Copolymerization of Ethylene with Vinyl Acetate by Trialkylaluminum–Lewis Base–Peroxide Catalyst

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ABSTRACT: Study was carried out on the behavior of the copolymerization of ethylene with vinyl acetate by specific combinations of trialkylaluminum–Lewis base–peroxide used as catalysts. A few of these gave higher activity than did a usual low-temperature free-radical initiator, and the copolymerization products obtained thereby were richer in vinyl acetate content as well as higher in molecular weight than was the random copolymer by the free-radical copolymerization. Solvent fractionation and thin-layer chromatography analyses revealed that the total product by the ternary system consisted of two different kinds of copolymer fractions. One was identical in characteristics with the random copolymer by the free-radical initiator and the other was identified with a copolymer exhibiting a high alternating tendency. ESR studies employing a spin-trapping agent, 2,4,6-tri-*tert*-butylnitrosobenzene for the ternary system of trimethylaluminum–γ-butyrolactone–acetyl peroxide, showed that the coordinated methyl radical formed in this system transformed quantitatively into the growing-end radicals of both ethylene and vinyl acetate, with the coordinated state retained throughout, thus confirming that the copolymer with high alternating character was formed by the mechanism of coordinated radical polymerization.

The ternary catalyst system consisting of some specific combinations of trialkylaluminum, Lewis base, and peroxide was found capable of readily polymerizing ethylene under the mild conditions of room temperature and 60 kg/cm^2.[1] ESR spectral analyses employing a bifunctional spin-trapping agent, 2,4,6-tri-*tert*-butylnitrosobenzene, showed that there form two different kinds of alkyl radicals in the ternary system, one being the coordinated alkyl radical, as we propose to call it, because it is to be regarded as being under some steric hindrance, and the other the usual free alkyl radical.[2] It was further confirmed that the formation of the high molecular weight polyethylene rests on the mechanism of the coordinated radical polymerization, i.e., the mechanism in which the coordinated alkyl radical attacks the activated ethylene molecules to bring about the initiation reaction followed by the propagation reaction, with the coordinated methylene growing-end radical retained throughout.

Investigation into the copolymerization behavior participated by these striking coordinated radicals constituted the next interesting step. We have already found, in our studies conducted under Professor Saegusa,[3] that the ternary catalyst system of triethylaluminum ($AlEt_3$)–zinc chloride ($ZnCl_2$)–carbon tetrachloride (CCl_4) enables copolymerization of ethylene and vinyl acetate (VAc) to give a mixture of the 1:1 alternating and the random copolymers. The present paper describes an attempt at copolymerizing the same monomer combination by using the ternary system of trialkylaluminum–Lewis base–peroxide. Interestingly, the copolymerization product was again found to be a mixture of the copolymer with high alternating character as well as high molecular weight and the random copolymer. Further investigations elucidated how the coordinated and the free radicals are related to the formation of these product copolymers.

Experimental Section

Materials. Vinyl acetate (VAc) (Wako Pure Chemical Ind.) was purified by the usual method. Petroleum ether (PE) (Wako Pure Chemical Ind.) was used without further purification. The other reagents used were the same as described in our previous papers.[1,2]

Catalyst Preparation and Copolymerization. Since the catalytic activity of the ternary system tends to decrease gradually if left standing after its preparation, it was prepared in situ, i.e., in the presence of the ethylene and VAc monomers, as was done in the case of our ethylene polymerization.[1] A typical example is as follows:

In a 50-ml pressure vessel, in which was placed a sealed glass ampule containing a solution of *tert*-butyl peroxyisobutyrate (1.0 mmol) in 5 ml of *n*-hexane, a solution of $AlEt_3$ (2.0 mmol) in 5 ml of *n*-hexane was added dropwise to a solution of γ-butyrolactone (BL) (2.0 mmol) in 5 ml of *n*-hexane at 0 °C under dry nitrogen with a magnetic stirrer in operation, and the mixture system was kept standing for 1 h. The vessel was closed after adding 5 ml (54 mmol) of VAc, and ethylene was introduced up to 60 kg/cm^2 (7 g, 250 mmol) to crush the ampule, thus bringing the catalyst components into contact. The copolymerization, which started immediately, was allowed to continue under stirring at room temperature (ca. 20 °C) for 18 h.

