

Synthesis of Polyesters as Binders for Deinkable Inks. II. Kinetics and Mechanism of Polyesterification Between *o*-Phthalic Anhydride and Neopentyl Glycol in Bulk at 200°C

M. J. CALLEJO CUDERO, M. M. C. LÓPEZ-GONZÁLEZ, E. CARAZO CHICO, J. M. BARRALES-RIENDA

Departamento de Química-Física de Polímeros, Instituto de Ciencia y Tecnología de Polímeros, C.S.I.C.
Juan de la Cierva, 3, E-28006 Madrid, Spain

Received 4 October 1996; accepted 5 March 1997

ABSTRACT: The kinetics of the polyesterification in bulk at 200°C between *o*-phthalic anhydride and neopentyl glycol (2,2-dimethyl-1,3-propanediol) in a nonequimolecular ratio and in the absence of an external catalyst was investigated. The formation of the monoester and two dimeric compounds by uncatalyzed heating of *o*-phthalic anhydride with neopentyl glycol was virtually complete after dissolution of the anhydride. The data were analyzed statistically by a mathematical method due to Fradet and Maréchal for the estimation of the orders of reaction. This statistical adjustment of the data analysis supports the assumption that the kinetics of polyesterification in the absence of both the solvent and catalyst may be fitted to several orders of reaction over all the conversion. At first, our experimental data may be fitted to 3, or $\frac{3}{2}$, or 2, etc., overall orders. The results establish that the overall kinetic order of the polyesterification depend upon the goodness of the experimental results and cannot be only selected by means of a correlation coefficient. If this last criterium is adopted, the polyesterification at low, medium, as well as at high conversions may be 3 as the most probable one, order one with respect to acid group concentration, and order two with respect to alcoholic group concentration, in agreement with Flory's predictions. A mechanism consistent with the most plausible kinetic results ($I_{m,n} = 0.9990$ and $m, n = 1, 2$) is proposed. It consists of a dimerization of the alcoholic groups followed by an attack of the acid to the dimer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2409–2431, 1997

Key words: polyester; polyesterification; ^{13}C -nuclear magnetic resonance; ^1H -nuclear magnetic resonance; structural analysis; volumetry; kinetics of polyesterification; mechanism of polyesterification

INTRODUCTION

In this article, we intend to apply a kinetic analysis to a polyesterification in bulk to obtain infor-

mation on its kinetics and mechanism. The selection of the present system is for two reasons: on the one hand, because of its possible application as a binder for deinkable inks, and on the other, to study a polyesterification reaction in bulk without solvent and an external catalyst. Nowadays, due to the toxicity, as well as to some other problems of different character created by the use of organic solvents, some industrial polyesterifications are being carried out in the bulk at temperatures

Correspondence to: J. M. Barrales-Rienda.
Contract grant sponsor: CICYT.
Contract grant number: PB-92-0773-03-1.

above 160°C. At the same time, reaction time, stripping of solvent, etc., are shortened very appreciably.

Very often, when one intends to make a critical analysis on polyesterification or copolyesterification with the only object being to systematize the experimental data from the existing bibliography, one finds that there exists a lack of agreement between the diverse mechanistic interpretations which have been proposed on the processes.¹⁻⁴ In some cases, the conclusions which have been attained for a series of identical experimental data, even from the same experimental results, can be quite different from one author to another.

Before carrying out an analysis of the present experimental data, independently of how the analysis is done, it is necessary to keep in mind a series of considerations, and, subsequently, to the analysis, we should have to conclude on its validity in the light of the results. There can be no doubt that these assumptions can facilitate the kinetic analysis.

Flory⁵⁻⁹ took into account only the experimental results for high degrees of conversion, namely, above 80%. Under these circumstances, the data of esterification reactions of small monofunctional molecules as well as the polyesterification give a rate equation of order three. However, some years later, the same experimental results were again analyzed, but at this time, the whole reaction was taken into account. For instance, it was found that they fitted a $\frac{5}{2}$ -order rate equation¹⁰ or a succession of a second- and third-order rate equations.^{11,12}

In the present work, we carried out the polyesterification in nonequimolecular concentrations. Finally, we would like to make mention of the tremendous importance which can be played by the medium of reaction, especially as in our case, when the polyesterification is done without solvent and by using an excess of one of the starting products. Some authors, using several procedures, have shown that some polyesters are not true solutions,¹³⁻¹⁵ and for this reason, they do not fulfill one of the basic requirements of the theory of Flory.

¹³C-NMR spectroscopy was employed in a previous article¹⁶ to analyze the structures formed during the polyesterification in bulk at 200°C between *o*-phthalic anhydride and neopentyl glycol. This experimental technique suffers from a series of inconveniences, especially when, as in our case, high accuracies are required in the quantification of structures just below of 2% for a reliable kinetic

analysis. Therefore, to achieve better precision, we made use of ¹H-NMR spectroscopy. Also, we determined the molar concentration of acid groups by volumetry.

EXPERIMENTAL

Reactives and Technique of Polyesterification

Reactives and the technique of polyesterification have been described elsewhere.¹⁶ The structures that can be formed will be designated similarly as was done in a previous article.¹⁶ The underlined letters will indicate protons whose resonance is being observed in every case.

¹H-NMR Spectroscopy

¹H-NMR spectra were recorded at room temperature on a Gemini 200 spectrometer at 200 MHz, in deuteriochloroform (CDCl₃) solution with a concentration lower than 8%, to improve their resolution.¹⁷ To obtain quantitative spectra, we used pulse sequences of 90° with a delay time of 2 s. The spectra were registered after 256 scans. Chemical shifts are referenced to the resonance of CDCl₃ [7.24 ppm from (CH₃)₄Si]. The ¹H-NMR chemical shifts of the starting products are gathered in Table I.

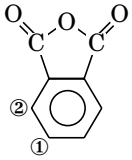
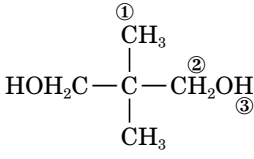
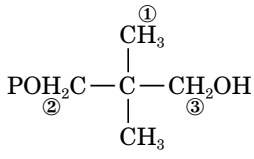
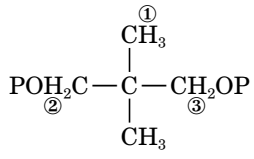
¹³C-NMR Spectroscopy

¹³C-NMR spectra were carried out on a Gemini 200 spectrometer at 50.28 MHz and at room temperature (23°C) on 20% (w/v) DMSO-*d*₆ solutions. To obtain quantitative spectra, we used an "inverse gated decoupling" sequence, with an acquisition time of 0.7 s, a delay between pulses of 30 s, and 300 scans. Chemical shifts are referenced to the central resonance of DMSO-*d*₆ (39.5 ppm from TMS). The area of the signals was calculated by planimetry and triangulation.

Volumetry

For the experimental determination of the number of acid groups by volumetry, we took 1 or 2 g of the sample depending on the acid number to be expected. They were dissolved in 25–50 mL of a mixture of toluene/ethyl alcohol (2/1, v/v) at room temperature. The resulting solution was titrated with alcoholic KOH 0.1N using an alcoholic

Table I $^1\text{H-NMR}$ Chemical Shifts in CDCl_3 Solution at Room Temperature (23°C) of Reactives and All Structures Which Can Present Neopentyl Glycol (N, 0.96 mol) in a Sample Isolated After 10 Min of Its Polyesterification with *o*-phthalic Anhydride (P, 0.68 moles) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in Bulk at 200°C)

Structure	δ (ppm)		
	1	2	3
	(7.88–7.95) ^a	(7.97–8.04) ^a	—
	0.79 (0.84) ^a	3.40 (3.42) ^a	— (3.36) ^a
	0.87–0.89	4.04	3.36
	0.98–1.01	4.06–4.09	

^a Chemical shifts of *o*-phthalic anhydride and neopentyl glycol as reactives.

solution of phenolphthalein as an indicator.¹⁸ All measurements were made in duplicate.

DESCRIPTION OF THE $^1\text{H-NMR}$ SPECTRA

We have not been able to find any remarkable article in which the $^1\text{H-NMR}$ spectroscopy was used to analyze and to follow the evolution of chemical structures of this type for kinetic purposes. A great number of the authors employed this technique to know the nature of the components and to establish the composition of the polyesters in multicomponent systems. However, there exists only a very reduced number of works in which the sequence distribution has been characterized.^{19–24}

Thus, Birley et al.^{19,20} employed $^1\text{H-NMR}$ spectroscopy for the assignation of protons of propyl-

ene glycol in its polyesterification with terephthalic acid. To obtain information about the secondary reactions which take place in the synthesis of poly(1,2-propylene *o*-phthalate), Maréchal et al.^{21,22} synthesized and characterized several model molecules. Andreis et al.²³ used $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectroscopies to determine the different structures which can adopt these glycolic units in the products of the polyesterification with maleic anhydride. More recently, Pétiaud et al.²⁴ determined the molar percentages of the different structures which can be formed during the polyesterification between terephthalic acid and ethylene glycol for samples of low molecular weight. There can be no doubt that Rybicky²⁵ and Marshall²⁶ are the authors which have given a more precise picture about how $^1\text{H-NMR}$ spectroscopy can be used to identify and to determine the components of the alkyd resins and their modified products.

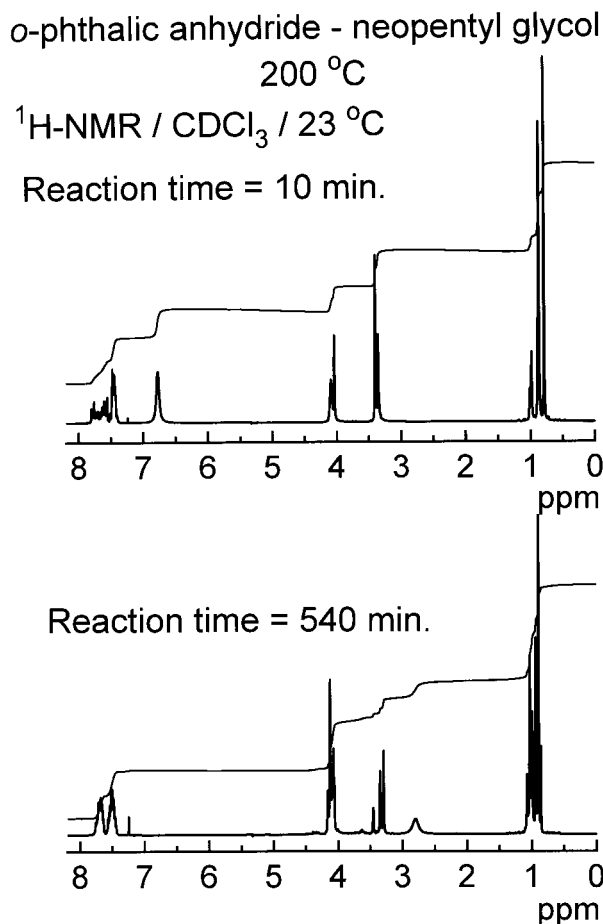


Figure 1 ¹H-NMR spectra recorded in CDCl₃ at room temperature (23°C) of two samples of the polyesterification between *o*-phthalic anhydride (*P*, 0.68 mol) and neopentyl glycol (*N*, 0.96 mol) ([—COOH]/[—OH]) = 0.7 in the bulk at 200°C, isolated after 10 and 540 min of reaction, respectively. Experimental conditions used: 256 scans; time between pulses, $D_1 = 2$ s; pulse 90°.

Our ¹H-NMR spectra obtained for each sample show, as can be observed in Figure 1, three clearly differentiated regions: (a) methylic region (0.79–1.01 ppm); (b) oxymethylene region (3.36–4.09 ppm); and (c) aromatic region (7.40–7.80 ppm). Furthermore, the spectra show another wide signal assignable to the alcoholic proton whose chemical shift depends upon the dilution of the sample, as already put forward by Fradet et al.²¹ and by Atta-ur-Rahman,²⁷ and the number of acid groups present in the sample. Thus, as can be observed in Figure 1, the ¹H-NMR spectrum of a sample isolated after 10 min of reaction with a molar concentration of acid groups of [—COOH] = 0.56₁ mol shows a wide band centered at 6.78 ppm.

However, for the sample isolated after 540 min with [—COOH] = 0.01₄ mol, this band shifts to 2.80 ppm. We have not observed, in any case, the proton of the free-acid group which would result from ring opening of the *o*-phthalic anhydride.

The structural analysis of the samples and its evolution as a function of the reaction time will be carried out in the zones where protons from neopentyl glycol units resonate. The free-acid moles in each one of the isolated samples through the polyesterification reaction will be obtained from the molar percentages of the esters formed at each time of reaction. The values, obtained in this way, will be checked against those resulting after the addition of diazomethane to the respective samples.

