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Isabelle Espinasse<sup>a</sup>; Roger Pétiaud<sup>a</sup>; Marie-France Llauro<sup>a</sup>; Alain Michel<sup>a</sup>

<sup>a</sup> Laboratoire des Matériaux Organiques à Propriétés Spécifiques, Vernaison, France

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# Multinuclear NMR Characterization of Co-cross-linking of Ethylene-co-vinylacetate and Ethylene-co-methylacrylate Polymer Blends in the Presence of Dibutyltin Oxide

ISABELLE ESPINASSE, ROGER PÉTIAUD, MARIE-FRANCE LLAURO  
AND ALAIN MICHEL\*

*Laboratoire des Matériaux Organiques à Propriétés Spécifiques, CNRS,  
BP 24, 69390 Vernaison, France*

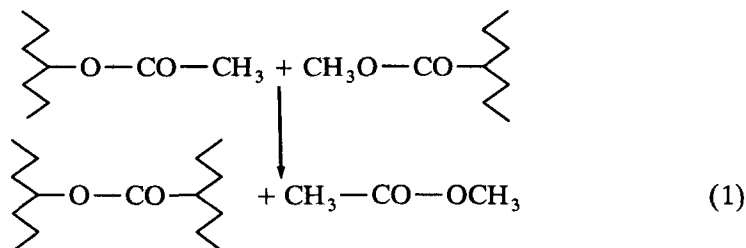
*(Received September 20, 1993)*

The co-cross-linking reaction of ethylene-co-vinylacetate (EVA) and ethylene-co-methylacrylate (EMA) polymer blends in the presence of dibutyltin oxide in the molten state is an interchain redistributive transesterification (ester–ester interchange reaction). It is shown with model esters, namely *n*-octyl acetate (1) and methyl nonanoate (2) in solution, that the efficient catalytic species are 1,3-acyl, alkoxy distannoxane from the reaction of esters with dibutyltin oxide. An intermolecular dimeric rearrangement between acyl and alkoxy dimeric distannoxanes from (1) and (2) esters occurs at ambient temperature without ligand exchange. Ligand exchange on tin atoms by reactions between free ester (1) and dimeric distannoxane occurs at higher temperature at both acyloxy and alkoxy tin sites. Reactions are characterized by multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$ ). Tetra acyloxy or tetra alkoxy distannoxanes are also efficient catalysts for this redistributive transesterification.

**KEY WORDS** Distannoxanes catalysts, polymer crosslinking in molten state, transesterification, NMR characterization.

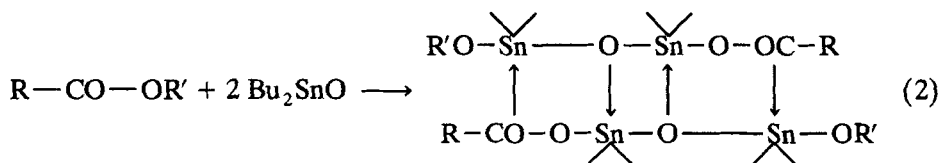
## INTRODUCTION

The reaction of ethylene-co-vinyl acetate (EVA) and ethylene-co-methylacrylate (EMA) polymer blends with dibutyltin oxide in the molten state leads to irreversible co-crosslinking of the copolymer chains [1]. The presence of methyl acetate indicates that some redistributive transesterification (interchain ester–ester interchange reaction) occurs, giving covalent crosslinking by the following reaction:

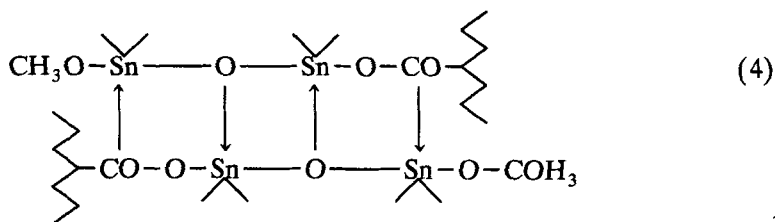
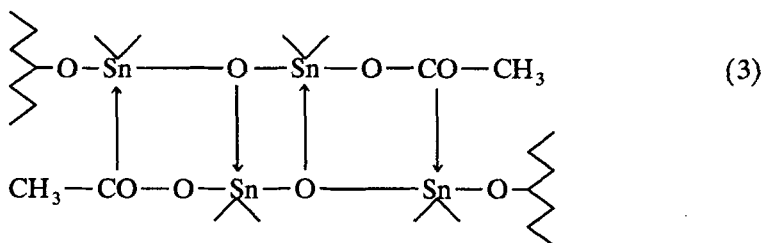


\* To whom all correspondence should be addressed.

The pseudo-kinetics of this cross-linking has been assessed by viscoelastic measurements of the dynamic storage modulus and by thermogravimetric analysis coupled with gas chromatography, which allows the measurement of evolved methyl acetate [2]. The observed variations of the storage modulus (Figure 1) are higher during the cross-linking of EVA/EMA blends than during the cross-linking of EVA (or EMA) alone, for experiments carried out in the same conditions [2]. Both cross-linkings, with EVA or EMA alone, are well explained by the formation of moisture-sensitive dimers of 1,3-acyloxy, alkoxy distannoxanes originating from the reaction of dibutyltin oxide on esters [3,4].



leading to cross-linking by dimeric distannoxane coordinated entities. In the case of EVA and EMA the cross-links have respectively the formulae (3) and (4):



In previous work [3,4], model compounds *n*-octyl acetate and methyl nonanoate were used to study the reaction between esters and dibutyltin oxide. In order to be in conditions close to rheological states, reactions were carried out at 200°C in bulk. It has been shown, with these two models esters, that under these conditions the reaction quickly leads (0.25 h) to the complete consumption of the organometallic oxide and produces, as a main product, one single dimer of 1,3-acyl, alkoxy distannoxane for formula (2). All attempts to crystallize these product failed, probably because of the C8 alkyl group. A mechanism of the attack of the dibutyltin oxide by the ester has been proposed [3,4].

Dimeric 1,3-acyloxy, alkoxy distannoxanes, obtained directly from the corresponding ester, were fully characterized by NMR; <sup>13</sup>C- and <sup>1</sup>H-NMR provided important complementary information in addition to classical <sup>119</sup>Sn-NMR. The

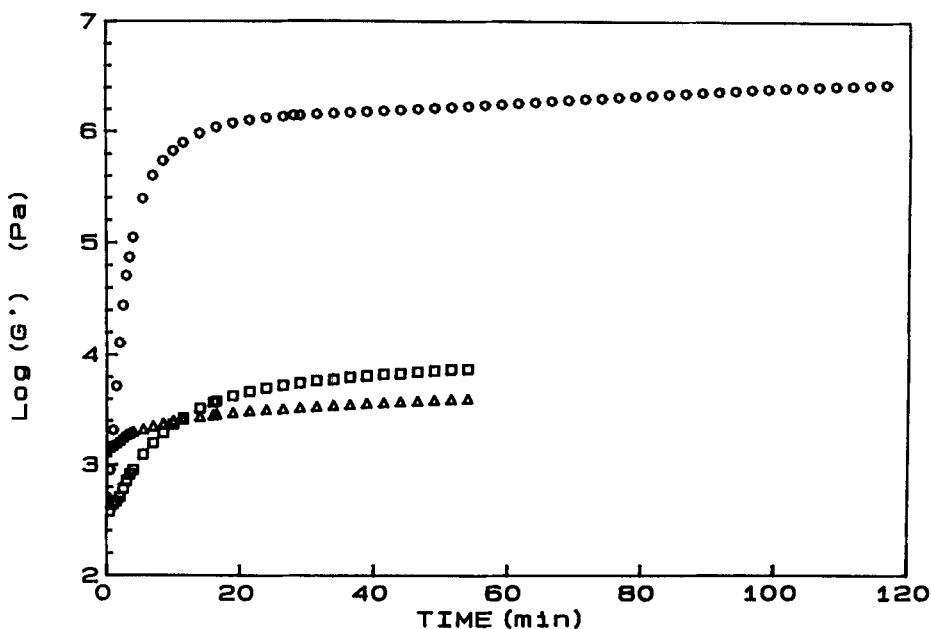


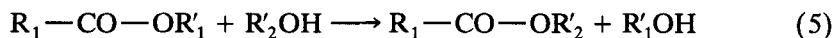
FIGURE 1 Storage modulus versus reaction time at 230°C: □, EVA + Bu<sub>2</sub>SnO; △, EMA + Bu<sub>2</sub>SnO; ○, EVA/EMA + Bu<sub>2</sub>SnO.

amount of by-products, some of which have not been identified, increased particularly at this temperature, if the ester was not in excess and if the reaction time was much longer than 15 min. For the reaction with *n*-octyl acetate, the formation of tributyltin acetate probably coming from the thermal degradation of the distannoxane, has been determined [3]. Tributyltin nonanoate was never observed in the reaction with methyl nonanoate.

