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Studies on the microstructure of the polymer obtained by chemical modification of poly(oxy-1-chloromethyl-ethylene-*co*-oxyethylene) (PECH–PEO) with phenolate

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Abstract

Poly(oxy-1-chloromethylethylene-*co*-oxyethylene) copolymer (PECH–PEO) has been modified chemically by phenolate, producing dehydrochlorination as a side reaction, because of its basic character. The comonomer composition of the resulting poly(oxy-1-chloromethylethylene-*co*-oxyethylene-*co*-oxy-1-methyleneethylene-*co*-oxy-1-phenoxy-methylethylene) can be quantitatively determined by ^{13}C NMR spectroscopy. A series of copolymeric models were synthesized to make the complete assignment of all the signals appearing in the spectrum of the tetrapolymer. The various ^{13}C NMR signals in the spectra were assigned to dyads, triads or tetrads of all the possible comonomer sequences and in some cases to the tacticity. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Chemical modification; PECH–PEO; Comonomer sequence

1. Introduction

High resolution NMR spectroscopy is a particularly useful technique for determining the microstructure of a polymer when the spectral resolution is sufficient to resolve the resonances of the specific sequences [1]. Some polymeric systems can be synthesized by chemically modifying preformed polymers. When chemical modification is incomplete or side reactions occur, the polymers obtained fall into the category of copolymers with different repeating units. Quantitative applications of the NMR technique are able to determine the composition of the copolymers and the assignment of compositional dyads or triads can help to determine the distribution of the different structural units along the main chain. These structural studies can also give valuable information about the mechanism and kinetics of the modification processes that have been used to obtain the copolymer. Moreover, the tactic nature of some copolymers can be determined if the different signals are well resolved.

The fact that some applications require functional polymers means that these polymers must be synthesized with well established structures [2]. Of the materials that are commercially available, polymers that contain chlorine are suitable starting products for synthesizing new functional polymers which can be used in several new technologies. Poly(epichlorohydrin)) (PECH) [3,4] and its ethylene oxide copolymer (PECH–PEO) [5] are of particular interest because their chlorine atoms are not directly attached to the main chain and they can be nucleophilically substituted.

In previous articles [6,7], we studied the chemical modification of PECH with phenolate and we observed the formation of vinylether moieties in the main chain arising from the undesired dehydrochlorination. To test whether the modification reaction depends on the chemical microenvironment, we quantified the different structural units and characterized the microstructure of the modified polymer, paying particular attention to the comonomer distribution. More recently, we have studied the chemical modification of PECH–PEO copolymer with phenolate [8] in an attempt to obtain new polymers which are related to polystyrene resins with a more flexible polar backbone and a lower proportion of aromatic rings than the modified PECH homopolymer. We quantified the percentage of different units in the modified polymers and elucidated the comonomer sequence of the tetrapolymer obtained on the basis of the assignments made by polymeric models which had been synthesized for this purpose.

This article describes the procedure for assigning the different comonomer sequence signals in the ^{13}C NMR spectra of the tetrapolymers obtained by chemical

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modification of PECH–PEO with sodium phenolates. This procedure includes the synthesis and characterization of different polymeric models which are specially designed to help in the microstructure study.

2. Experimental

2.1. Materials

Hexane was dried by refluxing over CaH_2 and distilled before use. Tetrahydrofuran (THF) was first refluxed over CaH_2 and then over sodium-benzophenone. It was used freshly distilled.

Tetrabutylammonium bromide (synthesis grade, Aldrich) was used as phase transfer agent and was dried over P_2O_5 under vacuum at room temperature.

Dry phenol (Probus) was prepared by fractional distillation. *p*-Benzyloxyphenol (Aldrich) was used as received. Sodium hydride (60% dispersion in mineral oil, Aldrich) and 3-*t*-butyl-4-hydroxy-5-methylphenyl sulphide (Santonox®) (Aldrich) were used without previous purification. Sodium methoxide (Aldrich) was dried under vacuum before use.

Phenylglycidylether (PGE) (Aldrich) was dried before use by fluxing it through an activated powder 4 Å molecular sieve column. Epichlorohydrin (EPC) (Fluka) was distilled and dried over 4 Å molecular sieve. Ethylene oxide (Fluka) (liquefied gas) was dried over CaH_2 at low temperature in a schlenck flask.

Sodium phenolate and sodium *p*-benzyloxyphenolate were prepared in a Schlenck flask by dropwise addition of a solution of phenol in THF over a suspension of pure NaH in anhydrous hexane under argon. Phenolates were filtered off under argon and washed several times with mixtures of hexane/THF. The solvent was eliminated in the vacuum and sodium phenolates were stored in schlenck flasks under an inert atmosphere.

Poly(oxy-1-chloromethylethylene-*co*-oxyethylene) copolymer (PECH–PEO) 1:1 (Zeon Chemicals Inc.), inherent viscosity in NMP (η_{inh}) = 280 ml/g, measured at a concentration of ca. 2 g/l at 30°C, average molecular weight ($\overline{M_w}$) = 940 000 Da and polydispersity ($\overline{M_w}/\overline{M_n}$) = 2.4, was dried at 60°C under vacuum over P_2O_5.

2.2. Preparation of polymeric models

Poly(oxy-1-chloromethylethylene-*co*-oxyethylene) copolymers with different comonomer ratios were synthesized by polymerizing the corresponding monomers using a Vandenberg chelate catalyst [9].

Poly(oxyethylene-*co*-oxy-1-phenoxymethylethylene) with different comonomer ratios were obtained from the corresponding monomers by the same polymerization procedure.

Poly(oxyethylene-*co*-oxy-1-methyleneethylene) 1:1 copolymer and poly(oxy-1-chloromethylethylene-*co*-oxyethylene-*co*-oxy-1-methyleneethylene)terpolymers with different comonomer ratios were synthesized from PECH–PEO and sodium methoxide in THF.

Poly(oxy-1-chloromethylethylene-*co*-oxyethylene-*co*-oxy-1-methyleneethylene)terpolymer with 24:50:26 comonomer ratio was obtained by partial dehydrochlorination with a 1:0.5 chlorine/methoxide molar ratio in THF.