After the copolymerization, the unreacted ethylene was purged from the vessel. The reaction mixture, treated with a small amount of methanol for decomposing the catalyst system, was subjected to extraction with methylene chloride. The copolymerization product was isolated by evaporating the methylene chloride, solvent *n*-hexane, and unreacted VAc monomer under reduced pressure.

For comparative purposes, the usual free-radical copolymerization was also performed under similar conditions except for the low-temperature free-radical initiator, isobutyryl peroxide, having been employed.

Thin-Layer Chromatography (TLC) of Copolymerization Product. The TLC analysis of the copolymerization product was performed as was described in our previous paper,[3] applying the procedure proposed by Inagaki et al.[4]

NMR Spectra. NMR spectra of the product copolymers were taken with the same instrument as described in our previous reports,[1,2] using tetramethylsilane as internal standard. The ratio of ethylene to VAc units in the copolymer was obtained from the peak area ratio of the peak at τ 5.10 (methine proton) or at τ 7.96 (acetyl protons) of VAc units to the multiplet from τ 8.1 to 9.0 (methylene protons) of ethylene and VAc units.

ESR Spectra. ESR measurements were carried out with the same instrument and similar procedures as described in our previous papers.[2] The addition of VAc to the mixture solution of the three catalyst components was made immediately before the solution was transferred into the ESR sample tube.

Molecular Weight. The molecular weight of the copolymer was measured with the same instrument as described in our previous paper,[1] in benzene at 40 °C.

Results and Discussion

Comparison with Random Copolymer by Free-Radical Initiator. The ternary catalyst system consisting of trialkylaluminum, Lewis base, and peroxide in some specific combinations, having been shown to be active in the polymerization of ethylene,[1] was also found to be capable of copolymerizing ethylene (7 g, 250 mmol, 60 kg/cm^2) with VAc (5 ml, 54 mmol) at room temperature. The copolymerizations performed by the ternary system of $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate and trimethylaluminum ($AlMe_3$)–BL–acetyl peroxide were compared with the usual free-radical copolymerization performed by a low-temperature initiator, isobutyryl peroxide, under similar conditions. The amount of the free-radical initiator was so determined as to make the isopropyl radical formed from its decomposition equal in quantity to that of the ethyl radical from the ternary system

Table I
Ternary Catalyst System Compared with Free-Radical Initiator in Ethylene–VAc Copolymerization[a]

Catalyst system		Copolymerization product		
	mmol	Yield, g	Ethylene content, mol %	$\overline{M}_n$[b]
$AlEt_3$–BL–*tert*-butyl peroxyisobutyrate	2.0–2.0–1.0	3.08	69	2,800
$AlMe_3$–BL–acetyl peroxide	2.0–2.0–1.0	2.86	71	2,600
Isobutyryl peroxide	5.67	1.78	81	1,300

[a] Copolymerization conditions: *n*-hexane, 15 ml; ethylene, 7 g (250 mmol, 60 kg/cm^2); VAc, 5 ml (54 mmol); at 20 °C for 18 h. [b] Molecular weight by VPO in benzene at 40 °C.

of $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate during the period of the polymerization time.[1] The results are listed in Table I. The activity was higher in the copolymerization performed by the ternary system than in the free-radical copolymerization. Furthermore, the total copolymerization product obtained by either of the ternary systems was found to be richer in VAc content as well as higher in molecular weight than that obtained by the free-radical initiator.

In order to account for these differences, solvent fractionations using methanol and petroleum ether (PE) were then carried out on the gross copolymerization product obtained by the system of $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate as well as on the product of the free-radical copolymerization, and the composition and molecular weight of each fraction obtained were determined. As is seen in Table II, the two fractions, one of which being insoluble to methanol and the other soluble in methanol as well as in PE/methanol (5/1) mixture, were common to either of the copolymerization products, and each pair of the corresponding fractions of the two products was found to approximate closely in composition as well as in molecular weight. These facts suggest that those fractions which were obtained by the ternary system were formed by the usual free-radical copolymerization. On the other hand, the fraction soluble in methanol while insoluble to PE/methanol (5/1) mixture, recovered in the amount of 34 wt % from the gross product formed by the ternary system, hardly has any counterpart in the copolymers produced by the peroxide only. It was further found that this fraction was approximately equimolar in composition and that, when compared with other two fractions, it was richer in VAc content as well as higher in molecular weight. All this indicates that this fraction copolymer is highly different in character from the product of the free-radical copolymerization.

