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Comonomer sequence assignment of the ^{13}C n.m.r. spectra of some poly(epichlorohydrin) derivatives obtained by nucleophilic substitution

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Poly(epichlorohydrin) [poly(oxy-1-chloro-methylethylene)] (PECH) has been modified chemically by basic nucleophiles, such as phenolate, producing dehydrochlorination as side reaction. The comonomer composition of the resulting poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethyl-ethylene-*co*-oxy-1-methyleneethylene) can be determined by quantitative ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy. Some polymeric models were synthesized in order to make accurate assignments, since most of the signals were not completely resolved. The various ^{13}C n.m.r. signals were assigned to comonomer sequences in the main chain, which were fitted to a Bernouillian statistical model. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Random and block copolyethers have numerous applications such as surfactants or polymeric electrolytes. Our most recent work deals with the preparation of functional polymers either by polymerization and copolymerization of functional monomers, or by chemical modification. Both procedures lead to similar functional polyethers although they have different advantages and drawbacks.

Ring-opening polymerization or copolymerization of *p*-functionalized glycidylic monomers by ionic-coordinative catalysts has been studied in previous works[1–4]. The modification of preformed polymers seems to be easier, since it is not necessary to synthesize the corresponding monomer. Moreover, the starting polymer can be chosen with the desired stereoregularity, molecular weight and polydispersity. However, some side reactions can take place during the modification process, leading to undesirable units remaining chemically attached to the polymer and which therefore cannot be removed.

Polymers with chloromethyl groups in the side chain are suitable starting materials for the synthesis of functional polymers, since these groups can be readily modified by substitution reaction with some nucleophilic agents under mild conditions. Of these polymers, poly(epichlorohydrin) is commercially available and its chemical modification has been studied extensively[5–9].

The modification of poly(epichlorohydrin) with highly basic nucleophiles, such as hydroxide or phenolates, involves dehydrochlorination as an undesired side reaction, so leading to vinylether units in the backbone. This undesired process was first observed by Nishikubo[10–11] with infra-red spectroscopy, although its extent was not quantified.

In the present paper we describe the microstructure of the polymers obtained from poly(epichlorohydrin) and sodium phenolate by ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy. From the spectra of a series of related polymers with several degrees of substitution and elimination, the various ^{13}C n.m.r. signals were assigned to the triad or dyad comonomer sequence of the terpolymer. Moreover, this technique enabled us to quantify the percentage of phenol-substituted, vinylether and remaining chloromethylated units, which cannot be determined directly by elemental analysis. By using resolution enhancement n.m.r. techniques, the stereosequences of some signals were also observed[12].

EXPERIMENTAL

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, and it was used freshly distilled.

Poly(epichlorohydrin) (PECH) (Aldrich)—inherent viscosity (η_{inh}) in *N*-methylpyrrolidone (NMP) of 234 ml g^{-1}, measured at a concentration of approximately 2 g l^{-1} at 30°C, weight-average molecular weight ($\bar{M}_w$) of 1 144 000 Da and polydispersity ($\bar{M}_w/\bar{M}_n$) of 2.49—was dried at 60°C under vacuum over P_2O_5.

Tetrabutylammonium bromide (TBAB) (synthesis grade, Fluka) was dried over P_2O_5 under vacuum at room temperature.

Phenylglycidylether (PGE) (Aldrich) was dried prior to use by fluxing it through an activated powder, 4 Å molecular sieve column.

Phenol (Probus), *p*-phenoxyphenol (Aldrich) and sodium hydride (60% dispersion in mineral oil, Aldrich) were used without previous purification.

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

PGE was polymerized with the aluminium isopropoxide/$ZnCl_2$ initiator system, following the reported procedure[13].

Substitution reaction of poly(epichlorohydrin) with sodium phenolate

Dry PECH (0.273 g, 2.95 mmol) was dissolved in anhydrous THF (15 ml) and a solution of sodium phenolate (0.343 g, 2.95 mmol) and dry TBAB (0.951 g, 2.95 mmol) in anhydrous THF (15 ml) was added under inert atmosphere. The reaction mixture was stirred at 60°C for 1 day in the dark. Then the modified polymer was filtered off to separate a very small amount of THF-insoluble fraction. The polymer solution was precipitated over water. The resulting polymer was purified by reprecipitating twice from THF over water and adding a small amount of 3-t-butyl-4-hydroxy-5-methylphenyl sulfide as a radical trapper in the last precipitation. The modified polymer was dried *in vacuo* at 50°C. Yield 98%. Modification degree 49% (from quantitative ^{13}C n.m.r. spectroscopy). Found chlorine content 9.02%.