Poly(oxyethylene-*co*-oxy-1-methyleneethylene-*co*-oxy-1-phenoxymethylethylene)terpolymer with a 50:22:28 comonomer ratio, obtained by treatment of 1:1 PECH–PEO with a mixture 1:1 of sodium phenolate and sodium methoxide in THF.

2.3. Substitution reaction of poly(oxy-1-chloromethylethylene-co-oxyethylene) with sodium phenolates

Dry PECH–PEO (0.214 g, 1.57 mmol) was dissolved in anhydrous THF (25 ml) and a solution of sodium phenolate (0.183 g, 1.57 mmol) and dry tetrabutylammonium bromide (TBAB) (0.507 g, 1.57 mmol) in anhydrous THF (25 ml) was added under an inert atmosphere. The reaction mixture was stirred at 60°C for 4 days in the dark. Then, the polymer solution was precipitated into water. The resulting polymer was purified by reprecipitating twice from THF into water and adding a small amount of 3-*t*-butyl-4-hydroxy-5-methylphenyl sulphide as a radical trapper in the last precipitation. The modified polymer was dried under vacuum at 50°C. The yield was 98%, the degree of substitution 57% and the degree of elimination 17% (from quantitative ^{13}C NMR spectroscopy). $\overline{M_w}$ = 1 120 000 Da.

Other samples of modified polymer were prepared at different reaction times and a phenolate/chlorine molar ratio of 1:2. In this way polymers with different comonomer percentages were obtained.

The same procedure was applied to the chemical modification of PECH–PEO with sodium *p*-benzyloxyphenolate, and, poly(oxy-1-(4-benzyloxy)phenoxymethylethylene-*co*-oxy-1-chloromethylethylene-*co*-oxyethylene) with a 26:24:50 comonomer ratio (yield = 97%) was obtained.

2.4. Instrumentation

^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 75.4 MHz, using 1,1,2,2-tetrachloroethane-d_2 as solvent. Substitution and elimination degrees were determined by integrating ^{13}C NMR signals under quantitative conditions, that is, with the sequence inverse gated decoupling and a delay time of 3 s. The resolution was enhanced by using an LB = 2, *zero-filling* and the Lorentz–Gaussian transformation technique [10], with factors of GF = 0.1 and GFS = 0.05.

Average molecular weights in mass and polydispersities were calculated on a SEC-MALLS system, made up of an HPLC Waters 510 pump, three columns (Shodex K-80M, PLgel 5 μ MIXED-D and PLgel 3 μ MIXED-E) and one precolumn (Shodex K-800 P). Two detectors were placed after the columns, a laser light scattering detector

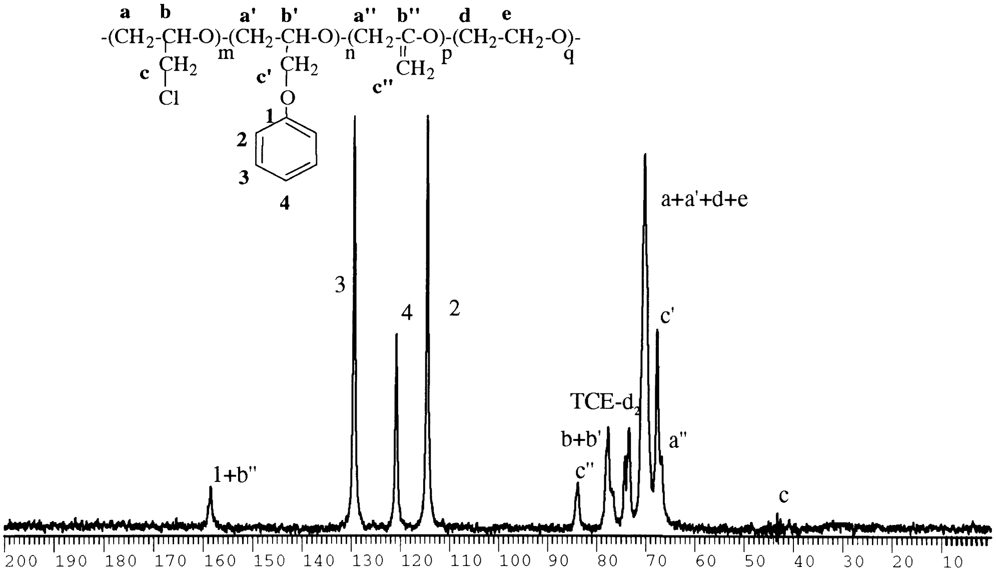
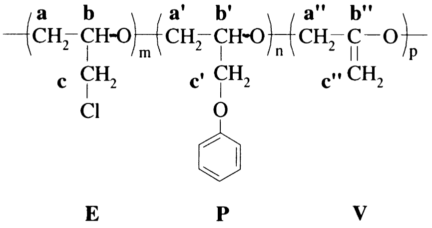


Fig. 1. ^{13}C NMR spectrum in deuterated tetrachloroethane of polymer obtained by chemical modification of PECH–PEO with phenolate.

Table 1

Assignment of the dyad and triad sequences of the different in the structural units of the ^{13}C NMR spectrum of poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethylethylene-*co*-oxy-1-methyleneethylene)



a		b		a′		b′	
δ (ppm)	Dyads	δ ppm)	Triads	δ (ppm)	Dyads	δ (ppm)	Triads
70.3	VE̲V	78.6	EE̲E EE̲P PE̲E PE̲P	70.2	VP̲	78.1	PP̲P-mm PP̲E EP̲P EP̲E
70.1	VE̲E	77.8	VE̲E VE̲P	69.7	PP̲-m	78.0	PP̲P-mr PP̲P-rm
69.4	EE̲-m PE̲	77.3	EE̲V PE̲V	69.5	PP̲-r	77.9	PP̲P-rr
69.1	EE̲-r	76.3	VE̲V		EP̲	77.0	VP̲P VP̲E
						76.8	PP̲V EP̲V
						75.6	VP̲V
a″		b″		c″		c′	
δ (ppm)	Dyads	δ (ppm)	Triads	δ (ppm)	Dyads	δ (ppm)	Dyads
67.2	VV̲	159.0	PV̲P	84.6	EV̲	67.9	PP̲ EP̲
66.7	PV̲	158.5	EV̲E	84.5	PV̲		
66.5	EV̲V	157.1	VV̲V VV̲E EV̲V VV̲P	84.3	VV̲		
66.4	EV̲E						