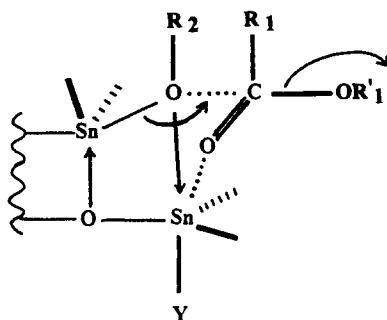
Tetraorganostannoxanes with short 1,3-organic ligands were discovered in 1914. Its dimeric structure was proved by x-ray analysis on some crystalline products [5]. More recently, pure, crystallizable tetraorganodistannoxanes were studied by <sup>119</sup>Sn-NMR in solution [6,7].

The unusual catalytic activity of different dimeric 1,3-disubstituted tetraorgano distannoxanes in urethane formation was first pointed out by Kanzana [8] and then investigated further by Otera [9].

Concerning transesterification, namely the following process:



where an ester is transformed into another through interchange of the alkoxy moiety (5), many organotin compounds turned out to be efficient catalysts. The first evidence of the catalytic properties of tributyltin alkoxides was reported by Pereyre et al. [10]. Other tin compounds were revealed as having catalytic properties of the same magnitude (R<sub>2</sub>Sn(OAc)<sub>2</sub>, R<sub>2</sub>SnCl<sub>2</sub>, R<sub>2</sub>SnO, etc. [1]. Later on, Otera [12–14] showed remarkably higher catalytic activity of crystalline distannoxanes which are easy to obtain and stable in air. A mechanism was proposed by Otera [13] involving



SCHEME I

the formation of an alkoxy distannoxane on one tin site in the initial step:



Scheme I shows the coordination of the ester on the neighboring tin sites, making the alcoholysis of the ester easier and providing a new ester due to the close proximity of the tin sites in dimeric distannoxanes.

In order to elucidate the exact function of dibutyltin oxide in the cross-linking of EVA/EMA blends, this work deals with the redistributive transesterification of model esters in solution and in less severe conditions than in the previous work (to reduce the side reactions observed previously [2,3]). The aim of this work is to characterize the active catalytic species and to study the exchange reactions taking place at the catalytic site, taking into account our previous work which described the reaction of dibutyltin oxide with esters, giving mostly 1,3-acyl, alkoxy distannoxane.

Since we have shown that dibutyltin oxide reacts with esters, although it is generally considered as a transesterification catalyst in reference to Otera (Reaction 5), it can no longer be considered as the active catalytic species in transesterification (5).

## EXPERIMENTAL

### Reagents

Dibutyltin oxide, *n*-octyl acetate, *n*-octadecyl acetate, and methyl nonanoate are commercial products (Aldrich). Ethylene-vinyl acetate (EVA) and ethylene-methyl acrylate (EMA) copolymers were kindly supplied by Atochem. The respective molar composition of acetate and acrylate units are 10.6 and 10.8%.

### Reactions of Dibutyltin Oxide with Copolymer in Molten State

EVA and EMA were mixed with 5% of dibutyltin oxide in the melt with an internal mixer (Haake Rheocord Mixer) equipped with a cam-type rotor. The mixer chamber temperature was set at 200°C and the stirring speed was increased quickly

to 50 rpm after the introduction of the polymer mixture. The molten polymeric medium was relaxed until a steady torque was reached.

### Reaction of Dibutyltin Oxide with Model Esters in Solution (Typical Procedure)

Equivalent molar amounts (0.032 mol) of both dibutyltin oxide and ester (methyl nonanoate or octylacetate) were mixed with 25 mL of tetrachloroethylene (TCE) in a reactor equipped with a magnetic stirrer and a reflux condenser. The mixture was heated for about 2 h under reflux. About 1 h, the mixture became clear. After removing the solvent and the excess ester under vacuum, an oily, pale yellow and translucent liquid was obtained. This liquid did not crystallize under cooling.

### Preparation of Diacetoxy, Tetrabutyl Distannoxane

Two methods are generally used: [15] reaction of acetic acid with dibutyltin oxide or partial hydrolysis of diacetoxy, dibutyl distannoxane. The second method was used, a white crystalline distannoxane was obtained.

### Preparation of 1,3-Dimethoxy, Tetrabutyl Distannoxane (in Dilute Solution)

This distannoxane was prepared by addition of water (0.031 g, 1.74 mM) to a solution of dimethoxy dibutyltin (10.250 g, 3.48 mM) in 10 mL of tetrachloroethylene. More generally dialkoxy, tetrabutyl distannoxane was prepared by reaction of dibutyltin oxide with the corresponding alcohol or carbonates [16].

Methyl alcohol formed during the reaction was not eliminated. There was a rapid exchange (at the NMR scale, 250 MHz) between free methyl alcohol and methoxy tin ligands, at room temperature. An average chemical shift value for methoxy protons was observed at  $\delta = 3.375$ . Characteristic spectral features are given in Table 1.

TABLE I

Characteristic NMR spectral features of dimeric symmetric distannoxanes

1,3,diacetoxy distannoxane		1,3,dimethoxy distannoxane
	<sup>1</sup> H-NMR	
$\delta \text{CH}_2(1)(\text{Bu}) = 0.920, 0.940$		$\delta \text{CH}_2(1)(\text{Bu}) = 0.955, 0.975$
$\delta \text{SnO}-\text{CO}-\text{CH}_3 = 1.880$		$\delta \text{SnOCH}_3 = 3.375$
	<sup>119</sup> Sn-NMR	
$\delta \text{Sn}(\text{endo}) = -219.4$		$\delta \text{Sn}(\text{endo}) = -174.1$
$\delta \text{Sn}(\text{exo}) = -229.8$		$\delta \text{Sn}(\text{exo}) = -180.1$
$^2\text{J Sn-Sn} = 122$		$^2\text{J Sn-Sn} = 164$
	<sup>13</sup> C-NMR	
$\delta \text{C1Bu} = 13.85$		$\delta \text{C1Bu} = 13.90$
$\delta \text{C2Bu} = 27.10; 27.25(^3\text{J} = 136)$		$\delta \text{C2Bu} = 27.60(^3\text{J} = 100)$
$\delta \text{C3Bu} = 27.60; 27.90$		$\delta \text{C3Bu} = 27.90; 28.10(^2\text{J} = 20)$
$\delta \text{C4Bu} = 27.55(^1\text{J} = 692-726)$		$\delta \text{C4Bu} = 19.25(^1\text{J} = 645-657)$
$\delta \text{C4Bu} = 29.40(^1\text{J} = 732-770)$		$\delta \text{C4Bu} = 22.50(^1\text{J} = 603-631)$
$\delta \text{SnO}-\text{CO}-\text{CH}_3 = 176.90$		$\delta \text{SnOCH}_3 = 50.60(^2\text{J} = 213)$
$\delta \text{SnO}-\text{CO}-\text{CH}_3 = 22.85$		

**Reaction of Dimethoxy, Tetrabutyl Distannoxane with Octyl Acetate (Typical Procedure) or Octyloxy, Acetoxy, Tetrabutyl, Distannoxane with Methyl Nonanoate or Diacetoxy, Tetrabutyl, Distannoxane with Octyl Acetate (or Methyl Nonanoate)**

21.4 mM of dimeric distannoxane and 42.8 mM of ester were mixed with 10 mL of tetrachloroethylene in a reactor equipped with a magnetic stirrer and a reflux condenser. The mixture was heated for 3 h at 120°C. A translucent oil was obtained and directly analyzed by NMR.

**NMR Spectroscopy**

High-resolution liquid NMR spectroscopy was carried out with a Bruker AC250 apparatus at 250 MHz for  $^1\text{H}$  and 62.9 MHz for  $^{13}\text{C}$  and with a Bruker AC 200 at 74.6 MHz for  $^{119}\text{Sn}$ . Tetrachloroethylene (TCE)/deuterated benzene ( $\text{C}_6\text{D}_6$ ) mixtures (2/1 by volume) were used as solvents. Chemical shifts values ( $\delta$ ) are given in ppm in reference to internal tetramethylsilane (TMS) for  $^1\text{H}$  and  $^{13}\text{C}$  and in reference to external tetramethyl tin for  $^{119}\text{Sn}$ .

**RESULTS AND DISCUSSION**

Dimeric 1,3-acyloxy,alkoxy distannoxanes have not been mentioned as catalytic entities in transesterification (5) by Otera, probably because he was not able to crystallize them or obtain them directly, [17] and they were moisture sensitive, particularly at the Sn–O–R bond when not stored in a solvent.

