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Synthesis of polyesters as binders for deinkable inks. III. Structural study by high resolution ^{13}C and ^{1}H n.m.r. spectroscopies of the copolyesterification between *o*-phthalic anhydride, oleic acid and neopentyl glycol in bulk at 205°C

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Analysis of the copolyesterification in bulk without any external catalyst at 205°C between *o*-phthalic anhydride, oleic acid and neopentyl glycol (2,2-dimethyl-1,3-propanediol) with a mole ratio ([–COOH]/[–OH]) = 0.70 has been carried out by high resolution ^{13}C and ^{1}H n.m.r. The different polymeric sequences and several monomeric structures formed during the copolyesterification have been identified and quantitatively determined. © 1997 Elsevier Science Ltd.

(Keywords: bulk copolyesterification; *o*-phthalic anhydride; oleic acid)

INTRODUCTION

Deinking is the key-technology for using waste paper as a fibre source in the production of graphic and sanitary papers. The flotation of waste paper is the predominating process for deinking. The ink must be easily removed from the page. This depends partially, to a first approximation, on the chemical nature of the ink components and their molecular interactions with the paper components. The composition of the binder resin employed has a crucial effect on the performance and properties of an inking system and especially on its possible deinking.

It has been found that the crosslinkable resin employed as binder, normally of the alkyd type[1–3], is the most important component which offers more difficulties for a good deinkability process. Therefore, the current research in this field is being addressed from a fundamental and exclusive point of view to the alkyd resin.

The functional groups of the alkyd resins have a great influence on the behaviour of the ink. Thus, for instance, the free carboxylic groups offer a high affinity for cellulose. On the other hand, if the alkyd resin presents a very elevated hydrophilic character, as can be the case with those resins which have been obtained from polyols, it is very good for deinking but they cannot be used because of the problems which they present during the printing process.

In the present paper we would like to focus our attention mainly on the differences between the present copolyester system and one without oleic acid described in previous papers[4,5]. A detailed analysis of structures should be very useful to establish relationships between copolyester structural composition and deinkable properties of newspapers printed with deinkable inks prepared with these copolyesters as binders and to see how these properties are affected by the copolyesterification time.

At present, the industrial production of some polyesters is being carried out in bulk at high temperatures (> 150–160°C). This has two fundamental advantages. On the one hand, it shortens the reaction time and consequently saves energy and on the other, it serves to diminish environmental pollution by decreasing the emission of toxic organic solvents which would occur if the azeotropic process were used.

We have used ^{13}C and ^{1}H n.m.r. spectroscopies to follow the evolution of functional groups and chemical structures as a function of the reaction time. A series of authors[6–13] among which we can distinguish Hvilsted[14–18] and more recently Pham *et al.*[19–21] have made clear that the ^{13}C n.m.r. spectroscopy is a very powerful tool to analyse structures and sequence distribution during the formation of polyesters and copolyesters. Besides, this technique has been also described[22] as the more adequate one for the characterization of natural oils which are employed to prepare alkyd resins. Marshall and Lander[23] used ^{13}C n.m.r. to characterize the fatty acids of a series of vegetable oils. The sensitivity of this technique to small variations in the chemical surrounding of

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the observed nucleus makes this technique suitable for the structural study of the present copolyesterification. Rybicky[24] and Marshall[25] have used ^1H n.m.r. for the identification and determination of components in alkyd and modification alkyd resins. Besides the main esterification reaction, side or secondary reactions can occur, for example, double bond isomerization[26–28], addition of hydroxyl groups to double bonds[6,28–31], decarboxylation, etherification, polymerization between chains of unsaturated acids[32,33], etc. and gelification processes[3,17,19,34–37]. Perhaps there are other important factors to be taken into account in the present research since when dealing with copolyesterifications carried out at high temperature in bulk some secondary reactions may take place.

Table 1 Composition (%) expressed as a function of the fatty acids content of oleic acid of a nominal purity of 65%. Values have been obtained by capillary column gas chromatography as indicated in the text

Fatty acids	Composition (%)	Fatty acids	Composition (%)
C 12:0	0.5	C 18:1 t	2.9
C 14:0	2.4	C 18:2 c	9.3
C 14:1	0.4	C 18:2 *trans* total	1.3
C 16:0	5.9	C 18:3 c	0.7
C 16:1	4.4	C 18:3 *trans* total	0.2
C 17:0	0.2	C 20:0	0.1
C 17:1	0.8	C 20:1	0.7
C 18:0	2.0	C 22:0	0.1
C 18:1 c ω 9	59.2	Others	5.8
C 18:1 c ω 7	3.1		

EXPERIMENTAL

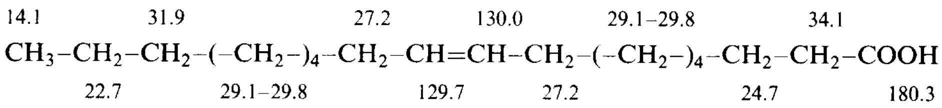
Materials

The *o*-phthalic anhydride (P), neopentyl glycol (2,2-dimethyl-1,3-propanediol) (N) and the preparation of diazomethane have been previously described[4]. Oleic acid (*cis*-9-octadecanoic acid) (O) (Fluka Chemie, A.G. Buchs, Switzerland) of a nominal purity of 65% and an m.p. = 1–3°C has been used without any previous purification. Its composition is given in *Table 1*. It has been estimated by column gas chromatography (CGLC). Chromatographic measurements were performed on a SP-2380 capillary column of 60 m length, 0.25 inner diameter and a film thickness of 0.25 μm. The column temperature programme was 20 min hold at 170°C followed by a 3°C min^{-1} ramp to 200°C. The injector and detector temperatures were 200 and 250°C, respectively. The column was operated using hydrogen as carrier with a flow rate of 2 ml min^{-1}. A splitter with a flow ratio of 100/1 has been used. The preparation of fatty acid derivatives was done according to the IUPAC 2.301 method.

This analysis has made clear that we have a mixture of fatty acids with a variable number of carbon atoms in the *n*-alkyl chain, namely from 12 to 22. From this point of view our oleic acid contains about ~ 35% of some other fatty acids, which participate in the copolyesterification process giving rise to very similar products which do not affect the structural analysis. They probably do not affect in any appreciable form the reactivities towards the trimethylopropane with respect to the oleic acid.

^{13}C n.m.r. spectroscopy

^{13}C n.m.r. spectra were carried out on a Gemini 200 spectrometer operating at 50.28 MHz and at room temperature (23°C) on undegassified 20% (w/v) $CDCl_3$ solutions in 5 mm i.d. tubes. Chemical shifts are referenced to the central resonance of $CDCl_3$ [77.00 ppm from $(CH_3)_4Si$]. Chemical shifts for oleic acid agree with those given in the literature[23,38,39]. Chemical shifts together with the oleic acid chemical structure are



$$\overset{14.1}{CH_3}-\underset{22.7}{CH_2}-\overset{31.9}{CH_2}-(\underset{29.1-29.8}{-CH_2-})_4-\overset{27.2}{CH_2}-\underset{129.7}{CH}=\overset{130.0}{CH}-\underset{27.2}{CH_2}-(\overset{29.1-29.8}{-CH_2-})_4-\underset{24.7}{CH_2}-\overset{34.1}{CH_2}-\underset{180.3}{COOH}$$

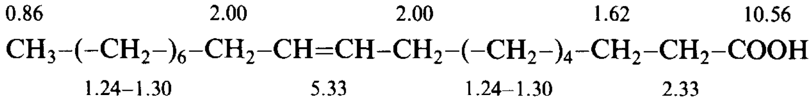
Scheme 1

^{13}C n.m.r. chemical shifts for other reagents have been previously described[4].

The multiplicity of the carbon atoms from the samples of the copolyesterification has been determined in a Bruker AM-200 spectrometer by means of a DEPT-135° experiment under the following experimental conditions: acquisition time, 0.7 s; delay between pulses, 3 s and 975 scans. The spin–lattice relaxation times T_1 were measured by the *inversion recovery method*, which is based on the following pulse sequence: $(180°-\tau-90°-t_a-t_d)_n$. In this sequence a t_d (delay between pulses) of 30 s, t_a (acquisition time) of 0.7 s, and the following τ values: 0.1, 0.2, 0.4, 0.8, 1.6, 3.0, 5.0, 10.0 and 30.0 s were adequate. This determination has been done using a sample isolated after 6 h of copolyesterification in bulk without any external catalyst at 235°C. Under these conditions this new sample is supposed to be at total completion, namely, 90% and 63% of acid and alcoholic groups, respectively. The experimental values are given in *Table 2*. It is important to mention that in the spectrum the signal corresponding to **ae/EA** and **O/ee/EA** structures does not appear as a consequence of the high conversion degree of this sample. These species which will be described later on, are only detected at the very beginning of the copolyesterification. 300 scans were considered to be good enough for our purposes. With the aim to carry out quantitative analysis, ^{13}C n.m.r. spectra were recorded by means of 'inverse gated decoupling' sequences. The acquisition time was 1 s. A sweep width of 15 000 Hz, 300 scans and a delay time of 30 s (3–5 times higher than T_1) have been used. The area of the signals were calculated by planimetry and triangulation.

^1H n.m.r. spectrometry

The ^1H n.m.r. spectra were recorded at room temperature (23°C) on a Gemini 200 and on a Bruker AM-200 spectrometer both operating at 200 MHz, in $CDCl_3$ solution with concentrations lower than 8% (w/v) to improve their resolution[11]. To obtain quantitative spectra, we have used pulse sequences of 90° with a delay time of 2 s. The spectra were recorded after 256 scans. Chemical shifts are referenced to the resonance of $CDCl_3$ [7.24 ppm from $(CH_3)_4Si$]. ^1H n.m.r. spectra of the reagents have been described elsewhere[5] and the chemical shifts of the oleic acid together with its chemical structure are



$$\overset{0.86}{CH_3}-\underset{1.24-1.30}{(-CH_2-)_6}-\overset{2.00}{CH_2}-\underset{5.33}{CH=CH}-\overset{2.00}{CH_2}-\underset{1.24-1.30}{(-CH_2-)_4}-\overset{1.62}{CH_2}-\underset{2.33}{CH_2}-\overset{10.56}{COOH}$$

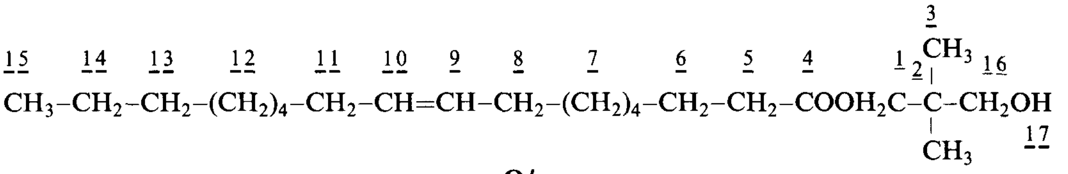
Scheme 2

Reaction with diazomethane

The procedure has been described previously[4].