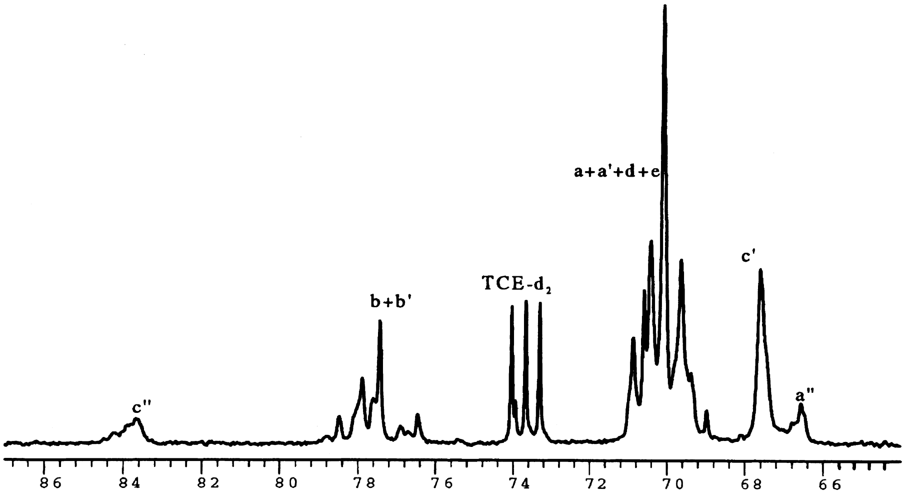


Fig. 2. Region between 65 and 86 ppm of the ^{13}C NMR spectrum of the modified PECH–PEO shown in Fig. 1.

(miniDAWN from Wyatt Technology Corporation) at the beginning and a refraction index detector (RID-6A from Shimadzu) at the end. The data were mathematically treated with the ASTRette 1.2 program for Macintosh, from Wyatt Technology. Working conditions were THF as solvent (MALLINCKRODT ChromAR HPLC), flux of 1.0 ml/min, helium as degasser and nearly 3×10^{-4} g of sample injected via a 100-μl loop.

3. Results and discussion

In a previous article [8], we studied the chemical modification of PECH–PEO with phenolate in order to find the best reaction conditions for high substitution degrees with minimum chain cleavage. We found that the phenolate/active chlorine molar ratio should be 1:2, the reaction temperature 60°C for one day and the solvent THF. In this way, a modified polymer with a 63% of degree of substitution without appreciable chain scission was recovered (98%). However, the basic character of the phenolate caused about 20% of dehydrochlorinated units and in the final material 17% of the chloromethylated units remained unaltered.

The overall tetrapolymer composition obtained by this modification procedure was evaluated by quantitative ^{13}C NMR spectroscopy (see Fig. 1). By integrating $\mathbf{c}''$ signals (CH_2 in the vinylether units) at 84 ppm, $\mathbf{b}+\mathbf{b}'$ signals (methine carbons in the main chain) at 78–79 ppm and **c** signals (chloromethyl group) at 43 ppm, the comonomer percentages were calculated, taking into account that the initial polymer is 1:1 molar ratio PECH/PEO. The percentage of the remaining chloromethylene units was confirmed by elemental analyses.

Previous studies [6,8] suggested that there is a mechanistic explanation for the degradative scission of the main chain in the reaction of PECH and PECH–PEO with nucleophiles. This mechanism was confirmed and it involves a nucleophilic attack of the phenolate on the methylene carbon next to a vinyl ether unit. Thus, in the ^{13}C NMR spectra of the modified polymers the methylketone end-groups that appear at 29.4 and 205 ppm can be identified. The presence of phenolate terminal groups, produced in the chain scission, cannot be detected because they overlap with different signals of the repetitive structural units.

In a previous study [7] we assigned the different comonomer sequence signals in the ^{13}C NMR spectra of the PECH modified with phenolate. On the basis of these results, here we have attempted to assign the whole microstructure of the modified PECH–PEO. The commercial starting PECH–PEO is a polymer which is atactic and completely regioregular, so we have dealt mainly with the comonomer distribution along the main chain. Since in this case there are four different repeating units, epichlorohydrin (E), ethylene oxide (O), vinylether (V) and phenylglycidylether (P), a considerable number of additional split signals can be expected, although many of them will overlap.

The assignment of the comonomer sequence was made on the basis of the PECH signals identified above (see Table 1) and the study of the ^{13}C NMR spectra of polymeric models synthesized for this purpose. We have prepared:

1. Two PECH–PEO copolymers with comonomer ratios of 93:7 and 56:44 which had been obtained by coordinative ring-opening polymerization [9] from epichlorohydrin and ethylene oxide. The spectra of these polymers and that of the commercial 1:1 PECH–PEO allow us to assign the split signals arising from E and O combinations for each carbon. In fact, Cheng [11] had assigned the complete microstructure of the PECH–PEO copolymer in DMSO-d_6, but for purposes of comparison, we recorded the spectra in deuterated tetrachloroethane and reviewed his study.
2. Two poly(oxyethylene-*co*-oxy-1-phenoxymethylethylene) copolymers in comonomer ratios of 52:48 and 17:83, synthesized by polymerization with the same