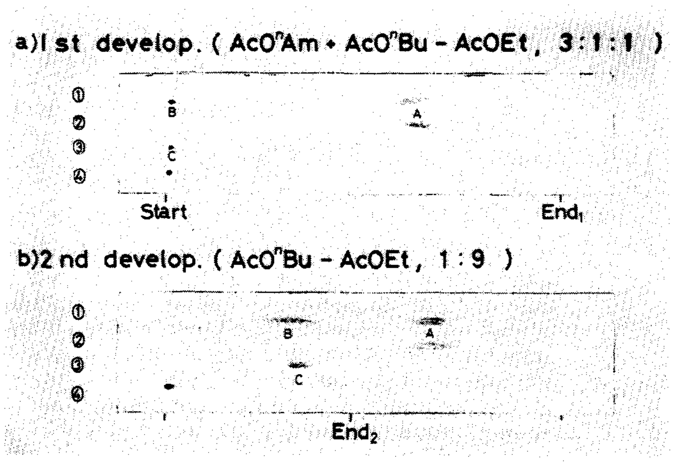


Figure 1. Thin-layer chromatograms of ethylene–VAc copolymers; (1) Ethylene–VAc copolymer obtained by $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate system; (2) ethylene–VAc copolymer obtained by isobutyryl peroxide; (3) ethylene–VAc 1:1 alternating copolymer obtained by $AlEt_3$–$ZnCl_2$–CCl_4 system; (4) poly-VAc.

This was brought out even clearer by thin-layer chromatography (TLC) analysis, as is shown in Figure 1. In the development during which two parts of ethyl acetate/*n*-butyl acetate (1/1) mixture was added dropwise to three parts of *n*-amyl acetate, the copolymerization product, spotted on the starting line, divided itself into two parts, A and B (Figure 1a). Similar developments were conducted not only on the two other ethylene–VAc copolymerization products, i.e., the random copolymer by the free-radical initiator, and the 1:1 alternating copolymer synthesized earlier by the ternary system of $AlEt_3$–$ZnCl_2$–CCl_4,[3] but also on the homopolymer of VAc. The R_f value of spot A is virtually identical to that of the free-radical random copolymer, clearly indicating that the spot A fraction was formed by the free-radical copolymerization. Spot B, in contrast, remained on the starting line in the first development, as did the spots of both the alternating copolymer and VAc homopolymer. In the second development with ethyl acetate/*n*-butyl acetate (9/1) mixture, spot B as well as the spot of the alternating copolymer moved up to positions of approximately equal R_f values, whereas the spot of poly-VAc again remained on the starting line (Figure 1b). This indicates that the spot B fraction is composed of copolymer having a perfectly or at least predominantly alternating

Table II
Solvent Fractionation of Ethylene–VAc Gross Copolymers as Obtained by Ternary Catalyst System and Free-Radical Initiator[a]

Fraction	Copolymer by $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate			Copolymer by isobutyryl peroxide		
	Recovered,[b] wt %	Ethylene content, mol %	$\overline{M}_n$[c]	Recovered,[b] wt %	Ethylene content, mol %	$\overline{M}_n$[c]
CH_3OH soluble						
PE–CH_3OH (5/1), insoluble	34	48	8000	Trace		
PE–CH_3OH (5/1), soluble	27	78	1300	64	79	1000
CH_3OH insoluble	39	82	3700	36	83	3000

[a] Copolymerization conditions: *n*-hexane, 15 ml; ethylene, 7 g (250 mmol, 60 kg/cm^2); VAc, 5 ml (54 mmol); catalyst, $AlEt_3$–BL–*tert*-butyl peroxyisobutyrate, 2.0–2.0–1.0 mmol, with yield, 3.08 g; catalyst, isobutyryl peroxide, 5.67 mmol, with yield, 1.78 g; at 20 °C for 18 h. [b] Relative percentage to total recovered copolymer. [c] Molecular weight by VPO in benzene at 40 °C.

