Polymerization of Ethylene by Trialkylaluminum–Lewis Base–Peroxide Catalyst

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ABSTRACT: Some specific combinations of trialkylaluminum, Lewis base, and peroxide were found to be capable of polymerizing ethylene under the mild conditions of room temperature and 60 kg/cm^2. As the Lewis base, γ-butyrolactone was particularly effective. Some other lactones, substances similar in structure to such lactones, and bidentate-type Lewis bases, such as *N,N,N',N'*-tetramethylethylenediamine and ethylene glycol dimethyl ether, also showed activity. Spectroscopic studies of the interaction between trialkylaluminum and some of the effective Lewis bases suggested that all those Lewis bases, including γ-butyrolactone, formed, with the trialkylaluminum, a 1:1 complex capable of taking on a chelate structure, a fact closely related to the activity of the catalyst system. The peroxides, of which those containing the carboxyl group were effective, were found to attack the 1:1 complex to release the alkyl radical from the trialkylaluminum. This radical was confirmed to be the initiating species of the actual polymerization by the fact that the isobutyl group was detected by IR analyses of the polyethylene obtained with the catalyst system containing triisobutylaluminum.

Recent years have brought to light several low-temperature radical initiating systems containing alkylaluminum, such as triethylaluminum ($AlEt_3$)–carbon tetrachloride (CCl_4),[1] $AlEt_3$–Lewis base–CCl_4,[2] trialkylaluminum–acyl peroxide,[3] and $AlEt_3$–Lewis base–acyl peroxide.[4] The monomers so far polymerized by these catalyst systems, however, were limited to common vinyl monomers. A single example of a similar catalyst system consisting of $AlEt_3$, group 2 metal halide, and CCl_4, applied to the polymerization of ethylene at room temperature and under low pressure has been described, where, however, only oligomers (heptamer and octamer) were obtained.[5]

The present paper describes the ethylene polymerization by the ternary catalyst system consisting of trialkylaluminum, Lewis base, and peroxide, a suitable combination of which components have led to the polymerization even at room temperature and under 60 kg/cm^2. Somewhat detailed studies on primary structural requirements for the Lewis bases and the peroxide to give higher activity, on interactions among those catalyst components, and on the initiating species of the polymerization are presented in this paper.

Experimental Section

Materials. Alkylaluminums (Texas Alkyls Inc.) were used without further purification. Lewis base reagents (Wako Pure Chemical Ind., or Tokyo Kasei Kogyo Co.) were dried over either anhydrous calcium sulfate or Molecular Sieves 4A, followed by distillation immediately before use. Peroxides (Nippon Oils & Fats Co.) were bubbled with nitrogen before use. Ethylene (polymerization grade) contained in a cylinder was used without further purification. All the solvents were dried and distilled over sodium or potassium under nitrogen.

Catalyst Preparation and Polymerization. Since the catalytic activity of the ternary system decreased gradually when all the components were mixed together and kept at room temperature, it was prepared in situ, i.e., in the presence of the ethylene monomer. A typical procedure is as follows:

In a 50-ml pressure vessel under dry nitrogen was placed a sealed glass ampule holding a solution of the peroxide (1.0 mmol) in 5 ml of *n*-hexane, and a solution of the Lewis base (2.0 or 4.0 mmol) in 5 ml of *n*-hexane was charged. A solution of $AlEt_3$ (2.0 mmol) in 5 ml of *n*-hexane was added dropwise at 0 °C with a magnetic stirrer in operation. The mixture system was kept standing, under stirring, for 1 h to allow completion of the complex formation. The ampule was crushed by ethylene introduced up to 60 kg/cm^2 (7 g), bringing all the catalyst components in contact. The polymerization, which started immediately, was allowed to continue under stirring at room temperature (ca. 20 °C) for a given period.

After the polymerization, the reaction mixture was treated with a small amount of 2-propanol and poured into methanol. The precipitated crude polyethylene was isolated together with the shattered glass fragments by filtration, and the former was separated from the latter by allowing it to rise to the surface of the water–methanol mixture system. The polyethylene was purified by filtration with kerosene at high temperature (90–120 °C) and further reprecipitated at room temperature.

IR Spectra. IR spectra of the polyethylene were taken with a spectrophotometer of Model DS-402 of Japan Spectroscopic Co., Ltd., using thin films. The quantity of the methyl group in the polyethylene was evaluated from the absorption intensity at 1380 cm^{-1}, which was calibrated with that of a blend sample consisting of linear polyethylene made from diazomethane and atactic polypropylene.

IR measurements of the catalyst components were also carried out with the same instrument in a KBr solution cell 0.1 mm thick under dry nitrogen.