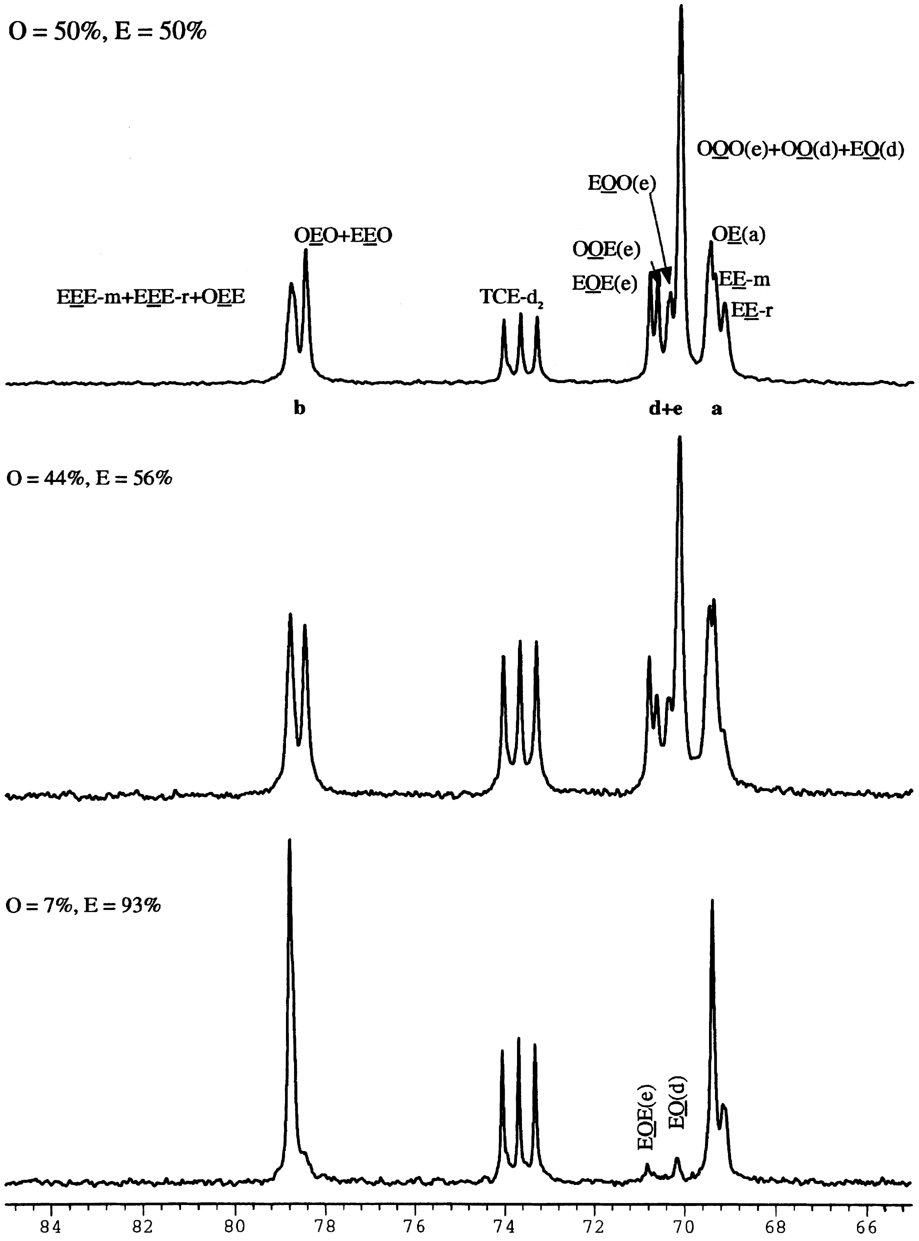


Fig. 3. Region between 66 and 84 ppm of the ^{13}C NMR spectrum in deuterated tetrachloroethane of the poly(1-chloromethylethylene-*co*-oxyethylene) copolymer in comonomer molar ratios of 50:50, 44:56 and 7:93.

initiator as before. These copolymers allow the sequences arising from O and P units, to be assigned.

3. Poly(oxyethylene-*co*-oxy-1-methyleneethylene) 1:1 synthesized by complete dehydrochlorination of commercial PECH–PEO 1:1 with sodium methoxide. This model allows the sequences arising from O and V units, to be studied.
4. Poly(oxy-1-chloromethylethylene-*co*-oxyethylene-*co*-oxy-1-methyleneethylene) terpolymer in a comonomer ratio of 24:50:26, obtained by partial dehydrochlorination of commercial PECH–PEO with sodium methoxide. From this polymer, the sequences arising from combinations of E, O and V can be assigned.
5. Poly(oxy-1-[*p*–benzyloxyphenoxy]methylethylene-*co*-oxy-1-chloromethylethylene-*co*-oxyethylene) terpolymer in a comonomer ratio of 21:29:50, obtained by chemical modification of commercial PECH–PEO with sodium *p*-benzyloxyphenolate. This polymer, which has no vinylic units, is a suitable model for assigning the sequences from P, E and O combinations.
6. Poly(oxyethylene-*co*-oxy-1-methyleneethylene-*co*-oxy-1-phenoxymethylethylene)terpolymer in a comonomer ratio of 50:22:28, obtained by treating 1:1 PECH–PEO with a mixture of sodium phenolate and sodium metoxide. From this model the sequences originated by O, P and V units can be assigned.

Table 2
Assignment of dyad and triad sequences of methine and methylene carbons in the main chain of the ^{13}C NMR spectrum of the poly(oxy-1-chloromethyl-ethylene-*co*-oxyethylene) copolymer

a		**b**		**d**		**e**	
δ (ppm)	Dyad	δ (ppm)	Triad	δ (ppm)	Dyad	δ (ppm)	Triad
69.5	OE̲	78.7	OE̲E	70.1	OO̲ EO̲	70.8	EO̲E
69.4	EE̲-m	78.6	EE̲E			70.6	OO̲E
69.1	EE̲-r	78.5	EE̲O OE̲O			70.4	EO̲O
						70.1	OO̲O

To confirm that the microstructure had been completely assigned we also took into account the spectra of several samples of tetrapolymer with different comonomer ratios which had been obtained by modifying PECH–PEO with sodium phenolate in different reaction conditions.

