Mechanism of Ethylene Polymerization by Trialkylaluminum— Lewis Base—Peroxide Catalyst

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ABSTRACT: Studies were conducted on the mechanism of ethylene polymerization by the ternary catalyst system consisting of certain specific combinations of trialkylaluminum, Lewis base, and peroxide. Comparison of the polymerization product by the ternary system of triethylaluminum (AlEt_3)— γ -butyrolactone (BL)—*tert*-butyl peroxyisobutyrate with those products brought about by two low-temperature free-radical initiators suggested that two different active sites were formed in the ternary system, *i.e.*, one responsible for the formation of solid polyethylene, and the site of the usual free-radical polymerization responsible for oily oligomers. The ESR analysis employing a bifunctional spin-trapping agent, 2,4,6-tri-*tert*-butylnitrosobenzene, disclosed that the sterically hindered alkyl radical which can be regarded as being in the coordinated state was formed along with the usual free alkyl radical from the trialkylaluminum. Participation was suggested on the part of the coordinated alkyl radical, as we propose to call it, in the initiation reaction for the solid polyethylene, since cyclopentene added to the ternary system showed only the *coordinated* ethyl radical quantitatively transformed into the cyclopentyl radical. IR and NMR measurements of AlEt_3 —BL complex in the presence of cyclopentene suggested possible activation of ethylene monomer by the complex in the polymerization system. The analysis for the ternary system both in the absence and presence of 4-methyl-1-pentene showed a possibility of the *coordinated* radical taking part in the propagation reaction with the coordinated state retained. Further direct support was obtained upon introduction of ethylene monomer to the ternary system containing trimethylaluminum when the *coordinated* methyl radical was found to be transformed into the *coordinated* methylene growing-end radical. These facts suggest that the formation of the solid polyethylene should rest solely on the mechanism of the *coordinated radical polymerization*, *i.e.*, the mechanism in which the *coordinated* alkyl radical formed from trialkylaluminum attacks the ethylene molecules which are in the activated state causing the initiation reaction followed by the propagation reaction, with the coordinated state retained throughout.

KEY WORDS Ethylene / Trialkylaluminum / Lewis Base / γ -Butyrolactone / Peroxide / Cyclopentene / 4-Methyl-1-Pentene / Spin Trapping / 2,4,6-Tri-*tert*-Butylnitrosobenzene / Coordinated Radical Polymerization /

We have already reported that the ternary catalyst system consisting of trialkylaluminum, Lewis base, and peroxide readily enables polymerizing of ethylene under mild conditions of room temperature and 60 kg/cm².¹ Among the Lewis base components, γ -butyrolactone (BL) was particularly effective. Some other lactones and bidentate-type Lewis bases also showed ac-

tivity. It was suggested that each of these Lewis bases formed 1:1 chelate complex with the trialkylaluminum, a fact closely related to the activity in the polymerization. The peroxides, of which those having the carboxyl group were effective, were noted to attack the chelate complex to release the alkyl radical from the trialkylaluminum. The alkyl radical so formed

was further confirmed to be the initiating species of the actual polymerization.

The present paper describes further findings on the working mechanism of the ethylene polymerization. ESR spectral studies employing a bifunctional spin-trapping agent revealed the generation of two different kinds of alkyl radicals in the ternary system, one being the usual free alkyl radical and the other being what we propose to call the *coordinated* alkyl radical, which can be regarded as being under some steric hindrance. The involvement of the *coordinated* alkyl radical in the initiation reaction was investigated by quantitative analyses of the adducts from one of the ternary systems to which cyclopentene was added. Similar investigation with respect to the propagation reaction was made in the presence of 4-methyl-1-pentene in the ternary system. Further studies were carried out on a different ternary system with the addition of ethylene monomer for direct examination of the growing-end radical of the polymerization.

EXPERIMENTAL

Reagents

Alkylaluminums. Commercially available alkylaluminums (Texas Alkyls Inc.) were used without further purification.

Lewis Base Reagents. Commercially available Lewis base reagents (Wako Pure Chemical Ind.) were dried over anhydrous calcium sulfate, followed by distillation under nitrogen.

Peroxides. Commercially available peroxides (Nippon Oils & Fats Co.) were bubbled with nitrogen before use.

Ethylene. Commercially available polymerization-grade ethylene contained in a cylinder was used without further purification.

Cyclopentene and 4-Methyl-1-Pentene. Commercially available guaranteed grades (Tokyo Kasei Kogyo, K.K.) were dried over anhydrous calcium chloride and then over anhydrous calcium sulfate, followed by distillation under nitrogen.

Solvents. The solvents used were commercially available guaranteed grades, which were further dried and distilled over sodium or potassium under nitrogen.

2,4,6-Tri-*tert*-Butylnitrosobenzene (TBNB). This spin-trapping reagent was synthesized in accord-

ance with the procedure developed by Inamoto, *et al.*²

Catalyst Preparation and Polymerization

The preparation of the ternary catalyst system and the polymerization of ethylene were performed by procedures similar to those dealt with in our previous paper.¹ A typical procedure is as follows.