NMR Spectra. NMR spectra of the catalyst components were obtained with a spectrometer of 100 MHz Model JNM-4H100 of Japan Electron Optics Lab. Co., Ltd., in a cyclopentane, benzene, or toluene solution under nitrogen.

Molecular Weight. The molecular weight of the polyethylene was measured with a vapor pressure osmometer Model 117 of Hitachi Co., in *o*-dichlorobenzene at 117 °C.

Interactions between Trialkylaluminum–Lewis Base Complex and Peroxide. In order to investigate the attack of the peroxide on the trialkylaluminum–Lewis base complex, the following two tests were performed by use of the most active of the catalyst systems, $AlEt_3$–γ-butyrolactone(BL)–*tert*-butyl peroxyisobutyrate.

Quantitative Determination of the Evolved Gas. A solution of *tert*-butyl peroxyisobutyrate in toluene was added to a solution of 1:1 $AlEt_3$–BL mixture in toluene. The reaction was made to take place at 50 °C until evolution of the gaseous products ceased. The evolved gas was collected in a gas buret sealed with a saturated aqueous solution of NaCl. An excess amount of water was added to the residual reaction mixture to collect the evolved gas in the same way. The captured gas was analyzed by gas chromatography.

Determination of Time Conversion of the Peroxide Decomposition. To a solution of 1:1 $AlEt_3$–BL mixture in toluene was added a given amount of a solution of *tert*-butyl peroxyisobutyrate in toluene. The mixture system was allowed to stand at given temperatures for required periods of time, then cooled in a dry ice–methanol bath. To this chilled reaction mixture was added an excess amount of cooled methanol to decompose $AlEt_3$. The quantity of unreacted peroxide was then determined by iodometry.

Results and Discussion

Behavior of Lewis Base. In order to elucidate the behavior of the Lewis base in the ternary catalyst system, polymerizability of ethylene by the system consisting of $AlEt_3$, *tert*-butyl peroxyisobutyrate, and one of the various Lewis bases used was determined, as shown in Table I. $AlEt_3$ and *tert*-butyl peroxyisobutyrate were chosen for these studies since the former is one of the most popular alkylaluminums, while the latter, highly soluble in solvent *n*-hexane, is quite stable by itself at the polymerization temperature.

Without Lewis base, no polymer was obtained, which

Table I
Effect of Lewis Bases on Ethylene Polymerization[a]

Lewis base			Polyethylene yield, g
	mmol	$\Delta\delta_{\mathrm{int}}$,[c] ppm	
[b]	0	0.72	0
γ-Butyrolactone (BL)	2.0	1.20	3.77
ε-Caprolactone	2.0	1.19	1.61
Ethylene carbonate	2.0	1.17	1.38
Dimethyl maleate	2.0	1.20	1.68
Ethyl acetate	4.0	1.20	0
Allyl acetate	4.0	1.19	0
Ethylene glycol diacetate	2.0	1.19	0.98
Ethylene glycol dimethyl ether (DME)	2.0	1.22	1.44
Veratrol	2.0	1.18	1.42
n-Butyl ether	4.0	1.21	0
Allyl ether	4.0	1.20	0
Tetrahydrofuran	4.0	1.20	0
N,N,N′,N′-Tetramethylethylenediamine (TMEDA)	2.0	1.30	1.61
Triethylamine	4.0	1.26	0
Pyridine	4.0	1.03	0
Dimethylacetamide	4.0	1.23	0
Dimethylformamide	4.0	1.21	0
Succinonitrile	2.0	1.18	0
Acetonitrile	4.0	1.18	0

[a] Polymerization conditions: $AlEt_3$, 2.0 mmol; *tert*-butyl peroxyisobutyrate, 1.0 mmol; *n*-hexane, 15 ml; ethylene, 7 g (60 kg/cm^2); at 20 °C for 16 h. [b] No Lewis base used. [c] Internal chemical shift, i.e., the difference between methyl and methylene proton shifts of $AlEt_3$ in its mixture system with each of the Lewis bases (one molar toluene solution, at 24 °C).

suggests that the Lewis base component is essential for the polymerization of ethylene.

Of the various Lewis bases examined, BL turned out to be the most effective in the polymerization. The system of $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate (2.0–2.0–1.0 mmol), prepared in situ, polymerized ethylene (7 g, 60 kg/cm^2) at room temperature to produce 3.77 g of polyethylene, filling the reaction vessel most to the brim after 16 h. Its molecular weight was estimated at 4100.

Lewis bases other than BL but effective in polymerizing ethylene under similar conditions were found to be those possessing either a ring structure like BL, such as ε-caprolactone and ethylene carbonate, or a structure of typical bidentate ligand in the classes of amines, ethers, and esters, such as *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and ethylene glycol dimethyl ether (DME). Succinonitrile, a bidentate type of nitrile, however, yielded no polymer.

