Direct Ethoxylation of Fatty Methyl Ester over Al-Mg Composite Oxide Catalyst

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ABSTRACT: For the purpose of estimating the reaction mechanism of the direct ethoxylation of a fatty ester in the presence of an Al-Mg composite oxide catalyst, a labeled fatty methyl ester $C_{11}H_{23}CO^{18}OCH_3$ containing ^{18}O isotope was synthesized and directly ethoxylated. The product was evaluated by gas chromatography–mass spectrometry (GC–MS). The GC–MS spectra showed that the ^{18}O isotope label was present only in the methoxy group at the molecular end of the ethoxylated fatty methyl ester. This supports the reaction mechanism of coordination anionic polymerization where the bond between the acyl and methoxy groups of the fatty methyl ester molecule was broken, caused by the bifunctional effect of the acid–base active sites; an intermediate chemisorption species was formed; and then ethylene oxide was addition-polymerized sequentially, in parallel.
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KEY WORDS: Al-Mg composite oxide catalyst, coordination anionic polymerization, direct ethoxylation, ethoxylated fatty methyl ester, ethoxylation, ethylene oxide, fatty methyl ester, nonionic surfactant, reaction mechanism, solid catalyst.

In the previous paper (1), we reported that the direct ethoxylation of a fatty methyl ester without active hydrogens in the molecule did not proceed in the presence of an ordinary homogeneous catalyst, such as NaOH (2), but readily proceeded over the novel metal ion-containing MgO, especially an Al ion-containing MgO catalyst. The resultant ethoxylated fatty methyl ester was a monoester-type nonionic surfactant which was substantially completely homogeneous.

Also, the possibility was proposed that the reaction proceeded by a coordination anionic polymerization mechanism on the surface of the solid catalyst, and that ethylene oxide was directly inserted between the acyl and methoxy groups of the fatty methyl ester.

In this paper, the tracer experiment with the ^{18}O stable isotope was carried out to reveal the insertion position of the ethylene oxide on the solid catalyst and to establish the ethoxylation reaction mechanism (3–5).

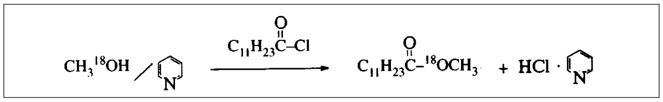
EXPERIMENTAL PROCEDURES

Synthesis of labeled methyl ester. The method used for synthesizing the fatty acid methyl ester labeled with an ^{18}O stable isotope (relative isotopic abundance 0.20%) is shown in Scheme 1 (6–7). To 80 mL of a solution of 0.6 g of ^{18}O-labeled methanol (EURISCO-TOP, Saint-Aubin Cedex, France: ^{18}O concentration 98.7 atom %, purity 99.1%) and 8.94 g of ordinary methanol (refined by distillation of methanol for high-performance liquid chromatography (HPLC), manufactured by Kanto Chemical, Tokyo, Japan) in pyridine (special grade pyridine, manufactured by Junsei Chemical (Tokyo, Japan) with added CaH_2, and distilled to be refined), 178 g (0.357 mol, 1.2 equivalents) of *n*-dodecanoyl chloride (special grade *n*-dodecanoyl chloride, manufactured by Tokyo Chemical Industry, Tokyo, Japan, and distilled to be refined) was added dropwise gradually for 1 h while the solution was vigorously stirred. Immediately after the addition of acid chloride was completed, 100 mL water was added to terminate the reaction. Organic substances were extracted in diethyl ether (Kanto Chemical) and dried with anhydrous magnesium sulfate (Kanto Chemical). Then the solvent was distilled away under reduced pressure to give 85.7 g of crude product. To remove polar substances that coexist in the product, the crude product was refined in an alumina column to give 55.7 g of methyl dodecanoate as the final product. The purity of the ^{18}O-labeled methyl dodecanoate was about 97% as determined by high-performance liquid chromatography (HPLC).