Fig. 2 shows the region between 85 and 65 ppm of the ^{13}C NMR spectrum of a PECH–PEO copolymer modified with phenolate in deuterated tetrachloroethane. The broad and poorly resolved signal appearing between 85 and 83 ppm has been attributed to the olephinic methylene carbon (**c**″) of the vinylic unit. The methynic carbons, **b** and **b**′, are split in the zone between 76 and 79 ppm. A more complicated pattern appears between 69 and 71 ppm, due to the overlapping of the sequence signals of the methylene carbons of

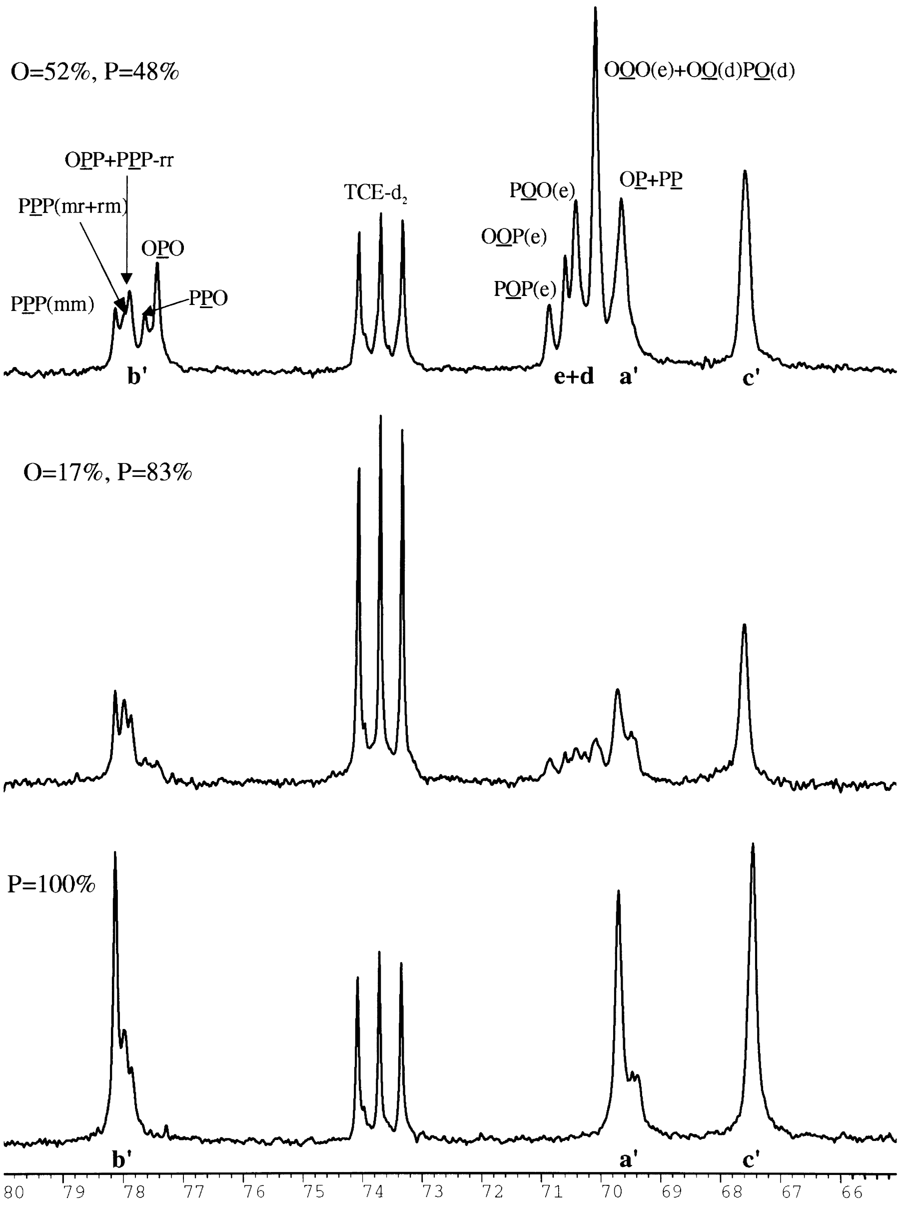


Fig. 4. Region between 66 and 80 ppm of the ^{13}C NMR spectrum in deuterated tetrachloroethane of the poly(oxythylene-*co*-oxy-1-phenoxymethylethylene) copolymers in comonomer ratios of 52:48 and 17:83, and poly(oxyl-1-phenoxymethylethylene).

Table 3
Assignment of the dyad and triad sequences of methine and methylene carbons in the main chain of the ^{13}C NMR spectrum of the poly(oxyethylene-*co*-oxy-1-phenoxymethylethylene) copolymer

a′		**b**′		**d**		**e**	
δ (ppm)	Dyad	δ (ppm)	Triad	δ (ppm)	Dyad	δ (ppm)	Triad
69.7	P$\underline{\text{P}}$-m	78.1	P$\underline{\text{P}}$P-mm	70.1	P$\underline{\text{O}}$ O$\underline{\text{O}}$	70.8	P$\underline{\text{O}}$P
69.5	P$\underline{\text{P}}$-r O$\underline{\text{P}}$	78.0	P$\underline{\text{P}}$P-mr P$\underline{\text{P}}$P-rm			70.6	O$\underline{\text{O}}$P
		77.9	P$\underline{\text{P}}$P-rr O$\underline{\text{P}}$P			70.4	P$\underline{\text{O}}$O
		77.6	P$\underline{\text{P}}$O			70.1	O$\underline{\text{O}}$O
		77.4	O$\underline{\text{P}}$O				

the E and P units, **a** and **a**′, and **d** and **e** of the oxyethylene unit. In the zone between 66 and 68 ppm two broad signals corresponding to the methylene carbons (**c**′ and **a**″) of the P and V units can be observed.

Before discussing the complete assignment of the sequence signals, it should be mentioned that, in general, methine and quaternary carbons in the main chain are triad-sensitive and methylene carbons are dyad-sensitive. The exception to this rule is the methylene carbon **e** of the oxyethylenic unit, which must be triad-sensitive according of their placement, although depending on their environment sensitivities could be higher. It is also important to note that the non-symmetry of the environment leads to non-equivalent sequences, so different ^{13}C chemical shifts should be expected for triads such as O$\underline{\text{O}}$P or P$\underline{\text{O}}$O.

Fig. 3 shows the region between 66 and 84 ppm of the ^{13}C NMR spectra of the PECH–PEO copolymers. The signals of the different sequences were assigned using empirical calculations [12] and the assignments made by Cheng [11]. Moreover, the intensity of the different dyads and triads E-centred must diminish when the percentage of ethylene oxide in the comonomer increases. It should be noted that the polymers we synthesized have a greater isotactic character, so the *meso* stereosequences are more intense and the spectra seem to be simpler. The E$\underline{\text{O}}$E triad of carbon **e** and the E$\underline{\text{O}}$ dyad of carbon **d** can be assigned unmistakably from the spectrum with the least percentage of ethyleneoxide. Table 2 collects the assignments of the different comonomer sequences from E and O units.