None of the monodentate Lewis bases examined was found to form a catalyst system active in the ethylene polymerization despite the fact that their concentration was doubled to match the number of coordinating sites with that of the bidentate Lewis base in the reaction system. This inactivity is at variance with the reported results of the polymerization of vinyl chloride, where monodentate Lewis bases, such as ethyl acetate and *n*-butyl ether, when combined with $AlEt_3$–benzoyl peroxide, were found to give active catalyst systems.[4]

As a first step to account for such differences in activity, the possibility of its being due to the disparity in the electron-donating ability of the Lewis bases toward $AlEt_3$ was studied. The NMR internal chemical shift, i.e., the difference between the chemical shifts of methyl and of methylene protons of $AlEt_3$, has been proposed as a measure of the electron-donating ability.[6] The internal chemical shifts of $AlEt_3$ and of the $AlEt_3$–Lewis base mixture were determined in the same way as was done by Hata et al.[7] The results, listed in Table I, show that the values of the internal chemical shifts are in no way correlated with the activities of the catalyst systems. This fact suggests that the electronic magnitude of the Lewis base coordination is not the only factor controlling the activity.

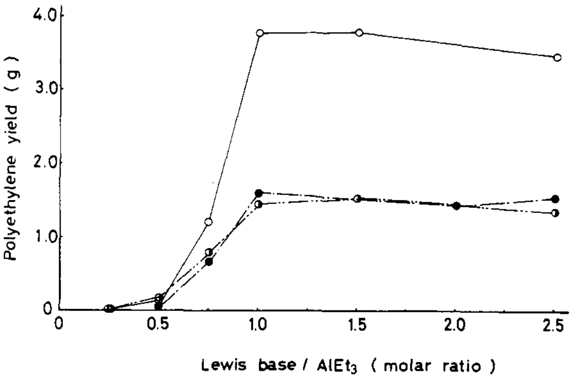

Figure 1. Ethylene polymerization as affected by varied Lewis base molar ratios to $AlEt_3$; (○) BL; (●) TMEDA; (◑) DME. Polymerization conditions: $AlEt_3$, 2.0 mmol; *tert*-butyl peroxyisobutyrate, 1.0 mmol; ethylene, 60 kg/cm^2 (7 g); *n*-hexane, 15 ml; at 20 °C for 16 h.

Another possibility that suggests itself is that only the bidentates, but not the monodentates, may be capable of assuming a particular coordinating structure toward $AlEt_3$ to participate in the polymerization activity. Special attention was therefore given to the behavior of the ethylene polymerization where BL, the most effective of the Lewis bases, and the typical bidentates, TMEDA and DME, were used.

The reversing of the order in which the catalyst components are added, accomplished by crushing, under ethylene pressure, an ampule containing a solution of $AlEt_3$ in the presence of the Lewis bases and *tert*-butyl peroxyisobutyrate, left none of the three runs with any solid polyethylene obtained. This fact suggests that the complex formation of alkylaluminum with the Lewis base prior to their contact with the peroxide is necessary to form an active catalyst system.

Polymerizations performed with varied amounts of the Lewis bases to a fixed amount of $AlEt_3$ gave Figure 1. No significant change in activity was observed for the monomer ratios beyond unity. However, as the monomer ratio is decreased from unity, the activity was seen to undergo significant decrease, nearly vanishing to null when the amount of the Lewis bases was half the amount of $AlEt_3$. No polyethylene was obtained when the amount of the Lewis bases was further reduced. These facts indicate the possibility that the 1:1 complex formation may be closely related to the polymerization activity.

As to the structural nature of the complex required for the activity in ethylene polymerization, the spectra of the mixture of $AlEt_3$ and the Lewis bases were examined in detail.

NMR spectra of TMEDA taken with varied amounts of $AlEt_3$ at different temperatures (24 and −60 °C) in cyclopentane are shown in Figure 2. Both the methyl and methylene proton signals observed in the higher and lower magnetic fields, respectively, tend to shift to the lower magnetic field with increased quantities of $AlEt_3$ in the mixture. Interestingly, the 1:1 mixture at 24 °C, leading to the highest activity, gives the chemical shifts of the methyl protons as well as of the methylene protons, (b), both of which are located at positions in the magnetic field higher than the geometrical averages of the respective counterparts of free TMEDA, (a), and of the 2:1 mixture, (c), for which the activity vanishes. Since there is little probability of free TMEDA being present in amounts greater than half the total TMEDA amounts in the 1:1 mixture, this fact is more suggestive of the formation of a 1:1 complex, in which the two nitrogen ligands in TMEDA are apparently equivalent toward the aluminum atom, rather than of the rapid equilibrium between free TMEDA and the