A solution of triethylaluminum (AlEt_3) (2.0 mmol) in 5 ml of *n*-hexane was added dropwise, at 0°C under dry nitrogen, to a solution of BL (2.0 mmol) in 5 ml of *n*-hexane contained in a 50-ml stainless steel vessel. The mixture was kept standing for 1 hr to allow completion of the complex formation. The vessel was closed after placing on the mixture solution a sealed glass ampoule containing a solution of *tert*-butyl peroxyisobutyrate (1.0 mmol) in 5 ml of *n*-hexane, and ethylene was introduced up to 60 kg/cm² (7 g) to crush the ampoule, bringing the catalyst components into contact. The polymerization, which started immediately, was allowed to continue at room temperature (*ca.* 20°C) for a given period.

Following polymerization, the reaction mixture was treated with a small amount of isopropanol 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 a high temperature (90–120°C), and further reprecipitated at room temperature. The filtrated methanol solution was subjected to evaporation under reduced pressure, and the liquid products, extracted from the residue with methylene chloride, were analyzed by gas chromatography, IR and NMR spectroscopy.

In order to examine possible wall effects of the polymerization pressure vessel, a polymerization run was carried out in a bottomed glass tube firmly attached within the pressure vessel sealed with aluminum metal.

ESR Spectra

ESR spectra were taken with an X-band spectrometer of Model JEC-360 of Japan Electron Optics Lab. Co., utilizing 100-KHz modula-

tion. To a solution of the trialkylaluminum—Lewis base complex in cyclopentane was added a solution of the peroxide in cyclopentane accurately measured off in the required ratio, followed by immediate transfer of the mixture solution into an ESR sample tube. The mixture in this tube, after having been kept standing under the required conditions, was treated with a cyclopentane solution of TBNB used in amounts approximately equimolar to the trialkylaluminum component, and then subjected to the measurement. The addition of cyclopentene or 4-methyl-1-pentene to the mixture system was done just before its transfer into the sample tube. Ethylene monomer was directly introduced under pressure (ca. 2 kg/cm²) into the sample tube immediately after the transfer of the mixture system of the three catalyst components at room temperature (ca. 20°C).

IR Spectra

IR measurements of the catalyst components were carried out with a spectrometer of Model DS-402 of Japan Spectroscopic Co., Ltd., in a KBr solution cell of 0.1-mm thickness under dry nitrogen. The liquid products were examined with the same instrument by the usual method.

NMR Spectra

NMR spectra of the catalyst components were obtained with a spectrometer of 100-MHz JNM-4H100 of Japan Electron Optics Lab. Co., Ltd., in a cyclopentane solution under dry nitrogen. The liquid products were examined with the same instrument in a deuteriochloroform solution.

Molecular Weight

The molecular weight of the solid polyethylene was measured with a vapor pressure osmometer (VPO) of K.G. Knauer, in *o*-dichlorobenzene at 117°C, using monodisperse polystyrene (Pressure Chemical Co., molecular weight: 4,000) as reference.

RESULTS AND DISCUSSION

Dual Site Character of Ternary Catalyst System

In order to investigate the working mechanism of the ternary catalyst system of trialkylaluminum—Lewis base—peroxide capable of polymerizing ethylene at room temperature and under a pressure of 60 kg/cm²,¹ the polymerization by

a very active catalyst system consisting of AlEt₃—BL—*tert*-butyl peroxyisobutyrate was compared with that by either of the two usual free-radical initiators with respect to the nature of their products. The free-radical initiators chosen were acetyl cyclohexylsulfonyl peroxide and isobutyryl peroxide, which cause generation of free methyl radical and free isopropyl radical, respectively, at the polymerization temperatures for the ternary system. The amount of either of the free-radical initiators was determined so as to make its decomposition rate, as calculated from the reference,^{3,4} approximately the same as that measured for the *tert*-butyl peroxyisobutyrate in the ternary catalyst system,¹ shown in Figure 1. The other conditions for the free-radical polymerizations were made to conform to those used with the ternary catalyst system, except that the polymerization using isobutyryl peroxide was performed at 25°C. The polymerization results are summarized in Table I. The ternary catalyst system gave, along with liquid products, solid polyethylene, having a molecular weight estimated at 2,870. On the other hand, no solid polyethylene was obtained by either of the free-radical initiators, which only gave liquid products. The liquid products by the ternary system as well as those by the free-radical initiators were confirmed by gas chromatography, IR and NMR measurements to consist of ethylene oligomers. These results suggest that the usual free-radical mechanism should be responsible for the ethylene oligo-

Figure 1. Peroxides compared for the rate of decomposition: —, AlEt₃—BL—*tert*-butyl peroxyisobutyrate (1.0—1.0—0.5 mmol in 15 ml of solvent at 20°C); ---, acetyl cyclohexylsulfonyl peroxide (4.75 mmol in 15 ml of solvent at 20°C); — · —, isobutyryl peroxide (4.45 mmol in 15 ml of solvent at 25°C).