The catalytic activities of 1,3-octanoxy,acetoxy distannoxane, 1,3-methoxy, nonanyloxy distannoxane, 1,3-diacetoxy distannoxane and 1,3-dimethoxy distannoxane were evaluated for the redistributive transesterification (ester–ester interchange reaction) of *n*-octyl acetate (ester 1) and methyl nonanoate (ester 2). The catalyzed reaction, in the presence of each of these four dimeric distannoxanes, leads to a complete random redistribution of alkoyl and acyl parts of these esters, after 4 h at 110°C. This randomization gives four esters which are characterized by their distinct carbonyl resonances at  $\delta = 169.75$ , 170.05, 172.60, and 172.95, respectively for ester (1), methyl acetate (3), octyl nonanoate (4) and methyl nonanoate (2). In another study [18] concerning the comparison of the catalytic activity of a series of tin compounds (dibutyltin oxide, dialkoxy dibutyltin, diacyloxy dibutyltin and the above-mentioned distannoxanes) toward the cross-linking of EVA/EMA polymer blends by redistributive transesterification at 200°C, the analogy was evidenced between results observed with model compounds in solution and with polymer blend in the molten state.

Moreover, by comparing the spectral features of these distannoxanes and those obtained after reaction with equimolar amount of the appropriate ester, the exchange reactions at the tin sites were defined. These exchange reactions are the basis of catalytic activity of distannoxanes in this redistributive transesterification.

Except for the 1,3-diacetoxy distannoxane, which is crystalline and more stable, these distannoxanes were prepared in dilute solution in tetrachloroethylene (TCE), where they were protected against hydrolysis. These mild conditions gave nearly pure distannoxanes compared with compounds prepared in the solid phase in bulk

TABLE II

Characteristic NMR spectral features of dimeric 1,3 acyloxy, alkoxy distannoxanes	
ester: octylacetate	ester: methyl nonanoate
<sup>1</sup> H-NMR	
$\delta$ CH <sub>2</sub> (1)(Bu) = 0.940, 0.970	$\delta$ CH <sub>2</sub> (1)(Bu) = 0.940, 0.965
$\delta$ SnOCH <sub>2</sub> - = 3.525	$\delta$ SnOCH <sub>3</sub> = 3.330
$\delta$ CH <sub>3</sub> CO-OCH <sub>2</sub> - = 3.965	$\delta$ C8O-CO-CH <sub>3</sub> = 3.505
$\delta$ SnO-CO-CH <sub>3</sub> = 1.865	$\delta$ SnO-CO-CH <sub>2</sub> - = 2.150
$\delta$ O-CO-CH <sub>3</sub> = 1.850	$\delta$ CH <sub>3</sub> O-CO-CH <sub>2</sub> - = 2.185
<sup>119</sup> Sn-NMR	
$\delta$ Sn(endo) = -214.5	$\delta$ Sn(endo) = -218.2
$\delta$ Sn(exo) = -182.5	$\delta$ Sn(exo) = -181.4
<sup>2</sup> J Sn-Sn = (72-205)	<sup>2</sup> J Sn-Sn = (72.5-217)
<sup>13</sup> C-NMR	
$\delta$ C1Bu = 13.90	$\delta$ C1Bu = 13.90
$\delta$ C2Bu = 27.45; 27.65	$\delta$ C2Bu = 27.50; 27.75
$\delta$ C3Bu = 27.75; 27.90	$\delta$ C3Bu = 27.80; 28.00
$\delta$ C4Bu = 24.95 ( <sup>1</sup> J = 657-688)	$\delta$ C4Bu = 24.45 ( <sup>1</sup> J = 662-693)
$\delta$ C4Bu = 22.35 ( <sup>1</sup> J = 488-520)	$\delta$ C4Bu = 22.35 ( <sup>1</sup> J = 608-636)
$\delta$ CH <sub>3</sub> -CO-OC8 = 20.55	$\delta$ CH <sub>3</sub> -O-CO-CH <sub>2</sub> CH <sub>2</sub> - = 25.25
$\delta$ CH <sub>3</sub> -CO-OSn = 23.30	$\delta$ Sn-O-CO-CH <sub>2</sub> CH <sub>2</sub> - = 26.40
$\delta$ CH <sub>3</sub> -CO-OCH <sub>2</sub> CH <sub>2</sub> - = 29.10	$\delta$ CH <sub>3</sub> -O-CO-CH <sub>2</sub> C7 = 34.00
$\delta$ SnOCH <sub>2</sub> CH <sub>2</sub> = 35.15	$\delta$ Sn-O-CO-CH <sub>2</sub> C7 = 36.20
$\delta$ SnOCH <sub>2</sub> - = 64.25	$\delta$ SnOCH <sub>3</sub> = 51.00
$\delta$ CH <sub>3</sub> -CO-OCH <sub>2</sub> - = 64.15	$\delta$ C8-CO-OCH <sub>3</sub> = 50.90
$\delta$ SnO-CO-CH <sub>3</sub> = 176	$\delta$ SnO-CO-C8 = 178.80
$\delta$ C8O-COCH <sub>3</sub> = 169.30	$\delta$ C8-CO-OCH <sub>3</sub> = 172.65

and at 200°C [3-4]. NMR analysis, made directly on the reaction medium, shows that tributyltin acetate is not detected (tin resonances at 84.4 and 91.5 ppm). Above all, if the ratio of dibutyltin oxide and ester is lower than 0.5, no other side products appear (no tin resonances between 160 and 240 ppm). The characteristic NMR features of the obtained distannoxanes from octyl acetate (ester 1) and methyl nonanoate (ester 2) are given in Table II.

The extreme simplicity of the <sup>119</sup>Sn spectra is shown in Figure 2: two tin sites with equal populations coupled to each other with two different coupling constants J<sub>1,2'</sub> and J<sub>1,2</sub> is typical of the well-known dimeric distannoxane structure (Scheme II). In the following schemes, figures, and formulae, butyl tin ligands will not be represented). The <sup>1</sup>H-spectrum shows two different methyl protons corresponding to butyl ligands attached to exo- and endocyclic tin atoms, distinct resonances for Sn-O-CH<sub>2</sub>- and CH<sub>3</sub>-CO-OCH<sub>2</sub>- of the initial octyl acetate (a similar difference between Sn-O-CH<sub>3</sub> and C8-CO-OCH<sub>3</sub> of methyl nonanoate) and also distinct resonances Sn-O-CO-CH<sub>3</sub> (and Sn-O-CO-CH<sub>2</sub>-) from the corresponding ones in the free esters (1) and (2). Although the <sup>13</sup>C spectra were sometimes saturated by the presence of an equal quantity of residual free ester, all resonances were almost completely assigned. The two different butyl groups typical of distannoxanes are well resolved at 62.9 MHz except for their methyl carbons: Carbons in the  $\alpha$  position to the tin atoms, both endo- and exocyclic, show <sup>1</sup>J Sn-C coupling constants values, characteristic of pentacoordination of the tin atoms in the dimeric distannoxane structure. Carbons from alkoxy and acyloxy groups directly attached to tin atoms are broad and deshielded resonances, compared with the corresponding ones in the free esters. Detailed assignments were fully discussed in



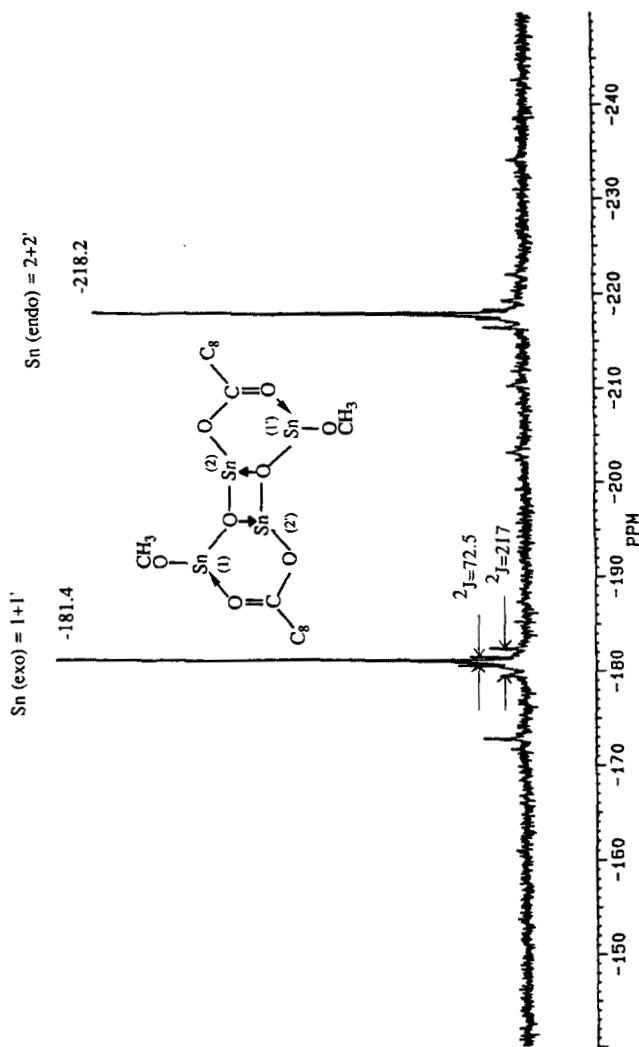
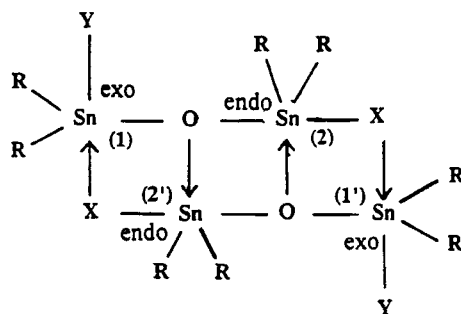


FIGURE 2 <sup>119</sup>Sn-NMR (74.6 MHz) spectrum of 1,3-methoxy,nonanyloxy distannoxane obtained in solution (Tetrachloroethylene) at 110°C from the corresponding ester and dibutyltin oxide.