Structural Analysis

Methylic Region

In this region, for short times of reaction, as can be appreciated in Figure 2(A), there appear three groups of signals, which can be clearly differentiated. The two methyl groups assignable to the **aa** structure of free neopentyl glycol are present as a singlet at 0.79 ppm. The esterification brings about a deshielding of this signal; for this reason, the monoester structure **ae** appears between 0.87 and 0.89 ppm, and the diesterified species **ee**, between 0.98 and 1.01 ppm. The order of appearance of these structures is identical to that described by some other authors for the distinct structures which can be adopted by the glycolic units of 1,2-propanediol in its polyesterification with several diacids as terephthalic acid,^{19,20} *o*-phthalic anhydride,²² and maleic anhydride.²³

As the polyesterification increases, we observe an overlapping of these regions, since a great number of signals appear for methyl groups from the mono- and diesters of neopentyl glycol as is depicted in Figure 1. This can be attributed to a molecular weight effect, which may probably have a decisive influence on the chemical shift of every pair of geminal methyl groups.

The integral (*I*) which corresponds to each one of these three groups of signals is proportional to the molar percentage of these structures in each one of the investigated samples. These percentages were estimated by applying the following expressions:

$$[\mathbf{aa}](\%) = 100 \cdot [I_{\mathbf{aa}}(-\text{CH}_3)]/I(-\text{CH}_3) \quad (1)$$

$$[\mathbf{ae}](\%) = 100 \cdot [I_{\mathbf{ae}}(-\text{CH}_3)]/I(-\text{CH}_3) \quad (2)$$

o-phthalic anhydride - neopentyl glycol
200 °C
¹H-NMR / CDCl₃ / 23 °C
Reaction time = 10 min.

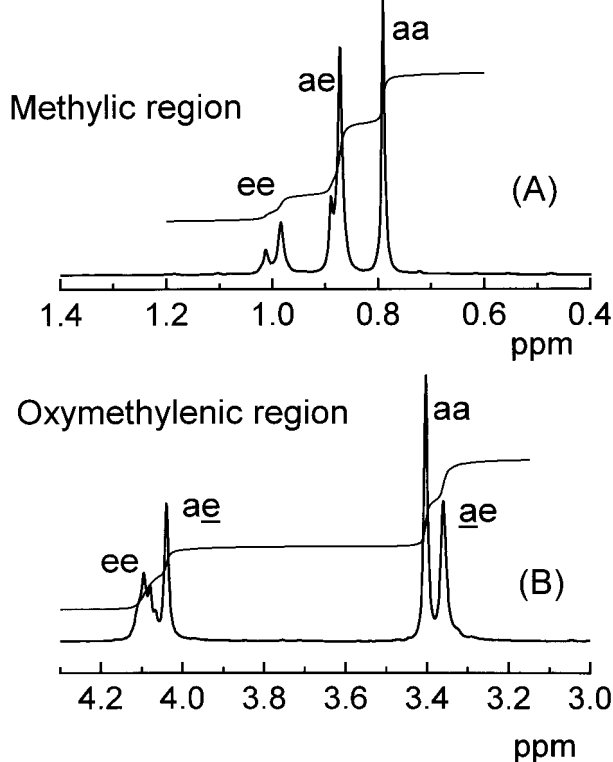


Figure 2 Expansions of the (A) methylic and (B) oxymethylenic regions of the ¹H-NMR spectra recorded in CDCl₃ at room temperature (23°C) of a sample isolated after 10 min of polyesterification of *o*-phthalic anhydride (*P*, 0.68 mol) and neopentyl glycol (*N*, 0.96 mol) ([—COOH]/[—OH]) = 0.7 in bulk at 200°C. aa, ae, and ee: free and mono- and diesterified *N*, respectively. The underlined letters indicate those protons whose resonance is being observed in every case.

$$[\text{ee}](\%) = 100 \cdot [I_{\text{ee}}(-\text{CH}_3)] / I(-\text{CH}_3) \quad (3)$$

where

$$I(-\text{CH}_3) = I_{\text{aa}}(-\text{CH}_3) + I_{\text{ae}}(-\text{CH}_3) + I_{\text{ee}}(-\text{CH}_3) \quad (4)$$

It is necessary to mention that the overlapping observed at high degrees of conversion has made it difficult to determine these molar percentages in the samples isolated at the end of the polymer-

ization. These values are shown in Table II and its representation as a function of time is given in Figure 3.

Oxymethylenic Region

In this region appear two very well differentiated groups of signals, as can be appreciated in Figure 2(B):

1. Those situated at the lower chemical shift have been assigned to the oxymethylenic protons with the free alcoholic group. Thus, at 3.36 ppm resonate those from the monoester ae, and the singlet at 3.40 ppm has been assigned to the —CH₂OH groups in the aa structure.

Table II Molar Percentages of Structures (%) as a Function of the Reaction Time *t*, of All Species Which Can Present Neopentyl Glycol (*N*, 0.96 mol) in Its Polyesterification with *o*-Phthalic Anhydride (*P*, 0.68 mol) ([—COOH]/[—OH]) = 0.7 in Bulk at 200°C

<i>t</i> (min)	<u>aa</u> (%)	<u>ae</u> (%)	<u>ee</u> (%)	Region
0 ^a	37	51	12	—
10	33	50	17	A
	34	49	17	B
20	30	52	18	A
	28	53	19	B
30	28	51	21	A
	23	53	24	B
40	21	55	24	A
	21	54	25	B
50	19	51	30	A
	18	54	28	B
60	16	50	34	A
	16	52	32	B
120	13	48	39	A
	12	49	39	B
180	10	48	42	A
	8	50	42	B
240	8	47	45	A
	7	50	43	B
360	8	45	47	A
	8	47	45	B
540	6	45	49	A
	5	46	49	B

Experimental values were obtained from the methylic (A) and oxymethylenic (B) regions of the ¹H-NMR spectra in CDCl₃ solution at room temperature. aa, ae, and ee: free, mono-, and diesterified *N*, respectively.

^a Molar percentages were estimated as described in the text. The values (mol/kg) for each structure given in eq. (20).

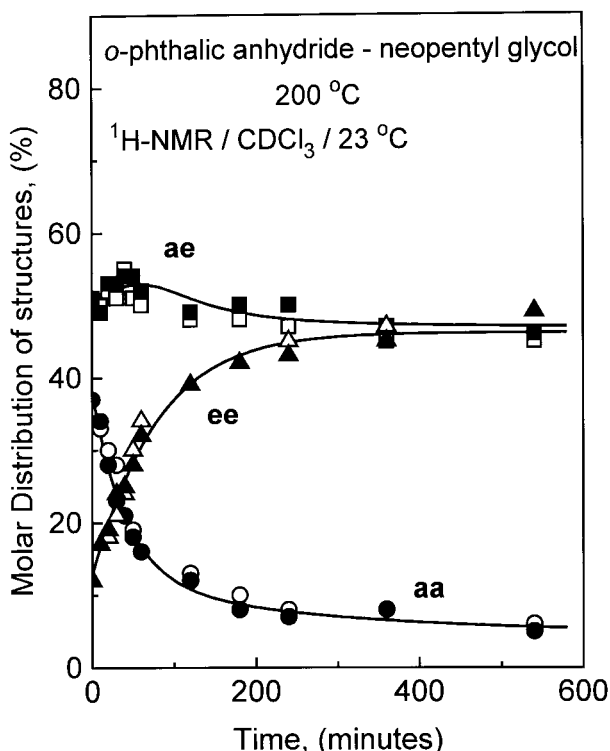


Figure 3 Molar distribution of structures (%) as a function of the reaction time t of all species which can be formed during the polyesterification between *o*-phthalic anhydride (P , 0.68 mol) and neopentyl glycol (N , 0.96 mol) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in bulk at 200°C. **aa**, **ae**, and **ee**: free and mono- and diesterified N , respectively. Open and solid symbols represent values estimated from the methylic and oxymethylenic regions, respectively. The $^1\text{H-NMR}$ spectra were recorded in CDCl_3 solution at room temperature (23°C).

- The esterified oxymethylenic protons appear as two groups of signals at 4.04 and 4.06–4.09 ppm. They were assigned to the monoester **ae** and diester **ee** structures, respectively. The signals due to this last structure are converted into more complicated ones and its molar percentage increased through the polyesterification process. As indicated by Pétiaud et al.,²⁴ protons from $-\text{CH}_2\text{OCOR}$ in the monoester of ethylene glycol and terephthalic acid resonate at 4.30 ppm, whereas those from the diesterified structure resonate at 4.60 ppm.

Molar percentages of each one of these three structures were estimated using the following expressions:

$$[\text{aa}](\%) = 100$$

$$\times [(I_{\text{aa}}(-\text{CH}_2\text{OH})/2)/I(-\text{CH}_2\text{O}-)] \quad (5)$$

$$[\text{ae}](\%) = 100 \cdot [I_{\text{ae}}(-\text{CH}_2\text{OH})/I(-\text{CH}_2\text{O}-)]$$

$$= 100 \cdot [I_{\text{ae}}(-\text{CH}_2\text{OCOR})/I(-\text{CH}_2\text{O}-)] \quad (6)$$

$$[\text{ee}](\%) = 100$$

$$\times [(I_{\text{ee}}(-\text{CH}_2\text{OCOR})/2)/I(-\text{CH}_2\text{O}-)] \quad (7)$$

where

$$I(-\text{CH}_2\text{O}-) = (I_{\text{aa}}(-\text{CH}_2\text{OH})/2)$$

$$+ I_{\text{ae}}(-\text{CH}_2\text{OH}) + (I_{\text{ee}}(-\text{CH}_2\text{OCOR})/2) \quad (8)$$

Although the signals from the **ae** and **ee** structures are partially overlapped at the beginning of the reaction, the $^1\text{H-NMR}$ spectra become more complicated with the degree of conversion and produce a total overlapping as can be observed in Figure 1. Then, the integral due to the diester may be calculated using the following expression:

$$I_{\text{ee}}(-\text{CH}_2\text{OCOR})$$

$$= I(-\text{CH}_2\text{OCOR}) - I_{\text{ae}}(-\text{CH}_2\text{OH}) \quad (9)$$

in which $I(-\text{CH}_2\text{OCOR})$ represents the integral of all esterified oxymethylenic protons.

Molar percentages obtained for each one of the structures are shown in Table II. Figure 3 shows a plot of their distributions against the reaction time.

Determination of the Free-acid Moles

The determination of the molar concentration of free acid was carried out from the oxymethylenic zone, as well as from the study of the $^1\text{H-NMR}$ spectra obtained after the addition of diazomethane to the different samples isolated during the polyesterification.

Oxymethylenic Region

The determination of the free-acid moles in each one of the samples was easily obtained from the molar percentage of the ester groups $[-\text{CH}_2\text{OCOR}](\%)$ using the following expression:

$$[-\text{COOH}](\text{moles}) = (2 \times 0.68)$$

$$- [([-\text{CH}_2\text{OCOR}](\%) \times 2 \times 0.96)/100] \quad (10)$$

Table III Molar Percentages of Functional Groups (%) as a Function of the Reaction Time t of the Free Alcoholic Groups $-\text{CH}_2\text{OH}$ and Esterified Oxymethylene Groups $-\text{CH}_2\text{OCOR}$ of Neopentyl Glycol (N , 0.96 mol) in Its Polyesterification with o -Phthalic Anhydride (P , 0.68 mol) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in Bulk at 200°C

t (min)	$[-\text{CH}_2\text{OH}]$ (%)	$[-\text{CH}_2\text{OCOR}]$ (%)	$[-\text{COOH}]$ (mol)	
			A	B
0 ^a	62.5 ₄	37.4 ₆	0.64 ₀	0.64 ₀
10	58.4 ₉	41.5 ₁	0.56 ₃	0.55 ₉
20	54.6 ₈	45.3 ₂	0.49 ₀	0.48 ₄
30	49.9 ₀	50.1 ₀	0.39 ₈	0.41 ₈
40	47.9 ₈	52.0 ₂	0.36 ₁	0.36 ₆
50	45.6 ₆	54.3 ₄	0.31 ₇	0.33 ₉
60	42.1 ₂	57.8 ₈	0.24 ₉	0.28 ₄
120	36.5 ₆	63.4 ₄	0.14 ₂	0.17 ₄
180	33.4 ₀	66.6 ₀	0.08 ₁	0.11 ₃
240	32.4 ₈	67.5 ₂	0.06 ₄	0.10 ₁
360	31.1 ₄	68.8 ₆	0.03 ₈	0.05 ₈
540	28.3 ₂	71.6 ₈	0	0.02 ₈

Experimental values obtained from the integrals of the oxymethylene regions of the $^1\text{H-NMR}$ spectra in CDCl_3 solution at room temperature (23°C). Moles of acid groups $-\text{COOH}$ calculated from the oxymethylene region (A) in the spectra of $^1\text{H-NMR}$ in CDCl_3 solution at room temperature (23°C) and recorded after the addition of an excess of diazomethane (B) to the different samples isolated during the polyesterification process.

^a See footnote ^a to Table II.

