/22

[a]Cited from Ref. 13.

results of more detailed work, it has been proposed that the addition re-
action takes place through a four-centered mechanism involving two
molecules of dialkylzinc and one molecule of an unsaturated ketone [13].
It is very likely that the steric effect mentioned above is related to this re-
action mechanism.

Since it has been concluded that either or both the conjugate addition
and the hydrogen abstraction takes place as the initial step of catalyst
formation, it is interesting to consider what follows these reactions. The
reaction product of the conjugate addition will be

$$\begin{array}{c} \backslash \quad | \\ CH{-}C{=}C{-} \\ / \qquad | \\ R \qquad OZnR \end{array}$$
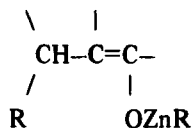
where R is an alkyl group from dialkylzinc. The reaction product of the
hydrogen abstraction will be

$$\begin{array}{c} R'{-}C{=}CH_2 \\ | \\ OZnR \end{array}$$
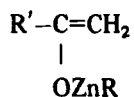
where R' is a vinyl or substituted vinyl group. Since enol-forms of vinyl
ketones are unstable [16, 17], it is probable that the above structures
may rearrange or react to form other species.

Saturated ketones are known to give aldol-type condensation products in the presence of dialkylzinc [18]. Species similar to that formed in the dialkylzinc-water catalyst were found to be formed. The reaction product of the hydrogen abstraction in the present system may possibly undergo similar reactions.

A difference between phenyl ketones and methyl ketones is found in the effect of the catalyst composition. The effect of the catalyst composition on conversion is shown in Figs. 1 and 2. All the methyl ketones show maximum values when the ratio of the ketone to diethylzinc is between ½ and 2, while the phenyl ketones do not. Methyl ketones in excess decrease the catalyst activity. This suggests the presence of unfavorable side reactions in the case of methyl ketones.
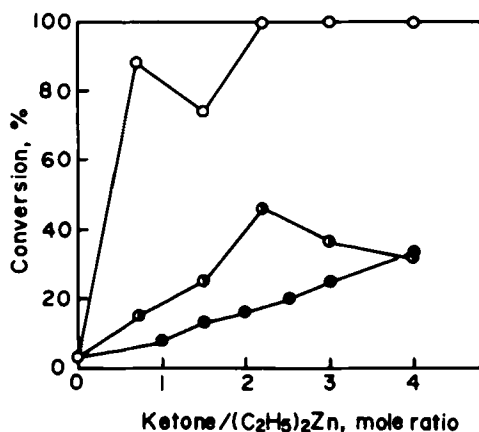
Fig. 1. Effect of the catalyst composition (1), phenyl ketones.
o: $CH_2=CHCOC_6H_5$. •: $CH_2=C(C_6H_5)COC_6H_5$. ◑: $C_6H_5CH=CHCOC_6H_5$.

The effect of the temperature of polymerization shown in Table 4 is also in accord with the above result. While acrylophenone, methyl vinyl ketone, and benzalacetone have cocatalytic reactivity of about the same degree at 50°C, big differences are found between them at elevated temperature. Compounds with higher reactivity toward hydrogen abstraction lose cocatalytic reactivity to a larger extent. This again suggests the presence of unfavorable side reactions in the case of methyl ketones. The aldol-type condensation mentioned above may be one of the related reactions.

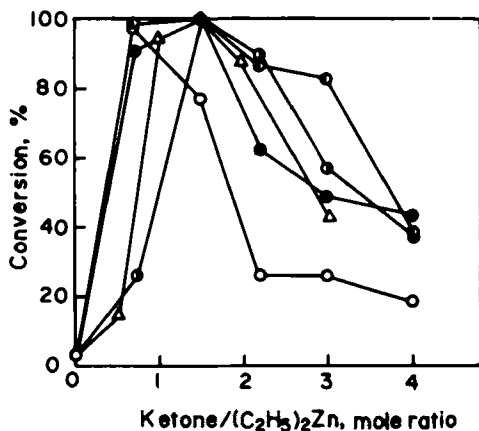It may be concluded that the conjugate adducts give, directly or through

Fig. 2. Effect of the catalyst composition (2), methyl ketones. Data for acetophenone from the Ref. 2. $\circ$: $CH_2=C(CH_3)COCH_3$.

