

# Identification and Determination of the Glyceride and Tris-(2-hydroxyethyl)isocyanurate Structures in the Average Macromolecule of a Polyester with Carbon-13-NMR Spectroscopy: Analysis of the Polyester Average Structure

MACIEJ SKARŻYŃSKI,<sup>1</sup> GRAŻYNA CYNKOWSKA,<sup>2</sup> LUIGI ABIS,<sup>3</sup> IWONA WAWER,<sup>4</sup> SILVIA SPERA<sup>3</sup>

<sup>1</sup> Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland

<sup>2</sup> University of Kentucky, Chandler Medical Center, Lexington, Kentucky

<sup>3</sup> The Guido Donegani Institute, EniChem, Novara, Italy

<sup>4</sup> Medical Academy, Department of Pharmacy, Warsaw, Poland

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**ABSTRACT:** The <sup>13</sup>C-NMR approach to quantitative analysis of a polyester resin synthesized from dimethylterephthalate, ethylene glycol, *tris*-(2-hydroxyethyl)isocyanurate (THEIC), and glycerol is presented. Various glyceride and isocyanurate structures formed during the esterification have been identified and analyzed, at first in simple model systems and then in the structure of the resin. The contents of particular structural units were determined as well as a hypothetical average macromolecule of the resin defined. The assignments of <sup>13</sup>C-NMR signals were made and correlated with the <sup>1</sup>H shifts using a 2D-HETCOR experiment. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 675–687, 1998

**Key words:** <sup>13</sup>C-NMR; <sup>1</sup>H-NMR; quantitative analysis; polyester resin; isocyanurate; glycerol; glyceride

## INTRODUCTION

Molecules at various degrees of substitution arise in the reaction of esterification carried out with trihydroxyl alcohols (triols), and so various triol moieties are present in the macromolecules of polyesters synthesized from triols and aromatic dibasic acids. The most common example is glycerol—its esterification yields five possible structures: 1-monoglyceride, 2-monoglyceride, 1,3-diglyceride, 1,2-diglyceride, and triglyceride (plus unreacted glycerol), as illustrated in Scheme 1.

Another example is *tris*-(2-hydroxyethyl)isocyanurate (THEIC); three different molecules (or moieties in a macromolecule of a polyester) are

formed during its esterification: monoester, diester, and triester (plus unestrified THEIC); see Scheme 2. (Numbers 1, 2, and 3 refer to the number of the signal in Fig. 2.)

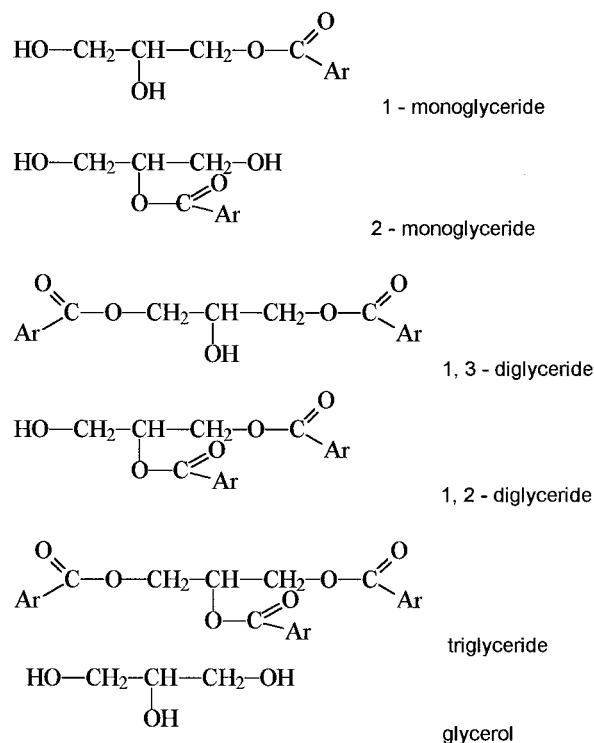
The problem of analysis of various glyceride structures has been approached in a number of published works regarding studies of fats and products of their processing.<sup>1–7</sup> Attention was given exclusively to tri- and diglycerides found in natural oils. Analysis of the carbonyl and olefin ranges of the <sup>13</sup>C-NMR spectra was the basis for the determination of the distribution of saturated and unsaturated chains between the 1,3- and 1,2-positions of glycerol and for the evaluation of the average esterification degree of glycerides in oils. More extensively, it was described by Sacchi et al. in a series of works<sup>4–7</sup>; the authors analyzed also the oxyalkyl range of the <sup>13</sup>C-NMR spectrum and proposed a rapid method for the determination of

Correspondence to: M. Skarżyński.