Synthesis of model molecules: neopentyl mono- and dioleates

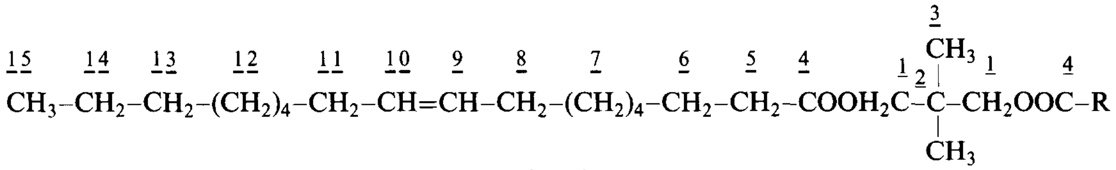
In a 250 ml three neck round bottom flask, with strong mechanical stirrer, double jacketed rectification column (back column), a Dean–Stark device to separate azeotropic mixtures, a water cooler condenser with anhydrous calcium chloride tube joined to a Dean–Stark device beyond the condenser and a nitrogen inlet tube, 10.4 g (0.01 mol) of neopentyl glycol and 28.25 g (0.01 mol) of oleic acid dissolved in 25 ml of xylene were heated to reflux. After 3 h the mass of reaction was cooled down to room temperature. The solvent was stripped off under reduce pressure. A quantitative analysis of the crude product by ^{13}C n.m.r. spectrometry has shown that it contains 48% of neopentyl monooleate, **O/ea**, 19% of neopentyl dioleate, **O/ee/O**, 7% of unreacted oleic acid and 26% of unreacted neopentyl glycol. Chemical structures for neopentyl mono- (**O/ea**) and dioleate (**O/ee/O**) are



$$\underset{15}{CH_3}-\underset{14}{CH_2}-\underset{13}{CH_2}-\underset{12}{(CH_2)_4}-\underset{11}{CH_2}-\underset{10}{CH}=\underset{9}{CH}-\underset{8}{CH_2}-\underset{7}{(CH_2)_4}-\underset{6}{CH_2}-\underset{5}{CH_2}-\underset{4}{COO}\underset{1}{H_2C}-\underset{2}{\overset{\overset{3}{CH_3}}{\underset{CH_3}{C}}}-\underset{16}{CH_2OH}\;\;\underset{17}{}$$

O/ea

Scheme 3



$$\underset{15}{CH_3}-\underset{14}{CH_2}-\underset{13}{CH_2}-\underset{12}{(CH_2)_4}-\underset{11}{CH_2}-\underset{10}{CH}=\underset{9}{CH}-\underset{8}{CH_2}-\underset{7}{(CH_2)_4}-\underset{6}{CH_2}-\underset{5}{CH_2}-\underset{4}{COO}\underset{1}{H_2C}-\underset{2}{\overset{\overset{3}{CH_3}}{\underset{CH_3}{C}}}-\underset{1}{CH_2}\underset{4}{OOC}-R$$

O/ee/O

where R represents an oleate residue, i.e. $-(-CH_2-)_7-HC{=}CH-(-CH_2-)_7-CH_3$.

Scheme 4

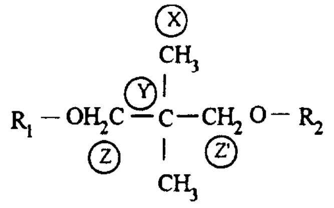
Analytical thin layer chromatography (t.l.c.) was performed on Merck-60 F_{254} silica gel plates of 0.2 mm thickness on aluminium plates. The spots were visualized under 254 nm light. The mobile phases were: *n*-hexane and *n*-hexane/acetone mixtures of 99/1; 96/4 and 90/10 (v/v). The purification of the above crude product was carried out by short column chromatography[40] on Merck-60 G (230–400 mesh) silica gel. A yellowish liquid was isolated by using *n*-hexane as eluent. Its ^{13}C n.m.r. spectrum showed signals which were very easily assigned to neopentyl dioleate (**O/ee/O**). Successive elutions with 200 ml portions of *n*-hexane/acetone mixtures from 90/10 to 50/50 (v/v) yielded a second product, which after identification by ^{13}C n.m.r. showed signals of a mixture of oleic acid and neopentyl monooleate. Finally, neopentyl glycol retained at the top of the column was eluted with acetone. The second product neopentyl monooleate (**O/ea**) was isolated by ion interchange chromatography[41] by using Amberlite IRA-410. 2 g of resin in its basic form as stationary phase, 180 mg of product and ethyl ether as eluent were used. Oleic acid retained along the column was recovered by eluting with 100 ml ethanol and 300 ml of mixture of chloroform/ethanol/hydrochloric acid (60/37/3).

(1) Neopentyl dioleate (**O/ee/O**). Yellowish liquid of $R_f = 0.07$ (*n*-hexane).

^{13}C n.m.r. (50.28 MHz, $CDCl_3$): δ (ppm) 14.1 (C-15); 21.8 (C-3); 22.7 (C-14); 25.0 (C-13); 27.2 (C-8, C-11); 29.1-29.8 (C-7, C-12); 31.9 (C-6); 34.3 (C-5); 34.6 (C-2); 69.0 (C-1); 129.7 (C-10); 130.0 (C-9) and 173.7 (C-4).

^1H n.m.r. (200 MHz, $CDCl_3$): δ (ppm) 0.86 (*t*, 3H, H-15); 0.94 (*s*, 6H, H-3); 1.23–1.28 (*a*, 20H, H-7, H-12, H-13 and H-14); 1.56–1.63 (*m*, 3H, H-6); 1.97–2.00 (*m*, 4H, H-8 and H-11); 2.29 (*t*, 2H, H-5); 3.85 (*s*, 2H, H-1); 5.32 (*t*, 2H, H-9 and H-10).

Table 2 Spin–lattice relaxation times T_1 of all the carbons from neopentyl glycol units of a sample isolated after 6 h of copolyesterification between *o*-phthalic anhydride (P, 0.54 mol), oleic acid (O, 0.25 mol) and neopentyl glycol (N, 0.95 mol) ([–COOH]/[–OH]) = 0.70 in bulk and without any external catalyst at 235°C. Values determined from the ^{13}C n.m.r. spectra in $CDCl_3$ at room temperature (23°C). **EE**: P diesterified; **aa**: N free; **ae**: N monoesterified with P (**ae/EE**) and O (**ae/O**); **ee**: N diesterified with P and O (**P/ee/P** and **O/ee/EE**)



R_1	R_2	X	Y	Z	Z′	Assignment
		T_1 (s) (δ ppm)				
H	H	1.7 (*21.0*)	8.8 (*36.1*)	0.3 (*69.8*)	0.3 (*69.8*)	**aa**
H	P	0.7 (*21.2*)	4.8 (*35.9*)	0.3 (*67.6*)	0.2 (*70.4*)	**ae/EE**
H	O	1.2 (*21.1*)	4.8 (*35.9*)	0.7 (*67.8*)	0.7 (*69.0*)	**ae/O**
P	P	0.6 (*21.5*)	2.1 (*34.6*) 2.6 (*34.5*)	0.2 (*70.2*)	0.2 (*70.2*)	**P/ee/P**
O	P	0.6 (*21.5*)	3.2 (*34.3*)	0.2 (*68.7*)	0.6 (*70.5*)	**O/ee/EE**

Proton and carbon atoms may be identified according to the *Scheme 4*.

(2) Neopentyl monooleate, (**O/ea**). Colourless liquid of $R_f = 0.1$ [*n*-hexane/acetone, 90/10 (v/v)].

^{13}C n.m.r. (50.28 MHz, $CDCl_3$): δ (ppm) 14.0 (C-15); 21.4 (C-3); 22.6 (C-14); 24.8 (C-13); 27.1 (C-8 or C-11); 27.1 (C-11 or C-8); 28.9-29.7 (C-7, C-12); 31.8 (C-6); 34.2 (C-5); 36.2 (C-2); 68.0 (C-16); 69.2 (C-1); 129.6 (C-10); 129.9 (C-9) and 174.5 (C-4).

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (ppm) 0.85 (*t*, 3H, H-15); 0.89 (*s*, 6H, H-3); 1.24–1.28 (*a*, 20H, H-7, H-12, H-13 and H-14); 1.51-1.60 (*m*, 3H, H-6 and H-17); 1.97–2.11 (*m*, 4H, H-8 and H-11); 2.31 (*t*, 2H, H-5); 3.27 (*s*, 2H, H-16); 3.91 (*s*, 2H, H-1); 5.32 (*t*, 2H, H-9 and H-10).

Protons and carbon atoms may be identified according to the *Scheme 3*.

Copolyesterification

The copolyesterification has been carried out in bulk, homogeneous phase and without any external catalyst by a procedure described in detail previously[4]. 80 g (0.54 mol, 2.16 mol kg^{-1}) of *o*-phthalic anhydride (P), 71 g (0.25 mol, 1.00 mol kg^{-1}) of oleic acid (O) and 99 g (0.95 mol, 3.80 mol kg^{-1}) of neopentyl glycol (N) were heated to a temperature of 205 ± 0.5°C, during 11 h.

The relation between acid and alcoholic groups was calculated by means of the expression

$$r = \frac{f \cdot \text{mol of P} + f' \cdot \text{mol of O}}{f'' \cdot \text{mol of N}} = \frac{2 \times 0.54 + 1 \times 0.25}{2 \times 0.95} = 0.70 \qquad (1)$$

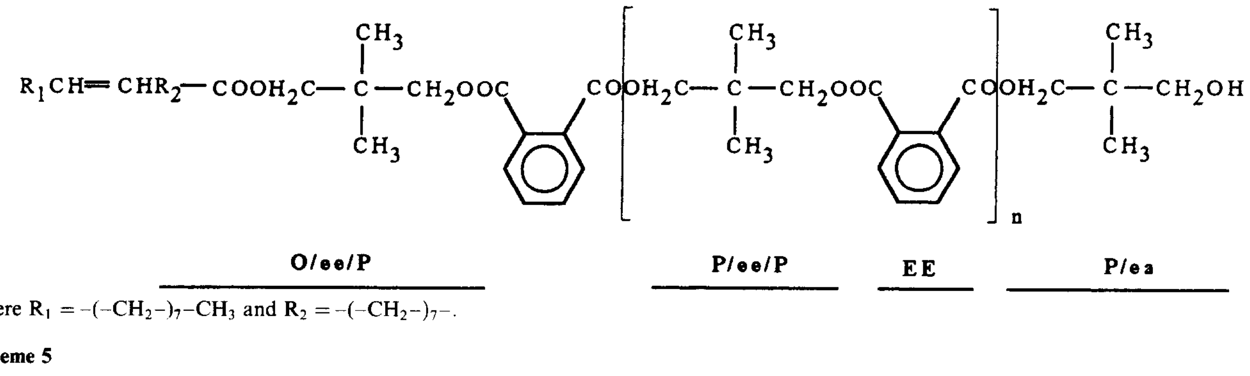
where f, f' and f'' represents the functionality of each one of the monomers.

The nomenclature employed to designate each one of the possible structures was described elsewhere[4]. In those cases in which is necessary to distinguish the carbon whose resonance is being observed, the letter which corresponds to the respective carbon atom has been underlined. The mononeopentyl mono-*o*-phthalate sequence **AE/ea** is equivalent to **ae/EA**.

DISCUSSION OF RESULTS

A sequence of the copolyesterification between *o*-phthalic anhydride, oleic acid and neopentyl glycol is depicted in *Scheme 5*.