Table III
Quantitative TLC Analysis of Ethylene-VAc Copolymer[a]

	Copolymer		
	Recovered,[d] wt %	Ethylene content, mol %	$\overline{M}_n$[e]
Fraction A[b]	64	80	1900
Fraction B[c]	36	54	7800

[a] Copolymerization conditions: catalyst, AlEt$_3$-BL-*tert*-butyl peroxyisobutyrate, 2.0-2.0-1.0 mmol; *n*-hexane, 15 ml; ethylene, 7 g (250 mmol, 60 kg/cm^2); VAc, 5 ml (54 mmol); at 20 °C for 18 h; yield, 3.08 g. [b] Fraction that moved up in the development during which two parts of ethyl acetate/*n*-butyl acetate (1/1) mixture was added dropwise to three parts of *n*-amyl acetate. [c] Fraction that remained on the starting line by the above development. [d] Relative percentage to total recovered copolymer. [e] Molecular weight by VPO in benzene at 40 °C.

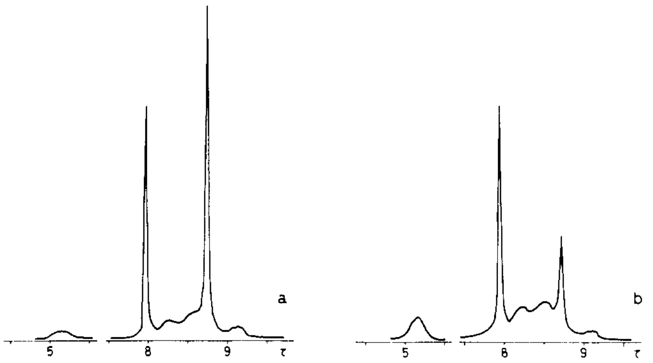


Figure 2. NMR spectra of ethylene-VAc copolymer fractions separated by quantitative TLC analysis (CDCl$_3$ solution): (a) fraction A; (b) fraction B.

structure with complete freedom from the VAc homopolymer.

The compositions of the fractions of spots A and B were determined by the quantitative TLC analysis. A fairly large sample of the gross copolymer was mounted in a band on the starting line of a special plate (20 × 20 cm^2, with a silica gel layer 1 mm thick) and was developed under the same conditions as used in the first development. From the gel layer were scraped off two bands, one having the R_f values equal to that of spot A and the other corresponding to spot B on the starting line, and each was extracted with acetonitrile. The results are listed in Table III, and the NMR spectra of the two fraction copolymers are shown in Figure 2.

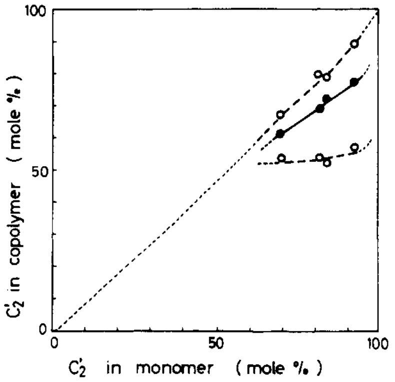


Figure 3. Copolymer composition curve in ethylene-VAc copolymerization by AlEt$_3$-BL-*tert*-butyl peroxyisobutyrate system. Copolymerization conditions: catalyst components, 2.0-2.0-1.0 mmol; *n*-hexane, 15 ml; at 20 °C for 18 h; (●) gross copolymer; (⊙) fraction A; (○) fraction B.

Fraction A was the ethylene-rich copolymer. Its NMR spectrum (Figure 2a) was found to be identifiable with that of the random copolymer obtained by isobutyryl peroxide, and its composition as well as molecular weight were also found to be close to those of the random copolymer (ethylene content, 81 mol %; mol wt, 1300).