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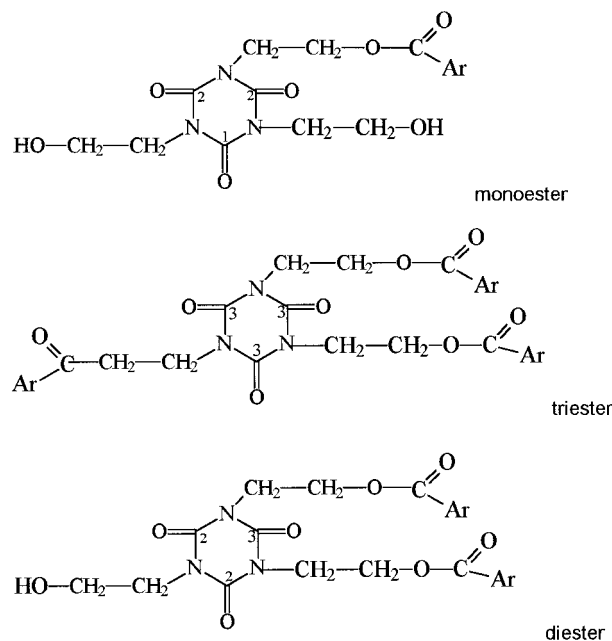
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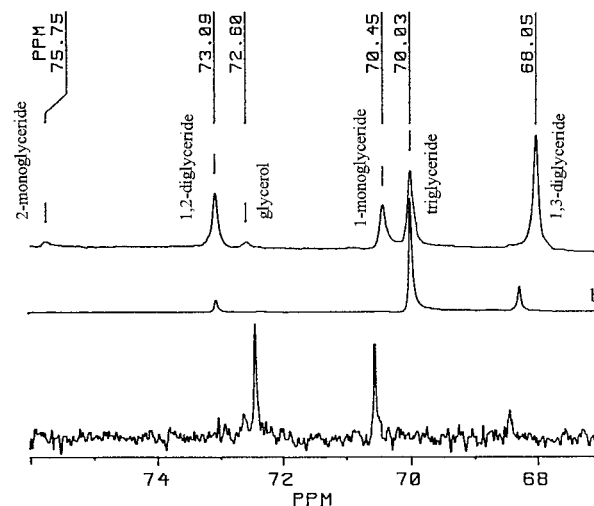


Scheme 1

the contents of 1,3- and 1,2-diglycerides in olive oils using  $^1\text{H-NMR}$  spectroscopy.<sup>6</sup> Jie et al.<sup>1</sup> and Gunstone<sup>3</sup> studied the spectra of synthetic triglycerides. Rabiller and Maze<sup>8</sup> analyzed most of



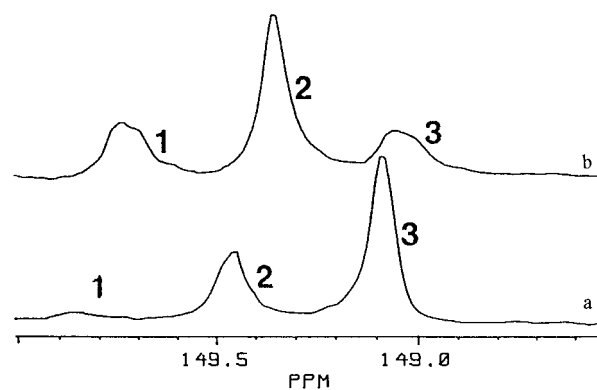
Scheme 2



**Figure 1**  $^{13}\text{C-NMR}$  (DEPT) spectra of CH glyceride groups in three mixtures (a, b, c) of benzoic acid glycerides.

the glycerides of propionic, lauric, and oleinic acids. The authors of a number of articles<sup>8-10</sup> applied  $^{13}\text{C-NMR}$  spectroscopy for studying the absolute configuration of natural glycerides. Preliminary results on the quantitative analysis of all possible glycerides and of glyceride moieties in polyester resins were reported previously.<sup>11,12</sup>

Hardly any articles in recent years<sup>13-16</sup> were devoted to studies of isocyanuric derivatives; they all apply solid-state CP/MAS  $^{13}\text{C-NMR}$  for monitoring either the formation of the isocyanuric ring<sup>13</sup> or its thermal degradation.<sup>15,16</sup> An approach to the quantitative analysis of THEIC structures at different degrees of substitution us-



**Figure 2**  $^{13}\text{C-NMR}$  signals of carbonyl carbon atoms of the isocyanuric ring in the products of esterification of 1 mol of THEIC (a) with 3 mol and (b) with 2 mol of benzoic acid; solutions in  $\text{CDCl}_3$ . Nos. 1, 2, and 3 correspond to the atom indices in Scheme 2.

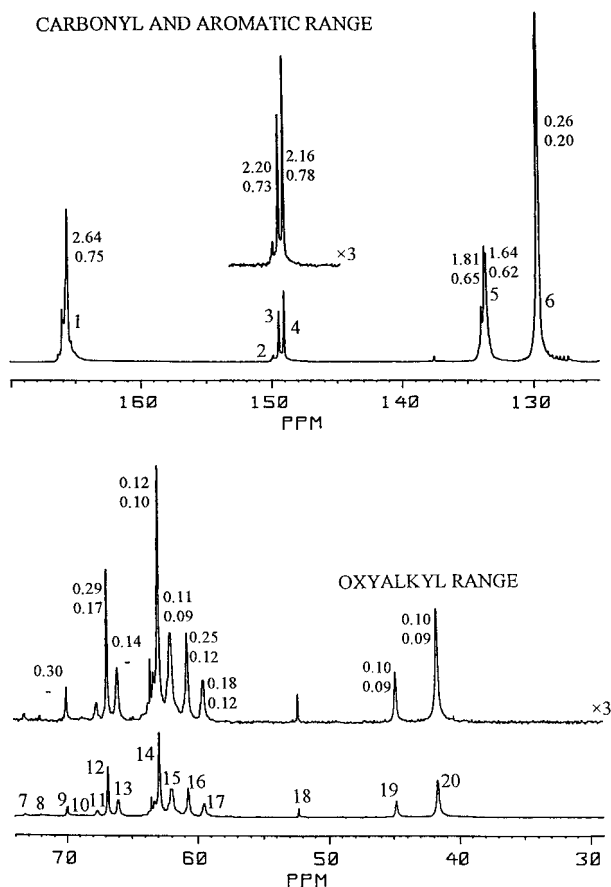
**Table I** Relative Contents (mol %) of Various Glyceride Structures in Products of Esterification of Benzoic Acid and of Dimethyl terephthalate with Glycerol (Mixtures b, c, and d)

Reactants	Glycerol	Monoglycerides		Diglycerides		Triglyceride
		1-	2-	1,3-	1,2-	
1M GL/3.0M BA	0.4	0.4	0.0	19.2	9.1	70.9
1M GL/2.5M BA	2.2	14.7	1.8	37.5	18.2	25.6
1M GL/0.4M DMT	22.5	49.7	5.9	16.3	6.0	0.0

GL, glycerol; BA, benzoic acid; DMT, dimethyl terephthalate.