Before going into a detailed analysis of structures we must say that the use of a commercial oleic acid does not introduce any problem or error on the results. It is well



where $R_1 = -(-CH_2-)_7-CH_3$ and $R_2 = -(-CH_2-)_7-$.

Scheme 5

documented that the chemical shift of the ester carbon and their close carbons in fatty acids are not affected by either the length of the alkylene chain or the double bond position at least in the series of fatty acids studied by Marshall and Lander[23]. Also, the structural analysis of the samples as a function of the reaction time has been fundamentally done on the nuclei of the alcoholic units. Thus, it has not been observed that fatty acids with chain lengths longer than twelve carbon atoms in the *n*-alkylene chain, have any appreciable influence on the mono-, di- and triesterified trimethylolpropane nucleus. For this reason, we must consider that our quantitative structural analysis is not affected by the actual commercial 'fatty acid' composition.

The study of the present ternary system will be made by comparison with the binary system *o*-phthalic anhydride-neopentyl glycol studied previously[4,5].

Structural study by ^{13}C n.m.r.

We have not observed in any case, either in the samples isolated through the copolyesterification process nor in a sample taken at the very beginning, i.e. just after the mixing of the three reacting monomers, any signal assignable either to the ring >C=O carbons of the *o*-phthalic anhydride or to the –COOH groups resulting from its opening and from the free oleic acid. From this fact, we can assume that the reaction between *o*-phthalic anhydride, oleic acid and neopentyl glycol takes place rapidly and quantitatively, just after they have been put together at 205°C.

The analysis has been carried out in the methylic, quaternary and oxymethylenic regions of neopentyl glycol and in the carboxylic region from *o*-phthalate and oleate residues.

Analysis of the neopentyl glycol structural distribution

(1) *Methylic region (13.9–21.6 ppm).* The position of the signals which appear in this region for the binary and ternary systems are similar, as can be seen in *Figures 1A* and *B*, except in the following:

(i) The splitting of the signal assigned to **ae**, which appears at 21.3 ppm for **ae/EE** and at 21.4 ppm for **ae/EA**. These two singlets are converted into one during the copolyesterification. Due to their overlapping, it has not been possible to determine separately their molar percentages.

(ii) The glycol esterification with oleic acid instead of *o*-phthalic anhydride produces a downfield shift of the methylic groups. Thus, the new signal at 21.2 ppm (*Figure 1B*) has been attributed to neopentyl glycol monooleate, **ae/O** (21.4 ppm in the model). This chemical shift is similar to 21.4 ppm described by Hvilsted[16] in terminal monoesterified neopentyl glycol sequences in copolyesters based on isophthalic acid, adipic acid and neopentyl glycol.

The **P/ee/P** and **O/ee/P** structures appear as a unique signal at 21.6 ppm. This chemical shift is very similar to 21.9 ppm described for diesters of similar structure[16]. On the other hand, it cannot be excluded that together with these diesters the **O/ee/O** structure in small quantities may also appear, say about 2–3%, since their methylic carbons resonate at 21.8 ppm in the model compound. Furthermore, it must be kept in mind that under the general structures **P/ee/P** and **O/ee/P**, all the possible combinations of neopentyl glycol diesters such as **AE/ee/EA**, **AE/ee/EE**, **EE/ee/EE**, **O/ee/EA** and **O/ee/EE** have to be considered.

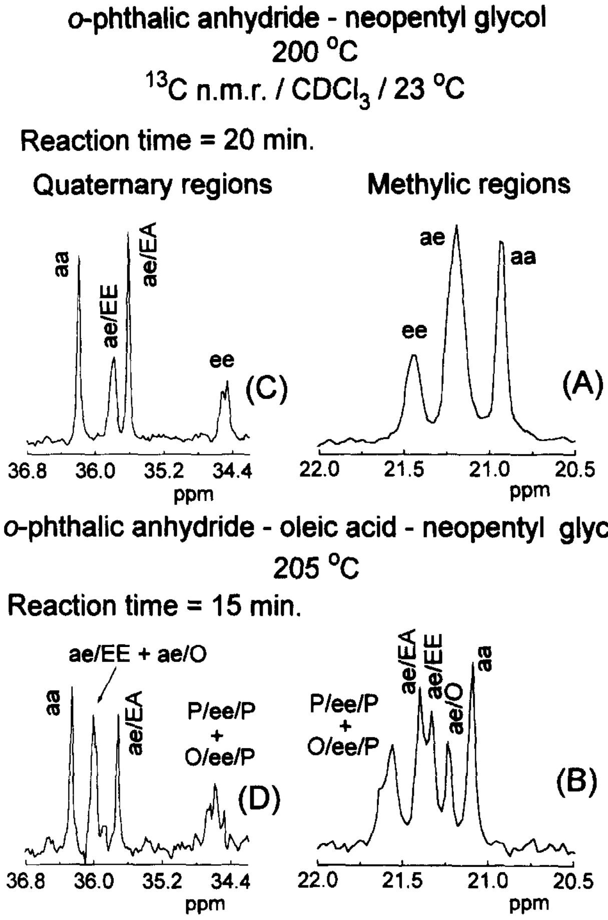


Figure 1 Expansions of the ^{13}C n.m.r. spectra methylic and quaternary regions in $CDCl_3$ at room temperature (23°C) of: (A) and (C) a sample isolated after 20 min of the reaction between *o*-phthalic anhydride (P, 0.68 mol) and neopentyl glycol (N, 0.96 mol) ([–COOH]/[–OH]) = 0.70 in bulk at 200°C and (B) and (D) a sample isolated after 15 min of copolyesterification between *o*-phthalic anhydride (P, 0.54 mol), oleic acid (O, 0.25 mol) and neopentyl glycol (N, 0.95 mol) ([–COOH]/[–OH]) = 0.70 in bulk without any external catalyst at 205°C. **EA** and **EE**: P mono- and diesterified, respectively. **aa**: N free; **ae**: N monoesterified with P (**ae/EA** and **ae/EE**) and O (**ae/O**); **ee**: N diesterified with P and O (**P/ee/P** and **O/ee/P**)

The analysis of the values of T_1 shown in *Table 2* confirms these assignments. The steric hindrance and the structural stiffness created by the *o*-phthalate residue decrease the mobility of the methyl groups in structures of the **ae/P** type. For this reason the monoester **ae/P** has a lower value of T_1 than **ae/O**. On the other hand, the diesterification of **ae/P** does not practically affect the methylic carbon relaxation time, T_1.

Chemical shifts of the methylic carbons in the different structures are given in *Table 3*. The molar percentage of structures, which are shown in *Table 4*, can be calculated by

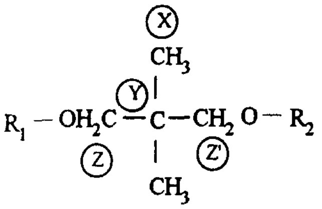
$$[\mathbf{aa}](\%) = 100 \times [\mathrm{aa}(\text{–}CH_3)/S(\text{–}CH_3)] \quad (2)$$

$$[\mathbf{ae/O}](\%) = 100 \times [\mathrm{ae/O}(\text{–}CH_3)/S(\text{–}CH_3)] \quad (3)$$

$$([\mathbf{ae/EA}] + [\mathbf{ae/EE}])(\%) = 100 \times [(\mathrm{ae/EA} + \mathrm{ae/EE})(\text{–}CH_3)/S(\text{–}CH_3)] \quad (4)$$

$$([\mathbf{P/ee/P}] + [\mathbf{O/ee/P}])(\%) = 100 \times [(\mathrm{P/ee/P} + \mathrm{O/ee/P})(\text{–}CH_3)/S(\text{–}CH_3)] \quad (5)$$

Table 3 ^{13}C and ^{1}H n.m.r. chemical shifts in $CDCl_3$ at room temperature (23°C) of samples isolated after 15 and 5 min of reaction of all structures which can present the neopentyl glycol (N, 0.95 mol) units in its copolyesterification with *o*-phthalic anhydride (P, 0.54 mol) and oleic acid (O, 0.25 mol) ([–COOH][–OH]) = 0.70 in bulk and without any external catalyst at 205°C. **EA** and **EE**: P mono- and diesterified, respectively; **aa**: N free; **ae**: N monoesterified with P (**ae/EA** and **ae/EE**) and O (**ae/O**); **ee**: N diesterified with P and O (**P/ee/P**, **O/ee/EA**, **O/ee/EE** and **O/ee/O**)


$$R_1-OH_2C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2O-R_2$$

			δ (ppm)				
Assignment	R_1	R_2	X	Y	Z	Z′	n.m.r.
aa	H	H	21.2	36.3	69.9	69.9	^{13}C
			0.82[a]		3.43	3.43	^{1}H
ae/O	H	O	21.2	36.0	67.8	69.1	^{13}C
			0.86[a]		3.29	3.87	^{1}H
ae/EA	H	P	21.4	35.7	67.2	70.4	^{13}C
			0.89–0.91		3.37	4.05	^{1}H
ae/EE	H	P	21.3	36.0	67.6	70.4	^{13}C
			0.89–0.91	-	3.37	4.05	^{1}H
P/ee/P	P	P	21.6	34.5–34.6	70.3	70.3	^{13}C
			1.00–1.04		4.09–4.11	4.09–4.11	^{1}H
O/ee/EA	O	P	21.6	34.5–34.6	69.1	70.5	^{13}C
			0.97–0.98		3.89	4.09–4.11	^{1}H
O/ee/EE	O	P	21.6	34.5–34.6	68.9	70.5	^{13}C
			0.97–0.98	-	3.89	4.09–4.11	^{1}H
O/ee/O	O	O	0.97–0.98		3.84	3.84	^{1}H

[a] These signals necessarily have also comprise methyl protons from oleate residues

where

$$S(-CH_3) = aa(-CH_3) + ae/O(-CH_3) + (ae/EA + ae/EE)(-CH_3) + (P/ee/P + O/ee/P)(-CH_3) \quad (6)$$

(2) *Quaternary region (34.5–36.3 ppm).* The signals appearing in this interval (*Figure 1D*) show a chemical shift and an evolution as a function of the reaction time quite similar to those observed for the binary system (*Figure 1C*) described in a previous paper[4].

The signal appearing at 36.0 ppm has been assigned to the quaternary carbon of the glycol when it is monoesterified not only with *o*-phthalic anhydride, giving place to an **ae/EE** structure, but also with oleic acid to give **ae/O**. This last structure shows this nucleus slightly shielded with respect to the position that it adopts in the model compound (36.2 ppm) and in a monoester quite similar formed between adipic acid and neopentyl glycol (36.2 ppm)[16].