Fraction B, on the other hand, was apparently an equimolar copolymer. Its NMR spectrum (Figure 2b) showed extremely small intensity of the peak at τ 8.72 corresponding to the long methylene units. These findings are taken to assign a structure with highly alternating character to the fraction B copolymer. Its molecular weight, moreover, is higher by far than that of the fraction A copolymer. Furthermore, the amounts of the fraction B copolymer recovered, it should be noted, exceed by far the quantity of the polymer that would have formed with one VAc molecule polymerizing with one ethylene molecule per trialkylaluminum of the ternary system, which is an indication of the fact that catalytical formation of the copolymer with high alternating tendency has actually taken place.

For further confirmation of these results, a series of copolymerizations was performed, each with the feed ratio of the two monomers varied, and each time the product copolymer was subjected to quantitative TLC analysis. The results are listed in Table IV, and the compositions of the gross and fraction copolymers are plotted in Figure 3. In each case the gross copolymers invariably separated into two fractions. As is seen in Figure 3, all fraction A spots rich in ethylene content

Table IV
Effect of Monomer Feed Ratios to Gross Product and Quantitative TLC Fractions in Ethylene-VAc Copolymerization[a]

Monomer		Copolymer					
		Gross product		Fraction A[b]		Fraction B[c]	
Ethylene, mmol	VAc, mmol	Yield, g	Ethylene content, mol %	Recovered,[d] wt %	Ethylene content, mol %	Recovered,[d] wt %	Ethylene content, mol %
290	22	2.09	77	60	89	40	57
290	54	2.84	72	69	79	31	52
250	54	3.08	69	64	80	36	54
250	108	3.41	62	67	72	33	54

[a] Copolymerization conditions: AlEt$_3$-BL-*tert*-butyl peroxyisobutyrate, 2.0-2.0-1.0 mmol; *n*-hexane, 15 ml; at 20 °C for 18 h. [b] Fraction that moved up in the development during which two parts of ethyl acetate/*n*-butyl acetate (1/1) mixture was added dropwise to three parts of *n*-amyl acetate. [c] Fraction that remained on the starting line by the above development. [d] Relative percentage to total recovered copolymer.

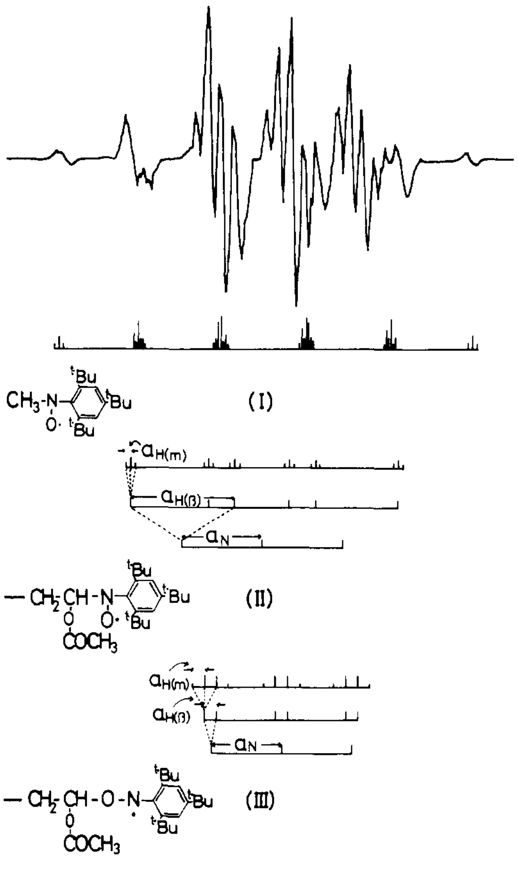


Figure 4. ESR spectrum of TBNB adducts for AlMe$_3$–BL–acetyl peroxide system (0.1–0.1–0.05 M solution of cyclopentane) kept standing at 20 °C for 30 min in presence of VAc monomer (in equimolar amount to AlMe$_3$).