Table I. Ternary catalyst system compared with free-radical initiators in ethylene polymerization^a

Initiator	Concn, mmol	Polymerization temp, °C	Polymerization products		
			Solid polyethylene		Oily oligomers
			Yield, g	M_w^b	Yield, g
AlEt ₃ —BL— <i>tert</i> -butyl peroxyisobutyrate	1.0—1.0—0.5	20	0.60	2,870	0.10
Acetyl cyclohexyl-sulfonyl peroxide	4.75	20	0	—	0.17
Isobutyryl peroxide	4.45	25	0	—	0.23

^a Polymerization conditions: *n*-hexane, 15 ml; ethylene, 7 g; 2 hr.^b Molecular weight by VPO in *o*-dichlorobenzene at 117°C.

mers in the polymerization by the ternary system, from which a particular site may be generated to cause the formation of the solid polyethylene.

Investigation into Solid Polyethylene Formation

For further investigation into the formation of the solid polyethylene, several polymerization runs with the ternary system of AlEt₃—BL—*tert*-butyl peroxyisobutyrate were carried out, using different polymerization periods. Each run gave, besides small amounts of oily oligomers, solid polyethylene, which increased in yield with increasing polymerization time, as shown in Table II. Interestingly, it was found that the molecular weight of the polyethylene obtained has a tendency to increase with increased polymerization time. This also suggests

the fact that the ternary catalyst system gives a particular propagating site other than the usual free-radical growing-end for the formation of the solid polyethylene.

Furthermore, another polymerization run was carried out in a bottomed glass tube tightly fitted in the pressure vessel with a packing piece of aluminum metal. As is shown in Table II, the activity for the solid polyethylene so obtained was, in consideration of the decreased reaction space, practically the same as when the glass tube was not used, and the polyethylene obtained either way was found to be of almost identical molecular weight. No wall effect of the stainless steel pressure vessel is thus seen in the formation of the solid polyethylene.

Detection of Coordinated Alkyl Radical

The initiating species of the ethylene polymerization was suggested to be the alkyl radical formed from the trialkylaluminum—Lewis base complex under the attack of the peroxide.¹ For further clarifying the behavior of the alkyl radical, the admixture system of AlEt₃—BL—*tert*-butyl peroxyisobutyrate was subjected to ESR analysis where a spin-trapping agent was employed. For the spin-trapping agent 2,4,6-tri-*tert*-butylnitrosobenzene was used and it is reported to be a bifunctional reagent because the steric effect it exerts on the oncoming radical leads to the formation of two different spin adducts.⁵ Spin trapping of the small-sized radicals, *i.e.*, methyl radical and primary alkyl radicals such as ethyl radical, gives the ordinary nitroxides, while the trapping of the bulkier radicals, *e.g.*, tertiary alkyl radicals such as 1-cyano-1-methyl ethyl radical or cyclic radicals such as

Table II. Polymerization behavior by AlEt₃—BL—*tert*-butyl peroxyisobutyrate catalyst^a

Polymerization time, hr	Solid polyethylene	
	Yield, g	M_w^b
2	0.79	2,610
5	1.63	2,800
10	1.80	3,030
16	3.77 ^d	4,100 ^d
16 ^c	3.38	3,960

^a Polymerization conditions: AlEt₃, 2.0 mmol; BL, 2.0 mmol; *tert*-butyl peroxyisobutyrate, 1.0 mmol; *n*-hexane, 15 ml; ethylene, 7 g (60 kg/cm²); at 20°C.^b Molecular weight by VPO in *o*-dichlorobenzene at 117°C.^c Polymerization was carried out in a glass tube closely fitted inside the pressure vessel having a sealed packing of aluminum metal.^d Experimental results shown in ref 1.

cyclohexyl radical, gives the anilino radical under the steric hindrance sustained by the *ortho* *tert*-butyl groups on the benzene ring.⁵

A solution of AlEt_3 —BL complex was mixed with a solution of *tert*-butyl peroxyisobutyrate, the three catalyst components being used in concentrations of the same order as in the ethylene polymerizations. This was followed by immediate treatment with a solution of TBNB used in amounts approximately equimolar to AlEt_3 . The ESR spectrum obtained without delay is shown in Figure 2. The prominent spectrum corresponding to the attached illustration was found to be in complete agreement with the spectrum for the case where the free ethyl radical formed in the mixture system of propionyl peroxide with triethylamine was trapped by TBNB under similar conditions. Therefore, the illustrated spectrum was assigned to ethyl 2,4,6-tri-*tert*-butylphenyl nitroxide (I) with the g values of 2.006, and the hyperfine splitting constants: $a_N = 13.6$ G, $a_{H(\beta)} = 18.0$ G, $a_{H(m)} = 0.8$ G. This fact signifies the generation of the free ethyl radical in the ternary catalyst system.

A more careful observation of the spectrum shown in Figure 2 permitted detection of another

Figure 2. ESR spectrum of TBNB adducts for AlEt_3 —BL—*tert*-butyl peroxyisobutyrate system (0.2—0.2—0.1 molar solution in cyclopentane) immediately after its preparation.

Figure 3. ESR spectrum of TBNB adducts for AlEt_3 —BL—*tert*-butyl peroxyisobutyrate system (0.1—0.1—0.05 molar solution in cyclopentane) kept standing at 20°C for 30 min after its preparation.

spectrum with minor intensity, which could not be assigned to the nitroxide I. The intensity of this spectrum was found to increase when the spin trapping with TBNB was made on the mixture system which had been kept standing for 30 min at room temperature after admixing of the three catalyst components, as shown in Figure 3. This is suggestive of the accumulation of a radical, different from the free ethyl radical, in the ternary system with the passage of time.