The quaternary carbons from **P/ee/P** and **O/ee/P** diesters appear between 34.5 and 34.6 ppm as two or three wide signals. The signal at lower chemical shift has a relaxation time slightly greater than the others (see *Table 2*). Then, it has been tentatively assigned to the mixed diester **O/ee/P** whose chemical shift is slightly lower than 34.9 ppm described elsewhere[16] for the mixed diester of *o*-phthalic and adipic acids with neopentyl glycol. We cannot rule out the existence of small quantities of **O/ee/O**, whose quaternary carbon appears at 34.6 ppm in the model. The chemical shifts of each one of these signals and their assignments are gathered in *Table 3*. Molar percentages calculated from this zone, given in *Table 4*, have been estimated by the expressions

$$[\mathbf{aa}](\%) = 100 \times [aa(-C-)/S(-C-)] \quad (7)$$

$$([\mathbf{ae/EE}] + [\mathbf{ae/O}])(\%) = 100 \times [(ae/EE + ae/O)(-C-)/S(-C-)] \quad (8)$$

$$[\mathbf{ae/EA}](\%) = 100 \times [ae/EA(-C-)/S(-C-)] \quad (9)$$

$$([\mathbf{P/ee/P}] + [\mathbf{O/ee/P}])(\%) = 100 \times [(P/ee/P + O/ee/P)(-C-)/S(-C-)] \quad (10)$$

where

$$S(-C-) = aa(-C-) + (ae/EE + ae/O)(-C-) + ae/EA(-C-) + (P/ee/P + O/ee/P)(-C-) \quad (11)$$

(3) *Oxymethylenic zone (67.2–70.5 ppm).* As can be observed in *Figures 2A* and *B*, the ternary system presents four new signals in this zone. All these signals are due to the presence of the oleate residue. At 67.8 ppm resonates the free oxymethylenic carbon of the monoesterified structure $\underline{a}$e/**O**, which appears at 68.0 ppm in the model compound. At 69.1 ppm resonates their esterified carbon a$\underline{e}$/**O**, whose chemical shift is

Table 4 Molar percentage of structures (%) as a function of the reaction time *t*, of all species which can present neopentyl glycol (N, 0.95 mol) in its copolyesterification with *o*-phthalic anhydride (P, 0.54 mol) and oleic acid (O, 0.25 mol) ([–COOH]/[–OH]) = 0.70 in bulk at 205°C. Values calculated from (A) methylic and (B) quaternary regions of the ^{13}C n.m.r. spectra and (C) from oxymethylenic region of the ^{1}H n.m.r., both in $CDCl_3$ solution at 23°C. **EA** and **EE**: P mono- and diesterified, respectively. **aa**: N free; **ae**: N monoesterified with P (**ae/EA** and **ae/EE**) and O (**ae/O**); **ee**: N diesterified with P and O (**P/ee/P**, **O/ee/P** and **O/ee/O**)

t (min)	**aa** (%)	**ae/O** (%)	**ae/EE** (%)	**ae/EA** (%)	**P/ee/P** (%)	**O/ee/P** (%)	**O/ee/O** (%)	Zone
5	28	14	37		21			A
	26	26		27	21			B
	26	14	40		10	8	2	C
15	21	14	39		26			A
	22	34		18	26			B
	20	13	40		13	12	2	C
30	18	14	38		30			A
	17	40		13	30			B
	17	13	39		18	10	3	C
45	16	13	39		32			A
	15	42		11	32			B
	15	13	40		18	12	2	C
60	15	12	39		34			A
	15	42		8	35			B
	14	11	41		19	12	3	C
90	15	11	39		35			A
	12	43		8	37			B
	12	10	42		20	14	2	C
120	14	11	39		36			A
	12	45		4	39			B
	12	10	38		21	16	3	C
180	11	10	40		39			A
	10	46		4	40			B
	9	10	39		25	15	2	C
240	10	10	38		42			A
	10	48		0	42			B
	8	10	38		27	15	2	C
360	9	10	39		42			A
	9	45		0	46			B
	7	9	38		29	15	2	C
540	8	10	37		45			A
	9	46		0	45			B
	7	9	38		29	15	2	C
660	7	9	37		47			A
	8	45		0	47			B
	7	9	38		29	15	2	C

69.2 ppm in the pure neopentyl glycol monooleate. In the system studied by Hvilsted[16] such nuclei appear at 68.1 ppm for the $-\underline{C}H_2OH$ and 69.3 ppm for the $-\underline{C}H_2OCOR$ in the neopentyl glycol monoadipate.

Together with **a̲e/O** resonates the oxymethylenic carbon esterified with an oleate residue from the mixed diester in which the *o*-phthalate residue has a free acid group, **O/e̲e/EA**. This assignment has been done keeping in mind that at the beginning of the copolyesterification the molar percentage of this last signal is larger than that obtained for the singlet of **a̲e/O** structure. As the reaction goes on both values become quite similar (see *Table 5*), since the **O/e̲e/EA** structure is disappearing. On other hand, the signal at 68.9 ppm has been assigned to the oxymethylene which is located close to the oleate residue in the mixed diester with a diesterified *o*-phthalate residue, **O/e̲e/EE**, whereas the carbon close to the *o*-phthalate residue, **O/ee̲/P**, appears at 70.5 ppm. This higher deshielding in the oxymethylenic carbons, $-\underline{C}H_2OCOR$, brought about by the presence of an aromatic ring[9,14–17,39,40] has been also observed by Hvilsted[16] in the mixed diester of neopentyl glycol with *o*-phthalic and adipic acids. Thus, he has described a chemical shift at 68.9 ppm for the aforementioned carbon when R is an adipate residue and 70.2 ppm when R is of aromatic nature. Therefore, we cannot rule out the presence of the **O/ee/O** structure, whose oxymethylenic carbons appear at 69.0 ppm in the model.

As can be observed in *Table 2*, the oxymethylenic carbons of the structures **ae/P** exhibit a lower T_1 than those of the **ae/O** structure, as a consequence of the steric hindrance and the structural stiffness created by the *o*-phthalate residue. On other hand, easiness of the hydroxyl group of the neopentyl glycol, **aa**, to form hydrogen bonds anchors the oxymethylenic extreme producing a decrease in the value of the relaxation time expected for the mentioned carbons.

As it may be expected and can be seen in *Figure 2B*, all the oxymethylenic carbons which are close to an *o*-phthalate group appear very close, and because of this

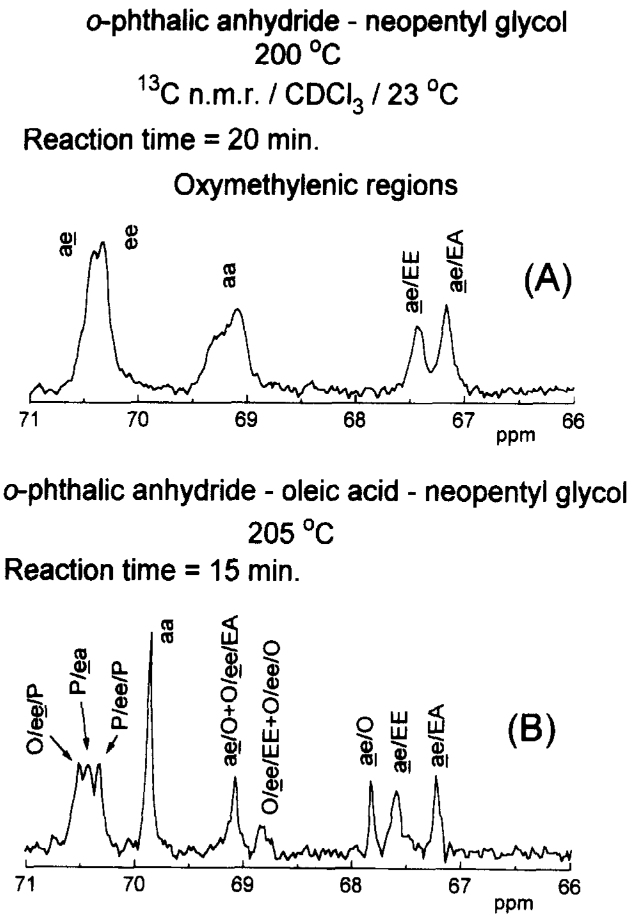


Figure 2 Expansions of the ^{13}C n.m.r. spectra oxymethylenic regions in $CDCl_3$ at room temperature (23°C) of: (A) a sample isolated after 20 min of the reaction between o-phthalic anhydride (P, 0.68 mol) and neopentyl glycol (N, 0.96 mol) ([-COOH]/[-OH]) = 0.70 in bulk and without any external catalyst at 200°C and (B) a sample isolated after 15 min of copolyesterification between o-phthalic anhydride (P, 0.54 mol), oleic acid (O, 0.25 mol) and neopentyl glycol (N, 0.95 mol) ([-COOH]/[-OH]) = 0.70 in bulk and without any external catalyst at 205°C. **EA** and **EE**: P mono- and diesterified, respectively. **aa**: N free; **ae**: N monoesterified with P (**ae/EA** and **ae/EE**) and O (**ae/O**); ee: N diesterified with P and O (**P/ee/P**, **O/ee/P**, and **O/ee/O**). The underlined letters represent the carbon $-\underline{C}H_2O-$ whose resonance is being observed in every case

it has not been possible to elucidate if such a residue would be mono-**AE** or diesterified **EE**, or to carry out the quantification of the aforementioned structures separately. The singlet which appears at 69.9 ppm has been assigned to the two methylene groups of the free neopentyl glycol **aa** and is deshielded as the reaction goes on, similarly to what happened in the binary system[4]. After 90 min of reaction, this singlet appears at 70.2 ppm, overlapping with the aforementioned signals. From this time of reaction it has not been possible to determine its molar percentage. All these assignments have been confirmed by the experimental results obtained after the addition of diazomethane and they will be described in detail later on. The chemical shifts of all these structures have been gathered in *Table 3*. The molar percentages of functional groups are shown in *Table 5* and they have been obtained from the area of every group of signals:

$$[\mathbf{aa}](\%) = 100 \times [\mathrm{aa}(-CH_2OH)/S(-CH_2O-)] \quad (12)$$

$$[\mathbf{a\underline{e}/O}](\%) = 100 \times [\mathrm{a\underline{e}/O}(-CH_2OH)/S(-CH_2O-)] \quad (13)$$

$$([\mathbf{a\underline{e}/O}] + [\mathbf{O/\underline{e}e/EA}])(\%) = 100 \times \left[\frac{(\mathrm{a\underline{e}/O + O/\underline{e}e/EA})(-CH_2OCOR)}{S(-CH_2O-)}\right] \quad (14)$$

$$([\mathbf{\underline{a}e/EA}] \text{ or } [\mathbf{\underline{a}e/EE}])(\%) = 100 \times \left[\frac{(\mathrm{\underline{a}e/EA \text{ or } \underline{a}e/EE})(-CH_2OH)}{S(-CH_2O-)}\right] \quad (15)$$

$$[\mathbf{O/\underline{e}e/EE}](\%) = 100 \times [\mathrm{O/\underline{e}e/EE}(-CH_2OCOR)/S(-CH_2O-)] \quad (16)$$

$$([\mathbf{P/ee/P}] + [\mathbf{a\underline{e}/P}] + [\mathbf{O/e\underline{e}/P}])(\%) = 100 \times [(\mathrm{P/eeP + a\underline{e}/P + O/e\underline{e}/P})(-CH_2OCOR)/S(-CH_2O-)] \quad (17)$$