The values are collected in Table III. The determination of the molar percentage of the free alcoholic groups as well as of the ester groups is direct by using the value of the integrals corresponding to $-\text{CH}_2\text{OH}$ [$I(-\text{CH}_2\text{OH})$] and $-\text{CH}_2\text{OCOR}$ [$I(-\text{CH}_2\text{OCOR})$], respectively. These values are also shown in Table III and are plotted against the reaction time in Figure 4.

Addition of Diazomethane

Its use for the esterification of the free carboxylic groups of the o -phthalic residues of the samples isolated during the polyesterification produces, in general, only very weak modifications in the $^1\text{H-NMR}$ spectra, as can be seen in Figure 5. We observe the appearance of a group of signals between 3.83 and 3.89 ppm which can be assigned to the methoxylic protons. The shift of alcoholic protons at a higher field (2.54 ppm), due to the disappearance of carboxylic groups and to a lower

concentration of the sample, was confirmed by their disappearance after the addition of D_2O .

The moles of free acid existing before the addition of diazomethane are equal to the moles of methoxylic residues which are present in each sample after the addition of this reactive. Its determination in each one of the samples is immediate if we use a known quantity of an internal or external reference. In our case, the calculations were carried out by using the signals from methyl groups from glycolic units as the internal reference. Its molar percentage, which is gathered in Table III, was obtained from the following expression:

$$[-\text{COOH}](\text{moles}) = 2 \times 0.96 \times [I(-\text{OCH}_3)/I(-\text{CH}_3)] \quad (11)$$

where $I(-\text{OCH}_3)$ and $I(-\text{CH}_3)$ are the integrals

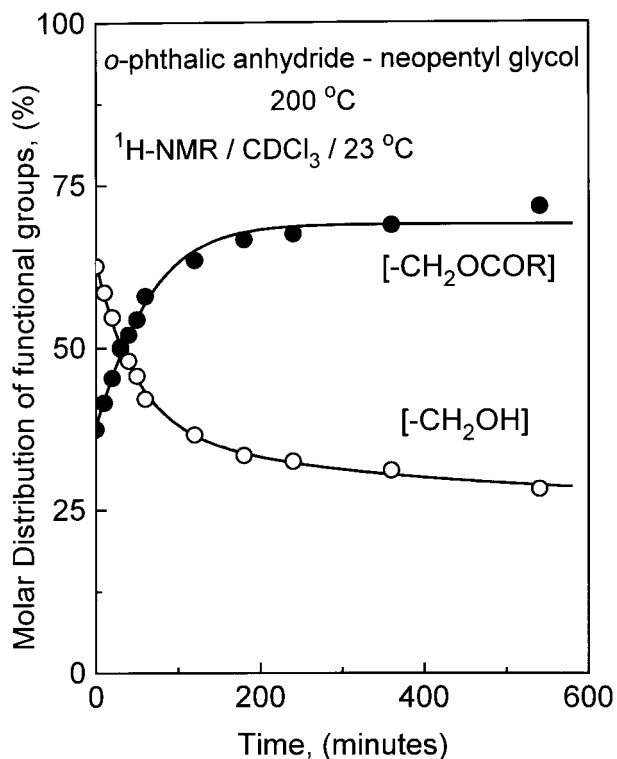


Figure 4 Molar distribution of functional groups (%) as a function of the reaction time t of the alcoholic $[-\text{CH}_2\text{OH}]$ and esterified oxymethylene $[-\text{CH}_2\text{OCOR}]$ groups in the polyesterification between o -phthalic anhydride (P , 0.68 mol) and neopentyl glycol (N , 0.96 mol) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in bulk at 200°C. The values were calculated from the respective integrals in the oxymethylene region of the $^1\text{H-NMR}$ spectra in CDCl_3 solution at room temperature (23°C).

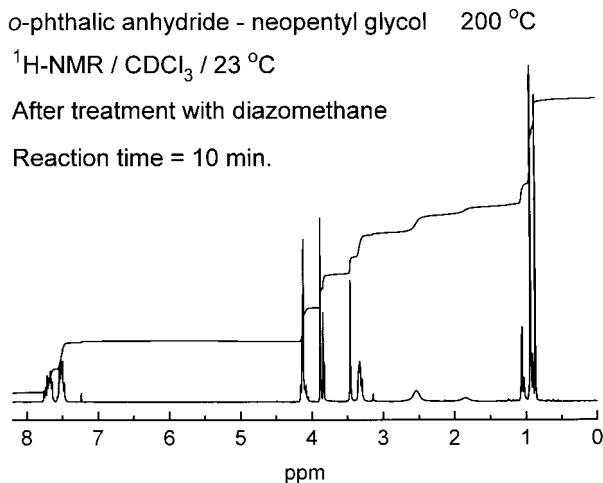


Figure 5 ¹H-NMR spectra recorded in CDCl₃ solution at room temperature (23°C) of a sample isolated after 10 min of the polyesterification between *o*-phthalic anhydride (*P*, 0.68 mol) and neopentyl glycol (*N*, 0.96 mol) ([—COOH]/[—OH]) = 0.7 in the bulk at 200°C, after the addition of an excess of diazomethane to the sample. This spectrum was obtained under the same experimental conditions as those for the spectrum shown in Figure 1.

corresponding to methoxylic and methylic groups, respectively.

DESCRIPTION OF THE ¹³C-NMR SPECTRA

The evolution of the different polymeric species formed during the polyesterification was also followed by ¹³C-NMR. The compounds give complex spectra whose structural analysis using CDCl₃ as solvent was described elsewhere.¹⁶ However, in the light of the results obtained using the NMR data analysis and volumetry, which will be described in detail later on, we considered it very convenient to carry out a ¹³C-NMR study in DMSO-*d*₆ to detect the different structures which may be present in the medium for short times of conversion. For higher degrees of conversion, it would be possible to detect, similarly as in CDCl₃, all the functional alcoholic groups of the chain ends from the neopentyl glycol monoesters **ae** and all the acid groups of the chain ends from the *o*-phthalate residues **AE**, as well as the total amount of diesterified neopentyl glycol, **ee**.

The ¹³C-NMR spectra in DMSO-*d*₆ show a time dependence quite similar to that shown when CDCl₃ is used as the solvent. They present also five quite well-differentiated regions, namely, me-

thylic, quaternary, oxymethylenic, aromatic, and carboxylic. Then, we analyzed and compared each one of these regions, in both solvents, excepting the aromatic one, for a sample isolated after 10 min of reaction.

Methylic Region

As can be observed in Figure 6(a), the use of DMSO-*d*₆ is inconvenient. The methylic groups of the neopentyl glycol in the **aa**, **ae**, and **ee** structures give a unique signal at 21.69 ppm. On the contrary, in the spectrum in CDCl₃, there appear three signals at 21.04, 21.37, and 21.54 ppm, respectively, which can be assigned to the aforementioned structures.

Quaternary Region

On the one hand, as we can see in Figure 6(a), when DMSO-*d*₆ is used, we lose the resolution shown by the neopentyl glycol monoester in CDCl₃. In this solvent, the **ae** structure gives two or three signals depending on the conversion degree. The evolution of these signals as a function of the reaction time allows us to make the assignment of the singlet at 35.68 ppm to the quaternary carbon of the monoester **ae/EA**, whereas the signals at 35.86 and 35.93 ppm were assigned to neopentyl glycol monoesters in which the second acid group of the *o*-phthalic ring is also esterified, i.e., structures of the **ae/EE** type. This type of groupings can come from dimers of the **ae/EE/ea** type or from chain-end structures as, for instance, **ae/EE/ee**.

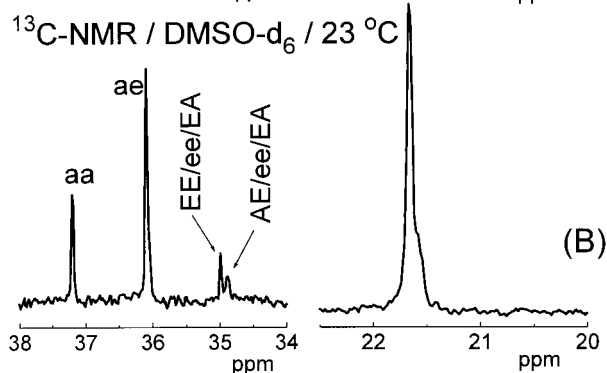
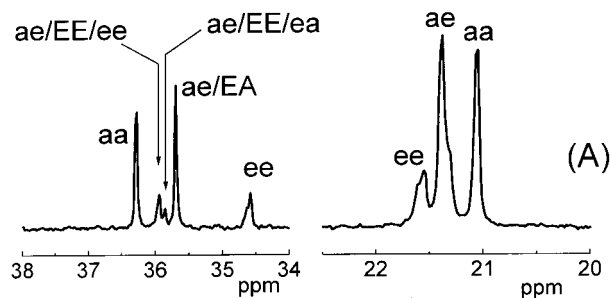
As the reaction increases, the signal which appears at higher chemical shifts is increased. Then, this signal may be assigned to monoesterified structures which are at the ends of the polymeric chain, whereas the signal appearing at a lower chemical shift, which is slightly decreasing along the process, may be attributed to structures of the **ae/EE/ea** type.

On the other hand, the use of DMSO-*d*₆ improves very slightly the resolution of the quaternary carbon of the diesterified neopentyl glycol, **ee**, as can be seen in the aforementioned Figure 6(a). In the ¹³C-NMR spectra obtained in both solvents of the sample isolated after 10 min of reaction appear two signals. Keeping in mind that for this time of reaction, as we will see later on, there do not exist in the medium of the reaction neopentyl glycol diesters in the middle of the polymeric chains, namely, structures of the **EE/ee/**

o-phthalic anhydride - neopentyl glycol

200 °C

Quaternary region Methylic region

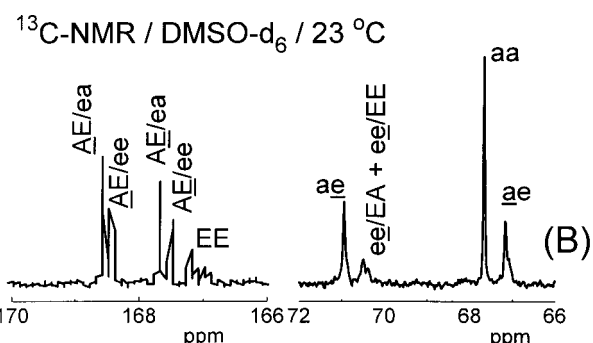
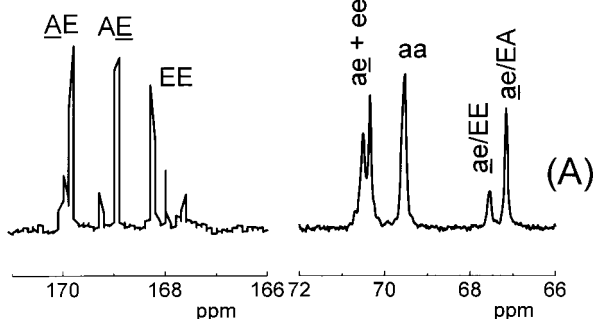
¹³C-NMR / CDCl₃ / 23 °C

6(a)

o-phthalic anhydride - neopentyl glycol

200 °C

Carboxylic region Oxymethylenic region

¹³C-NMR / CDCl₃ / 23 °C

6(b)

Figure 6 (a) Expansions of the methylic and quaternary zones of the ¹³C-NMR spectra in (A) CDCl₃ and (B) DMSO-*d*₆ at room temperature (23°C) of a sample isolated after 10 min of polyesterification between *o*-phthalic anhydride (*P*, 0.68 mol) and neopentyl glycol (*N*, 0.96 mol) ([—COOH]/[—OH]) = 0.7 in bulk at 200°C. **EA** and **EE**: mono- and diesterified *P*, respectively. **aa**: free *N*; **ae**: *N* monoesterified with *P*; **ee**: diesterified *N*. (b) Expansions of the oxymethylenic and carboxylic zones of the ¹³C-NMR spectra in (A) CDCl₃ and (B) DMSO-*d*₆ at room temperature (23°C) of a sample isolated after 10 min of polyesterification between *o*-phthalic anhydride (*P*, 0.68 mol) and neopentyl glycol (*N*, 0.96 mol) ([—COOH]/[—OH]) = 0.7 in the bulk at 200°C. **EA** and **EE**: mono- and diesterified *P*, respectively. **aa**: free *N*; **ae**: *N* monoesterified with *P*; **ee**: diesterified *N*. The underlined letters indicate those carbons whose resonance is being observed in every case.

EE type, both signals can only be attributed to structures of the **AE/ee/EA** and **EE/ee/EA** types. Considering the evolution of both signals and the effect exerted on the quaternary carbon of the neopentyl glycol by the esterification of the free-acid group, the signal which appears at a lower chemical shift can be tentatively assigned to the dimeric structure **AE/ee/EA**, whereas that appearing at a higher chemical shift, whose area increases with the time of reaction, can be attributed to structures of the **EE/ee/EA** types.