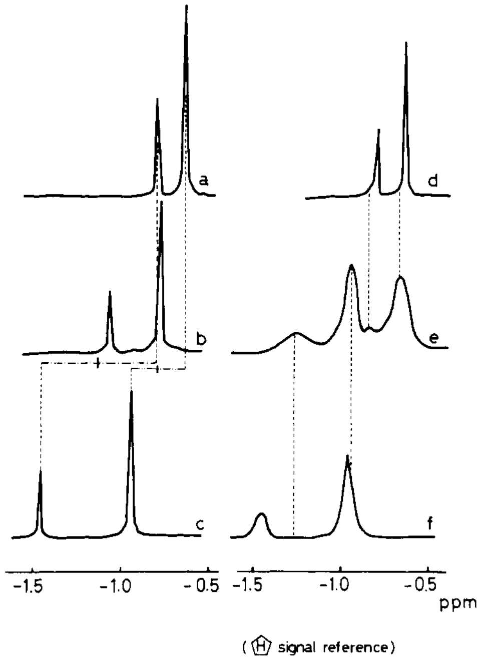

Figure 2. NMR spectra of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA): (a) free TMEDA at 24 °C; (b) 1:1 AlEt$_3$–TMEDA mixture at 24 °C; (c) 2:1 AlEt$_3$–TMEDA mixture at 24 °C; (d) free MEDA at −60 °C; (e) 1:1 AlEt$_3$–TMEDA mixture at −60 °C; (f) 2:1 AlEt$_3$–TMEDA mixture at −60 °C. (1.0 M TMEDA solution in cyclopentane for all cases.)

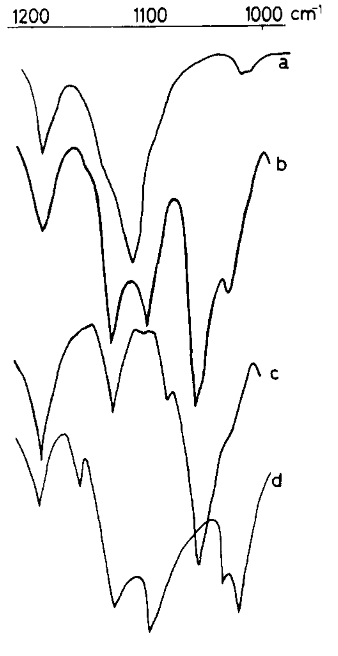

Figure 3. IR spectra of ethylene glycol dimethyl ether (DME): (a) free DME (0.1 M solution in cyclopentane); (b) 1:1 AlEt$_3$–DME mixture (0.1–0.1 M solution in cyclopentane); (c) 2:1 AlEt$_3$–D]ME mixture (0.2–0.1 M solution in cyclopentane); (d) HgCl$_2$–DME complex (measured as KBr tablet).

2:1 complex. At −60 °C, each of the proton signals for the 1:1 mixture was observed to split into a doublet, (e). Thus the 1:1 complex is denied of a simple chelate structure wherein the two nitrogen ligands coordinate equivalently to the aluminum atom. The mixture system was then cooled to −80 °C, but the chemical shifts of the split peaks remained at the same respective positions. These observations point to the ligand exchange being virtually frozen in such a low-temperature range. It is noteworthy, on the other hand, that neither pair of the chemical shifts for the 1:1 mixture coincides with the respective counterpart for free TMEDA, (d), or for the 2:1 mixture, (f). In order to investigate whether the sequence of the nitrogen–carbon and carbon–carbon bonds in TMEDA offers a passage through which the chemical shifts might in any way be affected, triisoamylamine was further subjected to NMR measurements under similar conditions with and without AlEt$_3$ added. No variation was observed in the chemical shift of its methyl protons (+0.71 ppm as measured from the proton signal of the solvent cyclopentane). Therefore, in the 1:1 AlEt$_3$–TMEDA complex, the aluminum atom, to which one of the nitrogens has coordinated, appears to be somehow interrelated with the other nitrogen, suggesting the possible configuration of a chelate structure, even at such low temperatures as bring the ligand exchange to a standstill.

Table II
Effect of Diethers on Ethylene Polymerization[a]

Diether	Polyethylene yield, g
Ethylene glycol dimethyl ether	1.44
Trimethylene glycol dimethyl ether	0.58
Tetramethylene glycol dimethyl ether	0.30

[a] Polymerization conditions: AlEt$_3$, 2.0 mmol; diether, 2.0 mmol; *tert*-butyl peroxyisobutyrate, 1.0 mmol; *n*-hexane, 15 ml; ethylene, 7 g (60 kg/cm^2); at 20 °C for 16 h.