$\bullet$: $(CH_3)_2=CHCOCH_3$. $\circledcirc$: $C_6H_5CH=CHCOCH_3$. $\circledcirc$: $\boxed{}$$-CH=CHCOCH_3$.
$\triangle$: $CH_3COC_6H_5$.

subsequent reactions, the catalysts that are capable of polymerizing propylene oxide more rapidly with better stability at high temperature.

Examination of Other Related Compounds

The following α, β-unsaturated aldehydes showed slight reactivity under similar polymerization conditions: acrolein, methacrolein, and crotonaldehyde. The following compounds were not effective as the cocatalyst: cinnamaldehyde, 2-furylacrolein (α,β-unsaturated aldehydes), methyl acrylate, methyl methacrylate, diethyl fumarate, diethyl maleate (α,β-unsaturated esters), vinyl acetate, and acrylonitrile. The compounds effective as cocatalysts seem to be practically limited to ketones.

ACKNOWLEDGMENT

Table 4. Polymerization of Propylene Oxide at 120°C[a]

Ketone	Ketone/$(C_2H_5)_2Zn$ (mole ratio)	$(C_2H_5)_2Zn$ (mole/liter)	Monomer (mole/liter)	Polymerization time (hr)	Conversion (%)	$[\eta]$
CH_2=CHCOC$_6$H$_5$	2.5	0.03	2	1	59.1	5.20
CH_2=CHCOCH$_3$	1.5	0.03	2	3.5	44.0	2.04
C_6H_5CH=CHCOCH$_3$	1.7	0.03	1.5	9	18.6	0.677

[a]Toluene as the solvent; polymerization in ampoules standing in an oil bath.

REFERENCES

[1] K. T. Garty, T. B. Gibb, Jr., and R. A. Clendinning, *J. Polym. Sci., Part A*, **1**, 85 (1963).

[2] R. Sakata, K. Takeuchi, H. Yoshii, K. Haga, and A. Onishi, *Makromol. Chem.*, **98**, 253 (1966).

[3] T. Tsuruta and R. Fujio, *Makromol. Chem.*, **75**, 208 (1964).

[4] T. Tsuruta and R. Fujio, *Makromol. Chem.*, **64**, 219 (1963).

[5] E. Landau and E. P. Irany, *J. Org. Chem.*, **12**, 422 (1947).

[6] J. G. Leuck and L. Cejka, in *Organic Syntheses*, Col. Vol. 1 (H. Gilman, ed.) Wiley, New York, 1932, p. 283.

[7] C. Mannich and G. Heilner, *Chem. Ber.*, **55**, 360 (1922).

[8] J. Matti and M. Perrier, *Bull. Soc. Chim. France*, **1955**, 525.

[9] L. I. Smith, W. W. Prichard, and L. J. Spillane, in *Organic Syntheses*, Col. Vol. 3 (E. C. Horning, ed.), Wiley, New York, 1955, p. 302.

[10] L. I. Smith and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **71**, 2672 (1949).

[11] L. I. Smith and R. E. Kelly, *J. Amer. Chem. Soc.*, **74**, 3307 (1952).

[12] G. S. Mironov, M. I. Farberov, and I. M. Orlova, *Zh. Obshch. Khim.*, **33**, 1512 (1963).

[13] Y. Kawakami, Y. Yasuda, and T. Tsuruta, *J. Macromol. Sci.–Chem.*, **A3**, 205 (1969).

[14] M. Hauser, *Chem. Rev.*, **63**, 311 (1963).

[15] T. Tsuruta and Y. Yasuda, *J. Macromol. Sci.–Chem.*, **A2**, 943 (1968).

[16] M. T. Rogers, *J. Amer. Chem. Soc.*, **69**, 2544 (1947).

[17] K. W. F. Kohlrausch, *Chem. Ber.*, **72B**, 2054 (1939), *Chem. Abstr.*, **34**, 5347[7] (1940).

[18] M. Ishimori, T. Hiraishi, and T. Tsuruta, *Kogyo Kagaku Zasshi*, **70**, 970 (1967).