The nonlabeled methyl dodecanoate was synthesized in the same manner as described above by using ordinary methanol instead of ^{18}O-labeled methanol.

Direct ethoxylation of fatty methyl ester. Into a 200-mL glass autoclave were placed 55.0 g of the ^{18}O-labeled or nonlabeled methyl dodecanoate and 1.5 g of the novel Al ion-containing MgO (8) catalyst. The air in the autoclave was replaced with nitrogen gas while the material was stirred. Then the temperature of the mixture was elevated to 180°C. Ethylene oxide (hereinafter referred to as EO: Mitubishi Chemical, Tokyo, Japan) was gradually introduced into the autoclave to start the reaction.

At that time, the temperature in the autoclave was kept at 180°C, and the pressure at 3 atm. After 17 g of EO (the average mole number of added EO was equivalent to 1.5) was



SCHEME 1

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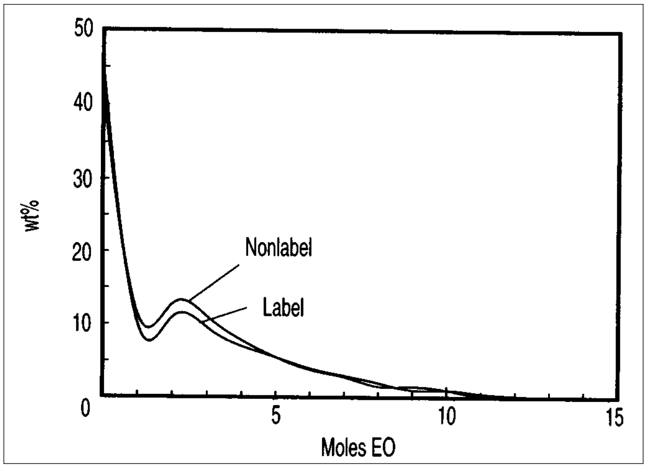


FIG. 1. Ethylene oxide (EO) distribution of methoxypolyoxyethylene dodecanoate (POE 1.5 mol).

supplied, the EO feed was stopped. Then, aging was carried out for 1 h. The reaction products were cooled, and the coexisting solid catalyst was filtered off to give the desired methoxypolyoxyethylene dodecanoate (POE, 1.5 mol). Figure 1 shows the EO distribution in the methoxypolyoxyethylene dodecanoate. The EO distribution was determined by the HPLC method (Shimazu LC-6A, Kyoto, Japan) with a UV detector (Shimazu SPD-10A), a Zorbax C8 column (DuPont, Boston, MA), and 76% acetonitrile aqueous solution as a mobile phase.

Analytical method. The labeling ratios of the ^{18}O-labeled and nonlabeled methyl dodecanoate, and the ^{18}O labeling positions in the methoxypolyoxyethylene dodecanoate were determined by GC–MS (SX-102; Jeol, Tokyo, Japan).

The analytical conditions for the GC–MS were as follows: column: HP-1, 0.32 mm × 25 m (Hewlett-Packard, Palo Alto, CA); carrier gas: He, split ratio: 56:1; injecting temperature: 250°C, column temperature: 120–300°C; ionization: ammonia CI; *m/z* range: 50–450 (0.5 s).

RESULTS AND DISCUSSION

Determination of labeling ratio of methyl dodecanoate. Figure 2 shows the respective magnified CI mass spectra for each fragment in the GC–MS spectra of the ^{18}O-labeled and nonlabeled methyl dodecanoate. M1–M4 are the fragment ions of methyl dodecanoate as indicated in Figure 2. The percentage in Figure 2 is the ratio [(M + 2)/{M + (M + 2)}] of the +2 mass peak [M + 2] to the sum of the main mass peak [M] and the +2 mass peak [M + 2] of each fragment.

The difference between the abovementioned +2 mass peak percentages of the ^{18}O-labeled and nonlabeled products represents the increment in mass caused by the ^{18}O labeling. Table 1 presents the increments in mass for each fragment of the methyl dodecanoate.