Also, varying the amounts of TBNB hardly affected the relative signal intensities of the nitroxide I and the adduct of the accumulated radical. This suggests that the TBNB molecule did not coordinate to the AlEt_3 —BL complex, but trapped the radicals formed in the system.

In order to track down the accumulated spin adduct, some modifications were made in the conditions of the ESR measurement. Fortunately, heating the spin-trapped system to 40°C just before the measurement resulted in the complete vanishing of the nitroxide I, leaving the spectrum of the accumulated adduct only, as shown in Figure 4. This spectrum is different from those of nitroxides in that it has a smaller g value, a smaller nitrogen coupling, and a larger hydrogen coupling at the *meta* positions on the benzene ring, all of these characteristics being attributable to an anilino radical. Furthermore, the hyperfine splitting of the protons at the β position consisting of

Figure 4. ESR spectrum of TBNB adduct, heated to 40°C, for AlEt_3 —BL—*tert*-butyl peroxyisobutyrate system (0.1—0.1—0.05 molar solution in cyclopentane) kept standing at 20°C for 30 min.

triplets (1:2:1) indicates the trapping of a primary radical. Since the sole possibility of the occurrence of a primary radical in the ternary system lies in the ethyl radical formed from the AlEt_3 —BL complex, the spin adduct was identified as *N*-ethoxy-2,4,6-tri-*tert*-butylanilino radical (II) ($g=2.003$, $a_N=10.6$ G, $a_{H(\beta)}=a_{H(m)}=2.3$ G).

Thus we have here the interesting fact that an ethyl radical that should hardly be susceptible to steric hindrance is trapped to form an anilino radical that was reported to be detectable only when a bulky radical was captured.⁵ This suggests that the ethyl radical so detected had been under some steric hindrance up to the moment of its being trapped. Such a state may be visualized in the ethyl radical coordinating itself to, say, the aluminum atom in the catalyst system, or in the unstable carbon-aluminum bond that is susceptible to homolytic cleavages to generate the ethyl radical. Our preceding paper showed that a mixture solution of the three catalyst components is capable, without the use of any additives, of generating up to one ethyl radical per AlEt_3 molecule.¹ Furthermore, this ethyl radical, to be discussed later, has been shown to behave quite differently from the usual free radical under the polymerization conditions. These facts suggest that the steric-

ally hindered state of the ethyl radical presents, in other words, a state in which the ethyl radical finds itself coordinated to, say, the aluminum atom in the catalyst system, or a state in which it can be regarded as virtually so coordinated. Therefore, we propose to call it the *coordinated* ethyl radical.

In order to confirm a more general occurrence of the *coordinated* alkyl radical from the trialkylaluminum in our ternary catalyst system, studies were conducted on other systems that proved active in the polymerization of ethylene,¹ with specific variations introduced in their constituent components.

The ternary system of trimethylaluminum (AlMe_3)—BL—acetyl peroxide was kept standing for 30 min at room temperature and then subjected to spin trapping with TBNB. The ESR spectrum obtained, shown in Figure 5, indicated the presence of two kinds of spin adducts, corresponding respectively to the attached illustrations.

Figure 5. ESR spectrum of TBNB adducts for AlMe_3 —BL—acetyl peroxide system (0.1—0.1—0.05 molar solution in cyclopentane) kept standing at 20°C for 30 min.

spectrum that was found precisely identifiable with that of the TBNB adduct of the free methyl radical formed from the decomposition of acetyl cyclohexysulfonyl peroxide. Therefore, it was assigned to methyl 2,4,6-tri-*tert*-butylphenyl nitroxide (III) ($g=2.006$, $a_N=12.8$ G, $a_{H(\beta)}=12.5$ G, $a_{H(m)}=0.8$ G).

For identification of the other spin adduct, ESR measurement was carried out immediately after the trapped system was heated to 40°C, as was done for the system of $AlEt_3$ —BL—*tert*-peroxyisobutyrate. This resulted in the sole spectrum exhibiting the characteristic feature of an anilino radical, as shown in Figure 6. The hyperfine splitting of the protons at the β position consisting of quartets (1 : 3 : 3 : 1) indicates that the adduct is assignable to *N*-methoxy-2,4,6-tri-*tert*-butylanilino radical (IV) ($g=2.003$, $a_N=10.8$ G, $a_{H(\beta)}=a_{H(m)}=2.0$ G).

The ternary system of triisobutylaluminum $Alisobu_3$ —BL—*tert*-butyl peroxyisobutyrate, allowed to stand for 30 min at room temperature and then spin-trapped, gave the spectrum shown in Figure 7, indicating likewise the formation of two kinds of spin adducts. This spectrum was further found to possess the same characteristic as were observed for the system of $AlEt_3$ —BL—*tert*-butyl peroxyisobutyrate. This reveals

Figure 6. ESR spectrum of TBNB adduct, heated to 40°C, for $AlMe_3$ —BL—acetyl peroxide system (0.1—0.1—0.05 molar solution in cyclopentane) kept standing at 20°C for 30 min.