Table 5 Molar percentage of functional groups (%) as a function of the reaction time *t*, of all species which can present neopentyl glycol (N, 0.95 mol) in its copolyesterification with o-phthalic anhydride (P, 0.54 mol) and oleic acid (O, 0.25 mol) ([-COOH]/[-OH]) = 0.70 in bulk and without any external catalyst at 205°C. These values have been obtained from oxymethylenic region of the ^{13}C n.m.r. spectra in $CDCl_3$, at room temperature (23°C). **EA** and **EE**: P mono- and diesterified, respectively. **aa**: N free; **ae**: N monoesterified with P (**ae/P** = **ae/EA** + **ae/EE**) and O (**ae/O**); **ee**: N diesterified with P and O (**P/ee/P**, **O/ee/P** = **O/ee/EA** + **O/ee/EE** and **O/ee/O**). The underlined letters indicate the carbon $-\underline{C}H_2O-$ whose resonance is being observed in each case

t (min)	**aa** (%)	**ae/O** (%)	**ae/O + O/ee/EA** (%)	**ae/EA** (%)	**ae/EE** (%)	**O/ee/EE + O/ee/O** (%)	**P/ee/P + ae/P + O/ee/P** (%)
5	27	7	11	13	7	2	33
15	22	7	10	10	9	4	38
30	19	6	9	6	12	4	44
45	17	6	8	5	14	5	45
60	16	6	8	4	16	6	44
90	—[a]	5	5	3	16	7	—[a]
120	—[b]	5	5	2	18	8	—[b]
180	—[c]	5	5	2	18	8	—[c]
240	—[d]	5	5	0	18	8	—[d]
360	—[e]	5	5	0	18	8	—[e]
540	—[f]	5	5	0	18	8	—[f]
660	—[g]	5	5	0	18	8	—[g]

[a,b,c,d,e,f,g] From 90 min of reaction, an overlapping of the oxymethylenic carbons of free neopentyl glycol and esterified with o-phthalic anhydride is produced. The whole values for the four signals are as follows: [a] 64%; [b] 62%; [c] 62%; [d] 64%; [e] 64%; [f] 64% and [g] 64%

where

$$S(\text{-CH}_2\text{O-}) = \text{aa}(\text{-CH}_2\text{OH}) + \underline{\text{a}}\text{e/O}(\text{-CH}_2\text{OH}) + (\text{a}\underline{\text{e}}\text{/O} + \text{O/}\underline{\text{e}}\text{e/EA})(\text{-CH}_2\text{OCOR}) + (\underline{\text{a}}\text{e/EA or }\underline{\text{a}}\text{e/EE})(\text{-CH}_2\text{OH}) + \text{O/}\underline{\text{e}}\text{e/EE}(\text{-CH}_2\text{OCOR}) + (\text{P/ee/P} + \text{a}\underline{\text{e}}\text{/P} + \text{O/e}\underline{\text{e}}\text{/P})(\text{-CH}_2\text{OCOR}) \quad (18)$$

Analysis of the structural distribution of acid groups

From 167.0 to 174.5 ppm we can clearly distinguish two zones (see *Figure 3*):

(1) *o-Phthalate residues zone.* The behaviour of the *o*-phthalic anhydride during the copolyesterification is similar to that observed in the binary system[4].

Thus, we have not detected any signal from the anhydride group (~ 162.6 ppm), and an increase of the conversion leads to a shielding of the signals due to all carboxylic groups of the sample (*Figure 3*). The assignments have been done following the same criteria given for the binary system[4], namely, by keeping in mind:

(A) The different possible combinations between a diacid, a monoacid and a dialcohol are shown in *Scheme 6*.

(B) The shielding produced by the esterification of the carboxylic and alcoholic groups from *o*-phthalate and alcoholic units, respectively.

Therefore, from high to low chemical shift, we can distinguish three regions, as can be seen in *Figure 3A*, which have been assigned by analogy to that described previously[4] as:

(i) The first two groups of signals which appear at lower field have been attributed to the free carboxyl group of the monoester **$\underline{\mathrm{A}}$E**: The first one, at 169.7 ppm has been assigned to structures of the **$\underline{\mathrm{A}}$E/ea** type, whereas the second one at 169.5 ppm has been attributed to structures of the **$\underline{\mathrm{A}}$E/ee** type. Both are transformed into a unique one as the conversion goes on (*Figure 3B*) and disappear at the end of the process (*Figure 3C*).

(ii) The esterified carboxylic carbon of the monoester **A$\underline{\mathrm{E}}$** also appear as two signals which can be assigned to **A$\underline{\mathrm{E}}$/ea** (169.2 ppm) and **A$\underline{\mathrm{E}}$/ee** (168.9 ppm) structures. They disappear when the reaction goes to completion.

(iii) The group of signals which appear between 168.3 and 167.9 has been assigned to the two ester groups of the diesterified structure, **EE**. In spite of its complexity, we can observe two well differentiated zones in *Figure 3B*: between 168.3 and 167.8 ppm resonate the carboxylate groups of the **E$\underline{\mathrm{E}}$/ea** structure, whereas the signals which appear between 167.6 and 167.4 ppm would be due to structures of the **E$\underline{\mathrm{E}}$/ee** type.

The molar percentage of free and esterified carboxylic groups gathered in *Table 6* have been estimated by the expressions

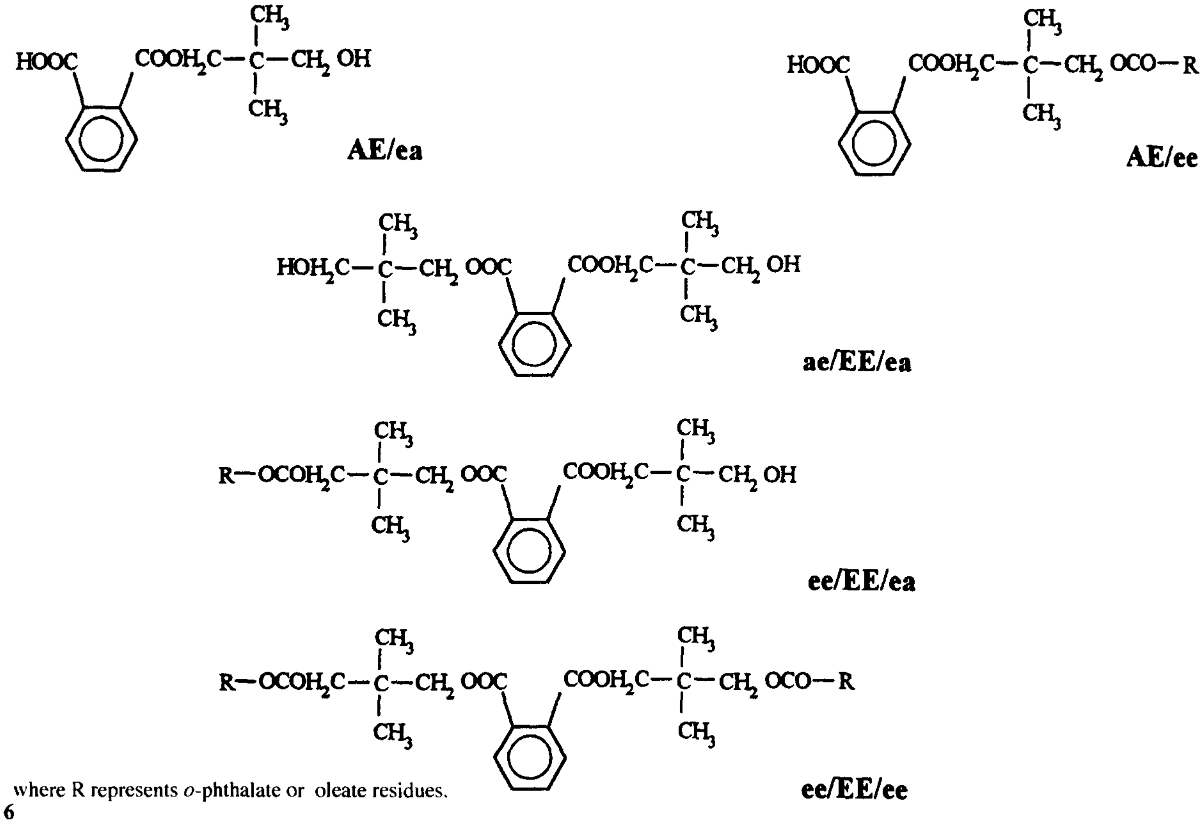
$$[\underline{\text{A}}\text{E}](\%) = 100 \times [\underline{\text{A}}\text{E}(\text{-COOH})/S(\text{-COO/P})] \quad (19)$$

$$[\text{A}\underline{\text{E}}](\%) = 100 \times [\text{A}\underline{\text{E}}(\text{-COO/P})/S(\text{-COO/P})] \quad (20)$$

$$[\text{EE}](\%) = 100 \times [\text{EE}(\text{-COO/P})/S(\text{-COO/P})] \quad (21)$$

where

$$S(\text{-COO/P}) = \underline{\text{A}}\text{E}(\text{-COOH}) + \text{A}\underline{\text{E}}(\text{-COO/P}) + \text{EE}(\text{-COO/P}) \quad (22)$$



where R represents *o*-phthalate or oleate residues.

Scheme 6

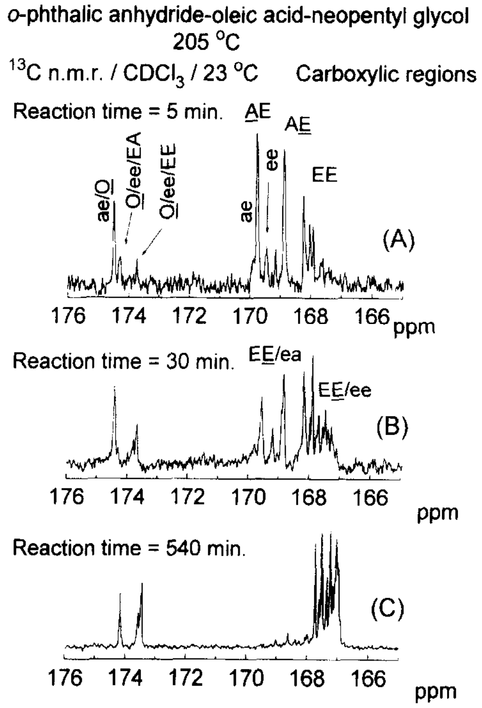


Figure 3 Expansions of the ^{13}C n.m.r. spectra carboxylic regions in $CDCl_3$ at room temperature (23°C) of a series of samples isolated after (A) 5, (B) 30 and (C) 540 min of copolyesterification between *o*-phthalic anhydride (P, 0.54 mol), oleic acid (O, 0.25 mol) and neopentyl glycol (N, 0.95 mol) ([–COOH]/[–OH]) = 0.70 in bulk and without any external catalyst at 205°C. **A**: free –COOH group from *o*-phthalate residue; **E** and **O**: esterified –COO– group from *o*-phthalate an oleate residue, respectively; **ae** and **ee**: N mono- and diesterified, respectively. The underlined letters indicate the carbon –$\underline{C}$OO– whose resonance is being observed in every case

Table 6 Molar percentage of functional groups (%) as a function of the reaction time *t*, of the *o*-phthalic anhydride (P, 0.54 mol) and oleic acid (O, 0.25 mol) esters which can be formed in its copolyesterification with neopentyl glycol (N, 0.95 mol) ([–COOH/[–OH]) = 0.70 in bulk and without any external catalyst at 205°C. The values have been obtained from the carboxylic region of the ^{13}C n.m.r. spectra in $CDCl_3$ at room temperature (23°C). **AE** and **EE**: P mono- and diesterified, respectively; **ae/O**: neopentyl glycol monooleate; **ee**: N diesterified with P and O (**O/ee/EA** and **O/ee/EE**). The underlined letter indicates the –$\underline{C}$OO– carbon whose resonance is being observed in each case

t (min)	**$\underline{A}$E** (%)	**A$\underline{E}$** (%)	**EE** (%)	**ae/$\underline{O}$** (%)	**$\underline{O}$/ee/EA** (%)	**$\underline{O}$/ee/EE** (%)
5	29	26	45	51	33	16
15	26	24	50	46	19	35
30	15	13	72	44	19	37
45	10	16	74	40	18	41
60	10	12	78	36	17	47
90	7	10	83	33	7	60
120	5	5	90	33	4	63
180	3	5	92	35	0	65
240	0	0	100	33	0	67
360	0	0	100	33	0	67
540	0	0	100	33	0	67
660	0	0	100	33	0	67

(2) *Oleate residue region.* As we have said before, we have not observed any signal due to the free oleic acid (180.3 ppm). This fact means that this acid is totally consumed at the very beginning of the copolyesterification and would yield to mono-, **ae/O**, and diesters **O/ee/O** and **O/ee/P**.