IR spectra of DME mixed with AlEt$_3$ were also measured, as shown in Figure 3. The specificity of the 1:1 mixture was also revealed. The distinctly split peaks (1091 and 1123 cm^{-1}), (b), were not observed for free DME, (a), nor for the 2:1 mixture, (c). The positions of the two specific peaks, (b), virtually coincide with those of the respective ether linkage absorptions of the 1:1 complex of mercuric chloride (HgCl$_2$) with DME, (d), for which complex a chelate structure has been proposed.[8]

The NMR measurements of DME showed the chemical shifts of both the methyl and methylene protons in the 1:1 mixture with AlEt$_3$ in cyclopentane to remain at the same positions as the system was successively cooled down to −80 °C (−2.14 and −2.42 ppm, respectively, as measured from the proton signal of the solvent). This fact also supports the chelate structure in the 1:1 AlEt$_3$–DME complex, if the ligand exchange were to be regarded as being kept at a standstill at such low temperatures, as was the case with the 1:1 AlEt$_3$–TMEDA complex.

The above spectral studies point to probable involvement of a chelate structure in the 1:1 complex of the typical bidentates, TMEDA and DME, with AlEt$_3$. Furthermore, the fact that high activities resulted in the polymerizations with the bidentates when used in equimolar amounts of AlEt$_3$ suggests that such a chelate structure has a vital part to play in imparting activity to the catalyst system.

In order to substantiate this consideration, the effect of the number of methylene units between ether linkage in diether on the polymerization activity was studied. The results are summarized in Table II. As the number of methylene units is increased, the yield of polyethylene decreases. This fact can easily be explained by assuming a chelate structure for the active complex and by taking into account the decreased stability of the complex with the increase in the size of its ring structure. These polymerizations, therefore, support the assumption that the chelate structure should take part in the activation of the catalyst system.

The behavior of BL, which showed the highest activity in the polymerizations performed but which has a somewhat

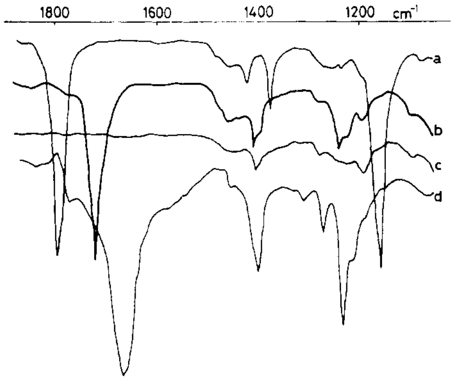

Figure 4. IR spectra of γ-butyrolactone (BL): (a) free BL; (b) 1:1 $AlEt_3$–BL mixture; (c) 2:1 $AlEt_3$–BL mixture; (d) 1:1 $SnCl_4$–BL mixture. (0.1 M BL solution for all cases.)

different structure from TMEDA or DME, was also studied in detail.

IR spectra of BL in cyclopentane are shown in Figure 4. The two absorption peaks assigned to the carbonyl group (1795 cm^{-1}) and the ether linkage (1155 cm^{-1}) in free BL, (a) shift in opposite directions (to 1721 and 1243 cm^{-1}, respectively) in the 1:1 mixture with $AlEt_3$, (b). The color of the 1:1 mixture was pale green. In the 2:1 mixture where the catalytic activity diminished, both the color and the absorptions by the carbonyl group and the ether linkage, (c), disappeared completely. The 1:1 mixture of BL with $AlEt_3$, (b), shows a similar shift for the carbonyl group and a larger shift for the ether linkage than its 1:1 mixture with stannic chloride ($SnCl_4$), (d). In the latter case, BL has been reported as coordinating to $SnCl_4$ only at the carbonyl oxygen and not at the ether oxygen.[9] Furthermore, the absorption intensity of the ether linkage of the 1:1 complex with $AlEt_3$ is relatively weaker than that with $SnCl_4$. These facts suggest that, in the formation of the 1:1 $AlEt_3$–BL complex, there is some possible participation of a chelate structure in which the aluminum atom is coordinated not only with the carbonyl oxygen but also with the ether oxygen.

NMR spectra also supported the $AlEt_3$–BL complex as differing in structure from the $SnCl_4$ complex. In cyclopentane, the chemical shifts by the protons at each position of BL complexed with either $AlEt_3$ or $SnCl_4$ shifted to the lower magnetic field when compared with those of free BL. In benzene, however, those by BL complexed with $AlEt_3$ shifted to the higher magnetic field contrary to the shifts in cyclopentane, while those by BL complexed with $SnCl_4$ shifted again to the lower magnetic field, as summarized in Table III. These results clearly indicate that the complex with $AlEt_3$ is of a different structure from that with $SnCl_4$ and that it is capable of interacting with the benzene molecule.

The studies so far described of the nature of the effective Lewis bases combine to suggest that it is possible for any of them to coordinate bidentately to $AlEt_3$ in the 1:1 complex and that the chelate structure formed therein participates in imparting activity to the ethylene polymerization.