Figure 7. ESR spectrum of TBNB adducts for $Alisobu_3$ —BL—*tert*-butyl peroxyisobutyrate system (0.1—0.1—0.05 molar solution in cyclopentane) kept standing at 20°C for 30 min.

that the isobutyl radicals, which are primary radicals formed in this ternary system, were trapped to give isobutyl 2,4,6-tri-*tert*-butylphenyl nitroxide (V) ($g=2.006$, $a_N=13.6$ G, $a_{H(\beta)}=18.0$ G, $a_{H(m)}=0.8$ G), and *N*-isobutyroxy-2,4,6-tri-*tert*-butylanilino radical (VI) ($g=2.003$, $a_N=10.6$ G, $a_{H(\beta)}=a_{H(m)}=2.3$ G).

Thus, not only the ethyl but also the methyl and isobutyl radical formed in the ternary system give the anilino radical adduct when trapped by TBNB. These facts suggest that our ternary catalyst system, active in the ethylene polymerization, generates the *coordinated* alkyl radical regardless of the kind of the trialkylaluminum employed.

This was supported by the fact that similar phenomena were observed regardless of the kind of the peroxides combined with the trialkylaluminum—Lewis base complex. The spin

Table III. TBNB spin adducts of radicals formed in trialkylaluminum—Lewis base—peroxide system

Ternary system ^a	Alkyl radical (R·) formed in the system	TBNB spin adduct ^b

		Concn, 10 ⁻⁵ mol/l	%	Concn, 10 ⁻⁵ mol/l	%
AlMe ₃ —BL—acetyl peroxide	Me·	2.68	62	1.67	38
AlMe ₃ —BL—propionyl peroxide	Me·	2.91	65	1.59	35
AlEt ₃ —BL—acetyl peroxide	Et·	2.13	49	2.22	51
AlEt ₃ —BL— <i>tert</i> -butyl peroxyisobutyrate	Et·	2.24	46	2.60	54
AlisoBu ₃ —BL— <i>tert</i> -butyl peroxyisobutyrate	isoBu·	1.85	44	2.36	56
AlEt ₃ —DME— <i>tert</i> -butyl peroxyisobutyrate	Et·	2.19	73	0.81	27

^a A solution of trialkylaluminum—Lewis base complex in cyclopentane was so mixed with a solution of peroxide at 0°C that the concentrations of the components were adjusted to 0.1–0.1–0.05 mol/l, and the mixture system was allowed to stand at 20°C for 30 min.

^b Spin-trapped by addition of a solution of TBNB in cyclopentane (0.5 mol/l) and ESR measurement was carried out at 20°C.

Table IV. Spin concentration of TBNB adducts for AlEt₃—BL—*tert*-butyl peroxyisobutyrate system^a

Additive ^b	Concn of AlEt ₃ , mol/l	TBNB spin adduct ^c

		Concn, 10 ⁻⁵ mol/l	%	Concn, 10 ⁻⁵ mol/l	%	Concn, 10 ⁻⁵ mol/l	%
—	0.2	4.37	47	4.93	53	—	—
Cyclopentane	0.1	2.24	46	2.60	54	—	—
Cyclopentane	0.1	2.52	49	0	0	2.59	51

^a A solution of AlEt₃—BL complex in cyclopentane (0.4 mol/l) was mixed with an equivolume solution of *tert*-butyl peroxyisobutyrate in cyclopentane (0.2 mol/l) at 0°C.

^b The catalyst system, upon addition of the compound, was allowed to stand at 20°C for 30 min.

^c Spin-trapped by addition of a solution of TBNB in cyclopentane (0.5 mol/l) to the system and ESR measurement carried out at 20°C.

trapping with TBNB for the ternary system of AlMe_3 —BL—propionyl peroxide led to the detection of both the nitroxide III and the anilino radical IV, and these only. The trapping for the system of AlEt_3 —BL—acetyl peroxide likewise gave both the nitroxide I and the anilino radical II. These facts also indicate that the radicals are generated not from the alkyl group in the peroxide, but solely from that in the trialkylaluminum.

A similar phenomenon was further observed when an effective Lewis base other than BL was employed. The spin trapping for the ternary system of AlEt_3 —dimethoxyethane (DME)—*tert*-butyl peroxyisobutyrate also gave both types of the adducts of the ethyl radical.

In order to gain more information on the radicals formed in the ternary catalyst system, quantitative analyses were carried out on the spin concentrations of the TBNB adducts for each of the systems tested, with necessary adjustments made in the measuring conditions. The percentage of the *coordinated* alkyl radical showed a tendency to increase as the size of the alkyl group in trialkyl aluminum complexed with BL increased, and BL, when complexed with AlEt_3 , was found to give the *coordinated* ethyl radical in much greater quantities and in much higher percentage than did DME. All this is summarized in Table III.