**Table II** Relative Contents (mol %) of Isocyanurate Structures at Different Degrees of Substitution in Products of Esterification of Benzoic Acid and of Dimethyl Terephthalate with THEIC

Reactants	Structure Content (mol %)			OH (mmol)	
	Mono-	Di-	Tri-	NMR	Titration
1M THEIC/3M BA	8.6	27.4	64.0	0.96	0.96
1M THEIC/2M DMT	13.3	30.9	55.8	—	—



**Figure 3** 75 MHz  $^{13}\text{C}$ -NMR spectrum of the PE resin. Signals are marked with indices from 1 to 20 (see Table III) and with relaxation times  $T_1$  measured without a relaxing agent (the upper values) and with  $\text{Cr}(\text{acac})_3$  in a concentration of 0.02M (the lower values).

ing  $^{13}\text{C}$ -NMR in solutions was carried out by Skarżyński et al.<sup>12,17</sup> Our continuing work on model systems and then on polyester resins encouraged us to propose a method of simultaneous identification and determination of all those structures in a nondestructive and relatively simple way using  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectroscopy.

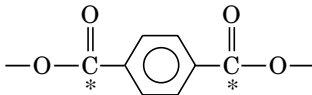
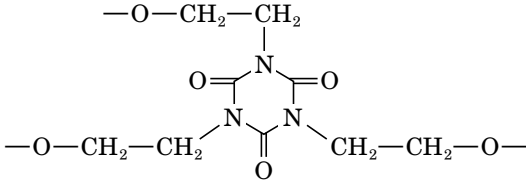
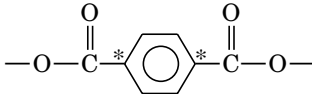
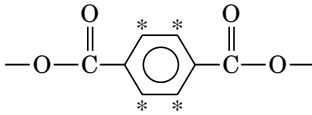
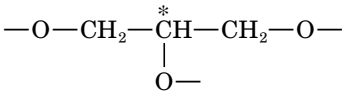
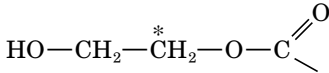
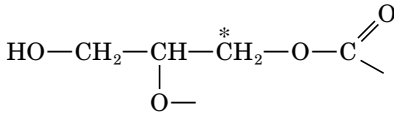
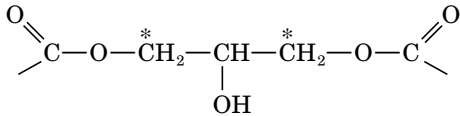
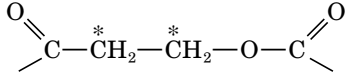
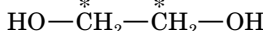
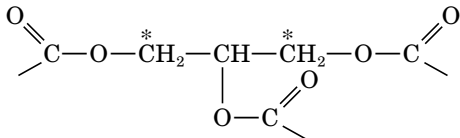
## EXPERIMENTAL

$^{13}\text{C}$ -NMR (25 MHz) and  $^1\text{H}$ -NMR (100 MHz) spectra were taken with a Bruker WP-100SY spectrometer.  $^{13}\text{C}$ -NMR (75 MHz) and  $^1\text{H}$ -NMR (300 MHz) spectra were obtained with a Bruker AM-300. The solvent used was  $\text{CDCl}_3$  at room temperature (25°C) and the internal standard of the chemical shift was tetramethylsilane (TMS), with 32K data points.

DEPT spectra were acquired assuming the average value of the heteronuclear carbon-proton coupling constant  $^1J_{\text{C-H}} = 141$  Hz, and the relaxation delay was 3 s, and acquisition time, 2.5 s. For quantification of the  $^{13}\text{C}$ -NMR spectrum of the resin, the gated proton decoupling (GAT-EDEC) technique with a 90° pulse and repetition delay of 13 s was applied.

Approximately 50% solutions of the resin without and with chromium acetylacetonate in a concentration of 0.02M as a relaxing agents were analyzed. Longitudinal relaxation times  $T_1$  were

**Table III** Assignments of  $^{13}\text{C}$ -NMR Signals of PE Resin

Signal Index	$\delta$ (ppm)	Assignment	No. C Atoms
1	167–174		2
2–4 <sup>a</sup>	150–149		3
5	135–133		2
6	131–129		4
7–11 <sup>b</sup>	73.6–67.8		1
12	67.0		2
13	66.3		2
			1
14	64–63		2
			2
			2

**Table III** *Continued*

Signal Index	$\delta$ (ppm)	Assignment	No. C Atoms
14	64–63	$\text{HO}-\overset{*}{\text{C}}\text{H}_2-\underset{\text{OH}}{\text{C}}\text{H}-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}$	1
		$\text{HO}-\overset{*}{\text{C}}\text{H}_2-\underset{\text{OH}}{\text{C}}\text{H}-\overset{*}{\text{C}}\text{H}_2-\text{OH}$	2
15	62.3	$\text{N}-\text{CH}_2-\overset{*}{\text{C}}\text{H}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}$	1–3 <sup>c</sup>
16	61.0	$\text{HO}-\overset{*}{\text{C}}\text{H}_2-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}$	1
		$\text{HO}-\overset{*}{\text{C}}\text{H}_2-\underset{\text{O}-\overset{\text{O}}{\parallel}{\text{C}}}{\text{C}}\text{H}-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}$	1
17	60.0	$\text{N}-\text{CH}_2-\overset{*}{\text{C}}\text{H}_2-\text{OH}$	1–3 <sup>c</sup>
18	52.6	$\overset{*}{\text{C}}\text{H}_3-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_5$	1
19	45.1	$\text{N}-\overset{*}{\text{C}}\text{H}_2-\text{CH}_2-\text{OH}$	1–3 <sup>c</sup>
20	42.0	$\text{N}-\overset{*}{\text{C}}\text{H}_2-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}$	1–3 <sup>c</sup>