Table 1 shows that about 4.6% of the methoxy positions (–OCH_3) in the ^{18}O-labeled methyl dodecanoate were labeled with ^{18}O.

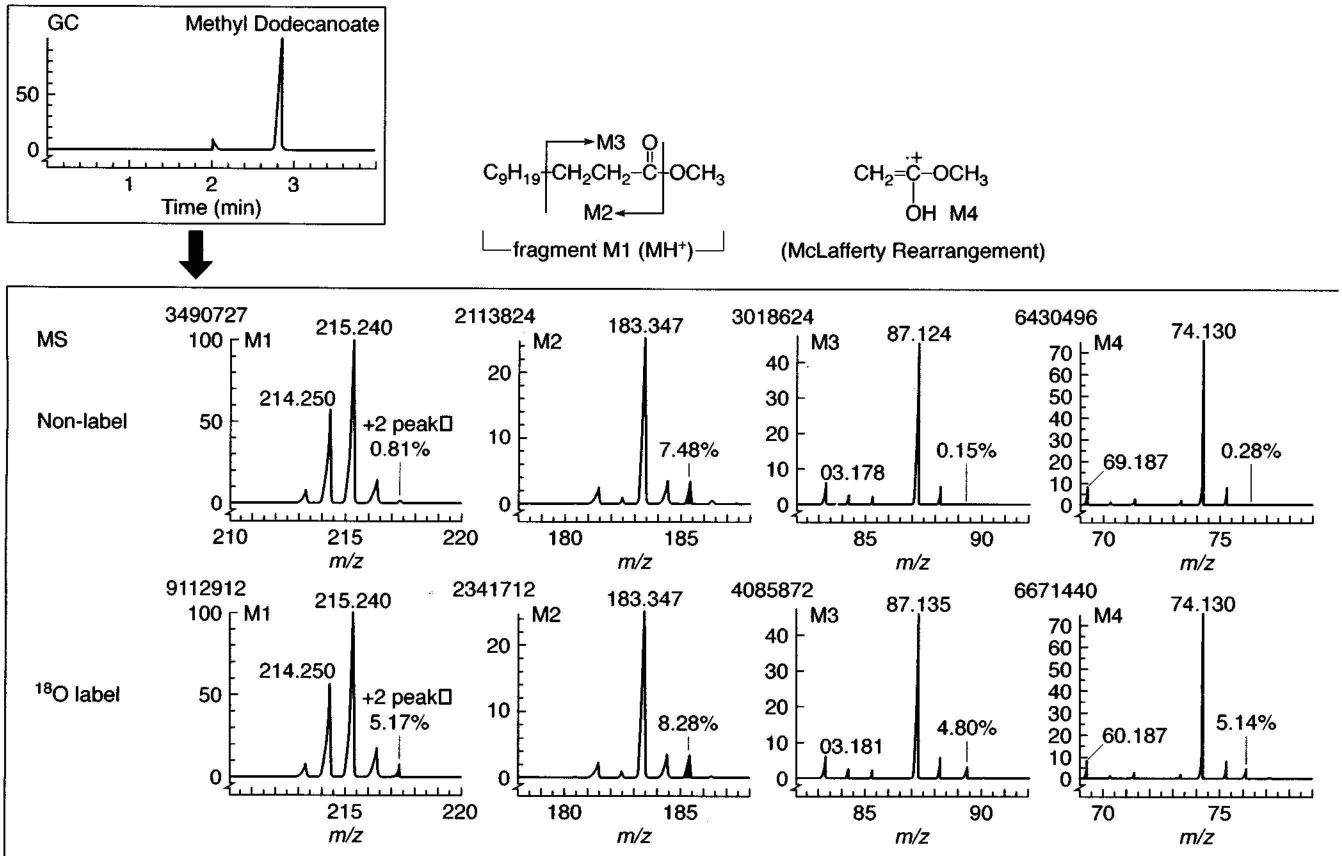


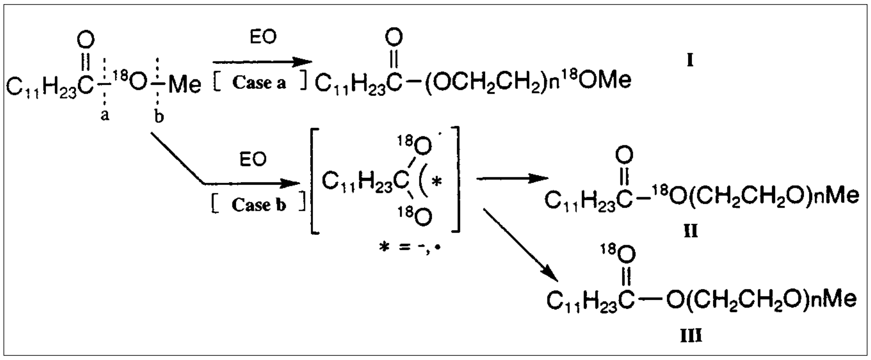
FIG. 2. Magnified mass spectra of fragments of methyl dodecanoate (raw material ester).

TABLE 1
Difference Between +2 Mass Peak of Each Fragment of the ^{18}O-Labeled and Nonlabeled Esters (%)

Fragment	M1	M2	M3	M4
^{18}O label	5.17	8.28	4.80	5.14
Nonlabel	0.81	7.48	0.15	0.28
Mass difference	+4.36	+0.80	+4.65	+4.86

Identification of EO insertion position. As regards the direct ethoxylation reaction of the fatty methyl ester over the Al-Mg composite oxide catalyst, the following is assumed. If the bond is broken as in Case a (Scheme 2) when the ^{18}O-labeled methyl dodecanoate dissociatively chemisorbs to an active site on the surface of the solid catalyst, a compound (**I**) containing the ^{18}O inserted at the methoxy position is produced. If the bond is broken as in Case b, compound (**II**) is produced, and if the oxygen of the methoxy groups is exchanged with that of the carbonyl group, compound (**III**) is produced, as shown in Scheme 2.

To identify the EO insertion position, the ^{18}O labeling position in the methoxypolyoxyethylene dodecanoate was determined by GC–MS. The respective magnified CI spectra for each fragment of the unreacted esters, 1-mole adducts and 2-mole adducts present in the ^{18}O-labeled plus nonlabeled methoxypolyoxyethylene dodecanoate (POE, 1.5 mol)