Thus, the signal appearing at 174.5 ppm in *Figure 3A* has been assigned to the neopentyl glycol monooleate, **ae/O**, whose carboxylic carbon resonates in the monoester model at 174.5 ppm. The signals at 174.2 and 174.3 ppm, which disappear as the reaction time goes up, have been assigned to structures of the **O/ee/EA** type. The singlet at 173.7 ppm shown in *Figure 3A* may be assigned to the carboxylate from the oleate residue of the mixed diester **O/ee/EE**. The existence of the diester **O/ee/O** (2–4%) cannot be completely ruled out, since its carboxylic carbons appear at 173.7 ppm in the pure neopentyl glycol dioleate. In the same way, we can appreciate in the aforementioned *Figure 3* that all these signals show a progressive shielding as the conversion goes up. All these assignments have been confirmed by the results obtained after the addition of diazomethane, as will be seen later on. The molar percentages of **ae/$\underline{O}$**, **$\underline{O}$/ee/EA** and **$\underline{O}$/ee/EE** structures have been determined by

$$[\mathbf{ae}/\underline{\mathbf{O}}](\%) = 100 \times [\mathrm{ae}/\underline{\mathrm{O}}(\text{–COO/O})/\mathrm{S}(\text{–COO/O})] \tag{23}$$

$$[\underline{\mathbf{O}}/\mathbf{ee}/\mathbf{EA}](\%) = 100 \times [\underline{\mathrm{O}}/\mathrm{ee}/\mathrm{EA}(\text{–COO/O})/\mathrm{S}(\text{–COO/O})] \tag{24}$$

$$[\underline{\mathbf{O}}/\mathbf{ee}/\mathbf{EE}](\%) = 100 \times [\underline{\mathrm{O}}/\mathrm{ee}/\mathrm{EE}(\text{–COO/O})/\mathrm{S}(\text{–COO/O})] \tag{25}$$

where

$$\mathrm{S}(\text{–COO/O}) = \mathrm{ae}/\underline{\mathrm{O}}(\text{–COO/O}) + \underline{\mathrm{O}}/\mathrm{ee}/\mathrm{EA}(\text{–COO/O}) + \underline{\mathrm{O}}/\mathrm{ee}/\mathrm{EE}(\text{–COO/O}) \tag{26}$$

These percentages are gathered in *Table 6*. They are similar, within the experimental errors of the technique, to the values estimated for the same structures from the oxymethylenic zone of neopentyl glycol, as can be very easily deduced by comparing *Tables 5* and *6*.

Structural study by ^{1}H n.m.r.

The ^{1}H n.m.r. spectra obtained for each one of the samples show some clearly differentiated zones, as can be seen in *Figure 4*. It is important to mention that the chemical shift of the signal assigned to the alcoholic proton depends on the dilution[27,42] and the total acid groups concentration of the samples. Thus, for a sample isolated after 5 min of reaction where [–COOH] = 0.45_8 mole, the $-CH_2O\underline{H}$ appears at 6.22 ppm (*Figure 4A*). This signal shifts to high field as the conversion goes up. So, the $-CH_2O\underline{H}$ appears at 2.44 ppm after 360 min of reaction (*Figure 4B*) where [–COOH] = 0.03_2 mol. The determination of the total acid groups concentration of each sample will be described in a forthcoming paper[43]. We have not observed in any case the acid proton which would result from the anhydride ring opening or from unreacted oleic acid.

(1) *Methylic region (0.82–1.04 ppm).* The signals have been tentatively assigned in samples isolated at low conversions since the system gets more complicated as the degree of conversion grows up (*Figures 4A* and *B*). The overlapping which all the methylic signals present prevents us from analysing the structural distribution in this zone.

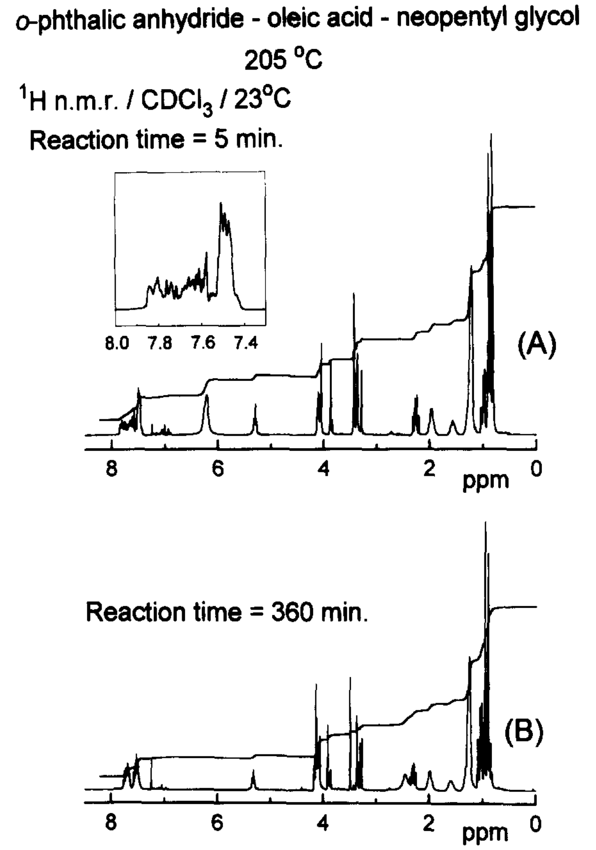


Figure 4 ^{1}H n.m.r. spectra in $CDCl_3$ at room temperature (23°C) of two samples isolated after (A) 5 and (B) 360 min of copolyesterification between *o*-phthalic anhydride (P, 0.54 mol), oleic acid (O, 0.25 mol) and neopentyl glycol (N, 0.95 mol) ([–COOH]/[–OH]) = 0.70 in bulk and without any external catalyst at 205°C. Experimental conditions were as follows: 256 scans; t_d = 2 s; pulse angle 90°

For a sample isolated after 5 min of reaction (*Figure 5B*), the singlet at 0.82 ppm has been attributed to the methylic protons of the free neopentyl glycol **aa**. As would be expected, the methylic protons from the aliphatic monoester, **ae/O**, appear more shielded than those from the aromatic ester, **ae/P**. The methyl group of the oleate residues must appear together with the **ae/O** giving rise to a triplet centred approximately at 0.86 ppm, similarly to what happens in the initial reagent and in model esters.

Finally, the diesterification produces a deshielding of the methylic nuclei. The higher aromatic nature of the substituents the higher deshielding. Thus, the methylic protons of the **O/ee/P** structures would appear at lower chemical shift than those of **P/ee/P** whose chemical shift is similar to that presented by the same structure in the binary system (*Figures 5A* and *B*). Furthermore, it is to be expected that together with **O/ee/P** signals the **O/ee/O** methyl groups will appear, since they resonate at 0.94 ppm in the diester model. All these chemical shifts are shown in *Table 3*.

(2) *Oxymethylenic zone (3.29–4.11 ppm).* The oxymethylenic protons with free alcoholic group of **aa** and **ae/P** structures appear with similar chemical shifts in both systems as can be observed in *Figures 5C* and *D*.

The new signal at 3.29 ppm may be assigned to the monoester **ae/O** (3.27 ppm in the pure neopentyl glycol monooleate). These protons are deshielded in comparison with those of **ae/P** as a consequence of the aliphatic nature of the oleate residue.

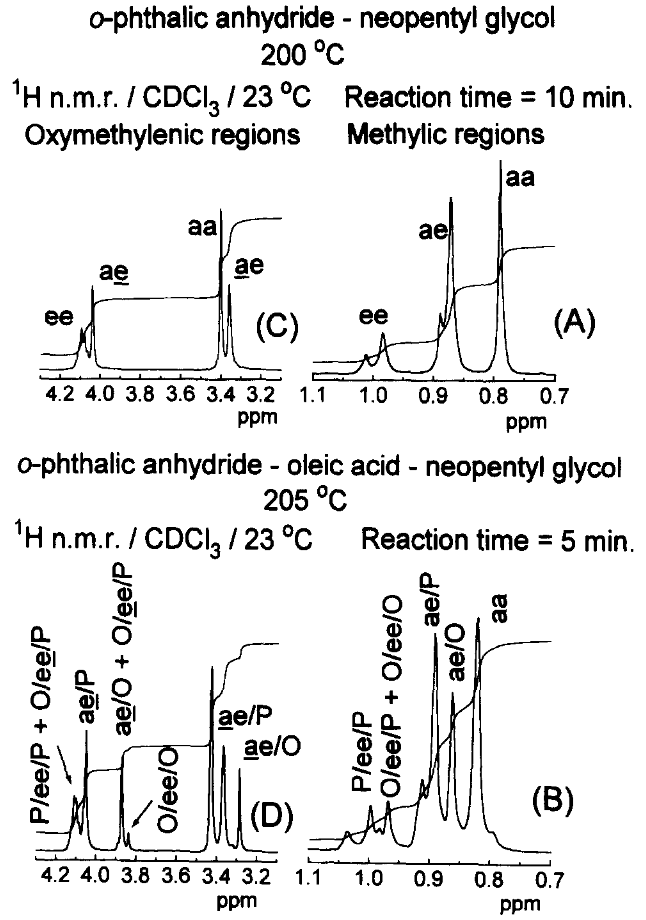


Figure 5 Expansions of the ^{1}H n.m.r. spectra methylic and oxymethylenic regions in $CDCl_3$ at room temperature (23°C) of: (A) and (C) a sample isolated after 10 min of the reaction between *o*-phthalic anhydride (P, 0.68 mol) and neopentyl glycol (N, 0.96 mol) ([–COOH]/[–OH]) = 0.70 in bulk without any external catalyst at 200°C, and (B) and (D) a sample isolated after 5 min of copolyesterification between *o*-phthalic anhydride (P, 0.54 mol), oleic acid (O, 0.25 mol) and neopentyl glycol (N, 0.95 mol) ([–COOH]/[–OH]) = 0.70 in bulk without any external catalyst at 205°C. **aa**: N free; **ae**: N monoesterified with P (**ae/P**) and O (**ae/O**); **ee**: N diesterified with P and O (**P/ee/P**, **O/ee/P** and **O/ee/O**). The underlined letter indicates the protons $-C\underline{H}_2O-$ whose resonance is being observed in every case

The inductive effect –I of the ester group produces a deshielding of the oxymethylenic protons when the alcoholic group is esterified ($-C\underline{H}_2OCOR$). As would be expected, the esterification with an aliphatic acid such as the oleic acid causes a smaller one than that produced by an aromatic residue. This effect has also been observed by Sepulchre *et al.*[44] in the poly(tetramethylene maleate-*b*-tetramethylene *o*-phthalate-*b*-tetramethylene succinate), *b*BMPS. The oxymethylenic protons in this copolymer which are esterified with succinic acid in sequences of the M(or P)$CH_2(CH_2)_2C\underline{H}_2S$ type, appear at 4.11 ppm, whereas in the poly(tetramethylene *o*-phthalate) these protons resonate at higher chemical shift, appearing at 4.33 ppm. Therefore, in our case, the new signals which appear at 3.84 and 3.87 ppm in *Figure 5D* have been assigned to oxymethylenic protons close to an oleate residue. Thus, the singlet at 3.84 ppm can be attributed to **O/ee/O** since this position agrees with that of the model compound. The signal at 3.87 ppm has been assigned to oxymethylenic protons in structures of the **ae/O** type (3.91 ppm in the model). Other small signals appear together with this last one at ~ 3.89ppm.