<sup>a</sup> Cf. Figure 1 and Table V.<sup>b</sup> Cf. Figure 2 and Table VI.<sup>c</sup> Dependent upon the degree of esterification of THEIC.

measured with the inversion–recovery pulse sequence. Solutions were not degassed.

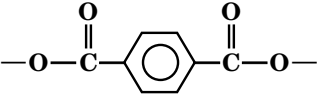
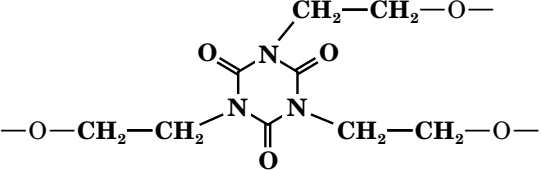
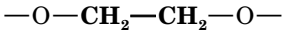
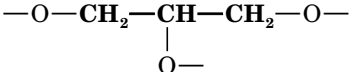
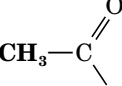

## RESULTS AND DISCUSSION

### Analysis of Glyceride Structures in Model Mixtures

Four samples containing various glyceride structures were prepared:

- The product of the reaction of 3 mol of benzoic acid with 1 mol of glycerol; the sample was drawn shortly after the beginning of the reaction;
- The sample drawn at the end of this reaction;
- The product of the reaction of 2.5 mol of benzoic acid with 1 mol of glycerol; and
- The polymer obtained as product of esterification of 0.4 mol of dimethylterephthalate with 1 mol of glycerol.

**Table IV** Calculated Structural Unit Contents (% by Weight) in the Average Structure of the PE Resin

	Structural Unit (Marked in Bold)	<i>M</i>	%
i		164	65.6
ii		210	18.7
iii		28	7.8
iv		41	3.3
v		15	0.2
vi		17	4.4

The range of 67–76 ppm in the  $^{13}\text{C}$ -NMR spectra with signals of carbon atoms in CH groups was analyzed. Each considered structure contains one CH group and so one signal in this range can be assigned to it. Unlike the signals of the  $\text{CH}_2$  groups, these signals do not overlap. No signals of other groups typical for polyesters, polyesterimides, or polyesterimideamides—in particular those from commonly used glycols—appear in this range either.

Comparison of relative intensities of the signals in the spectra of mixtures (a), (b), and (c) as well as evaluation of the  $\alpha$ - and  $\beta$ -substituent effects were the main criteria for making the assignments. Replacement of the glycerol hydroxyl groups in the  $\beta$ -position to CH with benzoate (yielding 1-monoglyceride and 1,3-diglyceride) results in an upfield shift of the CH signal by  $-2.2$  and  $-2.4$  ppm, successively. The effect of the substitution of successive  $\beta$ -hydroxyl groups of 2-monoglyceride is  $-2.7$  and  $-3.1$  ppm for 1,2-diglyceride and triglyceride, respectively. The  $\alpha$ -effect varies from  $+3.2$  ppm (for 2-monoglycer-

ide) through  $+2.6$  ppm (for 1,2-diglyceride) to  $+2.0$  ppm (for triglyceride). DEPT spectra of the three mixtures with assigned signals are shown in Figure 1.

The great advantages of using a proton–carbon polarization transfer technique (DEPT) are an increased sensitivity of a single measurement and a possibility of acquiring a spectrum much more rapidly since the proton—not carbon—relaxation times  $T_1$  become critical factors. However, the use of DEPT for quantitative measurements requires assuming the same values of the polarization transfer for each analyzed group, and so it can be reasonable only while comparing structures very close one to the other. Justness of this approximation for various benzoic acid glycerides was proved by repeating analyses of the same mixtures with the DEPT technique and with common for quantitative purposes the *inverse gated proton decoupling* (INVGATE) technique plus adding palladium acetylacetonate as a relaxing agent. Proportions of signals obtained in the two ways differed mostly within the range of ca. 5%—while

**Table V** Calculated Contents of Mono-, Di-, and Trisubstituted THEIC Structures in PE Resin

Structure	Relative Mol %	% per Weight in the Resin <sup>a</sup>
Monoester	25.6	4.5
Diester	33.0	5.8
Triester	41.4	7.2

<sup>a</sup> Values calculated for the structure unit C<sub>9</sub>H<sub>12</sub>N<sub>3</sub>O<sub>3</sub> with the sum of atomic weights  $M = 210$ ; see Table IV.

the DEPT spectra were acquired more than 10 times faster than were the INVGATE ones, and their signals were not broadened either by long-time averaging or by the use of a relaxing agent. The calculated relative contents (mol %) of individual glycerides in the mixtures are collected in Table I.