SCHEME 2

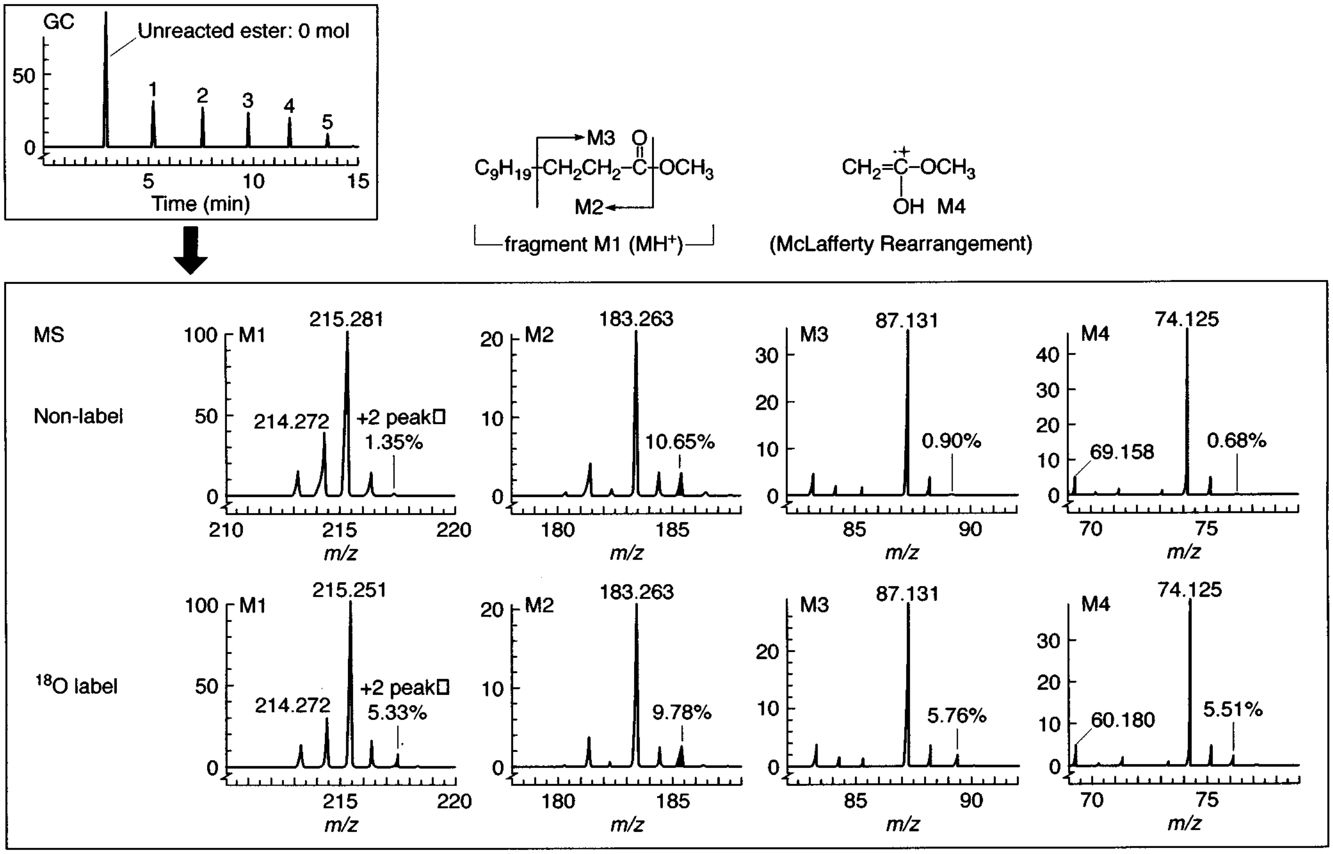


FIG. 3. Magnified mass spectra of fragments of unreacted methyl ester in POE, 1.5 mol: fragments M1, M2, M3, and M4 are the same as those of the raw material ester. See Figure 1 for abbreviation.