Investigation of the Initiation Reaction

Since oligomers were the only product in the polymerization of ethylene by means of either of the two free-radical initiators, the *coordinated* alkyl radical may participate in the formation of the solid polyethylene by use of the ternary catalyst system. In order to investigate the relevance of the *coordinated* alkyl radical in the initiation reaction of the ethylene polymerization, spin trapping was further carried out on the ternary system of AlEt_3 —BL—*tert*-butyl peroxyisobutyrate in the presence of cyclopentene instead of ethylene monomer. Cyclopentene was employed because it hardly homopolymerizes, and also because it enables distinction in the ESR spectra between the spin adduct of the ethyl radical formed from the ternary system and that of the cyclopentyl radical formed under the attack of the ethyl radical. The

concentration of each catalyst component was the same as described above for the detection of the alkyl radical, and cyclopentene was added in large excess of the catalyst component. The TBNB adducts of the radicals in the ternary system which had been kept standing after its preparation for 30 min at room temperature in

Figure 8. ESR spectrum of TBNB adducts for AlEt_3 —BL—*tert*-butyl peroxyisobutyrate system (0.1—0.1—0.05 molar solution in equivolume of cyclopentane) kept standing at 20°C for 30 min.

Figure 9. ESR spectrum of TBNB adduct, heated to 40°C, for AlEt_3 —BL—*tert*-butyl peroxyisobutyrate system (0.1—0.1—0.05 molar solution in equivolume of cyclopentane and cyclopentene) kept standing at 20°C for 30 min.

the presence of cyclopentene gave the ESR spectrum as shown in Figure 8. The observed spectrum, assignable to the nitroxide I, again indicates the presence of the free ethyl radical in the ternary system. On the other hand, a spectrum due to a new anilino radical was detected in place of that ascribable to the anilino radical II.

For identification of the new adduct observed, the spin-trapped mixture system was subjected to heating at 40°C, as previously done in the absence of cyclopentene, immediately before its ESR measurement. This resulted in the appearance of only the spectrum of the anilino radical, as shown in Figure 9. This spectrum is ascribable to the adduct of a primary radical because of the hyperfine splitting of the proton at the β position consisting of doublets (1:1). Furthermore, the g value and hyperfine splitting constants of this anilino radical were found to be approximately equal to the corresponding values of the adduct formed by the trapping of a cyclohexyl radical.⁵ These facts indicate that the adduct in the trapped system is identifiable as *N*-(2-substituted)cyclopentoxo-2,4,6-tri-*tert*-butyl-anilino radical (VII) resulting from the reaction with TBNB of the cyclopentyl radical that was formed from the cyclopentene under the attack of the radical ($g=2.003$, $a_N=10.9$ G, $a_{H(\beta)}=a_{H(m)}=1.9$ G).

Both the presence of the cyclopentyl radical and the complete vanishing of the *coordinated* ethyl radical upon addition of cyclopentene to the ternary catalyst system suggest that the ethylene polymerization should be initiated by the *coordinated* ethyl radical.

In order to gain more precise information on the radical transformation, a quantitative comparison was performed on the spin concentrations of the TBNB adducts of the radicals in the ternary system in the absence and presence of cyclopentene under properly adjusted conditions. The results are listed in Table IV. A solution of the three catalyst components in cyclopentane was diluted to half its concentration by the addition of the same solvent, and kept standing thereafter for 30 min at room temperature. The spin trapping performed on the mixture system caused no change in the ratio of the nitroxide I to the anilino radical II.

However, in the case where the solution was diluted to half its concentration by the addition of cyclopentene, the anilino radical II was no longer detected, with the anilino radical VII emerging instead in an approximately equal amount, while the ratio of the nitroxide I to the anilino radicals remained practically the same.

The observed quantitative transformation of the *coordinated* ethyl radical to the cyclopentyl radical, with no reaction on the part of the free ethyl radical, strongly points to the possibility that it should be the *coordinated* alkyl radical that initiates the polymerization of ethylene.

Possibility of Ethylene Activation

In order to investigate the possibility of the ethylene molecule being activated in the ternary catalyst system, cyclopentene, instead of ethylene monomer, was added to a solution of the $AlEt_3$ -BL complex in cyclopentane, and the mixture was subjected to IR and NMR spectral analyses.

The NMR chemical shift of the olefinic protons in cyclopentene, while undergoing hardly any change in the presence of free BL, showed a slight shift toward the lower magnetic field in the presence of the $AlEt_3$ -BL complex, as shown in Table V. This shift proved definite because similar results were obtained with the concentrations of the catalyst components and cyclopentene approximately halved or doubled. The chemical shifts of the methylene and methyl protons in $AlEt_3$ complexed with BL also

Table V. NMR chemical shift of olefinic protons in cyclopentene

System ^a	δ , ^b ppm	Δ , ^c ppm
Cyclopentene	-4.12	—
BL-cyclopentene (1:1)	-4.12	0
$AlEt_3$ -BL-cyclopentene (1:1:1)	-4.15	-0.03

^a 1.0 molar solution in cyclopentane. NMR measurement was carried out at 24°C.

^b Chemical shift as measured from the signal of cyclopentane protons.

^c Deviation from the chemical shift of the cyclopentene in cyclopentane.

shifted toward the lower magnetic field in the presence of cyclopentene, even when the cyclopentene present was in amounts equimolar to the complex, with both shifts increasing as its ratio to the complex was increased, as is seen in Table VI. Furthermore, the chemical shift of the γ -methylene protons in BL complexed with AlEt_3 , measured under the same conditions as in Table V, shifted by 0.07 ppm toward the higher magnetic field in the presence of cyclopentene, while their chemical shift in the free BL showed hardly any change even in the presence of cyclopentene. Similar phenomena were observed in the IR spectra of BL. The absorption peaks of the carbonyl group as well as those of the ether linkage in BL complexed with AlEt_3 were found to shift in the presence of cyclopentene, while the corresponding peaks in the free BL hardly showed any shift, as shown in Table VII.