#### Identification and Determination of Isocyanurate Structures in Model Mixtures

Mixtures of products of esterification of benzoic acid and of dimethyl terephthalate with THEIC were employed as model systems for the analysis. The <sup>13</sup>C-NMR spectrum of THEIC-benzoates consists of the following signals:

δ (ppm)	Carbon Atom
150.0–148.5	Carbonyl groups of aromatic ring
62.3	>N—CH <sub>2</sub> —*CH <sub>2</sub> —O—(C=O)—Ar
60.0	>N—CH <sub>2</sub> —*CH <sub>2</sub> —OH
45.1	>N—*CH <sub>2</sub> —CH <sub>2</sub> —OH
42.0	>N—*CH <sub>2</sub> —CH <sub>2</sub> —O—(C=O)—Ar

In the proposed analytical procedure, three signals of carbonyl carbon atoms of the aro-

matic ring in the range δ 150–148.5 ppm are considered. Esterification of an OH group of THEIC manifests in shifting the —C=O signal upfield by −0.5 ppm (ε substituent effect). Successive esterification of the two other hydroxyl groups (to diester and triester structures) shifts this signal twice by −0.5 ppm. This effect is observed in the chloroform solution (see Fig. 2); it does not occur in DMSO.

Let  $S_1$ ,  $S_2$ , and  $S_3$  denote the integral intensities of signals 1, 2, and 3, and let  $x$ ,  $x_i$ ,  $x_{ii}$ , and  $x_{iii}$  denote the relative mole contents of unsubstituted, mono-substituted, disubstituted, and trisubstituted structures in an analyzed mixture, respectively:

$$S_1 \sim 3x + x_i$$

$$S_2 \sim 2x_i + 2x_{ii} \quad (1)$$

$$S_3 \sim x_{ii} + 3x_{iii}$$

$$x + x_i + x_{ii} + x_{iii} = 100\% \text{ (or 1)} \quad (2)$$

If the absence of unreacted THEIC molecules is assumed, that is, if  $x = 0$ ,

$$S_1 \sim x_i$$

$$S_2 \sim 2x_i + 2x_{ii} \quad (3)$$

$$S_3 \sim x_{ii} + 3x_{iii}$$

$$x_i + x_{ii} + x_{iii} = 100\% \quad (4)$$

The integral intensities of the signals at 66.0 and 45.1 ppm are proportional to

$$3x + 2x_i + x_{ii} \quad (5)$$

**Table VI** Calculated Contents of Various Glyceride Structures, Identified in the Spectrum of the PE Resin

Signal	δ (ppm)	Structure	Relative Mol %	% per Weight in the Resin <sup>a</sup>
7	73.5	1,2-Diglyceride	7	0.2
8	72.3	Glycerol	(5)	—
9	70.2	1-Monoglyceride	45	1.6
10	69.0	Triglyceride	5	0.2
11	67.9	1,3-Diglyceride	38	1.3

<sup>a</sup> Values calculated for the structure unit —CH<sub>2</sub>—CH—CH<sub>2</sub>—,  $M = 41$ , see Table IV.

**Table VII Elemental Composition (%) and No. Atoms in the Average Macromolecule of the PE Resin**

Element	Elemental Composition		No. Atoms	
	Combustion	<sup>13</sup> C-NMR	Combustion	<sup>13</sup> C-NMR
C	56.7	57.7	52.0	52.9
H	4.5	4.5	49.1	49.5
N	3.9	3.7	3.1	2.9
O	34.9	34.0	24.0	23.4

while the intensities of the signals at 62.3 and 42.0 ppm are proportional to:

$$x_i + 2x_{ii} + 3x_{iii} \quad (6)$$

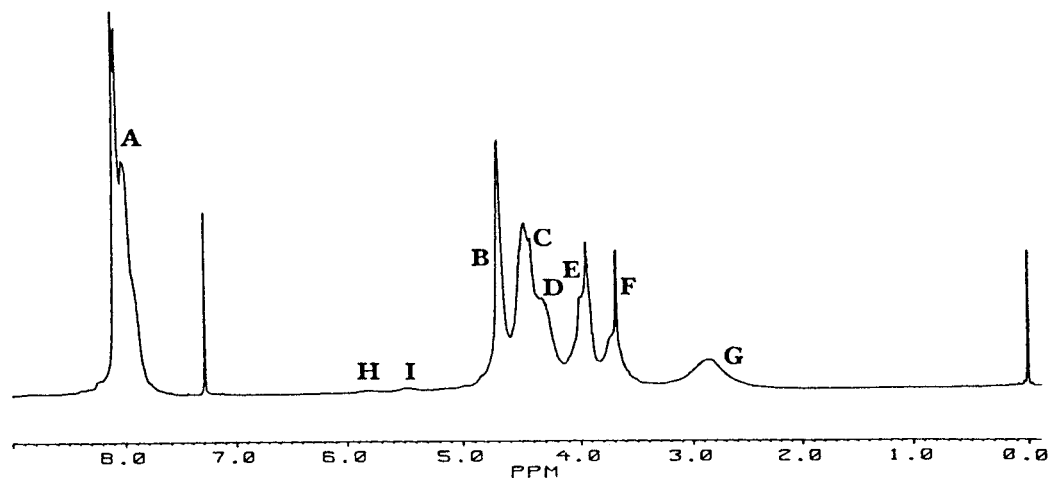
The addition of either (5) or (6) to (1) for forming a system of four equations with four unknowns gives a system with a zero determinant which can be solved parametrically or by taking any of the four unknowns as a parameter:

$$\begin{vmatrix} 3 & 1 & 0 & 0 \\ 0 & 2 & 2 & 0 \\ 0 & 0 & 1 & 3 \\ 3 & 2 & 1 & 0 \end{vmatrix} = \begin{vmatrix} 3 & 1 & 0 & 0 \\ 0 & 2 & 2 & 0 \\ 0 & 0 & 1 & 3 \\ 0 & 1 & 2 & 3 \end{vmatrix} = 0.$$