Oxymethylenic Region

Similarly to the above region and as can be observed in Figure 6(b), the information furnished by the DMSO-*d*₆ spectra on the oxymethylenic carbons with the free alcoholic group from the monoesterified structures, **ae**, is less than that obtained in CDCl₃, where we can observe two signals assignable to the two neopentyl glycol monoesters, **ae/EA** and **ae/EE**.

On the other hand, the oxymethylenic carbons

which are close to the esterified alcoholic groups are more well resolved in DMSO- d_6 . In this way, we can observe a singlet at 70.95 ppm assignable to \underline{ae} monoesters and two signals at 70.50 and 70.38 ppm which are attributed to the oxymethylene carbons of the neopentyl glycol diesters from structures of the $\underline{ee}/\underline{EE}$ and $\underline{ee}/\underline{EA}$ types. These two last structural groups resonate together in $CDCl_3$ at 70.34 ppm.

Carboxylic Region

Similarly to what happens in $CDCl_3$, in this region appear three very well differentiated zones when DMSO- d_6 is used, as can be seen in Figure 6(b). These zones can be assigned, from high to low chemical shifts, to the carboxylic carbons from the monoesterified *o*-phthalate residues \underline{AE} and \underline{AE} and diesterified \underline{EE} , respectively.

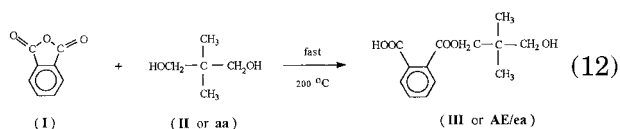
The assignments are the same as than those previously described¹⁶ in the case of $CDCl_3$, with the only difference that in DMSO- d_6 the position of the signals in the two first regions is inverted:

1. Thus, the singlet which appears at 168.62 ppm can be assigned to structures of the $\underline{AE}/\underline{ea}$ type, whereas that one appearing at 168.50 ppm may be assigned to carboxylic carbons of the free-acid groups of the neopentyl glycol diesters $\underline{AE}/\underline{ee}$ which are located at the chain ends.
2. Similar assignation can be made in the region where the esterified carboxylic carbons of the neopentyl glycol mono-*o*-phthalates resonate, namely, the singlet appearing at 167.74 ppm due to $\underline{AE}/\underline{ea}$ structures and the singlet at 167.58 ppm may be due to $\underline{AE}/\underline{ee}$ ones.
3. The groups of signals which appear at a higher field can be assigned to the carboxylic carbons of the \underline{EE} diesters. Similarly to what happens in $CDCl_3$, it has not been possible to make the assignation of this series of signals due to the complexity of the spectra.

The molar percentage of each one of the structures was estimated by an analogous form to that described in a previous work,¹⁶ i.e., from the area of the signals which appear in each one of these regions in the ^{13}C -NMR spectra. The values for the samples in DMSO- d_6 are similar to those obtained from the spectra registered in $CDCl_3$.

RESULTS

As put forward in a previous article,¹⁶ the reaction between *o*-phthalic anhydride and neopentyl glycol in the bulk at 200°C without a solvent or any external catalyst takes place rapidly and quantitatively, immediately after the reactives have been put together. It has not been possible to detect any trace of *o*-phthalic anhydride at the very beginning of the reaction. Furthermore, if we keep in mind that we have employed an excess of diol in the reactives, it will be possible to write the following reaction scheme:



A similar effect to this one of the instantaneous solution by reaction of the *o*-phthalic anhydride in alcohols for the formation of monoesters was observed by van der Zeeuw²⁸ during the esterification kinetic in the bulk and without a catalyst of *o*-phthalic anhydride with alcohols in a concentrated solution at 120°C for the preparation of monomeric plasticizers.

However, as described elsewhere,¹⁶ we cannot rule out the possibility of the formation of the structures of the $\underline{AE}/\underline{ee}/\underline{EA}$ and $\underline{ae}/\underline{EE}/\underline{ea}$ types at the beginning of the polyesterification process. Dimers of a similar nature were described by some other authors^{29–31} in the polyesterification between terephthalic acid and ethylene glycol; however, this system may be different with respect to structure and reactivity.

As we have already seen, the study by 1H -NMR has permitted to us not only the structural analysis of the samples but also the determination of the moles of free-acid groups which are present in each one of them. The results of this structural analysis are in agreement with those obtained using ^{13}C -NMR, as can be observed in Tables IV and V.

As we have already seen in a previous article,¹⁶ the direct quantitative estimation of $-COOH$ groups using high-resolution ^{13}C -NMR spectroscopy is not accurate enough, as is required, because of the interactive properties of the $-COOH$ group. For this reason, it can be thought that the estimation of the $-OH$ groups, which can be carried out from the relative areas of the different types of carbon atoms and later on to proceed by

Table IV Moles of Structures as a Function of the Reaction Time t of Some Species Which Can Present Neopentyl Glycol (N, 0.96 mol) in Its Polyesterification with *o*-Phthalic Anhydride (P, 0.68 mol) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in Bulk at 200°C

Structure	Time (min)												Zone
	0 ^a	10	20	30	40	50	60	120	180	240	360	540	
aa	0.35 ₈	0.30 ₇	0.28 ₈	0.23 ₀	0.21 ₁	0.16 ₃	0.16 ₃	0.11 ₅	0.08 ₆	0.06 ₇	0.05 ₈	0.05 ₈	A
		0.30 ₇	0.26 ₉	0.23 ₀	0.20 ₂	0.18 ₂	0.15 ₄	0.11 ₅	0.08 ₆	0.07 ₇	0.07 ₇	0.05 ₈	B
		0.32 ₆	0.27 ₈	0.25 ₀	0.21 ₁	0.20 ₂	0.16 ₃	0.14 ₄	0.14 ₄	— ^b	— ^c	— ^d	C
		0.31 ₇	0.28 ₈	0.26 ₉	0.20 ₂	0.18 ₂	0.15 ₄	0.12 ₅	0.09 ₆	0.07 ₇	0.07 ₇	0.05 ₈	D
		0.32 ₆	0.26 ₉	0.22 ₁	0.20 ₂	0.17 ₃	0.15 ₄	0.11 ₅	0.07 ₇	0.06 ₇	0.07 ₇	0.04 ₈	E
ee	0.11 ₈	0.16 ₃	0.19 ₂	0.23 ₀	0.24 ₀	0.29 ₈	0.29 ₈	0.37 ₄	0.41 ₃	0.44 ₂	0.46 ₁	0.46 ₁	A
		0.15 ₄	0.19 ₂	0.22 ₁	0.25 ₀	0.27 ₈	0.30 ₇	0.37 ₄	0.44 ₂	0.46 ₁	0.46 ₁	0.47 ₀	B
		0.15 ₄	0.19 ₂	0.21 ₁	0.26 ₉	0.26 ₉	0.30 ₇	0.35 ₅	0.41 ₃	— ^b	— ^c	— ^d	C
		0.16 ₃	0.17 ₃	0.20 ₂	0.23 ₀	0.28 ₈	0.32 ₆	0.37 ₄	0.40 ₃	0.43 ₂	0.45 ₁	0.47 ₀	D
		0.16 ₃	0.18 ₂	0.23 ₀	0.24 ₀	0.26 ₉	0.30 ₇	0.37 ₄	0.40 ₃	0.41 ₃	0.43 ₂	0.47 ₀	E

Experimental values were obtained from methylic (A), quaternary (B), and oxymethylenic (C) regions of the ¹³C-NMR spectra and methylic (D) and oxymethylenic (E) regions of the ¹H-NMR spectra, both in CDCl₃ solution at room temperature (23°C). **aa** and **ee**: free and diesterified N, respectively.

^a See footnote ^a to Table II.

^{b,c,d} From 240 min of reaction, an overlapping of the oxymethylenic carbons of free and diesterified neopentyl glycol is produced. The whole values are as follows: ^b 0.51₈ mol; ^c 0.50₄ mol; ^d 0.50₄ mol.

a smoothing of the experimental data, would be also used for the kinetic analysis.

Thus, the free alcoholic groups —CH₂OH from the dialcohol, **aa** (free diol, **II**) were estimated by ¹³C-NMR from the area of the signals of the free oxymethylenic groups, the quaternary carbon, and the geminal methyl groups. The average value of these three determinations is shown in the second column of Table VI.

The areas of the signals from the same nuclei

have been used to determine the molar percentages of the monoesterified diols, i.e., of free —OH groups from the compound (**III**) and in structures of the **EE/ea** type:

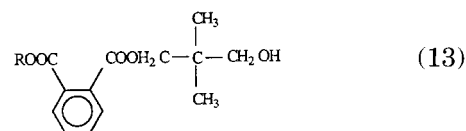


Table V Moles of Structures as a Function of the Reaction Time t of Some Species Which Can Present Neopentyl Glycol (N, 0.96 mol) in Its Polyesterification with *o*-Phthalic Anhydride (P, 0.68 mol) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in Bulk at 200°C

Structure	Time (min)												Zone
	0 ^a	10	20	30	40	50	60	120	180	240	360	540	
ae	0.48 ₁	0.49 ₀	0.48 ₀	0.49 ₉	0.50 ₉	0.49 ₉	0.49 ₉	0.47 ₀	0.46 ₁	0.45 ₁	0.44 ₂	0.44 ₂	A
		0.48 ₀	0.49 ₉	0.49 ₀	0.52 ₈	0.49 ₀	0.48 ₀	0.46 ₁	0.46 ₁	0.45 ₁	0.43 ₂	0.43 ₂	D
		0.47 ₀	0.50 ₉	0.50 ₉	0.51 ₈	0.51 ₈	0.49 ₉	0.47 ₀	0.48 ₀	0.48 ₀	0.45 ₁	0.44 ₂	E
ae/EA	0.40 ₂	0.33 ₆	0.26 ₉	0.22 ₁	0.19 ₂	0.13 ₄	0.12 ₅	0.07 ₇	0	0	0	0	B
		0.34 ₆	0.26 ₉	0.22 ₁	0.19 ₂	0.15 ₄	0.12 ₅	0.04 ₈	— ^b	0	0	0	C
ae/EE	0.07 ₉	0.16 ₃	0.23 ₀	0.28 ₈	0.31 ₇	0.36 ₅	0.37 ₄	0.39 ₄	0.43 ₂	0.42 ₂	0.42 ₂	0.43 ₂	B
		0.13 ₄	0.22 ₁	0.27 ₈	0.28 ₈	0.33 ₆	0.36 ₅	0.41 ₃	0.40 ₃	0.44 ₂	0.45 ₁	0.45 ₁	C

Experimental values were obtained from methylic (A), quaternary (B), and oxymethylenic (C) regions of the ¹³C-NMR spectra and methylic (D) and oxymethylenic (E) regions of the ¹H-NMR spectra, both in CDCl₃ solution at room temperature (23°C). **EA** and **EE**: mono- and diesterified P, respectively; **ae**: monoesterified N.

^a See footnote ^a to Table II.

^b Due to the smallness of the signal, it is quite difficult to be quantified.

Table VI Moles of Functional Groups —OH and —COOH as a Function of the Reaction Time t for the Polyesterification Between *o*-Phthalic Anhydride (P, 0.68 mol) and Neopentyl Glycol (N, 0.96 mol) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in Bulk at 200°C

t (min)	aa		ae/EA + ae/EE			
	(%) ^a	$[-\text{OH}]$ (mol)	(%) ^a	$[-\text{OH}]$ (mol)	$[-\text{OH}]_{\text{total}}$ (mol)	$[-\text{COOH}]_{\text{total}}$ (mol)
0 ^b	37	0.71 ₆	51	0.48 ₁	1.20 ₀	0.64 ₀
10	33	0.63 ₄	51	0.49 ₀	1.12 ₄	0.56 ₄
20	29	0.55 ₇	51	0.49 ₀	1.04 ₇	0.48 ₇
30	25	0.48 ₀	52	0.49 ₉	0.97 ₉	0.41 ₉
40	22	0.42 ₂	52	0.49 ₉	0.92 ₁	0.36 ₁
50	19	0.36 ₅	52	0.49 ₉	0.86 ₄	0.30 ₄
60	17	0.32 ₆	52	0.49 ₉	0.82 ₅	0.26 ₅
120	13	0.25 ₀	49	0.47 ₀	0.72 ₀	0.16 ₀
180	11	0.21 ₁	47	0.45 ₁	0.66 ₂	0.10 ₂
240	8	0.15 ₄	46	0.44 ₂	0.59 ₆	0.03 ₆
360	7	0.13 ₄	46	0.44 ₂	0.57 ₆	0.01 ₆
540	6	0.11 ₅	46	0.44 ₂	0.55 ₇	0

EA and **EE**: mono- and diesterified P, respectively. **aa** and **ae**: free and monoesterified N, respectively.

^a Molar percentages of structures obtained by arithmetic averaging of the respective percentages from the methylic, quaternary, and oxymethylenic zones of the ¹³C-NMR spectra in CDCl₃ at room temperature (23°C).