SCHEME II

previous work [3–4] where some NMR spectra were presented. A head-to-tail dimeric distannoxane entity, coming from the dissymmetric distannoxane monomer ( $R'O-Bu_2Sn-O-Bu_2Sn-O-CO-R$ ) associated through the carbonyl oxygen of the acyloxy ligands was indentified. The possibility of a ligand exchange (from an alkoxy to an acyloxy group and vice versa) at the tin atom is ruled out since it would give symmetrical monomer and a more complex tin spectra with two types of donor groups. Moreover, when ligand exchange has been observed in mixtures of dimeric distannoxanes [17,19,20] it was always from two different symmetric entities toward a dissymmetric one.

As for the two other distannoxanes, both symmetrical, their spectral features are much simpler, as shown in Table I.

In order to define the reactions occurring at the distannoxane catalytic site in cross-linking of EVA/EMA polymer blends, a series of reactions were investigated; adequate concentrations (and not catalytic ones) were chosen to allow, afterward, direct NMR analysis. Only a selection of spectra are presented here (or spectral features described), in order to support the discussion and to avoid repetition. The reaction of dibutyltin oxide with equimolar quantities of ester (1) and ester (2) [1/1/1 ratio] at  $110^\circ\text{C}$  was first investigated and compared successively with (i) a mixture at ambient temperature of alkoxy,acyloxy distannoxane from ester (1) and alkoxy,acyloxy distannoxane from ester (2) (ii) the reaction product of alkoxy,acyloxy distannoxane from ester (1) and ester (2) (iii) the reaction product of alkoxy,acyloxy distannoxane from ester (2) with ester (1); differences and analogies between spectral features of the distannoxanes entities are discussed. It is shown (*a*- and *b*-) that ligand exchanges occur at both alkoxy and acyloxy tin sites  $Sn-OR'$  and  $Sn-O-CO-R$ , mostly by an exchange between groups of the same nature ( $-OR'$  or  $-CO-R$ ) but not exclusively. These exchanges were evidenced by new  $^{13}\text{C}$  resonances, but also by new splittings in the  $^{119}\text{Sn}$  resonances coming from slightly different tin sites. These ligand exchanges do not occur at ambient temperature, whereas intermolecular dimeric rearrangement of the two different distannoxanes does.

To investigate exchange reaction at the distannoxane entity when only one type of exchange is possible (alkoxy exchange at the alkoxytin site or acyl exchange at the acyloxytin site) symmetrical distannoxanes were investigated with ester (1) and/or ester (2) (*-c*, *-d*, and *-e*). The kinetic aspect of these exchanges was not investigated in this work; reactions go to completion in 3 h in all cases, but these

catalysts have different catalytic activities [18]

**a Reaction of  $\text{Bu}_2\text{SnO}$  with Equimolar Amounts of Ester (1) and Ester (2) at  $110^\circ\text{C}$  [2 moles  $\text{Bu}_2\text{SnO}$ , 1 mole Ester (1), 1 mole Ester (2)]**

When both *n*-octyl acetate and methyl nonanoate react with dibutyltin oxide, which represents a model of cross-linking by transesterification observed with EVA/EMA blends, the two parent dimeric distannoxanes are expected and an hybrid one (at least in solution where the mobility of ester molecules is high enough, and also in the molten state as soon as the temperature is sufficient to have a homogeneous polymer blend). In fact, a broad endocyclic tin resonance, which is poorly resolved, is observed at high field (from  $\delta = -210$  to  $-225$  ppm:  $\text{Sn-O-CO-R}$ ) and a fine structure with four well-resolved resonances is observed at lower field (from  $\delta = -180$  to  $-185$  ppm) for exocyclic tin sites  $\text{Sn-OR}$ ; the same type of tin spectrum is obtained after reaction of the distannoxane of ester (1) with ester (2) and vice versa; a typical spectrum is shown in Figure 3. In order to assign the well-resolved exocyclic tin resonances, mixtures of equimolar amounts of the two distannoxanes at room temperature are analyzed; the same exocyclic tin pattern is obtained (Figure 4c). As shown on Scheme IIIA, intermolecular dimeric rearrangement with two monomer species would give three dimeric distannoxanes with four exocyclic tin sites, two of them are expected to have the same intensity ( $\Delta$  and  $\nabla$  sites in Figure 4). Assignments of the initial distannoxanes are indicated in Figure 4a and 4b. The nearly equal areas obtained from initial equimolar ester amounts (Figure 4c) indicate a random dimerization redistribution and, conse-

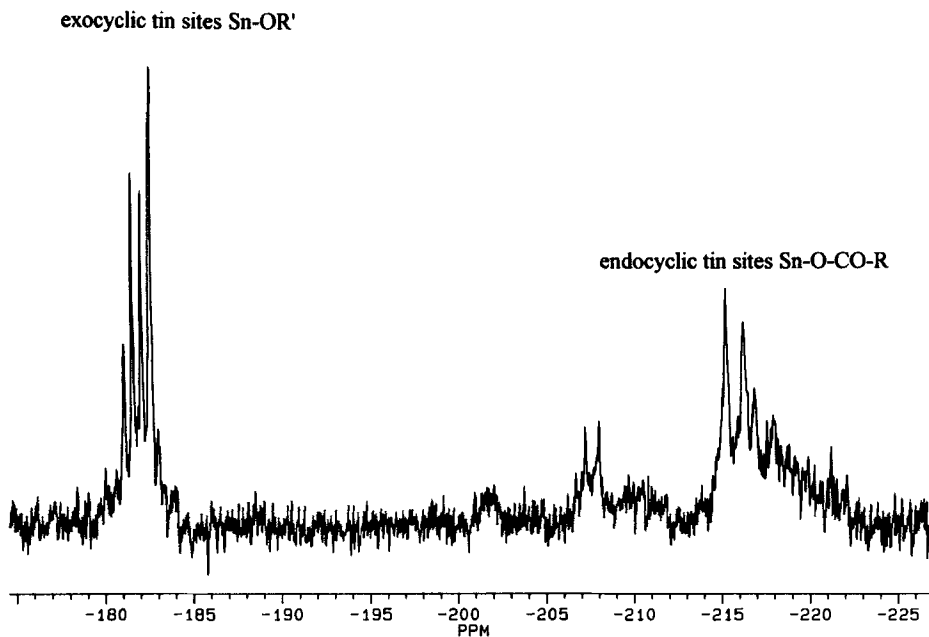


FIGURE 3  $^{119}\text{Sn}$ -NMR (74.6 MHz) spectrum obtained after reaction of octyl acetate (ester 1) with 1,3-methoxy,nonanyloxy distannoxane (distannoxane from ester 2). This typical spectrum is also observed in other cases (cf. text).