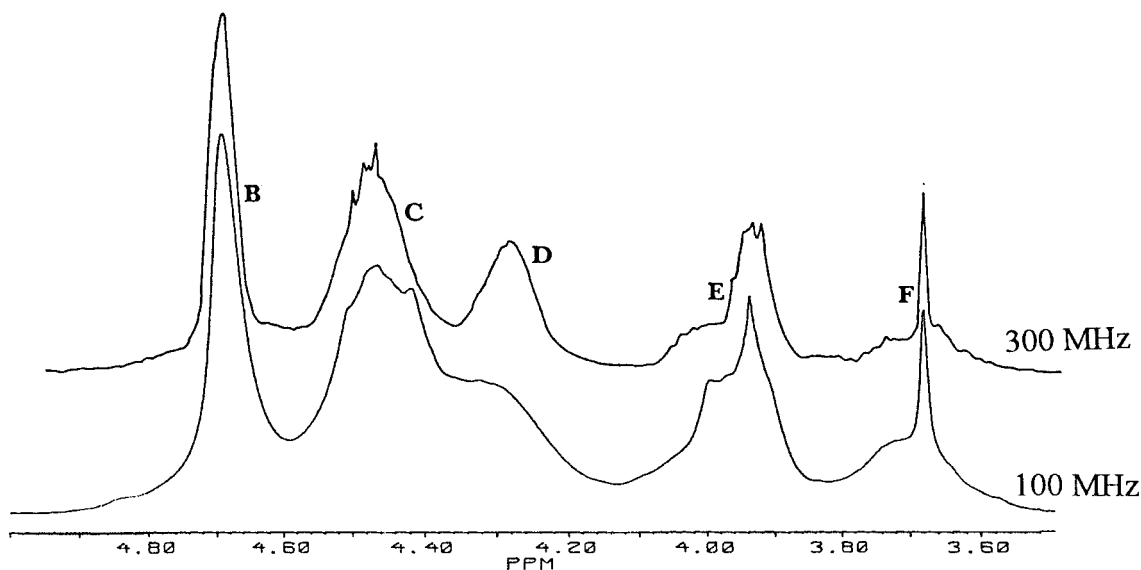
Any combination of four equations of the possible five behaves in the same way, so the problem, in practice, requires assumption of  $x = 0$  and calculation of the system (3) on the condition (4).

Relative mole contents of mono-, di-, and trisubstituted THEIC structures in two mixtures synthesized from 1 mol of THEIC and 3 mol of benzoic acid or 2 mol of dimethylterephthalate, calculated as described above, are shown in Table II.

To estimate the accuracy of the analysis, the number of millimoles of OH groups in 1 g of the mixture of THEIC benzoates was calculated from the NMR results and compared with the result of alkalimetric titration—in both cases, the same result of 0.96 was obtained. The proposed procedure is reasonable when the content of unreacted THEIC molecules is small (less than 5%), that is, if a stoichiometric excess of THEIC was not used for the reaction. It can be also applied, however, in the analysis of composed polyesters, polyesterimides, and polyesterimideamides synthesized from THEIC, glycerol, and various glycols even at total alcohol hydroxyl group excess since THEIC

**Figure 4** 100 MHz <sup>1</sup>H-NMR spectrum of the PE resin.





**Figure 5** Oxyalkyl region of the  $^1\text{H}$ -NMR spectrum of the PE resin at (lower trace) 100 MHz and (upper trace) 300 MHz.

is more reactive than those other alcohols, and so the content of unreacted isocyanurate molecules remains negligible.

#### Analysis of a Polyester Resin

Polyesters synthesized from terephthalic acid derivatives, ethylene glycol, THEIC, and glycerol were analyzed. The PE resin, for which a thorough analysis is described below, was obtained at mole proportions of dimethyl terephthalate/ethylene glycol/THEIC/glycerol = 4.0/3.6/1.0/1.0. Its  $^{13}\text{C}$ -NMR spectrum is shown in Figure 3. It consists of 20 signals marked in the figure with indices from 1 to 20 and assigned in Table III. Assignments were made using reference compounds—low molecular substances and test polymers synthesized at different proportions of reactants, as well as with some available literature data.<sup>18</sup>

The relaxation times  $T_1$  of carbon nuclei in structures assigned to signals 1–20 (Fig. 3) were measured. The longest  $T_1$  without a relaxing agent is 2.64 s, and the pulse repetition delay of its quintuple or 13 s was assumed as sufficient for quantification of the spectrum. In the cases of signals nos. 13, 14, and 16, more than one structure is assigned to a single signal—and so there are multiexponential relaxation decays with more than one time constant, and the three measured  $T_1$  values are, therefore, average ones. However, twofold elongation of the pulse repetition delay (to 26 s) was found not to

cause any observable change in the proportions of the measured signal intensities.

Any macromolecule of the resin PE can be divided into six irregularly repeated structural units defined in Table IV (marked with Roman numbers i–vi), involving the groups identified in Table III. Their mole contents in an average macromolecule of the resin are proportional to the following expressions  $P_i$ – $P_{vi}$ , where  $S_1$ – $S_{20}$  are integral intensities of signals 1–20, respectively:

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Structure i:	$P_i = (S_1 + S_5 + S_6)/8$
Structure ii <sup>a</sup> :	$P_{ii} = (S_2 + S_3 + S_4 + S_{19} + S_{20})/6$
Structure iii:	
(a) contribution of monosubstituted glycol structures:	
	$P_{iiia} = (S_{12} + S_{16} - 2S_7)/2$
(b) contribution of disubstituted glycol structures <sup>b</sup> :	
	$P_{iiib} = (S_{14} - 2S_8 - 2S_9 - S_{10})/2$
Structure iv <sup>c</sup> :	$P_{iv} = S_7 + S_9 + S_{10} + S_{11}$
Structure v:	$P_v = S_{18}$
Structure vi:	$P_{vi} = P_{iiia} + 2S_2 + (S_3 - 2S_2)/2 + S_7 + 2S_{10} + S_{11}$

---

<sup>a</sup> See also Table V.