^b See footnote ^a to Table II.

namely, from chain-end groups —CH₂OH, independently of the residual chain length where they are linked. The values tabulated in the fourth column of Table VI represent average values from these three determinations carried out simultaneously for **ae/EA** and **ae/EE** structures.

Experimental results on the polyesterification are gathered in Table VII. In the third column of this table are included the conversions of the polyesterification, with the only purpose being to make clear that for high conversions, perhaps for the higher ones, these samples are subjected to a much higher experimental relative error than are those obtained at lower conversions. In our case, the experimental percentages can be affected by a high relative error, if we keep in mind that they have been estimated from several and varied determinations, namely, by means of averages, additions, further differences, etc.

Therefore, to improve the accuracy in the quantitative determination of the —COOH groups by ¹³C-NMR, we also carried out an indirect measurement of the —COOH groups by using ¹H-NMR spectroscopy as a primary technique, since we need a higher accuracy in the quantification, namely, lower than 2%, to carry out a very precise kinetic analysis of the process. In this case, the quantification of the free-acid groups were done in two different ways: (i) using the percentages

of the —CH₂OCOR and —CH₂OH groups, and (ii) using the methyl esters obtained by derivatization of the acid group by reaction with diazomethane as has been indicated before. The values from ¹H-NMR indicated in the fifth column of Table VII correspond to the arithmetic mean of the free-acid groups obtained from these two zones.

We also estimated the moles of free acid of each one of the samples by volumetry. This technique furnished data independently of the type of structures which have been formed. In Table VII are also gathered the acid group concentrations determined by this technique, whose accuracies are much higher than 0.5%.

In Figure 7 is shown a plot of the acid group concentration $[-\text{COOH}]$ determined using ¹³C-NMR, ¹H-NMR, and volumetry as a function of the reaction time. From its inspection, it is easy to deduce that for the case of the data determined by ¹³C-NMR the differences with the volumetric ones are even larger. This fact is easily explainable if taken into account are the limits of sensibility and, especially, the relative errors of the ¹³C-NMR for samples obtained at high degrees of conversion with a low content of acid groups.

Therefore, because of the limits of detection of the ¹³C-NMR and ¹H-NMR techniques as well as because of the procedure followed in the quantification of structures and the determination of

Table VII Moles of Free Acid Groups [—COOH], esterified groups [—COO—], and Yields in the Polyesterification Between *o*-Phthalic Anhydride (**P**, 0.68 mol, 3.38₈ mol/kg), and Neopentyl Glycol (**N**, 0.96 mol, 4.78₃ mol/kg) ([—COOH]/[—OH]) = 0.7 in Bulk at 200°C

<i>t</i> (min)	¹³ C-NMR ^a			¹ H-NMR ^b			Volumetry ^c				
	[—COOH] (mol)	[—COO—] (mol)	Yield (%)	[—COOH] (mol)	[—COO—] (mol)	Yield (%)	[—COOH]		[—COO—]		Yield (%)
							(mol)	(mol/kg)	(mol)	(mol/kg)	
0 ^d	0.64 ₀	0.04 ₀	6	0.64 ₀	0.04 ₀	6	—	—	—	—	—
10	0.56 ₄	0.11 ₆	17	0.56 ₁	0.11 ₉	18	0.58 ₁	2.89 ₅	0.09 ₉	0.49 ₃	15
20	0.48 ₇	0.19 ₃	28	0.48 ₇	0.19 ₃	28	0.50 ₆	2.52 ₁	0.17 ₄	0.86 ₇	26
30	0.41 ₉	0.26 ₁	38	0.40 ₈	0.27 ₂	40	0.44 ₆	2.22 ₂	0.23 ₄	1.16 ₆	34
40	0.36 ₁	0.31 ₉	47	0.36 ₄	0.31 ₆	47	0.39 ₆	1.97 ₃	0.28 ₄	1.41 ₅	42
50	0.30 ₄	0.37 ₆	55	0.32 ₈	0.35 ₂	52	0.35 ₁	1.74 ₃	0.32 ₉	1.63 ₉	48
60	0.26 ₅	0.41 ₅	61	0.26 ₇	0.41 ₃	61	0.30 ₂	1.50 ₅	0.37 ₈	1.88 ₃	56
120	0.16 ₀	0.52 ₀	77	0.15 ₈	0.52 ₂	77	0.18 ₄	0.91 ₇	0.49 ₆	2.47 ₁	73
180	0.10 ₂	0.57 ₈	85	0.09 ₇	0.58 ₃	86	0.13 ₄	0.66 ₈	0.54 ₆	2.72 ₀	80
240	0.03 ₆	0.64 ₄	95	0.08 ₃	0.59 ₈	88	0.10 ₀	0.49 ₈	0.58 ₀	2.89 ₀	85
360	0.01 ₆	0.66 ₄	98	0.04 ₈	0.63 ₂	93	0.06 ₀	0.29 ₉	0.62 ₀	3.08 ₉	91
540	0	0.68 ₀	100	0.01 ₄	0.66 ₆	98	0.03 ₀	0.14 ₃	0.65 ₀	3.23 ₉	96

The data were obtained from ¹³C-NMR and ¹H-NMR spectroscopies recorded in CDCl₃ at room temperature (23°C) and by volumetry.

^a These values were calculated using a least-mean-squared procedure from the average molar percentages of all carbons from free and monoesterified neopentyl glycol species (see Table VI).

^b These values were calculated using a least-mean-squared procedure of the free acid moles obtained from the oxymethylene region, on the one hand, and from the methoxylic region from the same samples after treatment with diazomethane, on the other (see fourth and fifth columns of Table III).

^c Values obtained by volumetry made with 0.1*N* ethanolic potassium hydroxide solution in a ethanol–toluene solution of the samples.

^d See footnote ^a to Table II.

—COOH groups, both experimental techniques are not entirely recommendable to have reliable quantitative experimental data at high conversions. However, the volumetry furnishes a higher degree of self-confidence than do the above aforementioned techniques for high as well as for low concentrations of acid groups. In any case, the number of acid groups estimated by volumetry is superior to that estimated by either of the two other NMR spectroscopic techniques as can be appreciated graphically in Figure 7.

In spite of all of this, if we compare the moles of **ae/EA** which were formed at each time of the reaction, which are shown in Table V, with the concentration of free-acid groups, which is shown in the second column of Table VII, we can observe a very small but significant difference between both series of values. Such a difference must be attributed to the existence of structures with free-acid groups, as can be, for instance, the dimer **AE/ee/EA** and the end chain of the **EE/ee/EA** type. In general, we can employ the nomenclature **P/ee/EA** to refer to functional acid groups at the chain ends, where **P** represents mono-*o*-phthalate **AE** or di-*o*-phthalate **EE** residues. In the Table

VIII are shown the concentration expressed in mol/kg of **ae/EA** and functional groups **P/ee/EA** in each one of the samples.

On the other hand, the neopentyl glycol diesters **ee**, estimated by ¹³C- and ¹H-NMR, may belong to structures of the **P/ee/EA** or **EE/ee/EE** types, i.e.:

$$\begin{aligned}
 [\mathbf{ee}] &= [\mathbf{AE/ee/EA}] + [\mathbf{EE/ee/EA}] \\
 &\quad + [\mathbf{EE/ee/EE}] \\
 &= [\mathbf{P/ee/EA}] + [\mathbf{EE/ee/EE}] \quad (14)
 \end{aligned}$$

Therefore, the neopentyl glycol diesters which are situated in the middle of the polymeric chains **EE/ee/EE** can be very easily estimated mathematically from the **ee** concentrations, which are shown in the third column of Table VIII, and the functional groups **P/ee/EA**. The estimated values for these **EE/ee/EE** structures are also shown in Table VIII.

The dependence of each one of these species, X_i , as a function of time, t , was obtained using a least-mean-squared method (Peakfit package). The dependence of the molecular species whose

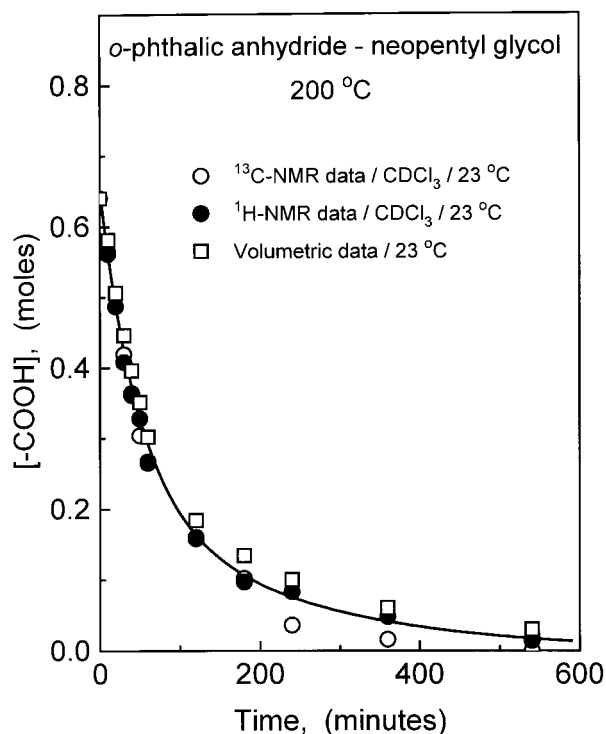


Figure 7 Moles of acid groups [—COOH] as a function of the reaction time t in the polyesterification between *o*-phthalic anhydride (P , 0.68 mol) and neopentyl glycol (N , 0.96 mol) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in the bulk at 200°C obtained by volumetry and by ^{13}C -NMR and ^1H -NMR spectroscopies recorded in CDCl_3 at room temperature.

concentrations decrease as a function of the reaction time was fitted with correlation coefficients higher than 0.9 to exponential functions of the following type:

$$[X]_i = A_{0i} \cdot \exp(-t/A_{1i}) \quad (15)$$

Molecular species whose concentration is growing as a function of the polyesterification time, such as the monoester **ae/EE**, were fitted with correlation coefficients higher than 0.98 to double exponential functions of the following type:

$$[X]_i = A_{0i} \cdot \exp(-t/A_{1i}) + A_{2i} \cdot \exp(-t/A_{3i}) \quad (16)$$

The dependence of the diesters which are located in the middle of the polymer chains, **EE/ee/EE**, was fitted to an exponential function similar to that proposed by Bacaloglu et al.³²:

$$[X]_i = \exp\left(A_{0i} + A_{1i} \cdot t + A_{2i} \cdot t^2 + A_{3i} \cdot \ln t + A_{4i} \cdot \frac{1}{t}\right) \quad (17)$$

where A_{0i} , A_{1i} , A_{2i} , A_{3i} , and A_{4i} are coefficients which depend on the molecular species being considered.

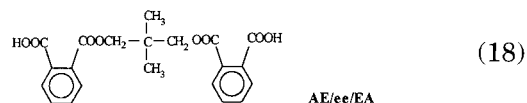
The dependence of all the molecular species as a function of the reaction time is shown in Figures 8–10. Solid and dashed lines represent curves for the best fitting. The concentrations at each reaction time given by these fitted curves for each of the species are shown in Table IX; they represent smoothed values.

Structures at Zero Time of Reaction

The mol/kg of each one of the molecular structures appearing just after the mixing of the reactives can be estimated from the values given in Table IX using a mass balance. To do this, it is very important to take into account the fact that we have not been able to detect any trace of *o*-phthalic anhydride at the very beginning of the polyesterification.