The modification process was repeated with a reaction time of 4 and 7 days, giving polymers with a degree of modification of 60% and 61%, respectively.

The same procedure was applied to the preparation of poly(oxy-1-*p*-phenoxyphenoxymethylethylene-*co*-oxy-1-methyleneethylene) from PECH and sodium phenoxyphenolate. The degree of modification was 45% (from ^{13}C n.m.r. spectroscopy); the amount of chlorine was non-detectable. Yield 34%.

Elimination reaction of poly(epichlorohydrin) with sodium methoxide

Dry PECH (0.273 g, 2.95 mmol) was dissolved in 30 ml of anhydrous THF, and sodium methoxide (0.239 g, 4.43 mmol) was added under inert atmosphere. The reaction mixture was stirred at 60°C for 1 day in the dark. The polymer solution was precipitated over water. The resulting polymer was purified by reprecipitating twice from THF over water and was then dried *in vacuo* at 50°C. The yield of poly(oxy-1-methyleneethylene) was almost quantitative.

The procedure above was repeated with use of a lower proportion of sodium methoxide in order to obtain poly(oxy-1-chloromethylethylene-*co*-oxy-1-methyleneethylene) copolymers with different degrees of elimination.

Reaction of poly(epichlorohydrin) with sodium methoxide and phenolate

Dry PECH (1.769 g, 19.1 mmol) was dissolved in 50 ml of anhydrous THF, and sodium methoxide (0.516 g, 9.6 mmol) and sodium phenolate (1.109 g, 9.6 mmol) were added under inert atmosphere. The reaction mixture was stirred at 60°C for 1 day in the dark. The polymer solution was precipitated over water. The resulting polymer was purified by reprecipitating twice from THF over water and was then dried *in vacuo* at 50°C. Yield 60%. Degree of elimination 37%, degree of substitution 47% (from ^{13}C n.m.r. spectroscopy). Chlorine content 4.70%.

The procedure above was repeated with different proportions of sodium methoxide and phenolate in order to obtain poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethylethylene-*co*-oxy-1-methyleneethylene) with several comonomer percentages.

Instrumentation

^{13}C n.m.r. spectra were recorded on a Varian Gemini 300 spectrometer at 75.4 MHz, using 1,1,2,2-tetrachloroethane-d_2 as solvent. Chemical modification and elimination degrees were determined by integrating ^{13}C n.m.r. signals under quantitative conditions, that is with the sequence

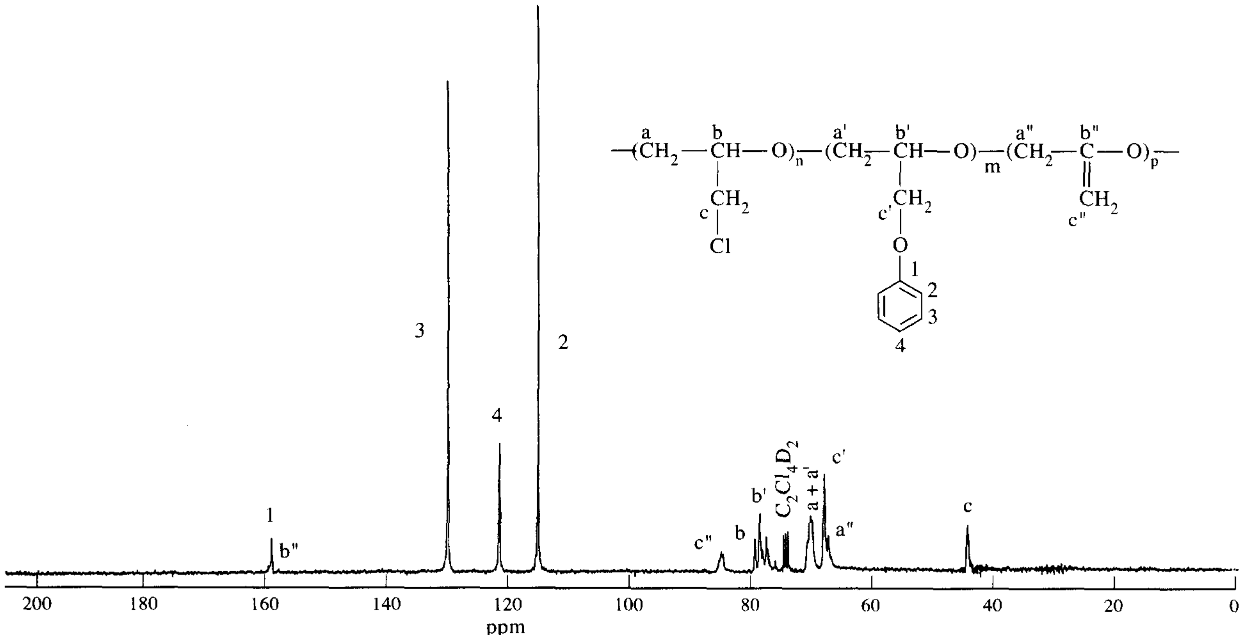

Figure 1 ^{13}C n.m.r. spectrum of poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethylethylene-*co*-oxy-1-methyleneethylene). Comonomer molar composition: 29:49:22