Table VI. NMR chemical shifts of methylene and methyl protons in AlEt_3

Cyclopentene/ AlEt_3 ^a , molar ratio	δ_{CH_2} , ^c ppm	δ_{CH_3} , ^c ppm
— ^b	1.77	0.56
1	1.75	0.54
2	1.73	0.52
4.3	1.69	0.49

^a Cyclopentene was added to a 1.0–1.0 molar solution of AlEt_3 and BL in cyclopentene. NMR measurement was carried out at 24°C.

^b No cyclopentene was used.

^c Chemical shift as measured from the signal of cyclopentane protons.

Table VII. IR absorptions of carbonyl group and ether linkage in BL

System ^a	$\nu_{\text{C=O}}$, cm^{-1}	$\nu_{\text{C-O-C}}$, cm^{-1}
BL	1795	1155
BL—cyclopentene (1:1)	1796	1157
AlEt_3 —BL (1:1)	1721	1243
AlEt_3 —BL—cyclopentene (1:1:1)	1711	1257

^a 0.2 molar solution in cyclopentane. IR measurement was carried out at 20°C.

All these phenomena combine to indicate that the double bond in cyclopentene interacts with the AlEt_3 —BL complex. Therefore, this fact suggests that, in the actual polymerization system, there are not only free ethylene molecules but also those that are activated by the complex, and it is further considered possible that the ethylene molecules so activated may participate in the initiation as well as in the propagation steps in the polymerization reaction.

Investigation of the Propagation Reaction

With a view to investigating the possible relationship between the coordinated radical and the propagation reaction in which the activated ethylene may take part, study was made on the behavior of the radicals in the ternary system of AlEt_3 —BL—*tert*-butyl peroxyisobutyrate in the presence of 4-methyl-1-pentene, instead of ethylene monomer, as it generates a secondary alkyl radical under the attack of any radical. The ternary system which had been kept standing for 30 min at room temperature in the

Figure 10. ESR spectrum of TBNB adducts for AlEt_3 —BL—*tert*-butyl peroxyisobutyrate system (0.1—0.1—0.05 molar solution in equivolume of cyclopentane and 4-methyl-1-pentene) kept standing at 20°C for 30 min.

presence of 4-methyl-1-pentene was subjected to spin trapping with TBNB to give the ESR spectrum shown in Figure 10. The measurement conditions were the same as when cyclopentene was used. This spectrum, besides indicating the presence of the nitroxide **I** responsible for the free ethyl radical, also shows the presence of two other adducts in the mixture system.

For identification of these two new adducts, reference was made to the report on a secondary alkyl radical generating two types of TBNB adducts, one being the nitroxide and the other the anilino radical,⁵ and the isopropyl radical from the decomposition of isobutyryl peroxide was spin-trapped, with its related spectrum obtained as in Figure 11. Comparison of this with the preceding figure shows that each of the two pairs of the corresponding adducts is quite identical in the g -value and hyperfine constants. This finding should assign the two adducts to *sec*-alkyl 2,4,6-tri-*tert*-butylphenyl nitroxide (**VIII**) ($g=2.006$, $a_N=13.3$ G, $a_{H(\beta)}=22.2$ G, $a_{H(m)}=0.8$ G) and *N-sec*-alkoxy-2,4,6-tri-*tert*-butylanilino radical (**IX**) ($g=2.003$, $a_N=11.0$ G, $a_{H(\beta)}=a_{H(m)}=1.8$ G), respectively.

Furthermore, a careful inspection of these spectra shows that the anilino radical **IX** is greater in intensity than the nitroxide **VIII** for the ternary system trapped in the presence of 4-methyl-1-pentene, while the reverse is true for the system of isobutyryl peroxide. This was confirmed by comparing the spin concen-

trations of these adducts measured under properly adjusted conditions. As shown in Table VIII, the secondary alkyl radical, formed from 4-methyl-1-pentene through attack by the *coordinated* ethyl radical, is trapped to form predominantly the anilino radical **IX** rather than the nitroxide **VIII**, quite in contrast to the trapping of the free secondary alkyl radical. These results are taken to suggest that there is but small possibility of the *coordinated* ethyl radical attacking the free 4-methyl-1-pentene to form the free propagating-end radical, or, in other words, that the propagation step of the polymerization most probably progresses with the radical at the propagating end maintained in the coordinated state throughout.

Behavior of Coordinated Radical in Presence of Ethylene

In order to furnish further direct proof for the interesting polymerization mechanism in which the *coordinated* radical may take part, ethylene monomer was introduced into one of the ternary systems for spin-trapping. The catalyst system was purposely made to have $AlMe_3$ as its alkylaluminum component, which was combined with BL and acetyl peroxide. This enabled spectral differentiation of the methyl radical released by $AlMe_3$ from the methylene radical formed by the methyl radical attacking ethylene monomer. The spin adducts of the radicals in the ternary system which had been allowed to stand after its preparation for 30 min at room temperature in the presence of ethylene monomer under a pressure of 2 kg/cm² gave the ESR spectrum shown in Figure 12. The observed spectrum, assignable to the nitroxide **III**, again shows the presence of the free methyl radical in this system. On the other hand, in place of the spectrum of the anilino radical **IV**, a different spectrum due to an anilino radical, was detected.