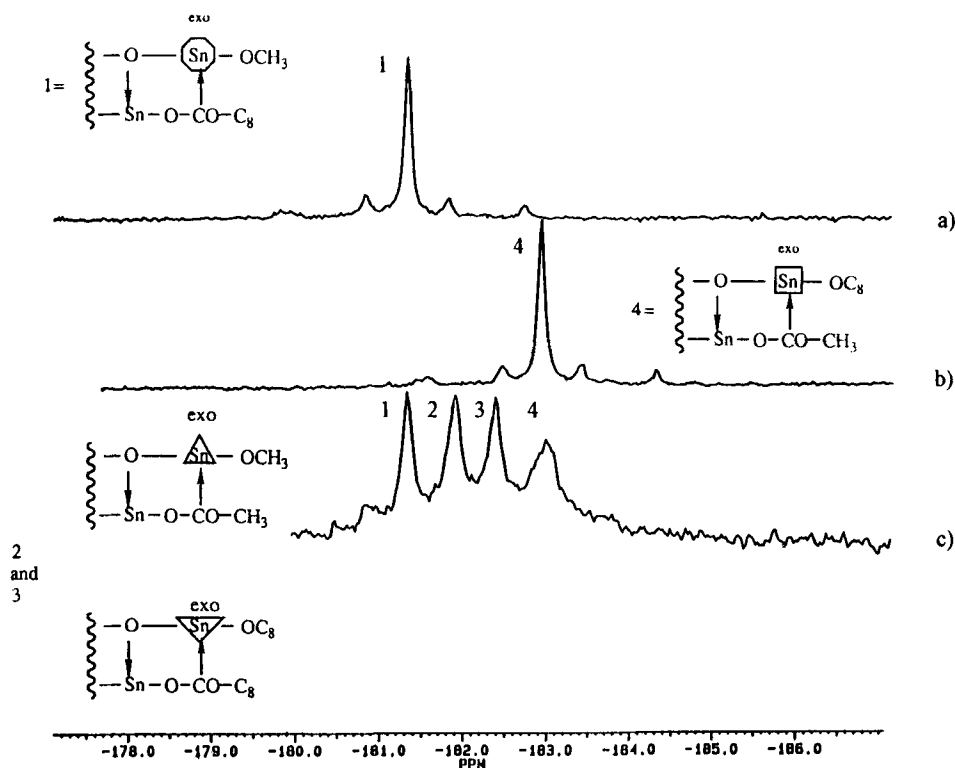


FIGURE 4  $^{119}\text{Sn}$ -NMR (74.6 MHz) spectra: enlargement of exocyclic tin sites region for slightly different 1,3-alkoxy,acyloxy distannoxanes: a) 1,3-methoxy,nonanyloxy distannoxane. b) 1,3-octyloxy,acetoxy distannoxane. c) mixture of equimolar amounts of the previous distannoxanes.

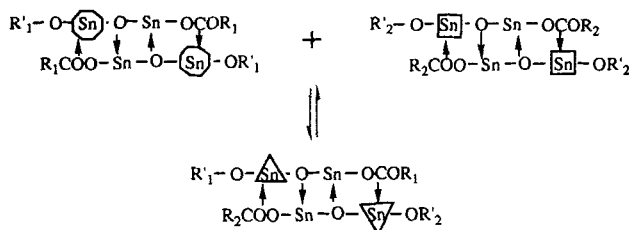
quently, equal thermodynamical stability of the three dimeric entities in spite of obviously different steric factors. The lack of resolution of the four endocyclic acyloxy tin sites is probably due to lower effects on their chemical shift values ( $\beta$  and  $\gamma$  effects in the case of exocyclic sites and  $\gamma$  and  $\delta$  in the endocyclic ones).

#### **b Reaction of the Distannoxane from Methyl Nonanoate (Ester 2) with Octyl Acetate (Ester 1) at 110°C [1 mole $\text{Bu}_2\text{SnO}$ + 1 mole Ester (2) Followed by 1 mole Ester (1).]**

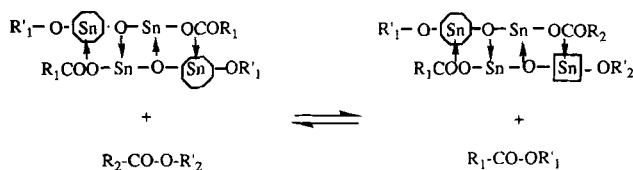
Exchange reaction between a free ester (1) and the dimeric distannoxane from ester (2) [present in excess of ester (2)] was evidenced at temperatures about 100°C. Random redistribution occurs between alkoxy groups (and acyloxy) from ester (2) and (1) involved in the distannoxane structure ( $^{119}\text{Sn}$  and  $^{13}\text{C}$  NMR); concerning free esters, a random redistributive transesterification was shown by the presence of four free esters ( $^1\text{H}$  and  $^{13}\text{C}$  NMR). As for the distribution between free ester and the ester involved in the distannoxane form, it depends of the initial ratio. In the present case, one mole of dibutyltin oxide for two moles of esters gives a ratio 3/1 for the two different forms (free/tin borne ester ratio).

When *n*-octyl acetate (1 mol) is treated at 110°C during a few hours with a solution of the dimeric distannoxane obtained with methyl nonanoate (1 mol

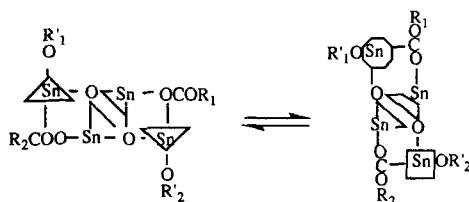
A: Intermolecular dimeric rearrangement of dimeric distannoxanes (ambient temperature) : random redistribution of monomeric species through three dimeric species.



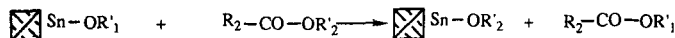
B: Hypothetical concomitant exchange reaction of both alkoxy and acyloxy ligands between free esters and 1,3-acyloxy, alkoxy dimeric distannoxane ( $T > 100^\circ\text{C}$ )



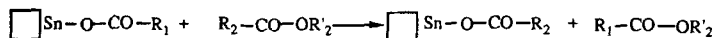
C: Hypothetical intra-dimeric rearrangement of 1,3-acyloxy, alkoxy dimeric distannoxanes.



D: Exchange reaction between the alkoxy groups (from free ester) and the tin alkoxy site of dimeric distannoxanes (  $\otimes$  )



E: Exchange reaction between the acyl groups (from free ester) and the tin acyloxy site of dimeric distannoxanes (  $\square$  )



SCHEME III

dibutyltin oxide, 1 mol methyl nonanoate), the tin spectrum of the solution shows the same pattern for exocyclic tin sites as previously observed in the case of the random redistribution between the two parent distannoxanes at room temperature (Fig. 4c). This indicates ligand exchange between free ester and dimeric distannoxanes at *both alkoxy- and acyloxy-bearing tin sites*. As a matter of fact, a ligand exchange of only alkoxy groups ( $\text{OR}'_1$  and  $\text{OR}'_2$ ) should give two exocyclic tin sites ( $\circ$  and  $\square$  Figure 4). The  $^{13}\text{C}$  spectrum shows not only the characteristic resonances of nonanyl oxytin  $\text{Sn-O-CO-C8}$  (carbonyl at  $\delta = 178.80$  and methylene carbons in  $\alpha$  and  $\beta$  position to the carbonyl at  $\delta = 36.20$  and  $26.40$ ) and methoxytin ( $\text{Sn-O-CH}_3$ ) methyl resonance at  $\delta = 36.20$ , but also new resonances

typical of acetoxytin  $\text{Sn-O-CO-CH}_3$  and  $\text{Sn-O-C8}$ . These new resonances at  $\delta = 176.10, 23.30, 64.20,$  and  $35.15$  are easily assigned to carbonyl, methyl carbon of acetoxytin group, carbons in the  $\alpha$  and  $\beta$  positions to the alkoxytin oxygen, respectively. These assignments were based on previous ones with 1,3-octyloxy, acetoxy distannoxane (Table I).

Reaction between a stannoxane from ester (2) and an ester (1) (and vice versa), produces the same pattern as the reaction of both esters with dibutyltin oxide (which gives the same spectral pattern as that obtained when mixing the two distannoxanes from ester (1) and ester (2) at room temperature (obtained in the presence of residual esters not engaged in the distannoxane form); that is, four exocyclic tin sites. However, an important difference is observed concerning the free esters: in the first two cases, there are four free esters, therefore redistribution occurred at  $110^\circ\text{C}$ , whereas it does not occur at room temperature. One hypothesis to consider is that a free ester reacts with a dimeric distannoxane by a similar mechanism which has been proposed with dibutyltin oxide [2,3] leading to ligand exchange at both exocyclic and endocyclic sites and a recombination of alkoxy ( $\text{R'O-}$ ) and acyl ( $-\text{CO-R}$ ) groups from ester (1), which should be possible because of the close proximity of these groups in the distannoxane structure.

If the reaction is written as indicated in Scheme IIIB, a random distribution of ester (1) and (2) between the distannoxane and the free form should occur. However, this scheme does not account for the  $^{13}\text{C}$  and  $^1\text{H}$  spectra of the reaction medium. They reveal the presence of four free esters, and four exocyclic tin sites, so, an intra-dimeric rearrangement (Scheme IIIC) should fall around the central planar square  $-\text{Sn-O-Sn-O}-$ . Consequently, this additional element has to be appended to the initial hypothesis: no strong and sufficient evidence can support a concomitant acyl and alkoxy group interchange at the neighboring sites.