inverse gated decoupling and a delay time of 3 s. The resolution was enhanced by using LB = 1, zero-filling and the Lorentz–Gaussian transformation technique[14] with factors of GF = 0.1 and GFS = 0.05.

Chlorine content was determined by Schöninger's method, which involves combustion of a sample on a platinum wire in a closed vessel.

RESULTS AND DISCUSSION

As has been previously mentioned, one of the main advantages in the modification of a preformed polymer is that its stereo- and regioregularity can be selected and no changes in the microstructure are expected during the process. In our case, the starting polymer was a commercial, completely regioregular and atactic PECH, so any study of the microstructure of modified polymers should deal mainly with the comonomer percentages and their distribution along the main chain.

Previous attempts to find the best reaction conditions for modifying PECH with sodium phenolate led us to the procedure described in the Experimental section. Modification reactions performed at 4 and 7 days led to similar modification degrees (60%), which suggested that a plateau had been reached. Therefore, some chloromethylated units always remain unchanged in the final polymer.

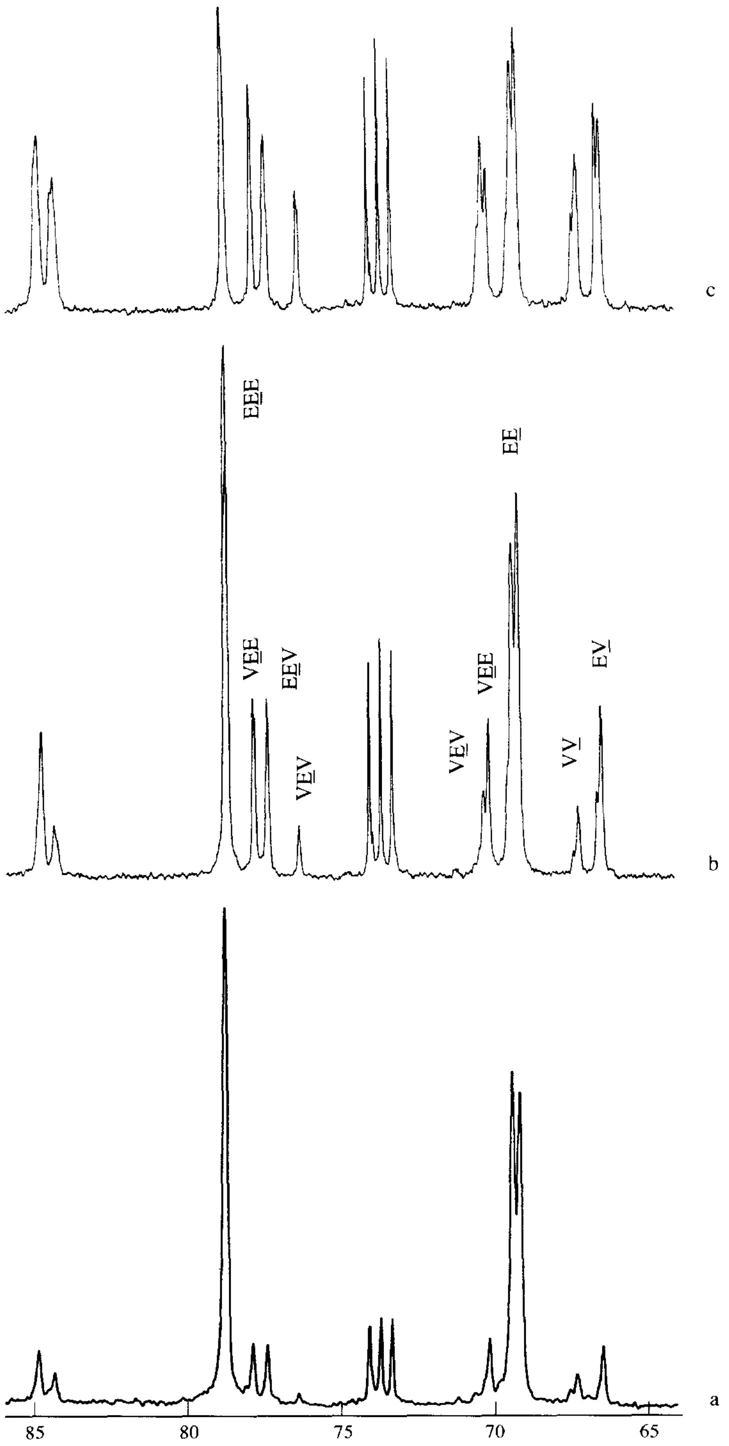

Figure 2 ^{13}C n.m.r. spectra (region between 65 and 85 ppm) of poly(oxy-1-chloromethylethylene-*co*-oxy-1-methyleneethylene). Comonomer molar composition: 90:10 (a), 80:20 (b) and 60:40 (c)