The second polymeric model, poly(oxyethylene-*co*-oxy-1-phenoxymethylethylene), was studied using a similar strategy, although there are no references in the literature about its microstructure. Fig. 4 shows the zone of the ^{13}C NMR spectra which corresponds to the aliphatic carbons of the structural units of the copolymers with comonomer ratios of 52:48 and 17:83, and a sample of poly(phenylglycidylether) homopolymer which we had synthesized previously [13]. As can be seen, in this zone there are considerable number of signals corresponding to the different sequences of carbons **a**′, **b**′, **d** and **e**. Due to the coordinative polymerization initiators used in the synthesis of these polymers, a highly isotactic character can be observed in the P$\underline{\text{P}}$P triad. In these copolymers, two different dyads for **a**′ and four different P-centred triads for **b**′ could be expected. Signals from P$\underline{\text{P}}$P and O$\underline{\text{P}}$O triads are easy to assign because of their chemical shifts and the differences in their homopolymer spectrum. In contrast, P$\underline{\text{P}}$O and O$\underline{\text{P}}$P triads, which appear in the middle, can be assigned by taking into account that the most important effects for substituents in δ are those with the oxygen directly attached to the carbon considered (α position) [11]. For this reason, the O$\underline{\text{P}}$P triad is more deshielded than P$\underline{\text{P}}$O for carbon **b**′. The methylene carbon **a**′ of the P unit was assigned by comparing the spectrum of the copolymer (molar ratio 12:83) with that of the homopolymer.

As far as the O-centred sequences are concerned, and as in the example above, two dyads and four triads are expected for carbon **d** and carbon **e**, respectively. The assignment was made by making empirical calculations, comparing how the intensity of the signals varied with the comonomer ratio and considering the statement above.

Unlike the carbons of the main chain, the methylene

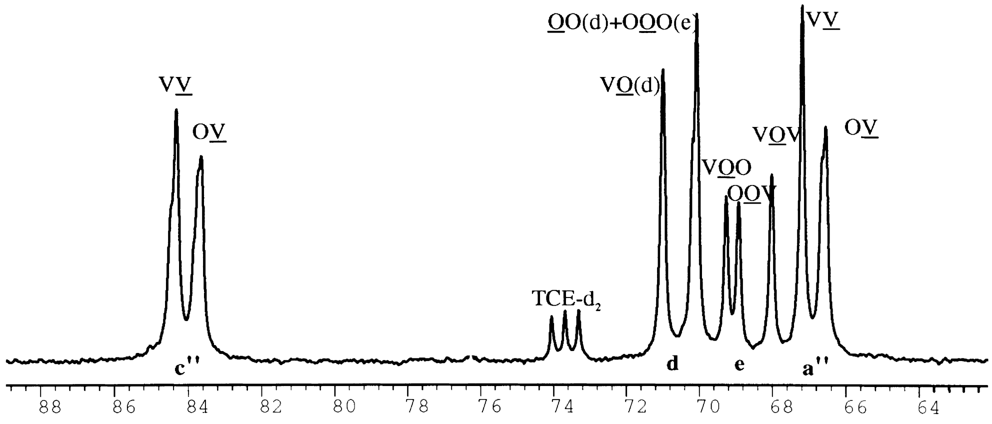


Fig. 5. Region between 64 and 88 ppm of the ^{13}C NMR spectrum in deuterated tetrachloroethane of the poly(oxyethylene-*co*-oxy-1-methyleneethylene) copolymer (1:1 comonomer molar ratio).

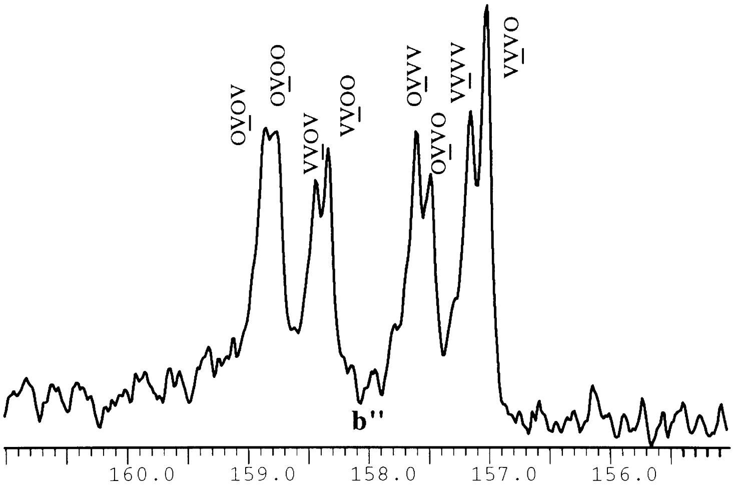


Fig. 6. Region between 156 and 160 ppm of the ^{13}C NMR spectrum in deuterated tetrachloroethane of the poly(oxyethylene-*co*-oxy-1-methyleneethylene) copolymer (1:1 comonomer molar ratio).

carbon $\mathbf{c}'$ of unit P does not present any splitting at this magnetic field intensity. The assignments made from this polymeric model are collected in Table 3.

The V- and O-centred comonomer sequences can be assigned by studying the poly(oxyethylene-*co*-oxy-1-methyleneethylene) 1:1 spectrum (see Fig. 5). The spectrum of the completely dehydrochlorinated PECH [7] makes it possible to unmistakably assign the $\mathrm{V\underline{V}}$ dyads for carbons $\mathbf{c}''$ and $\mathbf{a}''$ at 84.3 and 67.2, respectively. Therefore, signals at 83.6 and 66.6 ppm can be assigned to the $\mathrm{O\underline{V}}$ dyad, which is slightly split due to its higher sensitivity. As far as the assignment of the carbons of the oxyethylene unit is concerned, it must be mentioned that the $\mathrm{O\underline{O}}$ (**d**) dyad and $\mathrm{O\underline{O}O}$ (**e**) triad have been above identified, and so it is straightforward to assign the $\mathrm{V\underline{O}}$ (**d**) dyad to the signal at 71.0 ppm because of its intensity. The signals at 69.3, 68.9 and 68.0 ppm must correspond to the three other signals from the O-centred triads of carbon **e**. Taking into account the shielding effect of the neighbouring vinylic units, the signal at 68.0 must be due to the $\mathrm{V\underline{O}V}$ triad. The other two signals can be assigned by considering that, in the $\mathrm{V\underline{O}O}$ triad, the oxygen in the β position has a stronger deshielding effect because of its greater positive character (mesomeric effect).