Effect of Alkylaluminums. In order to investigate the effect of alkylaluminums on the catalytic activity for the polymerization of ethylene, studies were conducted as to how the kind of an alkyl group in trialkylaluminum and the number of alkyl groups on aluminum affect the yield of polyethylene.

When combined with BL and *tert*-butyl peroxyisobutyrate, both trimethylaluminum ($AlMe_3$) and triisobutylaluminum (Al-*i*-Bu_3) were found to be similar in catalytic activity to $AlEt_3$, as shown in Table IV.

Table III
NMR Chemical Shifts of Methylene Protons in γ-Butyrolactone (BL)[a]

	α-Methylene protons		β-Methylene protons		γ-Methylene protons	
System	δ[b] ppm	Δ,[c] ppm	δ,[b] ppm	Δ,[c] ppm	δ,[b] ppm	Δ,[c] ppm
BL	5.30		5.85		3.55	
$AlEt_3$–BL (1:1)	5.35	+0.05	6.10	+0.25	3.70	+0.15
$SnCl_4$–BL (1:1)	5.05	−0.25	5.85	0	3.45	−0.10

[a] NMR measuring conditions: one molar solution in benzene at 24 °C. [b] Chemical shift as measured from the signal of benzene protons. [c] Deviation from the chemical shift of free BL.

Table IV
Effect of Alkylaluminums on Ethylene Polymerization[a]

Alkylaluminum	Polyethylene yield, g
$AlMe_3$	3.24
$AlEt_3$	3.77
Al-*i*-Bu_3	2.93

[a] Polymerization conditions: trialkylaluminum, 2.0 mmol; BL, 2.0 mmol; *tert*-butyl peroxyisobutyrate, 1.0 mmol; *n*-hexane, 15 ml; ethylene, 7 g (60 kg/cm^2); at 20 °C for 16 h.

Table V
Effect of Peroxides on Ethylene Polymerization[a]

Peroxide	Polyethylene yield, g
b	0
Acetyl peroxide	2.96
Propionyl peroxide	2.80
Isobutyryl peroxide	2.67
Benzoyl peroxide	0.60
tert-Butyl peroxyisobutyrate	3.77
tert-Butyl peroxybenzoate	0.82
tert-Butyl peroxyisopropylcarbonate	3.11
Acetylcyclohexylsulfonyl peroxide	3.83
tert-Butyl peroxide	0
Cumyl peroxide	0
tert-Butyl hydroperoxide	0
Cumene hydroperoxide	0

[a] Polymerization conditions: $AlEt_3$, 2.0 mmol; BL, 2.0 mmol; peroxide, 1.0 mmol; *n*-hexane, 15 ml; ethylene, 7 g (60 kg/cm^2); at 20 °C for 16 h. [b] No peroxide used.

When two alkylaluminums containing a halogen, i.e., diethylaluminum chloride ($AlEt_2Cl$) and ethylaluminum dichloride ($AlEtCl_2$), were employed under similar conditions, both gave only oily products with no solid polyethylene. These results suggest that trialkylaluminum is a requirement in forming the catalyst system active enough to produce high molecular weight polyethylene.

Behavior of Peroxide. The combination of trialkylaluminum with the Lewis base without any peroxide, it was found, did not afford any catalyst system active for the polymerization of ethylene. This fact indicates that the peroxide plays a key role in the ternary system.

In order to gain more insight into the catalyst system, the behavior of the peroxide was investigated with respect to its structural requirements in forming an effective system. The results obtained with the catalyst systems of $AlEt_3$ and BL combined with a variety of the peroxides are summarized in Table V. The effective peroxides were found to be those con-

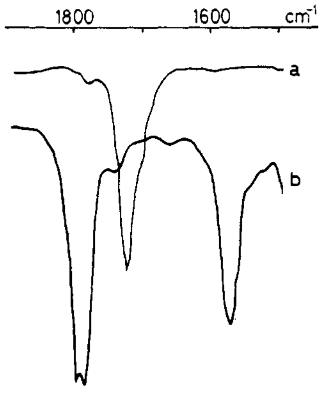

Figure 5. IR spectra of γ-butyrolactone and *tert*-butyl peroxyisobutyrate: (a) 1:1 $AlEt_3$–BL mixture (0.1–0.1 M solution in toluene); (b) equimolar reaction mixture of 1:1 $AlEt_3$–BL complex (0.2–0.2 M solution in toluene) with *tert*-butylperoxyisobutyrate (0.2 M solution in toluene) at 50 °C for 2 h.

taining the carboxyl group, acyl peroxides, and peroxy esters. However, hardly any polyethylene was obtained with alkyl peroxides or hydroperoxides. These findings suggest that the carboxyl group may participate in the initiation process through its interaction with the trialkylaluminum–Lewis base complex.