The other way to account for those spectra consists of an independent interchange of alkoxy and acyl groups (Schemes IIID and IIIE) with the corresponding groups on the distannoxane structure. The fact that redistributive transesterification is catalysed by symmetric distannoxanes (either dialkoxy or diacetoxy) as well as by alkoxy, acyloxy distannoxanes—four free esters are obtained from two initially introduced—is a strong argument in favor of this mechanism which grants independent acyl and alkoxy exchanges, does not exclude concomitant ones, and does not require the intra-dimeric rearrangement (Scheme IIIC). These independent exchanges were evident from the distannoxane structures, as described below.

### **c Reaction of Dimeric Diacetoxy Distannoxane with Methyl Nonanoate (Ester 2)** **[Initial Molar Ratio: $\text{Sn-O-CO-CH}_3 / \text{CH}_3\text{-O-CO-C8} = 2; 3\text{h at } 180^\circ\text{C}$ ]**

The typical dimeric distannoxane structure is mostly preserved as indicated by (i) two  $\text{CH}_3(\text{Bu})$  shown by  $^1\text{H}$  NMR, (ii) the typical group of four peaks for C2 and C3 from butyl groups attached to endo and exocyclic tin atoms shown by  $^{13}\text{C}$  NMR, (iii) two coupled tin sites shown by  $^{119}\text{Sn}$  NMR spectra. Moreover, diacyloxy distannoxanes are the main organotin species present in the medium, as indicated by the characteristic chemical shifts of the tin sites (left part of Table I in comparison to alkoxy, acyloxy distannoxanes chemical shift values given in Table II). However, the tin sites give very broad (or split into several peaks) resonances

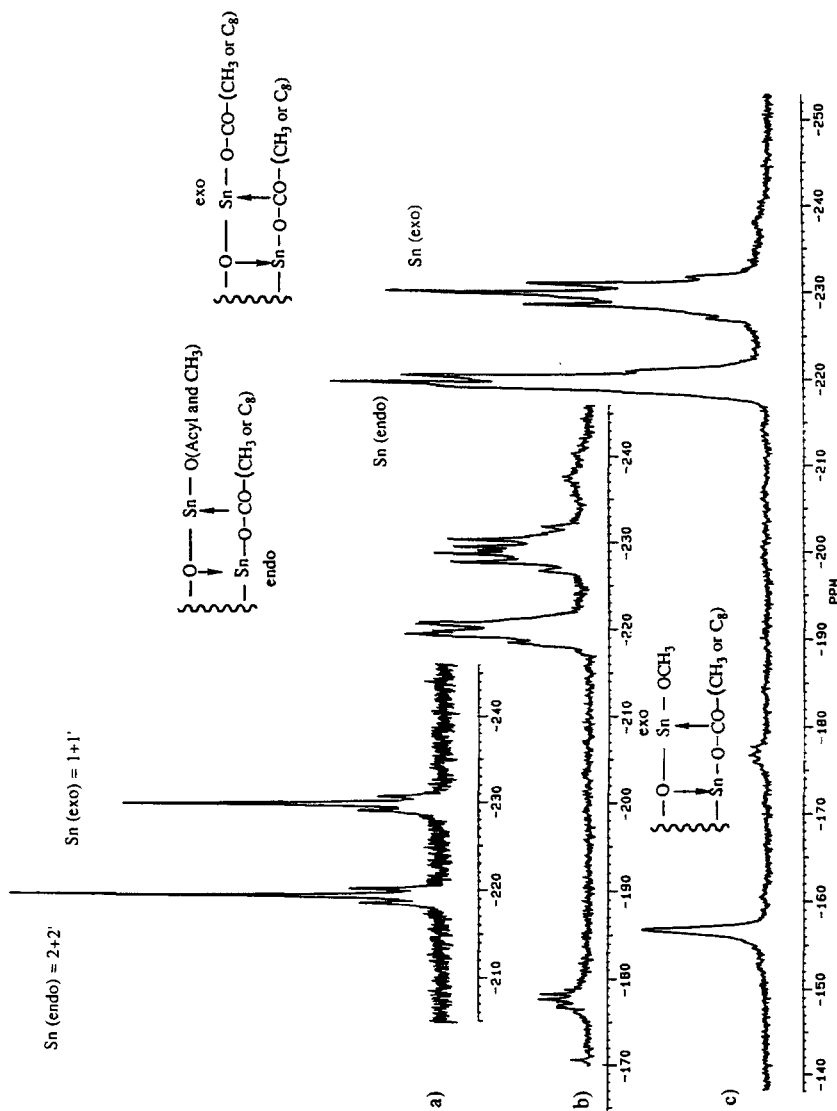
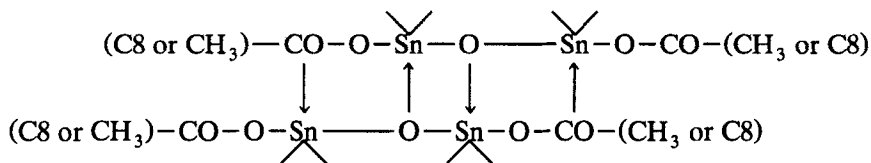
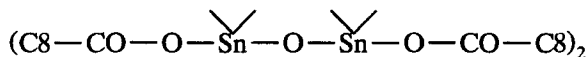


FIGURE 5  $^{119}\text{Sn}$ -NMR (74.6 MHz) spectra: a) initial dimeric 1,3-diacetoxy distannoxane; b) after 15 min at 180°C with methyl nonanoate; c) after 3h at 180°C with methyl nonanoate. Initial molar ratio  $\text{Sn-O-CO-CH}_3/\text{C}_8\text{-O-CO-CH}_3 = 2$ .

compared with the initial ones (Figure 5). These splittings, particularly well resolved at the less deshielded exocyclic tin site resonance region ( $\delta = -230$ ), are well explained by an important number of slightly different tin sites. The different possible exocyclic tin sites come from all combinations of diacyloxy distannoxanes which comprise both acetoxytin and acyloxy (2) tin with the general formula:



Because of the release of methyl acetate at this temperature, giving rise to a distannoxane richer in (O-CO-C8) acyloxy ligands, a simplified structure is expected, which is observed experimentally (Figure 5c). At completion, only one tin resonance should be observed, which was not reached in the situation corresponding to Figure 5c, when the following pure distannoxane is obtained:



The same phenomenon should occur at the endocyclic tin site which is split less than the previous one. A tin by-product is formed ( $\delta = 156.50$ ) which is not yet identified. The formation of tributyltin acetate is observed in very small quantities (in both  $^{119}\text{Sn}$  and  $^{13}\text{C}$  spectra, as already observed [2-3] at  $200^\circ\text{C}$ , without solvent, and at long reaction times or at higher contents of dibutyltin oxide).

$^{13}\text{C}$  spectral features give complementary information. Since the carbonyl group of the acetoxytin sites is observed at  $\delta = 177.00$ , as in the initial distannoxane, a new tin acyloxy resonance appears at  $\delta = 179.90$  assigned to  $\text{Sn}-\text{O}-\underline{\text{C}}\text{O}-\text{C8}$  (Table II). Two other peaks are easily assigned to the methylene carbons in the  $\alpha$  and  $\beta$  position to the carbonyl group of this tin acyloxy ( $\delta = 36.55$  and  $26.55$ , respectively) by comparison with the chemical shifts of the same carbons (Table II) observed in the alkoxy, acyloxy distannoxane obtained from methyl nonanoate.