Neopentyl Glycol Balance

If we assume that neopentyl glycol (4.78₃ mol/kg) produces the ring opening of all the *o*-phthalic anhydride to give compound **III**, according to the reaction represented by eq. (12), there are 1.39₅ mol/kg of neopentyl glycol in the medium of the reaction to continue the polyesterification. However, as can be observed in Table IX, the best fitting for this species **aa** predicts a higher concentration at the beginning of the process. Therefore, we can assume that a small percentage of glycol may simultaneously open two rings of two molecules of *o*-phthalic anhydride to give the dimer **AE/ee/EA**:



This possibility is supported by the fact that the best fitting of the dependence of the functional groups **P/ee/EA** as a function of time predicts 1.17₉ mol/kg for the aforementioned chain-end functional groups. If we assume that the **EE/ee/**

Table VIII Molar Concentrations of Glycolic Units Which Are Linked to Chain-end *o*-Phthalate Groups, P/ee/EA, and in the Middle of These Same Chains, EE/ee/EE, Which were Formed During the Polyesterification Between *o*-Phthalic Anhydride (P, 3.38₈ mol/kg) and Neopentyl Glycol (N, 4.78₃ mol/kg) ([—COOH]/[—OH]) = 0.7 in Bulk at 200°C

<i>t</i> (min)	[ae/EA] ^a (mol/kg)	[ee] ^a (mol/kg)	[P/ee/EA], (mol/kg) ^b			[EE/ee/EE] (mol/kg) ^c		
			¹³ C-NMR	¹ H-NMR	Volumetry	¹³ C-NMR	¹ H-NMR	Volumetry
0 ^d	2.01 ₁	0.59 ₀	1.18 ₉	1.18 ₉	1.18 ₉	0	0	0
10	1.70 ₄	0.79 ₇	1.06 ₆	1.11 ₁	1.20 ₁	—	—	—
20	1.34 ₄	0.93 ₁	1.04 ₁	1.06 ₆	1.18 ₆	—	—	—
30	1.10 ₄	1.09 ₄	0.99 ₁	0.97 ₁	1.12 ₆	0.10 ₃	0.12 ₃	—
40	0.96 ₀	1.22 ₉	0.84 ₅	0.84 ₅	1.02 ₀	0.38 ₄	0.38 ₄	0.20 ₉
50	0.72 ₀	1.40 ₂	0.80 ₀	0.86 ₀	1.03 ₅	0.60 ₂	0.54 ₂	0.36 ₇
60	0.62 ₄	1.54 ₆	0.75 ₆	0.77 ₁	0.88 ₆	0.79 ₀	0.77 ₅	0.66 ₀
120	0.31 ₂	1.85 ₃	0.38 ₈	0.46 ₃	0.60 ₈	1.46 ₅	1.39 ₀	1.24 ₅
180	— ^e	2.07 ₄	—	—	—	—	—	—
240	0	2.18 ₄	0.27 ₅	0.38 ₀	0.50 ₀	1.90 ₉	1.80 ₄	1.68 ₄
360	0	2.25 ₆	0.08 ₀	0.22 ₀	0.30 ₀	2.17 ₆	2.03 ₆	1.95 ₆
540	0	2.34 ₀	0	0.08 ₀	0.15 ₀	2.34 ₀	2.26 ₀	2.19 ₀

Values deduced from the free acid concentration determined by ¹H- and ¹³C-NMR spectroscopies and by volumetry. **EA** and **EE**: mono- and diesterified P, respectively. **ae/EA**: N monoesterified with P; **ee**: N diesterified with P (**P/ee/EA** and **EE/ee/EE**).

^a Arithmetic averaging of all the experimental determinations.

^b [P/ee/EA] = [—COOH]_{free} - [ae/EA].

^c [EE/ee/EE] = [ee] - [P/ee/EA].

^d At zero time of reaction, the molar values were estimated as explained in the text.

^e Its estimation is not possible due to the smallness of the signal.

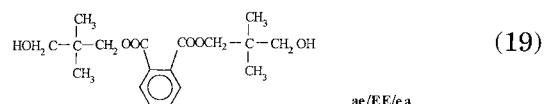
EA structures are not instantaneously formed, and therefore their initial concentration may be considered equal to zero, we will have, theoretically, 0.59₀ mol/kg of **AE/ee/EA** structures. Furthermore, according to eq. (12), a extrapolated value of 2.01₁ mol/kg at zero time of the reaction for **ae/EA** structure have been found. It is shown in Table IX.

Therefore, from the initial 4.78₃ mol/kg of neopentyl glycol, 0.59₀ mol/kg were consumed in the formation of the **AE/ee/EA** structures and 2.01₁ mol/kg in the formation of **ae/EA** structures. If all this is right, 2.18₂ mol/kg of unreacted neopentyl glycol would have to remain in the reaction medium. This quantity is still high with respect to that predicted using the best fitting for this glycol.

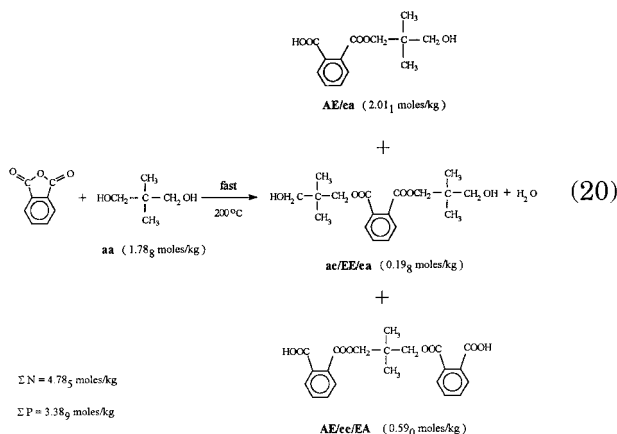
o-Phthalic Anhydride Balance

With respect to the *o*-phthalic anhydride, 1.17₉ mol/kg of the initial 3.38₈ mol/kg were consumed in the formation of the dimer **AE/ee/EA**. Then, in the reaction medium, it will remain hypothetically 2.20₉ mol/kg, from which only 2.01₁ mol/kg are consumed to yield the monoester **ae/EA**. All these facts seem to be indicative that probably there will exist also an instantaneous process in which every molecule

of *o*-phthalic anhydride will consume two molecules of neopentyl glycol, yielding approximately 0.19₈ mol/kg of **ae/EE/ea** structures:



According to the above, we may write the following scheme of reactions which also includes the mass balance:



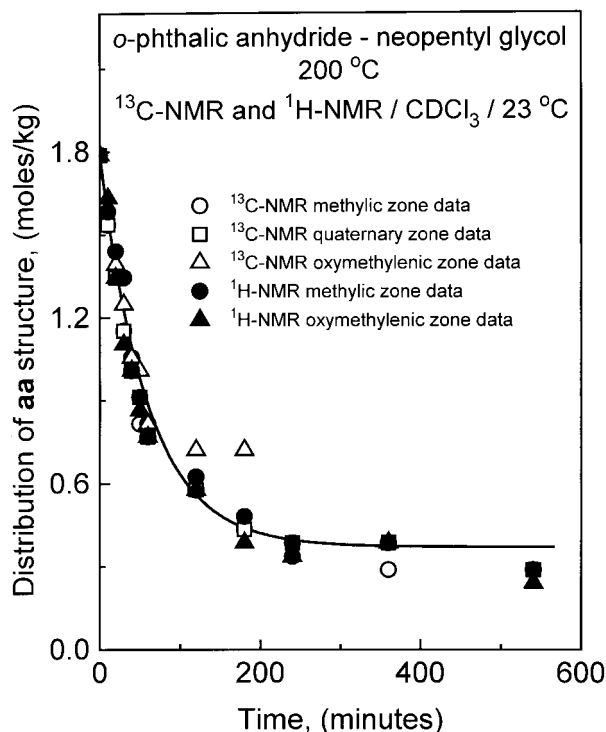


Figure 8 Dependence of the free neopentyl glycol (**aa**) concentration as a function of the reaction time t in the polyesterification between *o*-phthalic anhydride (P , 3.38₃ mol/kg) and neopentyl glycol (N , 4.78₃ mol/kg) ($[-\text{COOH}]/[-\text{OH}] = 0.7$) in the bulk at 200°C. The experimental data were obtained from ^{13}C -NMR (open symbols) and ^1H -NMR (full symbols) spectroscopies recorded in CDCl_3 at room temperature (23°C). The solid line represents the curve for the best fitting with a correlation coefficient of $R^2 = 0.96_2$.

Similarly, we may also estimate the concentration of every structure for the first sample isolated after 10 min of reaction. This is possible since there do not exist any neopentyl glycol diesters in the middle of the polymeric chains in growth, i.e., $[\text{EE}/\text{ee}/\text{EE}] = 0$. Therefore, according to the values which have been predicted by the best fitting, which are shown in the second row of Table IX, the mass balance can be finally expressed as follows:

- (A) For neopentyl glycol, $\Sigma N = 1.56_9$ mol/kg as the structure of the **aa** type + 1.66₀ mol/kg as **ae/EA** + 0.79₃ mol/kg as structures **ae/EE** + 1.11₄ mol/kg as functional groups **P/ee/EA** = 5.13₆ mol/kg.
- (B) For *o*-phthalic anhydride, $\Sigma P = 1.66_0$ mol/kg as **ae/EA** + 0.79₃ mol/kg as **ae/EE** + 1.11₄ mol/kg as end-chain acid groups **P/ee/EA** = 3.56₇ mol/kg.

These overall quantities indicated in the above sections (A) and (B) are slightly higher than the initial concentrations of 4.78₃ mol/kg of neopentyl glycol and 3.38₃ mol/kg of *o*-phthalic anhydride which have been put together at the beginning of the polyesterification reaction. Such a difference may be attributed to the existence in the reaction medium of dimeric structures of the **AE/ee/EA** and **ae/EE/ea** types.

If this is true, for instance, the mol/kg of neopentyl glycol which are forming part of the **AE/ee/EA** structures may be estimated by subtracting the initial concentration of neopentyl glycol in mol/kg to the moles given by (A) (5.13₆ mol/kg - 4.78₃ mol/kg = 0.35₃ mol/kg). Then, the chain-end structures of the **EE/ee/EA** type may

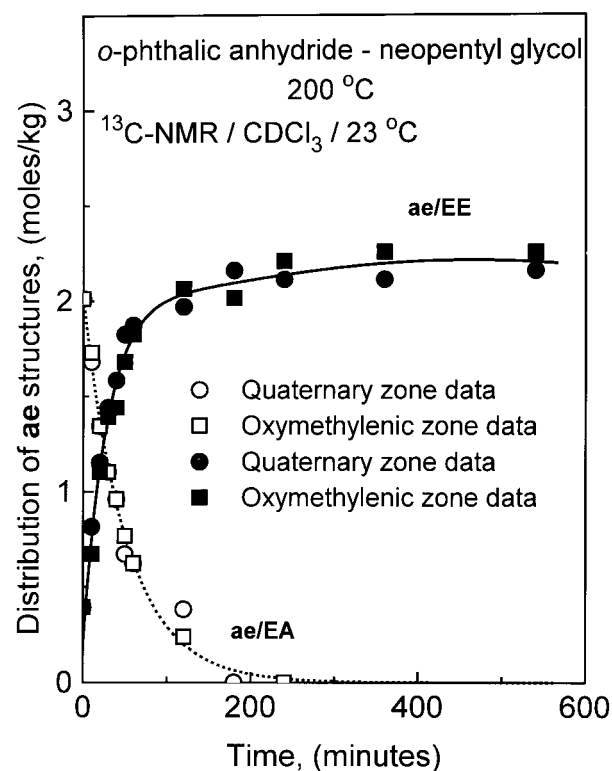


Figure 9 Dependence of the neopentyl glycol monoesters (**ae/EA** and **ae/EE**) concentrations as a function of the reaction time t in the polyesterification between *o*-phthalic anhydride (P , 3.38₃ mol/kg) and neopentyl glycol (N , 4.78₃ mol/kg) ($[-\text{COOH}]/[-\text{OH}] = 0.7$) in the bulk at 200°C. (\circ , \square) Open symbols from the monoester **ae/EA**. (\bullet , \blacksquare) Full symbols from the monoesterified structure **ae/EE**. The data were obtained from the (circles) quaternary and (squares) oxymethylenic regions of the ^{13}C -NMR spectra recorded in CDCl_3 at room temperature (23°C). The lines are the best-fitting curves: the solid line for a correlation coefficient of $R^2 = 0.98_5$ and the dashed line of $R^2 = 0.99_2$.

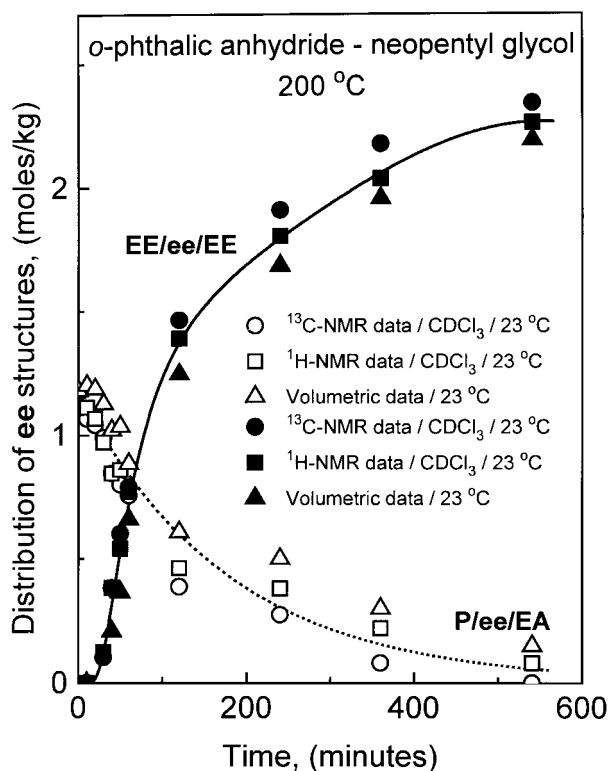


Figure 10 Dependence of the neopentyl glycol diesters (**EE/ee/EE** and **P/ee/EA**) concentrations as a function of the reaction time t in the polyesterification between *o*-phthalic anhydride (P , 3.38_8 mol/kg) and neopentyl glycol (N , 4.78_3 mol/kg) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in the bulk at 200°C). Open symbols represent data for diesters of the **P/ee/EA** type. Full symbols represent data for diesterified structures which are in the middle of the polymeric chains, **EE/ee/EE**. The data were obtained from (circles) ^{13}C -NMR and (squares) ^1H -NMR spectroscopies recorded in CDCl_3 at room temperature (23°C) and (up triangles) volumetry. The solid line represents the best-fitting curve with a correlation coefficient of $R^2 = 0.98_9$, and the dashed curve, a correlation coefficient of $R^2 = 0.93_6$.

be estimated from the number of the chain-end acid groups as

$$\begin{aligned} &1.11_4 \text{ mol/kg (P/ee/EA)} \\ &- 2 \times 0.35_3 \text{ mol/kg (AE/ee/EA)} \\ &= 0.40_8 \text{ mol/kg (EE/ee/EA)} \end{aligned}$$

On the other hand and similarly, we can calculate the amount of *o*-phthalic anhydride forming part of the **ae/EE/ea**-type structures from the *o*-phthalic anhydride moles given by (B) and the initial concentration of *o*-phthalic anhydride

(3.56_7 mol/kg $- 3.38_8$ mol/kg = 0.17_9 mol/kg). Also, similarly, the moles of end structures of the **ae/EE/ea** type can also be calculated using

$$\begin{aligned} &0.79_2 \text{ mol/kg (ae/EE)} \\ &- 2 \times 0.17_9 \text{ mol/kg (ae/EE/ea)} \\ &= 0.43_4 \text{ mol/kg (ae/EE/ee)} \end{aligned}$$

It is worth mentioning that the molar percentages estimated as seen above are similar to those obtained from the ^{13}C -NMR spectra in CDCl_3 and $\text{DMSO-}d_6$, within the experimental errors of the own technique. This fact validates the concentrations which have been previously estimated for each one of the structures mentioned above. After 20 min of reaction, this type of estimation is complicated because of the existence in the reaction medium of structures of the **EE/ee/EE** type.