For identification of the anilino radical, the trapped system was heated to 40°C and then subjected to ESR measurements which resulted in the appearance of its spectrum alone, as shown in Figure 13. This spectrum was found to have the same g value and hyperfine splitting constants as exhibited by the anilino radical **II** from $AlEt_3$ as well as by the anilino radical

Figure 11. ESR spectrum of TBNB adducts of the decomposed radical of isobutyryl peroxide (0.1 molar solution in cyclopentane) at 20°C.

Table VIII. Spin concentration of TBNB adducts for AlEt_3 —BL—*tert*-butyl peroxyisobutyrate system in the presence of 4-methyl-1-pentene

Trapped system			TBNB spin adduct ^d			
Radical initiator	Additive	Concn of radical initiator, mol/l
			Concn, 10^{-5} mol/l	%	Concn, 10^{-5} mol/l	%
AlEt_3 —BL— <i>tert</i> -butyl peroxyisobutyrate ^a	4-Methyl-1-pentene ^b	0.1—0.1—0.05	0.21 ^c	8	2.39 ^c	92
Isobutyryl peroxide ^c	—	0.1	0.56	73	0.21	27

^a A solution of AlEt_3 —BL complex in cyclopentane (0.4 mol/l) was mixed with an equivolume solution of *tert*-butyl peroxyisobutyrate in cyclopentane (0.2 mol/l) at 0°C.

^b The mixture system, upon addition of 4-methyl-1-pentene, was allowed to stand at 20°C for 30 min.

^c The solution in cyclopentane was kept standing at 20°C for 30 min.

^d Spin-trapped by addition of a solution of TBNB in cyclopentane (0.5 mol/l) and ESR measurement carried out at 20°C.

^e Besides ethyl 2,4,6-tri-*tert*-butylphenyl nitroxide I in concentration of 2.53×10^{-5} mol/l.

Table IX. Spin concentration of TBNB adducts for AlMe_3 —BL—acetyl peroxide system^a in presence of ethylene

Additive	TBNB spin adduct ^c

	Concn, 10 ⁻⁵ mol/l	%	Concn, 10 ⁻⁵ mol/l	%	Concn, 10 ⁻⁵ mol/l	%	Concn, 10 ⁻⁵ mol/l	%
—	2.68	62	—	—	1.67	38	—	—
Ethylene ^b	2.81	60	0	0	0	0	1.85	40

^a A solution of AlMe_3 —BL complex in cyclopentane (0.2 mol/l) was mixed with an equivolume solution of acetyl peroxide in cyclopentane (0.1 mol/l), and the mixture system was allowed to stand at 20°C for 30 min in absence and presence of ethylene.

^b 2 kg/cm² at 20°C.

^c Spin-trapped by addition of a cyclopentane solution of TBNB (0.5 mol/l) and ESR measurement carried out at 20°C.

Figure 12. ESR spectrum of TBNB adducts for AlMe_3 —BL—acetyl peroxide system (0.1—0.1—0.05 molar solution in cyclopentane) kept standing at 20°C for 30 min in presence of ethylene under 2 kg/cm^2 .

Figure 13. ESR spectrum of TBNB adduct, heated to 40°C , for AlMe_3 —BL—acetyl peroxide system (0.1—0.1—0.05 molar solution in cyclopentane) kept standing at 20°C for 30 min in presence of ethylene under 2 kg/cm^2 .

VI from AlisoBu_3 . Therefore, the adduct thus observed was assigned to *N*-(2-substituted)ethoxy-2,4,6-tri-*tert*-butylanilino radical (X) resulting from the trapping of the propagating end of ethylene ($g=2.003$, $a_N=10.6\text{ G}$, $a_{H(\beta)}=a_{H(m)}=$

2.3 G).

The findings mentioned above clearly indicate that the *coordinated* methyl radical participates in the polymerization of ethylene with the coordinated state retained, but that the free methyl radical does not.

In order to account quantitatively for this phenomenon, measurement was conducted on the spin concentrations of the adducts trapped for the ternary catalyst system in the absence and presence of ethylene monomer under properly adjusted conditions. The results are summarized in Table IX.

It was clearly revealed that virtual quantitative transformation of the *coordinated* methyl radical into the *coordinated* propagating-end radical took place in the presence of ethylene monomer, but that hardly any change occurred in the amount of the free methyl radical even in the presence of ethylene.

CONCLUSION

The studies so far described strongly suggest that the ethylene polymerization under mild conditions by the ternary catalyst system consisting of trialkylaluminum, Lewis base, and peroxide should rest solely on the mechanism of the *coordinated radical polymerization*, i.e., the mechanism in which the *coordinated* alkyl radical formed from the trialkylaluminum attacks the ethylene molecules which are probably activated, to bring about the initiation reaction followed by the propagation reaction, with the coordinated state retained throughout.

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