<sup>b</sup>  $P_{iiib}$  value is overstated if the unreacted glycol molecules are present.

<sup>c</sup> See also Table VI.

The above expressions for  $P_i$ – $P_{vi}$  were composed involving as many signals as possible for two reasons—First, that random errors related to intensity measurements are being averaged

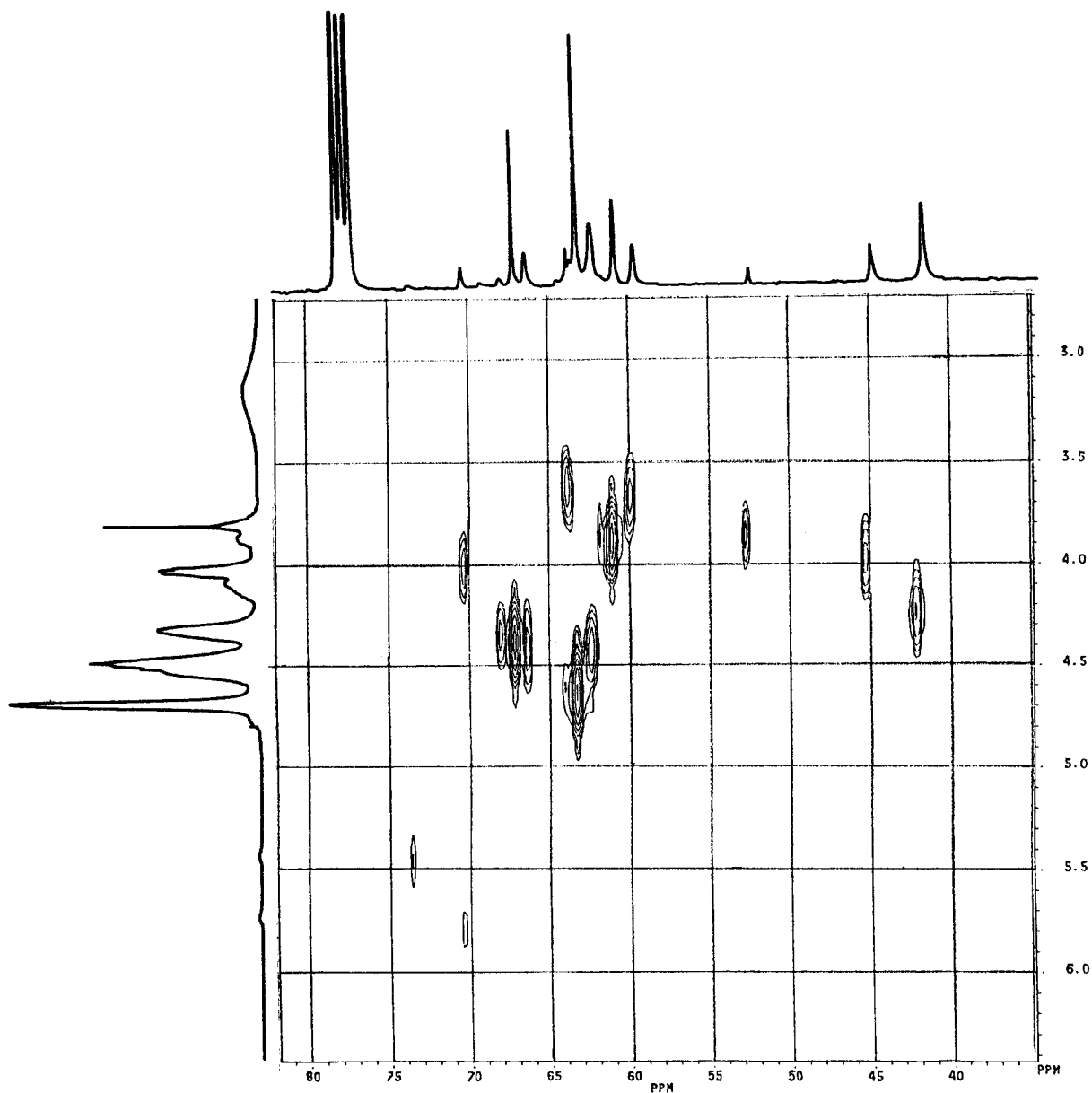
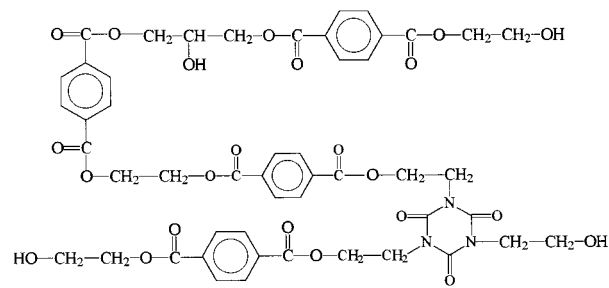


Figure 6 Oxyalkyl part of the  $^{13}\text{C}$ - $^1\text{H}$  HETCOR spectrum of the PE resin.

and, second, values with gross errors can be currently corrected and eliminated. The requirement for the total content of structures i-vi to be 100% leads immediately to the calculation of mole contributions of particular structures in the average macromolecule. Their contributions per weight may be simply calculated when the molecular weights of the structural units are known. Results of the analyses are compiled in Tables IV-VI.