KINETIC ANALYSIS OF EXPERIMENTAL DATA

During the kinetic analysis, we are going to use the following symbols:

- x ester group concentration $[-\text{COO}-]$ at time t
- a initial concentration of acid groups $[-\text{COOH}]$
- b initial concentration of alcoholic groups $[-\text{OH}]$
- m order of reaction in acid groups
- n order of reaction in alcoholic groups
- d overall order of reaction ($d = m + n$)
- $k_{m,n}$ overall rate constant of polyesterification
- $I_{m,n}$ correlation coefficient.

For the kinetic analysis, we are going to follow a procedure developed by Fradet and Maréchal.¹⁻⁴ The general equation rate can be written as

$$dx/dt = k_{m,n} \cdot (a - x)^m \cdot (b - x)^n \quad (21)$$

and its numerical integration yields

$$G_{m,n}(x) = \int_0^x f_{m,n}(x) \cdot dx = \int_0^t k \cdot dt = k \cdot t \quad (22)$$

where

$$f_{m,n}(x) = 1/[(a - x)^m \cdot (b - x)^n] \quad (23)$$

Table IX Smoothed Molar Concentration (mol/kg) Using a Least-mean-squared Procedure for all the Species Which Were Detected in the Polyesterification Between *o*-Phthalic Anhydride (P, 3.38 mol/kg) and Neopentyl Glycol (N, 4.78₃ mol/kg) ([—COOH]/[—OH]) = 0.7 in Bulk at 200°C

<i>t</i> (min)	[aa] (mol/kg)	[ae/EA] (mol/kg)	[ae/EE] (mol/kg)	[P/ee/EA] (mol/kg)	[EE/ee/EE] (mol/kg)
0	1.78 ₈	2.01 ₁	0.39 ₆ ^a	1.17 ₉	0
10	1.56 ₉	1.66 ₀	0.79 ₃	1.11 ₄	0
20	1.38 ₃	1.37 ₁	1.12 ₉	1.05 ₃	0.01 ₅
30	1.22 ₆	1.13 ₂	1.38 ₂	0.99 ₆	0.12 ₂
40	1.09 ₄	0.93 ₅	1.57 ₂	0.94 ₁	0.31 ₄
50	0.98 ₂	0.77 ₂	1.71 ₃	0.89 ₀	0.52 ₇
60	0.88 ₇	0.63 ₈	1.81 ₇	0.84 ₁	0.72 ₃
120	0.55 ₈	0.20 ₂	2.05 ₂	0.60 ₀	1.37 ₃
180	0.43 ₈	0.06 ₄	2.09 ₄	0.42 ₈	1.62 ₇
240	0.39 ₅	0.02 ₀	2.12 ₈	0.30 ₅	1.79 ₄
360	0.37 ₃	0.00 ₂	2.20 ₀	0.15 ₅	2.05 ₉
540	0.37 ₀	0	2.20 ₅	0.05 ₆	2.26 ₃

EA and **EE**: mono- and diesterified P, respectively. **aa**: free N; **ae**: N monoesterified with P (**ae/EA** and **ae/EE**); and **ee**: diesterified P.

^a Determined as was explained in the text.

To determine the kinetic equation which better reproduces our experimental results [*t*, *x*(*t*)], the problem is reduced to find the integral $G_{m,n}(x)$ which is the best adjusted to a straight line passing through the origin and slope equal to *k*.

The calculation of the integral of a determined function *f*(*x*) may be expressed by

$$\int_a^b f(x) \cdot dx = F(b) - F(a) \quad (24)$$

where $F'(x) = f(x)$. When *F*(*x*) is known, we shall have resolved the problem by means of an analytical integration. But, generally, *F*(*x*) is not known and then the problem is solved by numerical integration approximating

$$\int_a^b f(x) \cdot dx \approx \int_a^b \varphi(x) \cdot dx \quad (25)$$

where $\varphi(x)$ is a function of a known integral, generally a polynomial. On the one hand, Fradet and Maréchal² used the method of trapezes³³ and, on the other hand, Laporte et al.³⁴ used the method of Simpson for the determination of the values of the rate constant. In the present work, we use the method of Gauss³⁵ because of its properties of great accuracy and rapid convergence for a small number of values of the function to be integrated within the integration interval.

This method is based in the formula of the quadrature of Gauss:

$$\int_{-1}^1 f(t) \cdot dt = \sum_{i=1}^n A_i \cdot f(t_i) \quad (26)$$

which ensures to us that, if we choose adequately the abscissa *t_i* and the coefficients *A_i*, formula (26) is exact for all the polynomials of degree equal or smaller than 2*n* - 1.

The abscissa *t_i* turns out to be the roots of the Legendre's polynomials *P_n*(*t*), namely, $P_n(t_i) = 0$. The coefficients *A_i* are obtained by solving the linear systems:

$$\begin{aligned} \sum_{i=1}^n A_i \cdot t_i^{2n-2} &= 2/(2n - 1) \\ \sum_{i=1}^n A_i \cdot t_i^{2n-1} &= 0 \end{aligned} \quad (27)$$

To apply the Gauss' formula (26) to a general case, it is sufficient to carry out a change of variable,

$$\int_a^b f(x) \cdot dx = [(a - b)/2] \cdot \sum_{i=1}^n A_i \cdot f(x_i) \quad (28)$$

where

$$x_i = [(a + b)/2] + [(a - b)/2] \cdot t_i \quad (29)$$

where t_i are the roots of the Legendre's polynomials $P_n(t)$.

The application of the method of Gauss to our function (22) has proved to be completely satisfactory for all values of (m, n) . We obtained a convergence of the integral $G_{m,n}(x)$ with a number of experimental data equal or smaller than nine and an error less than 1×10^{-8} .

In this way, we calculated the numerical integrals for the experimental points. To do this, we varied m and n between 0 and 3 by $\frac{1}{2}$ steps, i.e., we consider the cases in which m and n are integers or semi-integers according to the following conditions:

$$0 \leq m \leq 3 \quad (30)$$

$$0 \leq n \leq 3 \quad (31)$$

$$0 \leq (m + n) = d \leq 3 \quad (32)$$

To determine the best fitting, we gauged the correlation coefficient $I_{m,n}$, by checking in each case the goodness of the fitting by means of the correlation coefficient of the data $[t, G_{m,n}(x)]$ and the standard deviation $S_{m,n}$. When the reaction is carried out under nonstoichiometric conditions, as in the present case, i.e., in excess of diol $b > a$, it is possible to determine m and n , if we take the precaution that the conversion is equal or higher than 70% and the error of the titration is as low as possible, i.e., below 1%.

As we already mentioned above, in the conventional analysis of experimental data of a polyesterification, it is normal to use experimental data obtained at low as well as at medium and high conversions, contrarily to what is done in the classical kinetic chemistry of small molecules where analyzed are only experimental results for very low degrees of conversion, namely, where the initial conditions of the medium does not undergo any type of apparent change. In the kinetics of polyesterification, possibly because its technological interest and owing to the pioneering works by Flory,⁵⁻⁹ more attention has been paid to medium and high conversions. For this, and for some other reasons given by Fradet and Maréchal,^{1,2} it is necessary to make use of very precise data at high conversions. Thus, we are going to employ the data of $[-\text{COOH}]$ obtained directly by volumetry.

The results of the present analysis are collected in Table X. For illustrative purposes, we plotted in Figure 11 our experimental results by kinetic

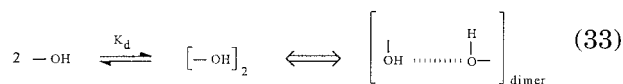
equations with the higher correlation coefficients of 0.9990 ($m, n = 1, 2$) and 0.9989 ($m, n = \frac{3}{2}, 0$). As can be easily appreciated, the experimental data fit very well to both equations over the whole range of conversions studied.

Clearly, therefore, the present series of experimental data can be represented and described by an overall rate equation of order three ($I_{m,n} = 0.9990$), or three-halves ($I_{m,n} = 0.9989$), or two ($I_{m,n} = 0.9979$), etc. It is very sad to say that to decide the order of the reaction and, consequently, the mechanism we must use a correlation coefficient, which is practically identical except in the three-four figure. This is a tremendous conclusion of our analysis. We are going to give only an example for the mechanism which shows the higher correlation coefficient.

MECHANISM

At the present time, esterification reactions as well as their reverse, i.e., their respective hydrolysis reactions, may be classified according to the different prototypes which were proposed years ago by Ingold.³⁶⁻³⁸ According to the kinetic analysis that we have done so far, the more plausible orders of reaction, with a correlation coefficient of $I_{1,2} = 0.9990$, correspond to an overall rate equation of order three, order one with respect to acid group concentration, and order two with respect to alcoholic group concentration (see Table X).

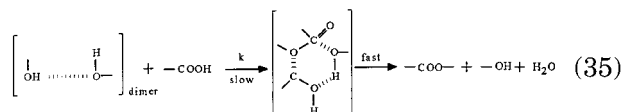
We may consider that alcohol dimers



in which

$$K_d = [(-\text{OH})_2] / [-\text{OH}]_{\text{free}}^2 \quad (34)$$

may participate in an esterification mechanism in which the attack of the acid to the dimer is the slow step of the reaction:



The reaction rate equation is then given by

$$d[-\text{COO-}] / dt = k \cdot [-\text{COOH}] \cdot \left[\begin{array}{c} | \\ \text{OH} \cdots \cdots \text{H} \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \right]_{\text{dimer}} \quad (36)$$

Table X Polyesterification Under Nonstoichiometric Conditions and Without An External Catalyst Between *o*-Phthalic Anhydride and Neopentyl Glycol in Bulk at 200°C; Initial Concentrations^a: Acid Groups [—COOH] = 3.19₁ mol/kg and Alcoholic Groups [—OH] = 5.98₃ mol/kg

$m,$ [—COOH] ^{<i>m</i>}	$I_{m,n}$						
	n [—OH] ^{<i>n</i>}						
	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$	3
0	0.8428	0.8632	0.8823	0.9001	0.9163	0.9309	0.9439
$\frac{1}{2}$	0.9173	0.9340	0.9486	0.9612	0.9717	0.9803	
1	0.9777	0.9862	0.9924	0.9966	0.9990		
$\frac{3}{2}$	0.9989	0.9979	0.9955	0.9921			
2	0.9757	0.9694	0.9629				
$\frac{5}{2}$	0.9301	0.9235					
3	0.8846						

Dependence of the correlation coefficients $I_{m,n}$ on the different pairs of the tested values of (m, n) in acid [—COOH] and alcohol [—OH]. The values for $I_{m,n} \geq 0.99$ are indicated in the shadowed background.