The peroxides found to be effective when used with $AlEt_3$ also gave active catalyst systems with other trialkylaluminums. Under similar conditions, for example, acetyl peroxide and propionyl peroxide, in combination with $AlMe_3$ and Al-i-Bu_3, respectively, yielded 2.90 and 2.55 g of polyethylene, respectively.

In order to study the role of the peroxides containing the carboxyl group in initiating the ethylene polymerization, the interaction between the $AlEt_3$–BL complex and *tert*-butyl peroxyisobutyrate, one of the most effective peroxides, was investigated by IR spectroscopy (Figure 5). Upon addition of an equimolar amount of *tert*-butyl peroxyisobutyrate to the complex solution, the carbonyl absorption of the $AlEt_3$–BL complex (1721 cm^{-1}), (a), disappeared completely and instead the absorption due to free BL (1795 cm^{-1}) appeared, (b). This can be accounted for by considering that the peroxide, attacking the complex, caused it to release its BL.

Besides the absorption band mentioned above, two characteristic bands are observed at 1785 and 1570 cm^{-1} in the spectrum, (b). The former coincides with the carbonyl absorption of *tert*-butyl peroxyisobutyrate, suggesting that not all of the peroxide added in an equimolar amount had been consumed. The latter coincides with the absorption observed for the product of $AlEt_3$ reacted with an equimolar amount of isobutyric acid, i.e., the model compound when one of the decomposed fragments of *tert*-butyl peroxyisobutyrate adds itself to $AlEt_3$. This suggests that the peroxide, attacking the $AlEt_3$–BL complex, decomposes to release isobutyroxy radical, which in turn reacts with $AlEt_3$ to form the isobutyroxyaluminum compound.

Gas evolution occurred during the reaction of the peroxide with the $AlEt_3$–BL complex. The analyses of the gaseous products are shown in Table VI. The constituents were ethane and ethylene, including a small amount of compounds having four carbon atoms. Their total volume measured was in good agreement with the value calculated on the assumption that a single ethyl group was released from $AlEt_3$. Addition of excess water to the reaction mixture further evolved ethane, the amount of which was in agreement with the assumption that two ethyl groups per aluminum were left unreacted with the peroxide. These results are taken to suggest that the peroxide plays the role of releasing an alkyl radical by attacking the complex.

Table VI
Results of Quantitative Analyses[a] of Gas Evolved from $AlEt_3$-γ-Butyrolactone-*tert*-Butyl Peroxyisobutyrate System

	After reaction of the three components only[b]		After further decomposition of the reacted mixture by excess water[c]	
Evolved gas	Exptl, ml	Calcd, ml	Exptl, ml	Calcd, ml
Ethane	96.7		237.5	
Ethylene	11.4		0	
C_4 compds[d]	6.7		4.4	
Total[e]	121.5	121.9	246.3	243.8

[a] Analysis conditions: dimethylsulfolane column; at 25 °C. [b] Reaction conditions: $AtEt_3$, 5.0 mmol; BL, 5.0 mmol; *tert*-butyl peroxyisobutyrate, 5.0 mmol; toluene, 5 ml; at 50 °C for 2 h. [c] Decomposition conditions: to reaction mixture was added dropwise 5 ml of water at 25 °C. [d] These were found to consist of *n*-butane, 1-butene, isobutene, and *trans*-2-butene. [e] Calculated values were derived by assuming evolution of ethane only.

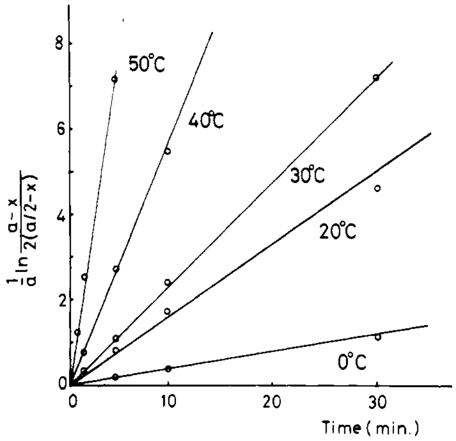

Figure 6. Analysis of *tert*-butyl peroxyisobutyrate consumed. Reaction conditions: 1:1 $AlEt_3$–BL complex, 0.885 mmol; *tert*-butyl peroxyisobutyrate, 0.885 mmol; toluene, 9.46 ml.