The data included in Tables IV-VI and the average molecular weight ( $1100 \pm 50$ , determined



$\text{C}_{50}\text{H}_{49}\text{N}_3\text{O}_{23}$

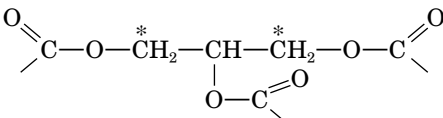
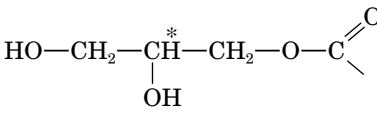
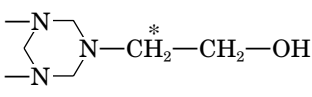
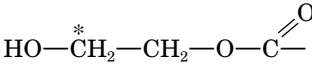
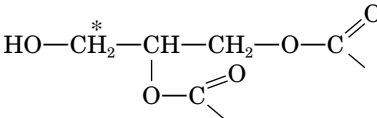
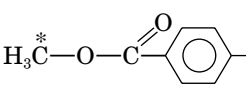
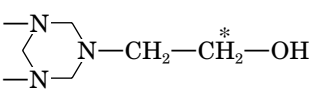
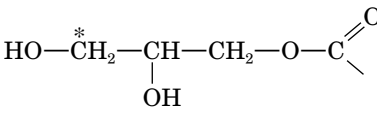
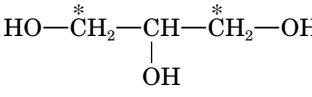
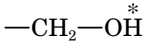
$M_n=1059$

Scheme 3

**Table VIII Chemical-shift Ranges in NMR Spectrum for Protons in All Identified PE Resin Structures**

Structure	Group	No. Protons	$\delta$ Range (ppm)	Chemical Shift (ppm)
	CH	4	8.8–7.7	8.2
	CH	1	5.9–5.7	5.8
	CH	1	5.6–5.3	5.4
	OH <sup>a</sup>	1	4.9–4.6	4.7
	CH <sub>2</sub>	4	4.9–4.3	4.6
	CH <sub>2</sub>	4	4.7–4.2	4.4
	CH <sub>2</sub>	2	4.7–4.2	4.4
	CH <sub>2</sub>	2	4.6–4.3	4.4
	CH <sub>2</sub>	2, 4, or 6 <sup>b</sup>	4.6–4.2	4.4
	CH	1	4.5–4.2	4.3
	CH <sub>2</sub>	4	4.5–4.1	4.3
	CH <sub>2</sub>	2, 4, or 6 <sup>b</sup>	4.5–4.0	4.2

Table VIII Continued

Structure	Group	No. Protons	$\delta$ Range (ppm)	Chemical Shift (ppm)
	CH <sub>2</sub>	4	4.4–4.1	4.2
	CH	1	4.2–3.8	4.0
	CH <sub>2</sub>	2, 4, or 6 <sup>b</sup>	4.2–3.8	4.0
	CH <sub>2</sub>	2	4.3–3.6	3.9
	CH <sub>2</sub>	2	4.3–3.6	3.9
	CH <sub>3</sub>	3	4.0–3.7	3.8
	CH <sub>2</sub>	2, 4, or 6 <sup>b</sup>	3.8–3.5	3.6
	CH <sub>2</sub>	2	3.8–3.4	3.6
	CH <sub>2</sub>	4	3.8–3.4	3.6
	OH <sup>a</sup>	1	3.4–2.2	2.8

<sup>a</sup> The quoted values of the absorption ranges and maxima for the OH protons should be taken as approximate.

<sup>b</sup> Dependent upon the degree of esterification of THEIC.

osmometrically) completely define the structure of a hypothetical average macromolecule of the resin, and a number of real molecules may be composed, more or less close to it. One of them (C<sub>50</sub>H<sub>49</sub>N<sub>3</sub>O<sub>23</sub>, M = 1059) is drawn in Scheme 3.

Elemental composition of the average macromolecule may be reckoned from the NMR data or

established by combustion analysis. The results obtained by the two ways are in a good agreement (see Table VII), which "macroscopically" confirms the correctness of the <sup>13</sup>C-NMR analysis.

Despite much lower spectral resolution, it is often more convenient to use <sup>1</sup>H-NMR rather than <sup>13</sup>C-NMR since it also provides essential

structural information, and the spectrum is acquired in much shorter time as well as problems with the relaxation processes are not so substantial. A 100 MHz proton-NMR spectrum of the resin PE chloroform solution is shown in Figure 4; its oxyalkyl region (3.5–5.0 ppm) together with that of the spectrum acquired at 300 MHz are shown in Figure 5. Exact assignments have been made with the help of literature data<sup>6,19,20</sup> and those obtained with the 2D  $^{13}\text{C}$ — $^1\text{H}$  heteronuclear correlation experiment. The oxyalkyl part of the 300 MHz HETCOR spectrum is shown in Figure 6. Chemical shift values for proton resonances in all identified PE resin structures are specified in Table VIII.

It is not possible to make an exact quantitative  $^1\text{H}$ -NMR analysis of the polyester because of overlapping signals corresponding to protons in a majority of the structures. The data in Table VIII, however, can form a basis for various semiquantitative approaches, which employ a number of approximations depending on its actual composition. An attempt was made by us<sup>21</sup> for the resin PE, and the hypothetical average macromolecule of the resin was determined as  $\text{C}_{51.7}\text{H}_{50.9}\text{N}_{2.7}\text{O}_{24.3}$  (cf. Table VII:  $\text{C}_{52.9}\text{H}_{49.7}\text{N}_{2.9}\text{O}_{23.4}$  is the result of the detailed  $^{13}\text{C}$ -NMR approach, and  $\text{C}_{52.0}\text{H}_{49.1}\text{N}_{3.1}\text{O}_{24.0}$  is the result of an ordinary combustion analysis).

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