The considerable sensitivity of the quaternary carbon of the vinylic unit $\mathbf{b}''$ (see Fig. 6) at 158 ppm must be emphasized. In principle, a triad sensitive signal would be expected but there are eight different signals which correspond to pairs of tetrads. The most shielded pair of tetrads can be assigned to the $\mathrm{V\underline{V}VV}$ and $\mathrm{V\underline{V}VO}$ because of the chemical shift observed in the case of completely dehydrochlorinated PECH ($\delta\mathrm{V\underline{V}V} = 157.1$ ppm). The different tetrads can be assigned by correlation, using the same criterion as the carbon **e** triad of ethylene oxide. Table 4 shows the assignments made by these polymeric models.

Taking into account all the assignments made with the copolymeric models all the signals from different comonomer sequences with three different units need to be assigned. Fig. 7 shows the spectrum of the poly(oxy-1-chloromethylethylene-*co*-oxyethylene-*co*-oxy-1-methyleneethylene)terpolymer in a comonomer ratio of 24:50:26, obtained by partial dehydrochlorination of commercial PECH–PEO with sodium methoxide. In this spectrum, all the assignments, except the signals marked, have already been

Table 4
Assignment of the dyad, triad and tetrad sequences of the carbons in the structural units of the ^{13}C NMR spectrum of the poly(oxyethylene-*co*-oxy-1-methyleneethylene) copolymer

$\mathbf{a}''$		$\mathbf{b}''$		$\mathbf{c}''$		**d**		**e**	
δ (ppm)	Dyad	δ (ppm)	Tetrad	δ (ppm)	Dyad	δ (ppm)	Dyad	δ (ppm)	Triad
67.2	$\mathrm{V\underline{V}}$	158.8	$\mathrm{O\underline{V}OV}$	84.3	$\mathrm{V\underline{V}}$	71.0	$\mathrm{V\underline{O}}$	70.2	$\mathrm{O\underline{O}O}$
66.6	$\mathrm{O\underline{V}}$	158.7	$\mathrm{O\underline{V}OO}$	83.6	$\mathrm{O\underline{V}}$	70.2	$\mathrm{O\underline{O}}$	69.3	$\mathrm{V\underline{O}O}$
		158.4	$\mathrm{V\underline{V}OV}$					68.9	$\mathrm{O\underline{O}V}$
		158.3	$\mathrm{V\underline{V}OO}$					68.0	$\mathrm{V\underline{O}V}$
		157.6	$\mathrm{O\underline{V}VV}$						
		157.4	$\mathrm{O\underline{V}VO}$						
		157.1	$\mathrm{V\underline{V}VV}$						
		157.0	$\mathrm{V\underline{V}VO}$						

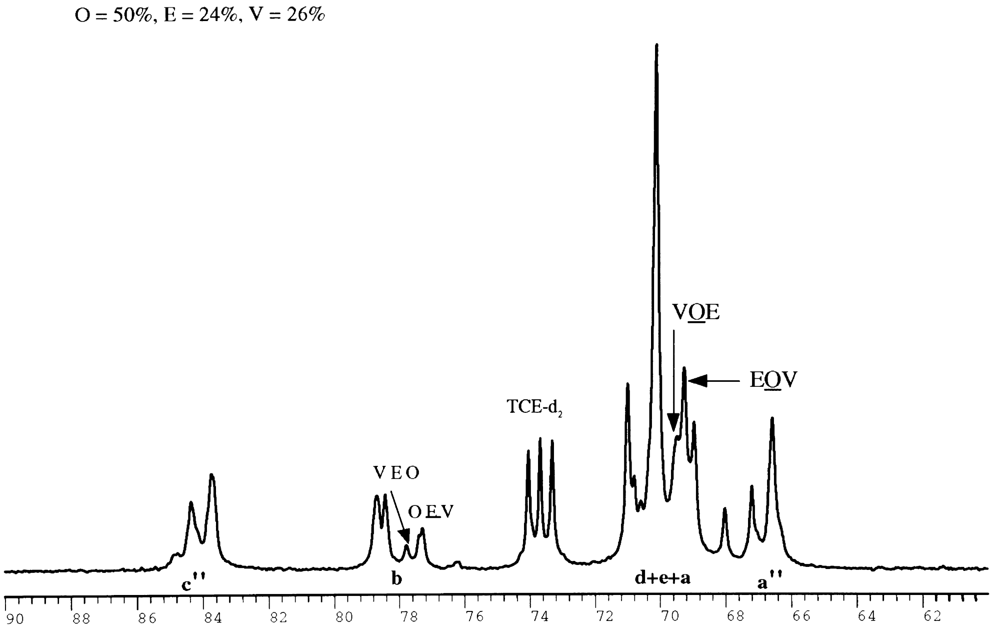


Fig. 7. Region between 62 and 90 ppm of the ^{13}C NMR spectrum in deuterated tetrachloroethane of the poly(oxy-1-chloromethylethylene-*co*-oxyethylene-*co*-oxy-1-methylene-ethylene)terpolymer in a comonomer ratio of 24:50:26.

discussed. Of the E-centred sequences, the OEV and VEO triads were empirically assigned on the basis of the EEE chemical shift and the effect that V and O units had on either the right or the left side. This effect was calculated from the assignments of EO and EV. At the chemical shifts calculated by this method, 77.8 and 77.4 ppm, triads VEO and OEV can be respectively found. Assuming a Bernouillian statistic, the intensities of these signals confirm this assignment. Of the O-centred sequences, the EOV and the VOE triads for carbon **e** still remain to be assigned. Empirical calculations indicate that EOV and VOO O must overlap, while VOE must correspond to the new signal at 69.5 ppm. Table 5 shows the new assignments.