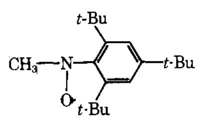
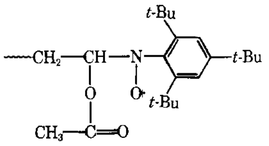
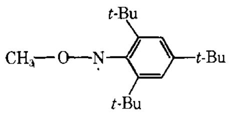
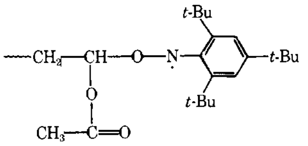
line up on a curve drawn with the assumed reactivity ratios of $r_1 = 0.6$ (for ethylene) and $r_2 = 1.0$ (for VAc). This indicates that the fraction copolymers which they represent are formed by the mechanism of the typical free-radical copolymerization. The copolymers represented by the fraction B spots, on the other hand, are all of approximately equimolar composition independently of the feed ratios of the two monomers, indicating that they are of high alternating character.

Investigation into Active Species of Copolymerization. In order, next, to investigate the active species of this ethylene–VAc copolymerization, one of the ternary catalyst systems was subjected to ESR analyses employing the bifunctional spin-trapping agent, 2,4,6-tri-*tert*-butylnitrosobenzene (TBNB), as described in our previous papers.[2,3] The catalyst system was purposely given AlMe$_3$ for its trialkylaluminum component to make possible spectral differentiation of the methyl radical released by the methyl group of the alkylaluminum from the methylene or secondary growing-end radical formed by the methyl radical attacking the ethylene or VAc molecule.

The spin trapping of the radicals formed in the ternary system of AlMe$_3$–BL-acetyl peroxide in the presence of VAc monomer gave the ESR spectrum shown in Figure 4. It indicates the presence of three kinds of adducts in this system, as illustrated in the figure. The emergence of the spectrum brought out in the uppermost illustration, assignable to methyl 2,4,6-tri-*tert*-butylphenyl nitroxide (I),[2] reveals the presence of the free methyl radical left unreacted with the VAc monomer. The spectrum shown in the middle illustration was found to be precisely identifiable with that of the sole spin adduct trapped for the system where a low-temperature free-radical initiator, acetyl cyclohexylsulfonyl peroxide, was decomposing in the presence of VAc monomer. Therefore, the adduct was assigned to 1-acetoxy-2-substituted ethyl 2,4,6-tri-*tert*-butylphenyl nitroxide (II) with the g value 2.006, and the hyperfine splitting constants $a_N = 12.5$ G, $a_{H(\beta)} = 17.2$ G, $a_{H(m)} = 0.8$ G. This indicates that part of the free methyl radicals formed in the ternary system attack the VAc molecules to transform into the VAc propagating end radicals. The spectrum represented by the bottom illustration has the characteristics of an anilino radical, but it quite differs from that of the adduct of the coordinated methyl radical[3] that should be generated in this system at the same time. A more careful scrutiny of the spectrum revealed that the hyperfine splitting of the protons at the β position consisted of doublets (1:1), which indicate the trapping of a secondary alkyl radical.[2] Since the sole possibility of the formation of a secondary radical lies in the propagating end radical of the VAc monomer, the adduct is assignable to *N*-(1-acetoxy-2-substituted) ethoxy-2,4,6-tri-*tert*-butylanilino radical (III) resulting from the trapping of the coordinated VAc end radical ($g = 2.003$, $a_N = 10.8$ G, $a_{H(\beta)} = a_{H(m)} = 1.8$ G). This fact signifies that the coordinated methyl radical also participates in the homopolymerization of VAc as well as in the ethylene homopolymerization,[2] i.e., it attacks the monomer to transform into the propagating end radical, while retaining its coordinated state throughout.

For further quantitative inquiries into the transformation of the radicals in the admixture system, measurement was carried out on the spin concentrations of the adducts trapped for the ternary system in the absence and presence of the VAc

Table V
Spin Concentration of TBNB Adducts for AlMe$_3$–BL–Acetyl Peroxide^a in Presence of VAc

	TBNB spin adduct^c							
								
Additive	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		
VAc^b	1.14	24	1.67	35	0	0	1.92	41

^{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 VAc. ^{b} Equimolar to AlMe$_3$. ^{c} Spin trapped by addition of a solution of TBNB in cyclopentane (0.5 mol/L) and ESR measurement carried out at 20 °C.