^aMolar values determined from the initial concentrations which have been estimated by extrapolation to zero time of reaction. These values are also shown in eq. (20).

and substituting the dimer concentration using eq. (34), we get

$$d[\text{—COO—}]/dt = k \cdot K_d \cdot [\text{—COOH}] \cdot [\text{—OH}]_{\text{free}}^2 \quad (37)$$

If we assume that the alcohol dimer concentration is low with regard to the total reactant concentration measured, i.e.,

$$[\text{—OH}]_{\text{free}} \approx [\text{—OH}]_{\text{total}} \quad (38)$$

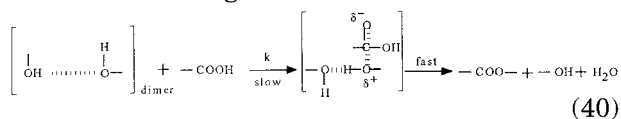
we can finally write that

$$d[\text{—COO—}]/dt = k \cdot K_d \cdot [\text{—COOH}]_{\text{total}} \cdot [\text{—OH}]_{\text{total}}^2 \quad (39)$$

Several studies on the ethanolysis of acyl chlorides in aprotic solvents have given place to kinetics of order three, first order with respect to the acyl halide and second order in ethanol.^{39–41} The apparent participation of two alcohol molecules has been explained^{41,42} in terms of a “push–pull”

mechanism of the type postulated by Swain⁴³ for reactions of substitution. Later on, Kevill and Foss⁴⁴ proposed an alternative mechanism in which, for the overall reaction, the tetrahedral intermediate which is formed in the first place is deprotonated or by a solvent molecule, giving a two-order kinetics, or by a second molecule of ethanol to give a third-order kinetics. Both giving the tetrahedral intermediate which supplies the reaction products. Ross⁴⁵ studied the reaction between benzoyl chloride and mononitrobenzoyl chloride with ethanol in acetone. He found that the reactions are a mixture of second and third orders. Ross⁴⁵ rationalized his results assuming that the transition-state determinant of the rate contains the substrate, the nucleophile, ethanol, and an acceptor for the hydrogen bond. One adequate acceptor can be, for instance, another ethanol molecule, an acetone molecule, or the chloride ion.

In our case, the activated complex would also have the following structure:



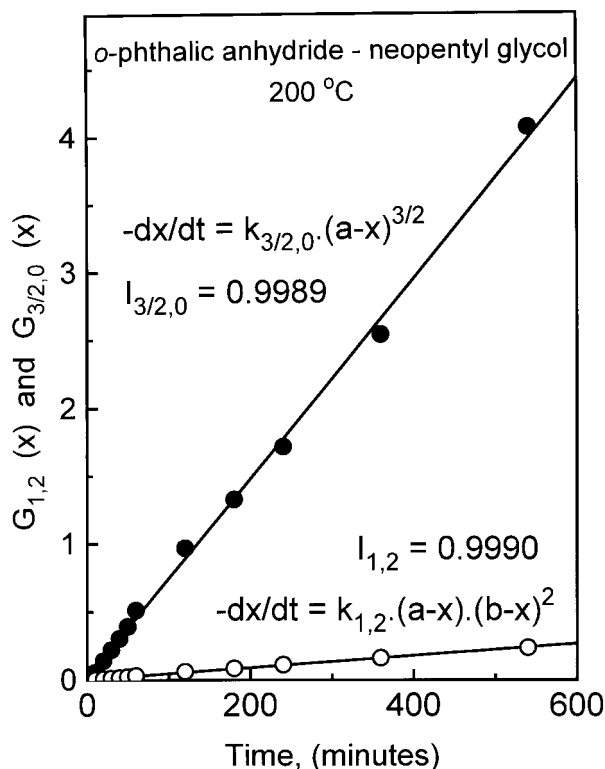


Figure 11 (○) Open circles, plot of the reaction function of order three, order one with respect to acid concentration, and order two with respect to alcohol concentration against time t . (●) Full circles, plot of the reaction function of three-halves order with respect to the acid concentration against time t for the polyesterification without external catalyst in nonequimolecular initial concentrations of *o*-phthalic anhydride (P , 0.68 mol) and neopentyl glycol (N , 0.96 mol) ($[-\text{COOH}]/[-\text{OH}] = 0.7$ in the bulk at 200°C.

Equation (39) would be in agreement with the experimental results found in the present work as it has been made clear in the representations made in Figure 11 and results given in Table X as well as by some others that fulfill the conditions imposed by the fitting to our experimental results.

DISCUSSION

So far, we have done a kinetic analysis of our data and we have proposed a possible mechanism:

1. Thus, it is well known that to obtain true and realistic kinetic data it is necessary to have available experimental data for the kinetic analysis obtained under standard conditions, namely, (i) they have to be ob-

tained at conversions as low as needed to not change the initial concentrations of reactives and (ii) the new products which have been formed remain diluted in the reaction medium in such a form, i.e., its concentration must be as low as possible, that they do not disturb the conditions of the medium as solvent, especially those concerning polarity and the dielectric constant. These two conditions are normally taken into account in reactions carried out in solution in classical kinetic chemistry of small molecules. In the bulk, reactives and products would form their own medium of reaction and therefore it will be a medium which is continuously changing in its properties. We must emphasize that if the reactions were carried out in the bulk these circumstances of the conversion and composition of the medium would have to be much stricter, i.e., the requirements to obtain valid kinetic data would have to be much more rigorous. Probably, it would have to work at conversions lower than 1–2%.

2. However, a great number of polyesterifications have been studied at high conversions and in some cases in the bulk. Recently, the preparation of polyesters at high temperatures was initiated, as in the present case. One intends to know the kinetics and mechanism through the whole; however, we would not forget that we are dealing with a system in which the concentration of reactives is changing in a continuous form as well as the formation of the products and also the conditions of the medium of reaction. Consequently, the interpretation of the kinetic data and their respective mechanisms of reaction would have to be made with a criterion quite different than those made in physical organic chemistry. It would not be possible to make comparisons with very simple systems, namely, small molecule systems.
3. Therefore, a kinetic and mechanistic analysis in the polyesterification reaction over all the reaction process would be incorrect, and it may only represent that the kinetics or the mechanism are better adjusted with the only criterion of a correlation coefficient at all, from the mathematic point of view. We can be sure that the kinetics, and, hence, the mechanism, in over all the range of conversion of our experimental data, can

be governed by a particular kinetic and its mechanism from the point of view of the traditional kinetochemistry. From the practical point of view, polyesterification reactions have been traditionally carried out at high conversions, and probably for this reason, a larger part of the experimental conditions are not correct to carry out a correct analysis of these processes. This is the reason of the great inconsistency of the experimental results which we can find in the literature when the data of polyesterification between diacids and glycols are analyzed.

- Independently of all of which we have said in the above sections, there is another very important factor concerning the quality of the experimental results, namely, from the point of view of how they have been obtained analytically, i.e., how they have been estimated in every case. On the one hand, we must take into account the details with which the structures are analyzed, i.e., the sensitivity of the experimental technique to detect species and, on the other, the accuracy with which these structures can be quantified in each case.

CONCLUSIONS

- The structural analysis using ^{13}C - and ^1H -NMR spectroscopies of the samples isolated as a function of reaction time has made possible the determination of the quantitative composition of each one of the molecular species which are present in each moment in the reaction medium.
- In the present study and according to the assumption made and confirmed by Flory,^{7,8} we have assumed that the acid group —COOH joined to the ring in the *o*-phenylenic position as well as the —OH groups from the oxymethylenic groups joined to a carbon with two geminal methyls —CH₃ each possess the same reactivity independently of the rest of the structure where they are linked.
- The experimental results have been fitted to an overall rate equation for different orders which are variable not only for the acid concentration but also for the alcohol concentration.
- It seems very hard to decide, using a series

of correlation coefficients varying in the three–four figure, which of them represents the overall process, i.e., from low to medium and to high conversions. We recommend special care in analyzing kinetic data and proposing a mechanism for such systems. It is interesting to take into account the importance which may be played by the medium of the reaction, formed by the reactives and the products which are being formed from them during the reaction, in a process that can be the polyesterification reaction.

M. J. C. C. gratefully acknowledges the financial support through a predoctoral grant from the Dirección General de Investigación y Capacitación Agrarias to carry out her doctoral thesis at the Instituto Nacional de Investigaciones Agrarias del Ministerio de Agricultura y Alimentación (Madrid). She is also grateful to the facilities given to her by the Departamento de Química-Física de Polímeros, Instituto de Ciencia y Tecnología de Polímeros (Madrid) C.S.I.C. for the realization of the present work. This work was partially supported by the CICYT through Grant PB-92-0773-03-1.

REFERENCES

- A. Fradet and E. Maréchal, *Adv. Polym. Sci.*, **43**, 51 (1982).
- A. Fradet and E. Maréchal, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 2905 (1981).
- A. Fradet and E. Maréchal, *J. Macromol. Sci.-Chem. A*, **17**, 859 (1982).
- A. Fradet and E. Maréchal, *J. Macromol. Sci.-Chem. A*, **17**, 881 (1982).
- P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).
- P. J. Flory, *J. Am. Chem. Soc.*, **59**, 466 (1937).
- P. J. Flory, *J. Am. Chem. Soc.*, **61**, 3334 (1939).
- P. J. Flory, *J. Am. Chem. Soc.*, **62**, 2261 (1940).
- P. J. Flory, *Chem. Rev.*, **39**, 154 (1946).
- A.-C. Tang and K.-S. Yao, *J. Polym. Sci.*, **35**, 219 (1959).
- M. Davies, *Research (Lond.)*, **2**, 544 (1949).
- M. Davies, *Trans. Faraday Soc.*, **34**, 410 (1938).
- D. H. Solomon and J. J. Hopwood, *J. Appl. Polym. Sci.*, **10**, 1431 (1966).
- E. G. Bobalek, E. R. Moore, S. S. Levy, and C. C. Lee, *J. Appl. Polym. Sci.*, **8**, 625 (1964).
- D. H. Solomon, B. C. Loft, and J. D. Swift, *J. Appl. Polym. Sci.*, **11**, 1571 (1967).
- M. J. Callejo Cudero, M. M. C. López-González, and J. M. Barrales-Rienda, *J. Polym. Sci. Polym. Chem. Ed.*, **34**, 1059 (1996).
- G. A. Russell, P. M. Henrichs, J. M. Hewitt, H. R.

- Grashof, and M. A. Sandhu, *Macromolecules*, **14**, 1764 (1981).
18. I.U.P.A.C., *Pure Appl. Chem.*, **33**, 411 (1973).
19. A. W. Birley, D. Kyriacos, and J. V. Dawkins, *Polymer*, **19**, 1290 (1978).
20. A. W. Birley, J. V. Dawkins, and D. Kyriacos, *Polymer*, **19**, 1433 (1993).
21. A. Fradet, M. Brigodiot, and E. Maréchal, *Makromol. Chem.*, **180**, 1149 (1979).
22. D. Judas, A. Fradet, and E. Maréchal, *Makromol. Chem.*, **184**, 1129 (1983).
23. M. Andreis, Z. Meic, and Z. Veksli, *Polymer*, **24**, 611 (1983).
24. R. Pétiaud, H. Waton, and Q.-T. Pham, *Polymer*, **33**, 3155 (1992).
25. J. Rybicky, *J. Appl. Polym. Sci.*, **23**, 25 (1979).
26. M. Marshall, *J. Oil Col. Chem. Assoc.*, **66**, 285 (1983).
27. Atta-ur-Rahman, *Nuclear Magnetic Resonance. Basic Principles*, Springer-Verlag, New York, 1986.
28. A. J. van der Zeeuw, *Chem. Ind. (Lond.)*, **22**, 978 (1969).
29. M. P. Vladimirova, V. V. Kiselev, V. A. Malykh, and A. S. Chegolya, *Khim. Volokna*, **1**, 17 (1976).
30. M. Krumpolc and J. Málek, *Makromol. Chem.*, **168**, 119 (1973).
31. M. Krumpolc and J. Málek, *Makromol. Chem.*, **171**, 69 (1973).
32. R. Bacaloglu, M. Mătieș, C. Csunderlik, L. Cotarcă, A. Moraru, J. Gros, and N. Marcu, *Angew. Makromol. Chem.*, **164**, 1 (1988).
33. A. Fradet, personal communication.
34. P. Laporte, A. Fradet, and E. Maréchal, *J. Macromol. Sci.-Chem. A*, **24**, 1269 (1987).
35. B. P. Demidovich and I. A. Maron, *Cálculo Numérico Fundamental*, 2nd ed., Editorial Paraninfo, Madrid, 1985, Chap. 16.
36. J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).
37. C. K. Ingold, *Structure and Mechanisms in Organic Chemistry*, Beel, London, 1953, Chap. XIV.
38. J. March, *Advanced Organic Chemistry. Reactions, Mechanisms and Structure*, 3rd ed., Wiley, New York, 1985, Chap. 10.
39. A. A. Ashdown, *J. Am. Chem. Soc.*, **52**, 269 (1930).
40. R. F. Hudson and B. Saville, *J. Chem. Soc.*, 4121 (1955).
41. W. R. Gilkerson, *J. Phys. Chem.*, **60**, 1142 (1956).
42. E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, Reinhart and Wiston, New York, 1959, p. 334.
43. C. G. Swain, *J. Am. Chem. Soc.*, **70**, 1119 (1948).
44. D. N. Kevill and F. D. Foss, *J. Am. Chem. Soc.*, **91**, 5054 (1969).
45. S. D. Ross, *J. Am. Chem. Soc.*, **92**, 5998 (1970).