All these results show that the main exchange takes place between the acyl group ( $-\text{CO}-\text{CH}_3$ ) initially engaged in the distannoxane structure and the acyl group ( $-\text{CO}-\text{C8}$ ) from the methyl nonanoate (ester 2), but some ligand exchange also occurs between acyloxy ( $-\text{O}-\text{CO}-\text{CH}_3$ ) and alkoxy ( $-\text{O}-\text{CH}_3$ ) groups at this temperature. This is clearly evidenced by the new tin resonances at  $\delta = -177$  (Figure 5). As shown in Table II, resonances from  $\delta = -182.5$  to  $-181.5$  correspond to exocyclic alkoxytin atoms in a typical alkoxy, acyloxy distannoxane structure. The observed resonance is slightly more deshielded, probably because the new distannoxane obtained in this case has three acyloxy and one alkoxy ligands. This is not strictly equivalent to the model compounds described in Table II. The corresponding endocyclic tin site expected in the range  $\delta = -214.5$  to  $-218.2$  is hidden by the broad resonance (centered at  $\delta = -219$ ) of the endocyclic tin site of the main product, namely a diacyloxy distannoxane with both acetoxy and acyloxy (2) ligands. The  $^1\text{H}$  spectrum also confirms the presence of



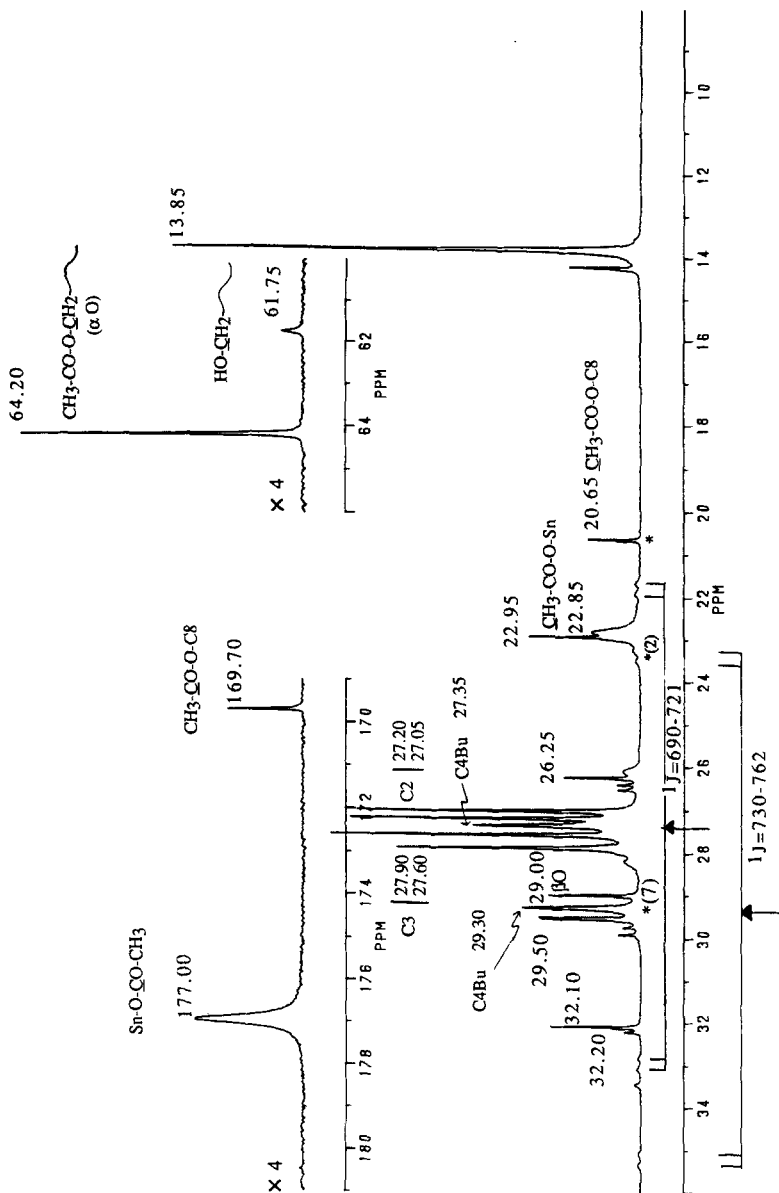


FIGURE 6  $^{13}\text{C}$ -NMR (62.9 MHz) spectrum obtained after reaction of 1,3-diacetoxy distannoxane with octyl acetate at  $120^\circ\text{C}$ , 3 h. \* (1): resonance of carbon (1) from alkyl group in octyl acetate; (1): same carbon as above in the corresponding distannoxane compound.

some Sn–O–CH<sub>3</sub> resonances at  $\delta = 3.330$ . In fact, many degradation reactions probably interfere with ligand exchanges at this temperature and during this time period. As a matter of fact, after 15 min at 180°C, exocyclic Sn–O–CH<sub>3</sub> representing 10% of the total distannoxane sites is observed, whereas it decreases to less than 2% after 3h (Figure 5b and 5c). However, the presence of these Sn–O–CH<sub>3</sub> tin sites, even if they are not stable at this temperature, accounts for the observed cross-linking of EVA in the presence of diacetoxy distannoxane. This cross-linking is not explained by an acyloxy exchange. Such drastic experimental conditions were chosen to explain this very surprising rheological observation (Figure 7).

**d Reaction of Dimeric Diacetoxy Distannoxane with Octyl Acetate (Ester 1) at 120°C, 3 h [Initial Sn–O–CO–CH<sub>3</sub>/ Ester (1) ratio = 2]**

In this case, no modification was observed in the tin spectra of the distannoxane (because of only one type of acyl groups, namely acetoxy ones) at room temperature, no Sn–O–C8 exocyclic tin site resulting from acyloxy/alkoxy exchange and extremely low quantities of other by-products at lower field are detected. The <sup>13</sup>C-NMR spectrum confirms that the initial diacetoxy distannoxane structure is unchanged (compare Figure 6 with corresponding values in Table I), except the presence of some unexplained octyl alcohol ( $\delta = 61.75$ ). This last reaction, which only gives rise to acyl exchange (that is, no change at all in the particular case described here where there is only one type of acyl group), demonstrates that with different acyl groups, for example, when diacetoxy distannoxane reacts with methyl nonanoate (the previous case), if mild conditions are used, only acyl (1)/acyl (2) exchange should occur. As a consequence, cross-linking of EVA in the presence of diacetoxy distannoxane at 200°C in the molten state (Figure 7b) can be explained by this secondary reaction which is not detected at 120°C on model compounds. Cross-linking of EMA in the presence of diacetoxy distannoxane is observed

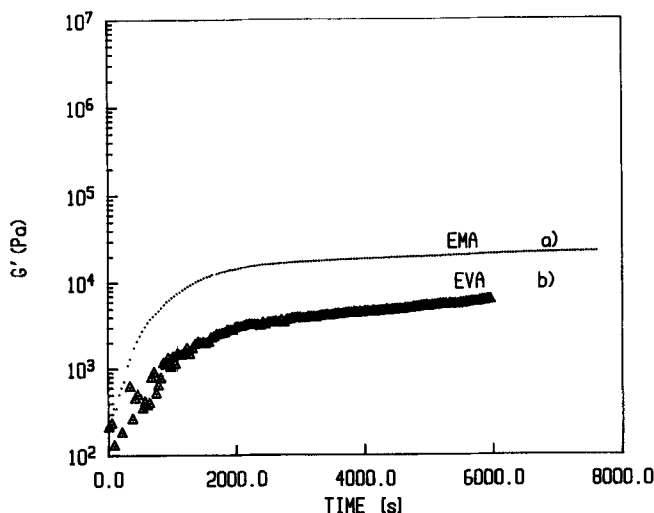
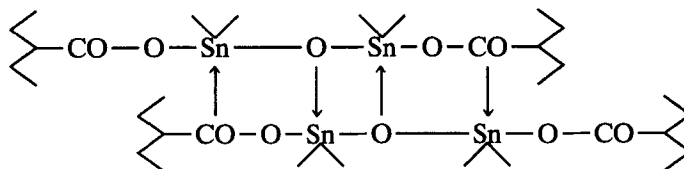


FIGURE 7 Storage modulus versus reaction time at 200°C: a) •, EMA b) Δ, EVA; in both cases with 1,3-diacetoxy distannoxane (5% w/w).

(Figure 7a) and the acyl exchange between polymeric  $\text{>CO-R}$  groups and  $\text{CH}_3\text{-CO}$ -groups of the distannoxane structure accounts for this observation. We may notice that release of methyl acetate would probably shift the equilibrium and at completion give a dense cross-link network



**• Reaction of Dimeric Dimethoxy Distannoxane with Octyl Acetate (Ester 1) at 120°C, 3 h. [Initial Ratio: Sn-O-CH<sub>3</sub>/ Ester (1) ratio = 2]**

The <sup>13</sup>C-NMR spectrum (Figure 8) shows, besides residual methoxy carbon (not differentiated from free methanol at  $\delta = 50.95$ ), a new resonance at  $\delta = 63.15$  from Sn-O-CH<sub>2</sub>-C7, less deshielded than the corresponding carbon in octyl acetate. Carbons in the  $\beta$  and  $\gamma$  positions to the oxygen of the octyloxy radical attached to the tin atom are observed at  $\delta = 34.55$  and 26.50, respectively. These results prove that alkoxy exchange occurs at the tin site. This reaction is confirmed by the presence of all resonances of methyl acetate resulting from this exchange.

No carbonyl resonance (expected at  $\delta = 176$ ) is observed, which should correspond to Sn-O-CO-CH<sub>3</sub> coming from the exchange between alkoxy and acyloxy groups. Moreover, all typical features of the carbons of butyl ligands in the initial dialkoxy distannoxane (right part of Table I compared with Fig. 8) are mostly unchanged (one C2 and two C3 shifts which are more deshielded, and two typical C4 shifts at  $\delta = 19.05$  and 22.35). A new C4 shift observed at  $\delta = 19.65$  corresponds to a new alkoxy tin site of the same nature as resonance at  $\delta = 19.05$  (endo-/or exocyclic). Carbons in the  $\beta$  and  $\gamma$  position to the oxygen in the octyloxytin are observed at  $\delta = 34.55$  and 26.50, respectively.