The reaction scheme suggested above was confirmed by kinetic analysis of the rate of consumption of *tert*-butyl peroxyisobutyrate, and may be written as follows:

$$AlEt_3\text{–BL complex} + t\text{-Bu-O-O-CO-}i\text{-Pr} \rightarrow Et_2AlA + Et\cdot + B\cdot + BL \quad (1)$$

$$AlEt_3\text{–BL complex} + B\cdot \rightarrow Et_2AlB + Et\cdot + BL \quad (2)$$

where $A\cdot$ and $B\cdot$ are either one of the radicals, i-PrCOO· or t-BuO· produced in the decomposition of *tert*-butyl peroxyisobutyrate.

Provided that reaction 1 is the rate-determining step, the rate of consumption of the peroxide for the case of its equimolar use with the $AlEt_3$–BL complex can be expressed by

$$-\frac{dx}{dt} = k(a-x)(a-2x) \quad (3)$$

where k, a, x, and t are the rate constant of reaction 1, initial concentration, amount of consumption of the peroxide, and reaction time, respectively.

Equation 3, upon integration, gives

$$kt = \frac{1}{a} \ln \frac{a-x}{a-2x} \quad (4)$$

The experimental results plotted according to eq 4 give Figure 6, which justifies the reaction scheme as formulated

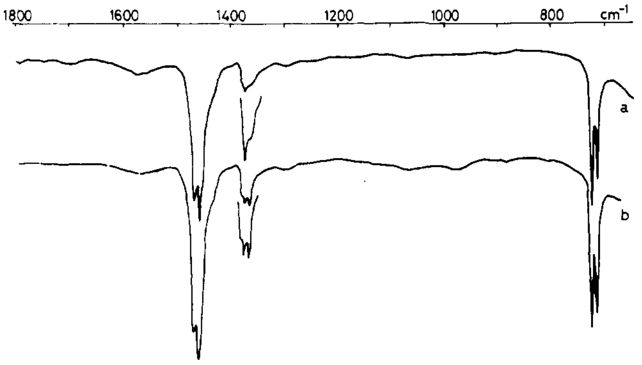

Figure 7. IR spectra of polyethylene: (a) prepared by $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate catalyst system; (b) prepared by Al-*i*-Bu_3–BL–propionyl peroxide catalyst system.

by eq 1 and 2. From the rate constants k for the different temperatures used, the activation energy was evaluated to be 11.6 kcal/mol.

To sum up, it was disclosed that the peroxide, in order to be effective in the ternary catalyst system, must contain the carboxyl group, and that as such its role consists in attacking the trialkylaluminum to induce the breakage of the aluminum–carbon linkage, thus providing an alkyl radical.

Initiating Species of Polymerization. In order to confirm that the alkyl radical formed by the attack of the peroxide on the trialkylaluminum–Lewis base complex is the initiating species of the polymerization of ethylene, the structure of the polyethylene obtained was studied by IR spectroscopy (Figure 7).

For the polyethylene obtained with the catalyst system consisting of $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate, (a), the absorption band due to the methyl group (1380 cm^{-1}) was observed besides those due to the methylene group (1470–1460 and 725–721 cm^{-1}). No absorption indicative of a double bond was noted in the region where it would be expected (910–889 cm^{-1}). On the basis of the quantity of the methyl group and the molecular weight of the polyethylene, the number of methyl groups was calculated to be ca. two per polyethylene molecule. While the ester carbonyl group, ether linkage, or isopropyl group formed by the decomposition of the peroxide would give absorption bands in their expected regions (1740–1730, 1150–1070, 1385, and 1365 cm^{-1}, respectively), if any of these constituted the end group of the polyethylene obtained ($\overline{DP}$ = ca. 150), no such absorption band was actually observed in the spectrum. These results are indicative of the polymerization being initiated by the ethyl radical and not by the radical from the peroxide and are further suggestive of the fact that the polymerization is terminated mainly by recombination, where no double bond is to be expected, and not by disproportionation, where a double bond is to be expected.

To substantiate these results, the polyethylene obtained with the catalyst of Al-*i*-Bu_3–BL–propionyl peroxide, (b), was further examined. Apart from the findings mentioned above, a band with two absorption peaks (1385 and 1365 cm^{-1}) was detected in the spectrum. This is an indication of the fact that the isobutyl group from Al-*i*-Bu_3 possibly serves to form the end group to the polyethylene, thus supporting the above discussion.

Conclusion

The requirements for the constituents of the ternary catalyst system of alkylaluminum–Lewis base–peroxide to make it active in the polymerization of ethylene are that the alkylaluminum should be of the trialkyl type, that the Lewis base should be of the bidentate type to give, with $AlEt_3$, a 1:1 complex capable of forming a chelate structure, and finally, that the peroxide should contain the carboxyl group. The studies on the interaction among the catalyst components suggested that the peroxide attacks the complex to release the alkyl radical and that the radical so formed initiates the polymerization.

The process involving the activation and polymerization of ethylene poses a no less interesting problem, which the authors propose to discuss in their forthcoming paper.

References and Notes

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