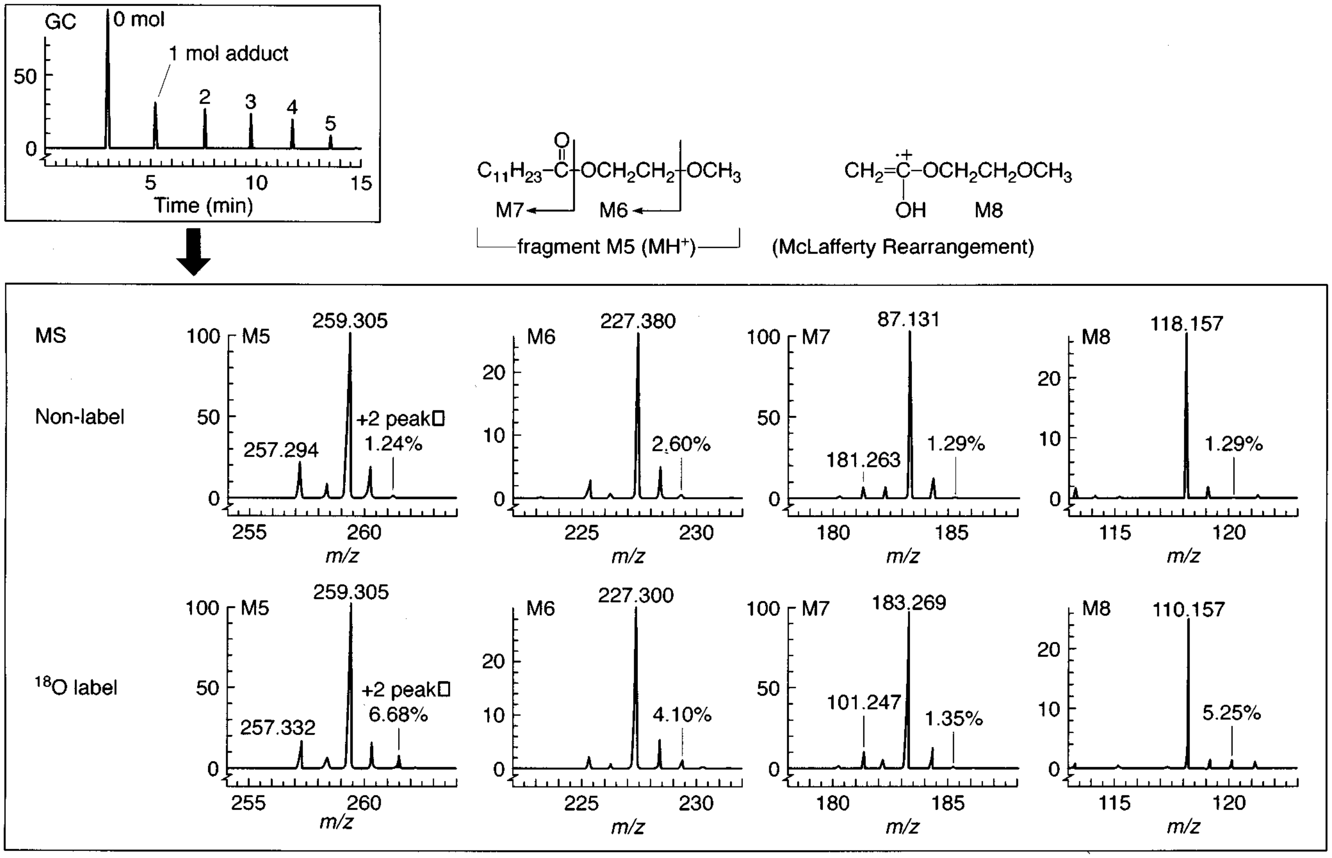


FIG. 4. Magnified mass spectra of fragments of 1-mol adduct in POE, 1.5 mol. See Figure 1 for abbreviation.

products are shown in Figures 3–5. The differences between the +2 mass peak percentages of the ^{18}O-labeled and nonlabeled products, that is, the increments in mass of the respective fragments caused by the ^{18}O labeling, are listed in Table 2.

Table 2 shows that the ^{18}O isotope present in the unreacted ester of the ^{18}O-labeled methoxypolyoxyethylene dodecanoate is positioned in the methoxy group of the methyl dodecanoate as in the raw material ester.

Moreover, it was determined that both the 1-mole adduct and the 2-mole adducts had structures in which the ^{18}O atoms were incorporated into the methoxy end groups. Accordingly, it is assumed that the direct ethoxylation reaction of the fatty methyl ester over the Al-Mg composite oxide catalyst proceeds by the mechanism whereby the bond is broken at (a), as shown in Scheme 2, when the methyl dodecanoate dissociatively chemisorbs to an active site on the surface of the solid catalyst to give a chemisorption intermediate, and that EO is added thereto. When bond (b) is broken on the surface of the catalyst, irrespective of the EO addition reaction, we assumed that the O atoms of the methoxy and the carbonyl groups will form a resonance structure and will be in the nonlocalized state to produce substance **III′**. However, no compounds in which the carbonyl groups were labeled as in substance **III′** were produced. This suggests that the bond at (b) was not broken.

$$C_{11}H_{23}\overset{\overset{^{18}O}{\|}}{C}\text{-}(OCH_2CH_2)nOCH_3$$

[**III′**]

Suggestion of direct ethoxylation reaction mechanism of fatty methyl ester. The intermediate chemisorption species present on the surface of the catalyst have not been identified. However, based on the above-described results, we assume that the direct ethoxylation reaction over the Al-Mg composite oxide catalyst proceeds by the mechanism shown in Scheme 3.