It cannot be very well resolved under the experimental conditions employed. It may be assigned to the oxymethylenes esterified with oleate residues in the mixed diester **O/e̲e/P**, since the esterification of **ae/O** with *o*-phthalic anhydride would produce a deshielding in the aforementioned protons. The oxymethylenic groups esterified with *o*-phthalate residues, **ae̲/P** and **P/ee/P**, appear in analogous position to those of the binary system (*Figures 5C* and *D*). Protons from **O/ee̲/P** structures would also resonate together with these latter ones. All these chemical shifts are gathered in *Table 3*.

The molar percentages of each one of these structures have been determined from the integrals I of each signal by the expressions

$$[\mathbf{aa}](\%) = 100 \times [(I_{\mathrm{aa}}(\text{-CH}_2\text{OH})/2)/I] \qquad (27)$$

$$[\mathbf{ae/O}](\%) = 100 \times [I_{\underline{\mathrm{a}}\mathrm{e/O}}(\text{-CH}_2\text{OH})/I] \qquad (28)$$

$$[\mathbf{ae/P}](\%) = 100 \times [I_{\underline{\mathrm{a}}\mathrm{e/P}}(\text{-CH}_2\text{OH})/I] \qquad (29)$$

$$[\mathbf{O/ee/O}](\%) = 100 \times [(I_{\mathrm{O/ee/O}}(\text{-CH}_2\text{O/O})/2)/I] \qquad (30)$$

$$[\mathbf{O/ee/P}](\%) = 100 \times [I_{\mathrm{O/\underline{e}e/P}}(\text{-CH}_2\text{O/O})/I] \qquad (31)$$

$$[\mathbf{P/ee/P}](\%) = 100 \times [(I_{\mathrm{P/ee/P}}(\text{-CH}_2\text{O/P})/2)/I] \qquad (32)$$

where

$$\begin{aligned} I = {} & (I_{\mathrm{aa}}(\text{-CH}_2\text{OH})/2) + I_{\underline{\mathrm{a}}\mathrm{e/O}}(\text{-CH}_2\text{OH}) \\ & + I_{\underline{\mathrm{a}}\mathrm{e/P}}(\text{-CH}_2\text{OH}) + (I_{\mathrm{O/ee/O}}(\text{-CH}_2\text{O/O})/2) \\ & + I_{\mathrm{O/\underline{e}e/P}}(\text{-CH}_2\text{O/O}) + (I_{\mathrm{P/ee/P}}(\text{-CH}_2\text{O/P})/2) \qquad (33) \end{aligned}$$

Due to the overlapping of the signals from **O/ee/P** and **P/ee/P** structures (*Figure 5D*), the value of the integrals of the protons of these structures have been calculated as:

(i) The oxymethylenic protons esterified with oleate residues ($\text{-C}\underline{\text{H}}_2\text{O/O}$) from the structures **ae̲/O** and **O/e̲e/P** gives rise to one signal. Therefore

$$\begin{aligned} I_{\mathrm{O/\underline{e}e/P}}(\text{-CH}_2\text{O/O}) = {} & I_{(\mathrm{a\underline{e}/O+O/\underline{e}e/P})}(\text{-CH}_2\text{O/O}) \\ & - I_{\mathrm{a\underline{e}/O}}(\text{-CH}_2\text{O/O}) \qquad (34) \end{aligned}$$

Moreover, in **ae/O** monoester the number of free oxymethylenic protons is equal to the number of esterified oxymethylenic protons. Thus, the integral for both types of protons must have the same value

$$I_{\mathrm{a\underline{e}/O}}(\text{-CH}_2\text{O/O}) = I_{\underline{\mathrm{a}}\mathrm{e/O}}(\text{-CH}_2\text{OH}) \qquad (35)$$

(ii) Similarly, we can calculate the contribution of the protons of the **P/ee/P** structures from the whole integral of the oxymethylenic protons esterified with *o*-phthalic anhydride $I(\text{-CH}_2\text{O/P})$ by applying:

$$\begin{aligned} I_{\mathrm{P/ee/P}}(\text{-CH}_2\text{O/P}) = {} & I(\text{-CH}_2\text{O/P}) - I_{\mathrm{a\underline{e}/P}}(\text{-CH}_2\text{O/P}) \\ & - I_{\mathrm{O/e\underline{e}/P}}(\text{-CH}_2\text{O/P}) \qquad (36) \end{aligned}$$

and by keeping in mind that

$$I_{\mathrm{a\underline{e}/P}}(\text{-CH}_2\text{O/P}) = I_{\underline{\mathrm{a}}\mathrm{e/P}}(\text{-CH}_2\text{OH}) \qquad (37)$$

and

$$I_{\mathrm{O/e\underline{e}/P}}(\text{-CH}_2\text{O/P}) = I_{\mathrm{O/\underline{e}e/P}}(\text{-CH}_2\text{O/O}) \qquad (38)$$

The molar percentages are gathered in *Table 4*. Its evolution as a function of the reaction time is shown in *Figure 6*. As can be seen in *Table 4*, the agreement between all the data is very good, which confirms once again not only the goodness of the results for ^{1}H n.m.r. as well as for ^{13}C n.m.r., but also the procedure followed in this case and the assignments which have been made in all the zones of the ^{1}H n.m.r. and ^{13}C n.m.r. spectra of the samples.

We wish to emphasize that the neopentyl glycol dioleate **O/ee/O** is detected by ^{1}H n.m.r. from the very beginning of the reaction and it is maintained constant throughout. The percentage is very small, say about 2–3%. This quantity is so small that such a structure has not been seen by ^{13}C n.m.r. under the experimental conditions in which the spectra have been recorded. This is probably due to the fact that these low percentages lie within the limits of error of the technique.

(3) *Aromatic zone (7.47–7.85 ppm).* In this zone three partially overlapped multiplets appear (*Figure 4*). According to the system poly(1,2-propylene *o*-phthalate) studied by Judas *et al.*[7] we have made the following assignments.

(i) The upfield protons (7.47–7.51 ppm) can be assigned to the nucleus in β and γ positions with respect to the substituents in the *o*-phthalic ring. They will be designated by H_2, H_3 and H_6.

(ii) From 7.58 to 7.72 ppm the protons H_4 and H_5 appear, situated in position α with respect to the ester groups.

(iii) Finally, in between 7.74 and 7.85 ppm the protons H_1 would resonate which are situated in α position with respect to the free carboxylic groups.

These assignments have been confirmed in two different ways:

(1) On the one hand, by the progress of the reaction. In fact, an increase of the conversion produces a progressive diminution of the area which corresponds to downfield multiplet assigned to H_1 protons, which disappears practically at the end of the reaction (*Figure 4*).

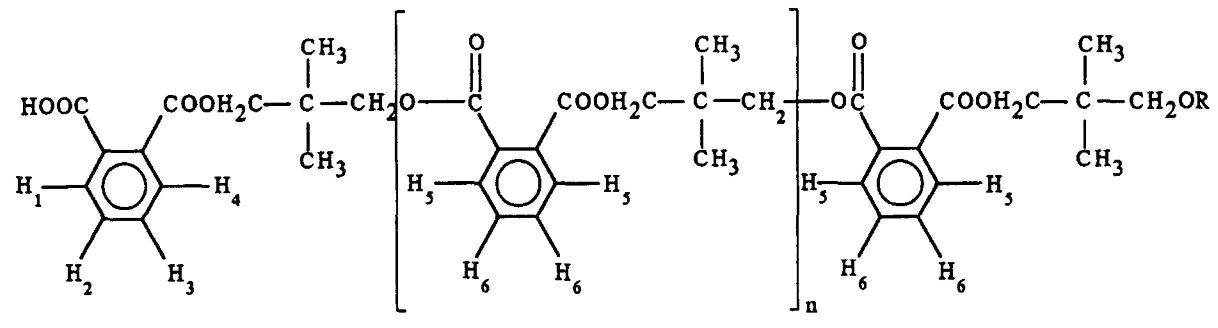
(2) On the other hand, the ^{1}H n.m.r. spectra of samples treated with diazomethane.

Structural analysis of the product of reaction with diazomethane

^{13}C n.m.r. spectra

With the only purpose to confirm the assignments, the chloroformic solutions of two samples isolated after 5 and 45 min of reaction have been treated with an excess of diazomethane[4]. The appearance of two signals due to the methoxy group at 52.6 and 52.5 ppm can be tentatively explained by the presence of **A̲E** monoester with different chain length in the untreated samples.

(1) *Methylic zone.* In the spectra given in *Figures 7A* and *B*, we observe the disappearance of the signal



Scheme 7

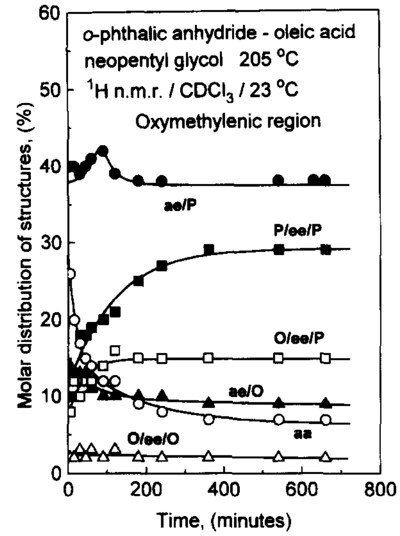


Figure 6 Molar distribution of structures (%) as a function of the reaction time *t*, of all species which can present the neopentyl glycol (N, 0.95 mol) in its copolyesterification with *o*-phthalic anhydride (P, 0.54 mol) and oleic acid (O, 0.25 mol) ([-COOH]/[-OH]) = 0.70 in bulk without any external catalyst at 205°C. Molar percentages have been obtained from the oxymethylenic zones of the ^{1}H n.m.r. spectra in CDCl$_3$ at room temperature (23°C). **aa**: N free; **ae**: N monoesterified with P (**ae/P**) and O (**ae/O**); **ee**: N diesterified with P and O (**P/ee/P**, **O/ee/P** and **O/ee/O**)

assigned to **ae/EA** as a consequence of its free carboxylic group esterification. The singlet at 21.4 ppm may be assigned to an **ae/P** structure, whose area is the total of those corresponding to **ae/EA** and **ae/EE** structures found for samples before the reaction with diazomethane.