## CONCLUSIONS

NMR spectroscopy has been shown to be a useful technique for investigating both the distannoxane structure and exchange reactions at the tin site. We must emphasize the fact that these results show that when a carbon changes in the  $\beta$  position to the tin atom <sup>119</sup>Sn, the effect on the carbons are much more important than the effect produced on the <sup>119</sup>Sn chemical shift. As a result, in these ligand exchange reactions at the tin site, <sup>13</sup>C-NMR was shown to be a particularly efficient method of analysis.

All the results prove that diacyloxy distannoxanes, dialkoxy distannoxanes, and alkoxy/acyloxy distannoxanes react with esters above 100°C leading to, respectively, acyloxy/acyloxy and alkoxy/alkoxy distannoxanes, and both groups exchange between those engaged in the distannoxane structure and those which are in the free-ester form. In mild conditions (about 100–110°C), these exchanges

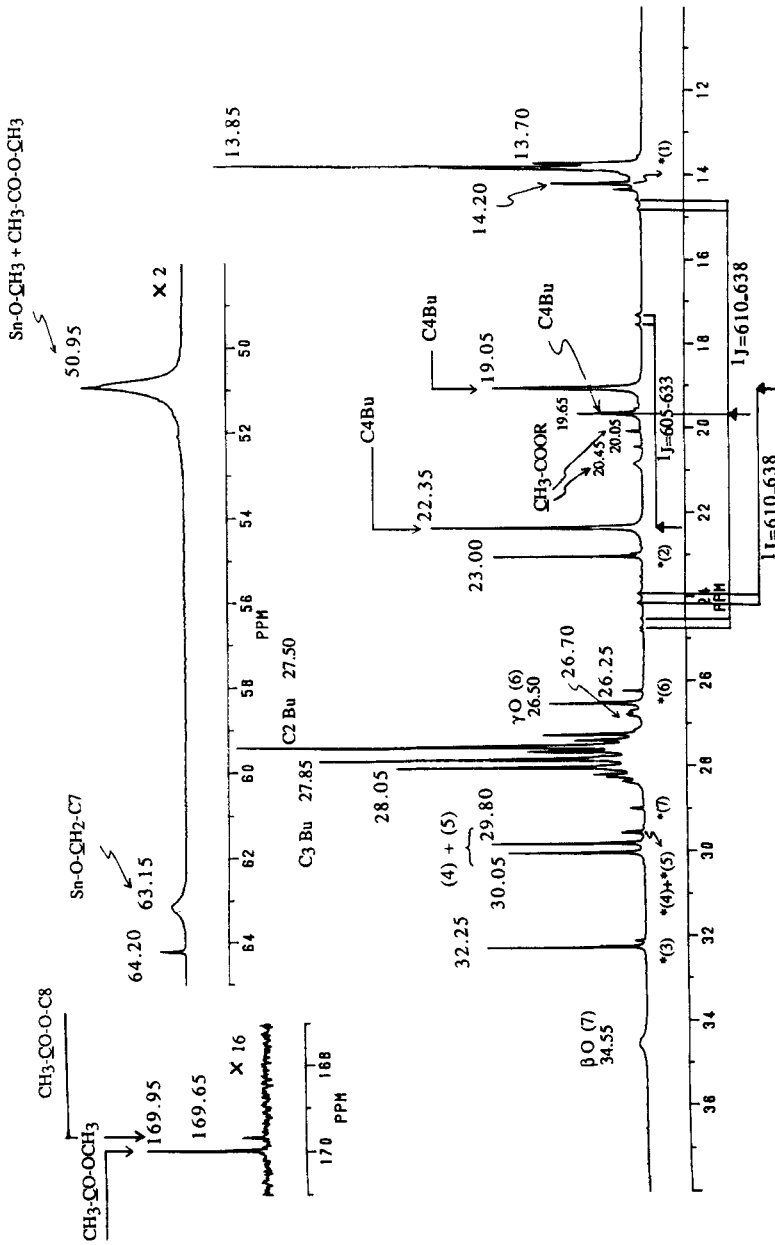


FIGURE 8  $^{13}\text{C}$ -NMR (62.9 MHz) spectrum obtained after reaction of 1,3-dimethoxy distannoxane with octyl acetate at  $120^\circ\text{C}$  3 h.

dominate, but in more drastic conditions (at 180°C with model esters), some alkoxy tin ligands are detected after reaction of the diacetoxy distannoxane with methyl nonanoate.

When used in catalytic amounts, in the presence of two different model esters, all these distannoxanes produce the redistributive transesterification of the esters, leading to four esters. This reaction occurs at random, giving, for example, equal amounts of the four esters, if equimolar amounts of the two initial esters were used.

Only one of these exchanges (acyloxy or alkoxy) is sufficient to account for the catalytic activity of the different distannoxanes tested in this work. Work is in progress [18] to elucidate whether the kinetics of the catalyzed reaction is more rapid when both types of exchanges are possible. In the latter case, that is with an alkoxy, acyloxy distannoxane, it is not yet elucidated if both exchanges occur in a concomitant way with recombination of the exchanged groups.

These results, obtained on model compounds, account for the cross-linking of EVA/EMA polymer blends in the molten state, and demonstrate that as soon as some alkoxy, acyloxy distannoxane entities are formed, they act as a catalyst toward the redistribution of  $\left\langle \text{O-CO-CH}_3 \text{ and } \text{CH}_3\text{-O-CO} \right\rangle$  ester groups, giving two other esters, methyl acetate and crosslinks  $\left\langle \text{O-CO} \right\rangle$

This transesterification will occur as soon as the polymer blend is homogeneous. Furthermore, the formation of the distannoxane catalytic entity depends on the dispersion of dibutyltin oxide in the polymer matrix.

It also appears that this reaction gives covalent cross-links, which are able to interchange again with another part of the polymer matrix, as long as distannoxane is still present in the medium. This interchange reaction is expected to give a sort of "mobile" cross-linking network. Of course, as soon as the temperature decreases, there is no more exchange reaction of an ester with a distannoxane entity and the network remains unchanged and "stiff."

Moreover, in the case of EVA/EMA blends, two types of cross-links coexist, (i) covalent cross-links between EVA and EMA chains able to interchange in molten state and (ii) three types of dimeric distannoxanes. As soon as the polymer blend is homogeneous, reaction of ester groups with dibutyltin oxide is expected to produce directly a random distribution of the three dimeric distannoxanes. If the formation of distannoxanes occurs rapidly, redistribution by an intermolecular dimeric rearrangement will give the same result. The release of methyl acetate probably shifts the distribution of both free ester and distannoxane species toward the formation of covalent cross-links and highly hindered distannoxane cross-links.

With dibutyltin oxide, which corresponds to a catalytic distannoxane entity produced *in situ* and borne by the polymer chain itself, the storage modulus is higher than with free distannoxanes previously obtained (Figure 9).

### Acknowledgments

The authors are indebted to Dr. C. Gondard for interesting discussions and useful suggestions.

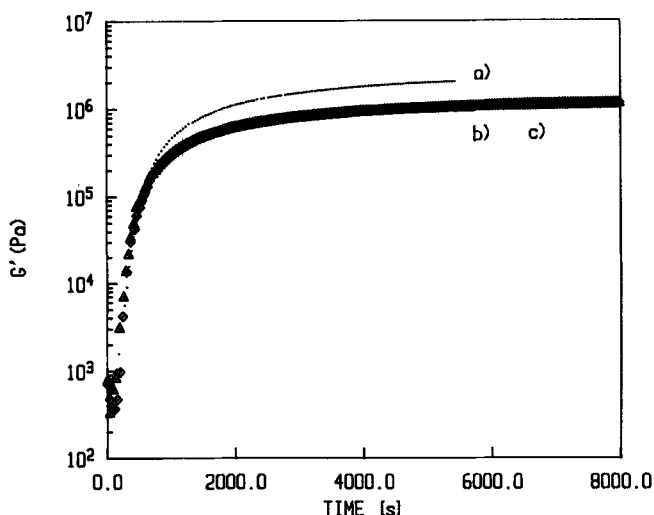


FIGURE 9 Storage modulus versus reaction time at 200°C of EVA/EMA polymer blend with 5% (w/w): a)  $\square$ , dibutyltin oxide; b)  $\Delta$ , alkoxy, acyloxy distannoxane (from octyl acetate); c)  $\diamond$ , 1,3-diacetoxy distannoxane.

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