That is, first, the dissociation of the fatty methyl ester into acyl cation and methoxy anion occurred by the bifunctional effects of the basic sites derived from the magnesium oxide present on the surface of the catalyst and the acid sites derived from the added aluminum ions, so that the intermediate chemisorption species were formed. Subsequently, EO was polarized, as a result of the strong affinity between the Al acid sites and EO. The methoxy anion attacked nucleophilically, and EO was polymerized by ring-opening. Moreover, the di-

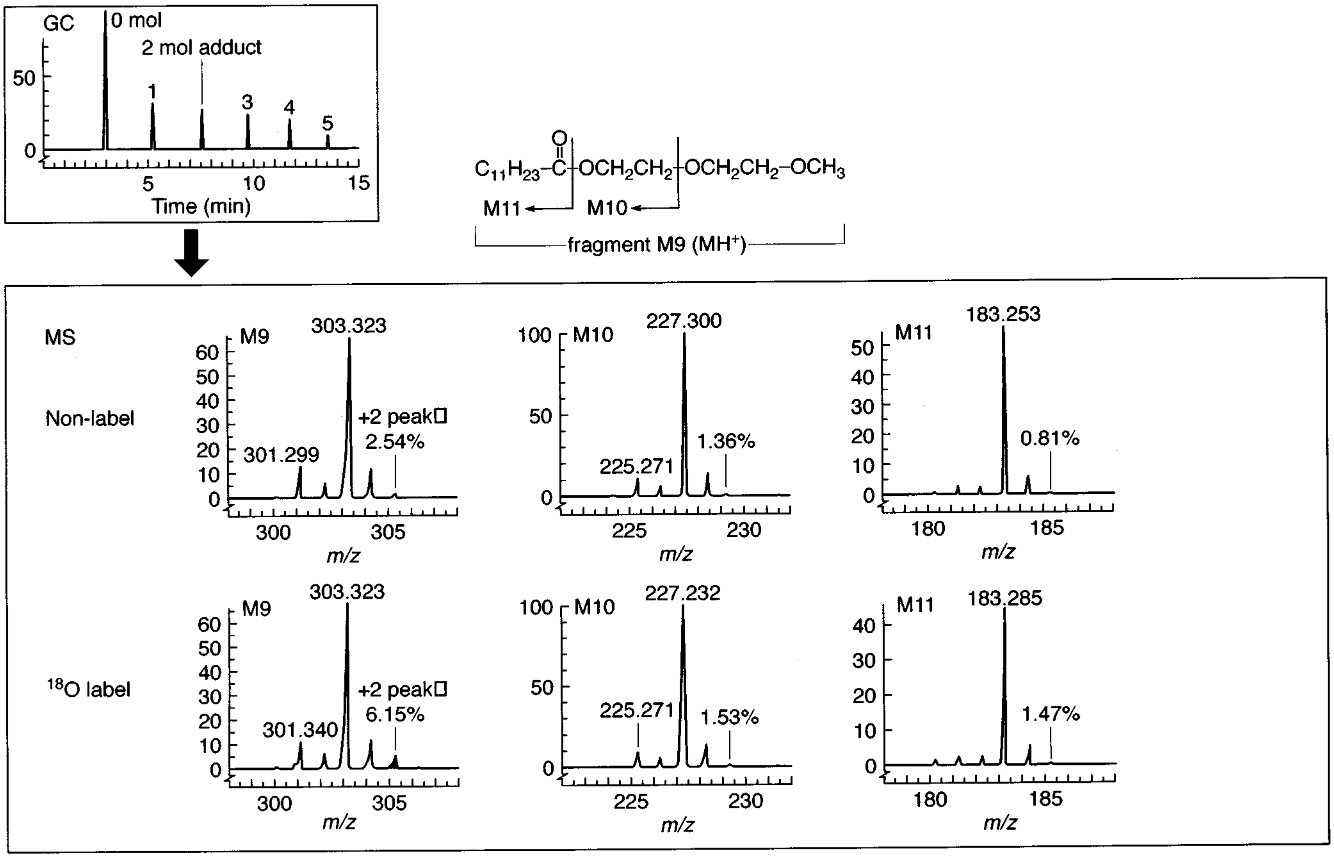


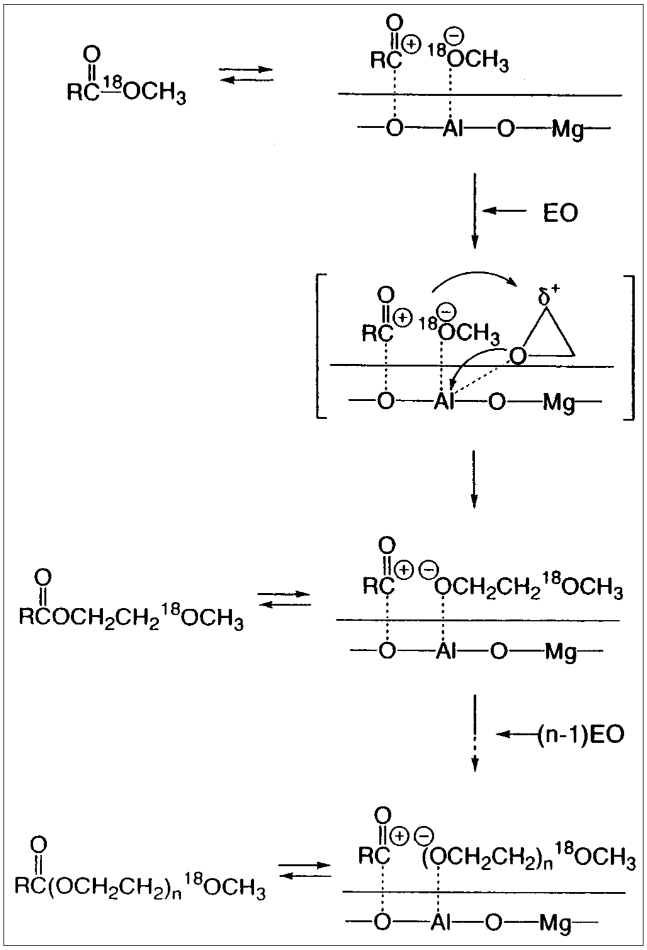
FIG. 5. Magnified mass spectra of fragments of 2-mol adduct in POE, 1.5 mol. See Figure 1 for abbreviation.

TABLE 2

Difference Between +2 Mass Peak of Each Fragment of the Unreacted Ester, 1-Mole Adducts and 2-Mole Adducts in the ^{18}O-Labeled and Nonlabeled Ethoxylates (%)

	Fragment	M1	M2	M3	M4
Unreacted ester	^{18}O label	5.33	9.78	5.76	5.51
	Nonlabel	1.35	10.65	0.90	0.63
	Mass difference	+3.98	−0.87	+4.86	+4.88
	Fragment	M5	M6	M7	M8
1-mol	^{18}O label	6.68	4.10	1.35	5.25
	Nonlabel	1.24	2.60	1.29	1.29
	Mass difference	+5.44	+1.50	+0.06	+3.96
	Fragment	M9	M10	M11	
2-mol	^{18}O label	6.15	1.53	1.47	
	Nonlabel	2.54	1.36	0.81	
	Mass difference	+3.61	+0.17	+0.66	

rect ethoxylation of the fatty methyl ester proceeded by the rebonding of the methoxyethoxy anion and by the acyl cation chemisorbing dissociatively to the surface of the catalyst. That is, by the coordination anionic polymerization mechanism, with the anionic species as the propagation end as shown in Scheme 3, the direct addition polymerization of EO to the fatty methyl ester occurred sequentially, in parallel, to give a homogeneous fatty methyl ester that was a substantially pure monoester.



SCHEME 3

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