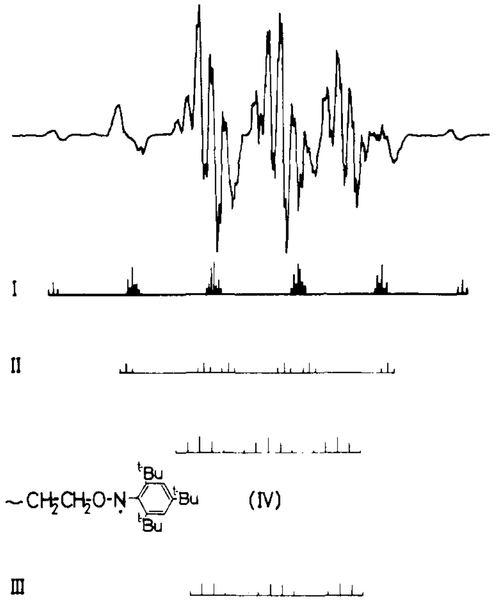


Figure 5. ESR spectrum of TBNB adducts for $AlMe_3$–BL–acetyl peroxide system (0.2–0.2–0.1 M solution of cyclopentane) kept standing at 20 °C for 30 min in presence of ethylene (2 kg/cm^2) and VAc (in equimolar amount to $AlMe_3$) monomers.

monomer, with necessary adjustment made in the measuring conditions. The results are summarized in Table V. It was clearly indicated that virtually quantitative transformation of the coordinated methyl radical into the coordinated propagating end radical occurred in the presence of the VAc monomer, but that only part of the free methyl radicals transformed into the free VAc growing end radical.

The radicals formed in this catalyst system in the presence of both the ethylene and VAc monomers were then examined by similar ESR spectral analysis. The spin trapping for the ternary system of $AlMe_3$–BL–acetyl peroxide to which was added the VAc monomer equimolar in amount to $AlMe_3$ followed by introduction of the ethylene gas sample under 2 kg/cm^2 gave the spectrum shown in Figure 5. This spectrum, compared with the spectra for this ternary system in the presence of the ethylene monomer[2] and of the VAc monomer, confirmed the generation of two kinds of nitroxide adducts and two kinds of anilino radical adducts. The former two are assignable to the nitroxide I corresponding to the free methyl radical[2] and nitroxide II corresponding to the free VAc propagating end radical. The latter two are identifiable with *N*-(2-substituted) ethoxy-2,4,6-tri-*tert*-butylanilino radical (IV) corresponding to the coordinated methylene radical indicating the presence of the propagating end of ethylene[2] and the anilino radical III corresponding to the coordinated VAc growing end radical. Since the random copolymer is formed by the free-radical copolymerization in accordance with the monomer reactivity ratios, these facts are taken to strongly suggest that it should be these coordinated propagating end radicals that are the sites which generate the ethylene–VAc copolymer with high alternating character.

This, together with the possibility we have indicated elsewhere[1] of these catalyst systems activating the ethylene monomer, and the fact that the ethylene–VAc copolymer is formed catalytically, further suggests that the mechanism of the coordinated radical polymerization as proposed in our previous papers[2] is likewise applicable to this copolymerization. Therefore, for the formation of the copolymer exhibiting the highly alternating character, we propose the mechanism of the coordinated radical copolymerization, i.e., the mechanism in which the coordinated alkyl radical formed from the trialkylaluminum very probably attacks both or at least either of the activated monomers to produce the coordinated initiating radical, from which the propagation reaction takes place, with the coordinated state retained, to yield the controlled copolymer sequence.

To bring out the underlying factors that control the alternating character achieved in the coordinated radical copolymerization calls for further extended investigations, through which the present authors hope to shed more light on this problem.

Conclusion

The ternary catalyst system of trialkylaluminum–Lewis base–peroxide was found capable of copolymerizing ethylene with VAc under mild conditions to form a mixture of the copolymer with high alternating character and the random copolymer. The catalytic formation of the former copolymer is effected by the mechanism which we propose to call the coordinated radical copolymerization, i.e., the mechanism in which the initiation and propagation reactions take place under the participation of the coordinated radicals, while the formation of the random copolymer is effected by the usual free-radical copolymerization.

References and Notes

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