The model studied next was poly(oxy-1-[*p*-benzyloxyphenoxy]methylethylene-*co*-oxy-1-chloromethyl-ethylene-*co*-oxyethylene)terpolymer in comonomer ratio of 21:29:50. It was assumed that the oxy-1-[*p*-benzyloxyphenoxy]methylethylene (P unit) has the same influence and chemical shift for the carbons studied as the p-phenylglycidylether. Fig. 8 shows the zone of its spectrum which corresponds to the aliphatic carbons in the main chain. Like the model above, most signals have already been assigned, so only new signals, obtained by combining three different structural units, are marked on this figure. Also like before, their assignment were made by taking into account the changes in the chemical shift originated by the different units and their relative positions. To confirm, we have also considered the integration of the deconvoluted spectrum, that fits fairly good with the calculated from the comonomer composition and the assumption of a Bernouillian statistic. The new assigned signals are collected in Table 5, in which a doublet due to the **c**′ carbon in the P unit can be observed. This carbon is dyad-sensitive, and the PP and EP dyads at 67.9 ppm have already been assigned. So, by elimination, the OP dyad can be assigned to the signal at 68.1 ppm. The intensities of these signals are also in accordance with those predicted by the statistics.

Table 5
Assignment of some of the triad sequences of methine (**b** and **b**′) and methylene carbon (**e**) in the main chain of the ^{13}C NMR spectrum of the poly(oxy-1-chloromethylethylene-*co*-oxyethylene-*co*-oxy-1-phenoxymethylethylene) copolymer

b		**b**′		**e**	
δ (ppm)	Triads	δ (ppm)	Triads	δ (ppm)	Triads
78.8	OEP	77.9	OPE	70.8	EOP POE
78.5	PEO	77.4	EPO	69.5	VOE
77.8	VEO	76.5	VPO OPV	69.3	VOP
77.4	OEV			69.2 69.0	EOV POV

Finally, the spectrum of poly(oxyethylene-*co*-oxy-1-methyleneethylene-*co*-oxy-1-phenoxymethylethylene)-terpolymer in a comonomer ratio of 50:22:28, represented in Fig. 9 enabled some triads corresponding to the **b**′ and **e** carbons to be assigned. Following a similar procedure as before, the signal at 76.5 ppm can be assigned to OPV and VPO triads from the carbon **b**′. However, triads VOP and POV from carbon **e** overlap with triads VOO and OOV at 69.3 and 69.0 ppm, respectively. These assignments were also confirmed by comparing statistical calculations and the

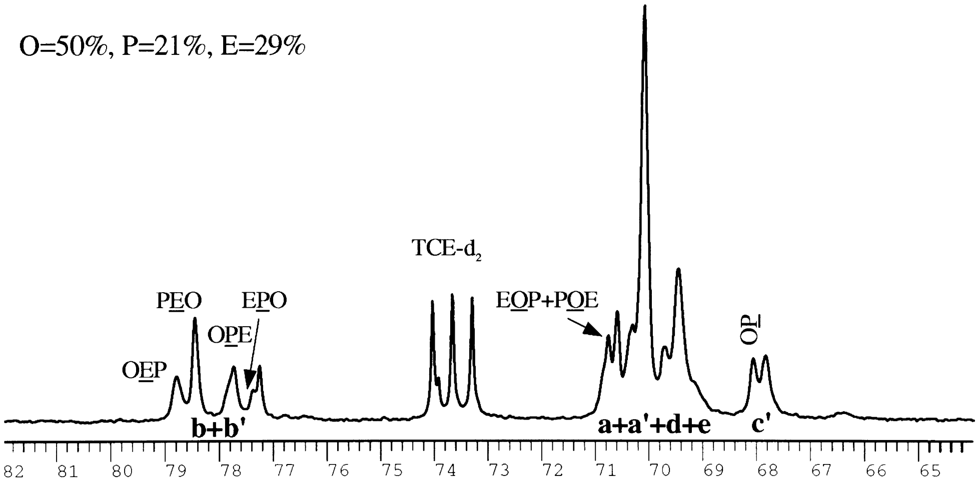


Fig. 8. Region between 65 and 82 ppm of the ^{13}C NMR spectrum in deuterated tetrachloroethane of the poly (oxy-1-[*p*-benzyloxyphenoxy]methylethylene-*co*-oxy-1-chloromethylethylene-*co*-oxyethylene)terpolymer in a comonomer ratio of 21:29:50.

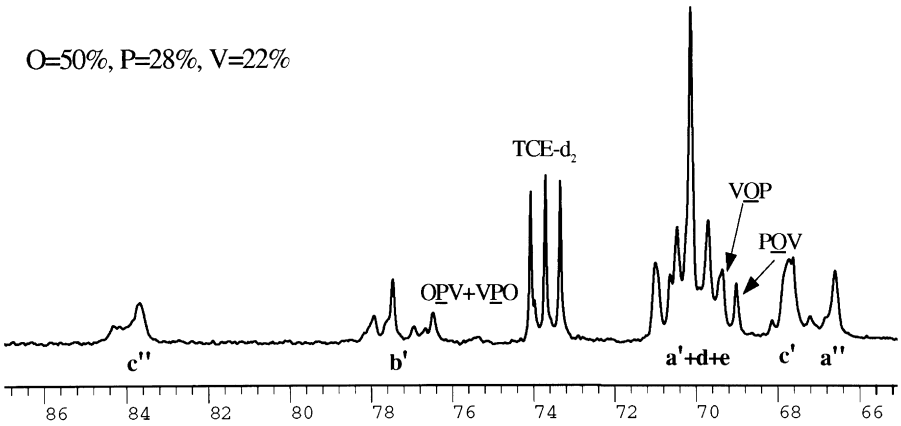


Fig. 9. Region between 66 and 86 ppm of the ^{13}C NMR spectrum in deuterated tetrachloroethane of the poly(oxyethylene-*co*-oxy-1-methyleneethylene-*co*-oxy-1-phenoxymethylethylene) terpolymer in a comonomer ratio of 50:22:28.

integration of deconvoluted spectra. Table 5 also shows the assignments.

All the assignments made here were confirmed by studying the spectra of some samples of modified PECH–PEO with phenolates in several comonomer percentages. The integrations of the different signals were made and compared with the calculations obtained from Bernouillian statistics leading to close values.

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