(2) *Quaternary zone.* The signal attributed to **ae/EA** also disappears (*Figures 7C* and *D*). The area of the signals at 36.0 and 36.1 ppm, assigned to **ae/EE** + **ae/O** structures, also comprises the area attributed to **ae/EA**.

(3) *Oxymethylenic zone.* We can also observe the disappearance of **ae/EA** in this region. The singlet at 67.7 ppm (*Figure 8B*) is due to the resonance of the **ae/EE** structure. Its intensity is the total of the two signals before the esterification with diazomethane.

We observe also a variation of the area of the signals which have been attributed to **ae/O**, **O/ee/EA** and **O/ee/EE** structures. The esterification with diazomethane of the free carboxylic group of the *o*-phthalate residue from **O/ee/EA** means that the signal at 69.1 ppm assigned to **ae/O** and **O/ee/EA** structure (*Figure 8A*) decreased its intensity in a percentage which is equivalent to an increase of the area of the signal at 68.8 ppm assigned to an **O/ee/EE** structure. In this way, after the addition of diazomethane, the estimated molar percentage of the neopentyl glycol monooleate is the same independently of the carbon which is being observed, **ae/O** or **ae/O**. For this reason, it is more probable that the **O/ee/O** structure resonates together with **O/ee/EE** in the spectra obtained before the diazomethane addition. On the contrary, if the structure **O/ee/O** would resonate together with **ae/O** structure, the areas of the signals assigned to **ae/O** and **ae/O** would be different after the diazomethane treatment. These results do confirm again the assignments previously made. In the same way, we have observed a downfield shift for **aa**, which resonates at 70.8 ppm (71.0 ppm in the initial reagent[4]).

(4) *Carboxylic zone.* As can be observed in *Figures 8C* and *D*, the esterification with diazomethane brings about the disappearance of the signals attributed to **AE** and an increase in the intensity of the signals due to the diesters, **EE**. In the same way, the signal assigned to the **O/ee/EA** structure disappears, but the area of the signal at 173.6 ppm assigned to an **O/ee/EE** structure increases.

^{1}H n.m.r. spectra

^{1}H n.m.r. spectra recorded after the diazomethane addition have not given any additional information. They are effectively the same as those of the untreated samples. The aromatic region only showed two very well defined multiplets, since the H$_1$ protons were shifted towards upfield as a consequence of the acid groups methylation.

In a forthcoming paper[43] we have proposed a chemical kinetic model for the copolyesterification between *o*-phthalic anhydride, oleic acid and neopentyl glycol in bulk at 205°C. The interpretation of experimental data for such complex reaction systems has been possible only by model simulation. The mechanism was based on very simple reactions. All relevant reactions were considered and a final selection of 12 reactions involving eight species was made.

CONCLUSIONS

(1) Low molecular weight copolyesters from the bulk copolyesterification at 205°C between *o*-phthalic anhydride, oleic acid and neopentyl glycol have been studied by ^{1}H and ^{13}C spectroscopies. The information has made possible the determination of the degree of conversion of acid and alcohol groups, the distribution of mono- and diesterified neopentyl glycol with *o*-phthalic anhydride and oleic acid and to characterize a series of structures. The changes found in the ^{13}C n.m.r. spectrum of the samples after treatment with diazomethane confirm

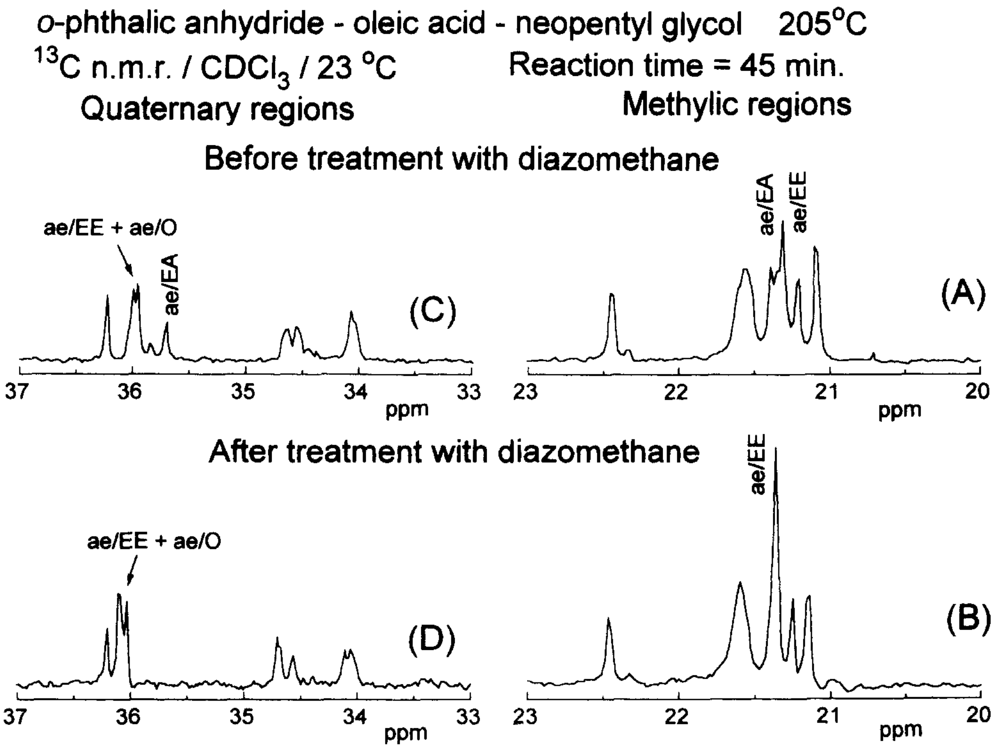


Figure 7 Expansions of the ^{13}C n.m.r. spectra methylic and quaternary regions in $CDCl_3$ at room temperature (23°C) of a sample isolated after 45 min of copolyesterification between *o*-phthalic anhydride (P, 0.54 mol), oleic acid (O, 0.25 mol) and neopentyl glycol (N, 0.95 mol) ([-COOH]/[-OH]) = 0.70 in bulk and without any external catalyst at 205°C, recorded (A) and (C) before and (B) and (D) after the addition of an excess of diazomethane. **A**: free -COOH group of *o*-phthalate residue; **E** and **O**: -COO- esterified group of *o*-phthalate and oleate residues, respectively; **ae**: N monoesterified with P (**ae/EA** and **ae/EE**) and O (**ae/O**)

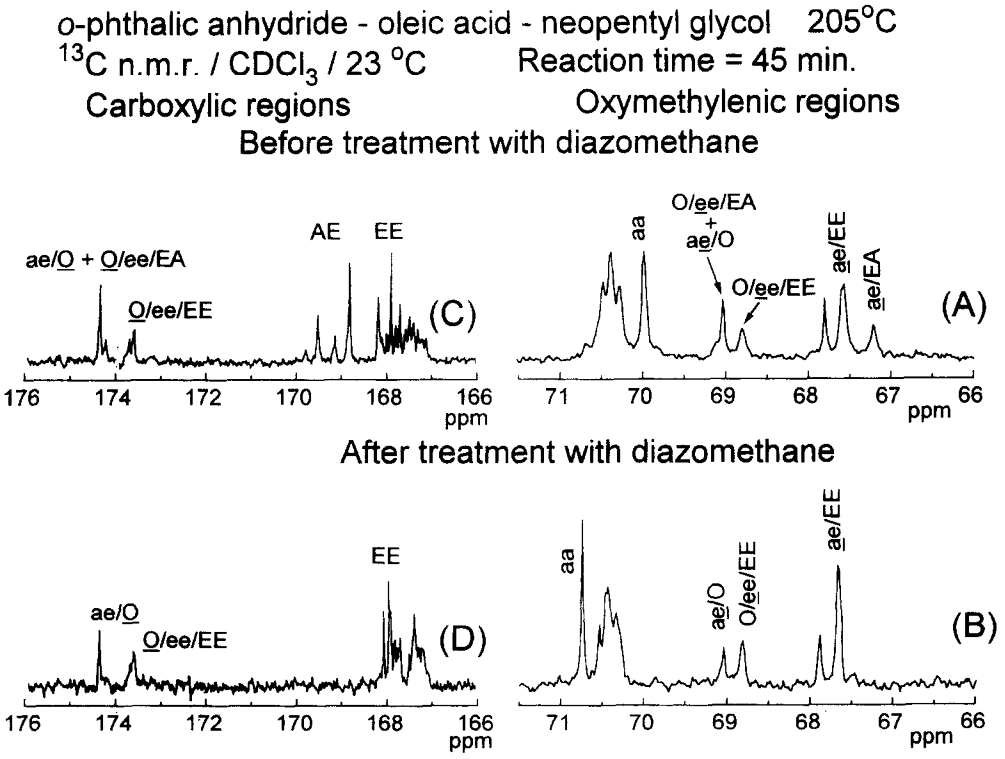


Figure 8 Expansions of the ^{13}C n.m.r. spectra oxymethylenic and carboxylic regions in $CDCl_3$ at room temperature (23°C) of a sample isolated after 45 min of the copolyesterification between *o*-phthalic anhydride (P, 0.54 mol), and oleic acid (O, 0.25 mol) with neopentyl glycol (N, 0.95 mol) ([-COOH]/[-OH]) = 0.70 in bulk without any external catalyst at 205°C, obtained (A) and (C) before and (B) and (D) after the addition of an excess of diazomethane. **A**: free -COOH group of *o*-phthalate residue; **E** and **O**: esterified -COO- group of *o*-phthalate and oleate residues, respectively; **aa**: N free; **ae**: N monoesterified with P (**ae/EA** and **ae/EE**) and O (**ae/O**); **ee**: N diesterified with P and O (**O/ee/EA** and **O/ee/EE**). The underlined letters indicate the carbon whose resonance is being observed in every case

the assignments for: (i) the two proposed structures of the **ae/P** monoester, **ae/EA** and **ae/EE**, (ii) the **O/ee/EA** and **O/ee/EE** diesters and (iii) the **AE** structures.

(2) This copolyesterification at high temperature, in bulk and without any external catalyst, has made clear that it is possible to prepare unsaturated polyesters at high conversions in short periods of time. We have not observed either the presence of secondary structures from isomerization, addition, decarboxylation and etherification reactions, polymerization between chains of unsaturated fatty acids at least within the limits of the experimental techniques employed or gels from crosslinking reactions as a consequence of the high temperature employed in the copolyesterification.

(3) The information furnished by the structural composition as a function of the reaction time is a very important source of data to establish subsequently a series of relationships between structure and deinking properties. Furthermore, the quantitative information afforded from ^{1}H and ^{13}C n.m.r. spectroscopies on the composition of the reaction medium and the evolution of each one of the functional groups and structures as a function of the reaction time have allowed us to carry out a detailed kinetic study. Its analysis by simulation of the copolyesterification process between *o*-phthalic anhydride, oleic acid and neopentyl glycol has been described elsewhere[43].

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