Furthermore, elimination processes usually compete with nucleophilic substitution, particularly when strong basic nucleophiles are used. So, in this reaction, in addition to functionalized phenolate and some remaining chloromethylated units, some vinylether can be expected. In previous works, chlorine elemental analysis enabled the proportion of non-substituted units to be calculated. However, in this case, elemental analysis is not a suitable method for accurate evaluation of the different ratios of the three comonomers and ^{13}C n.m.r. spectroscopy must be used.

Figure 1 shows the ^{13}C n.m.r. spectrum of one of the polymers modified with phenol. As can be seen, the highest signals correspond to the aromatic group which is introduced, but resonances at 158.5 and 84.3 ppm assigned to vinylether are also appreciable. Signals appearing in the region between 65 and 80 ppm are due to the carbons in the main chain. Moreover, at 43.6 ppm the methylene of the chloromethyl group can also be observed.

The splitting of the resonances associated with the carbons in the main chain can be attributed to the terpolymer sequence. A complete analysis of these fine structures can potentially provide information about polymer composition and about the influence of neighbouring units on the modification process. In this sense, very little information is given about copolymer sequences in PECH copolymers[15,16].

The overall terpolymer composition can be obtained by integrating the 84 ppm signal (CH_2 in the vinylether units, **c**″), the signals located at 75–79 ppm (methine carbons in the main chain, **b** and **b**′) and the 43.6 ppm signal (chloromethyl group, **c**) of the ^{13}C n.m.r. spectrum recorded under quantitative conditions.

For the comonomer sequence to be determined, a large number of triads, which cannot easily be assigned, need to be identified. Therefore, we compared the spectra of several polymeric models, most of which were synthesized for this purpose:

1. Poly(oxy-1-methyleneethylene) homopolymer, prepared from PECH and sodium methoxide as strong base. The ^{13}C n.m.r. spectrum of this polymer shows only three peaks: at 157.2 ppm (quaternary carbon, **b**″), at 84.3 ppm (methylene carbon, **c**″) and at 67.3 ppm (methylene carbon, **a**″).
2. PECH, commercial polymer. It shows signals at 78.7 ppm (methine carbon, **b**), at 69 ppm (methylene carbon in the main chain, **a**, split into two signals due to tacticity) and at 43.6 ppm (chloromethyl group, **c**).
3. Poly(phenylglycidylether) (PPGE) synthesized from PGE by using $AlP/ZnCl_2$ as initiator system[17]. The spectrum shows three peaks centred at 78.1 ppm (methine carbon, **b**′), at 69.8 ppm (methylene carbon in the main chain, **a**′) and at 67.8 ppm (pendant chain methylene carbon, **c**′). The signals corresponding to the carbons in the main chain are split off due to stereosequences.
4. Poly(oxy-1-chloromethylethylene-*co*-oxy-1-methylene-ethylene) in several comonomer ratios, synthesized from PECH by using different proportions of sodium methoxide. The ^{13}C n.m.r. spectra are shown in *Figure 2* (region between 65 and 85 ppm).
5. Poly(oxy-1-*p*-phenoxyphenoxymethylethylene-*co*-oxy-1-methylene-ethylene) obtained from PECH and sodium *p*-phenoxyphenolate in an equimolar ratio. In this case, no unmodified chloromethylated units remain in the polymer, as can be seen in *Figure 3* by the absence of the 43.6 ppm resonance from the chloromethyl group of ECH.
6. Poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxy-methylethylene-*co*-oxy-1-methyleneethylene) with several comonomer percentages, obtained by reacting PECH with mixtures of sodium phenolate and sodium methoxide in different ratios. *Figure 4* shows the zone between 65 and 85 ppm of their ^{13}C n.m.r. spectra.

The sequence placement can be determined taking into account the different possibilities of the triad sequences centred in epichlorohydrin (named E), in the vinylether moiety (named V) and in phenylglycidylether (named P).

Thus, for triad-sensitive carbons (methine and quaternary carbons in the main chain), 27 triads can be distinguished,

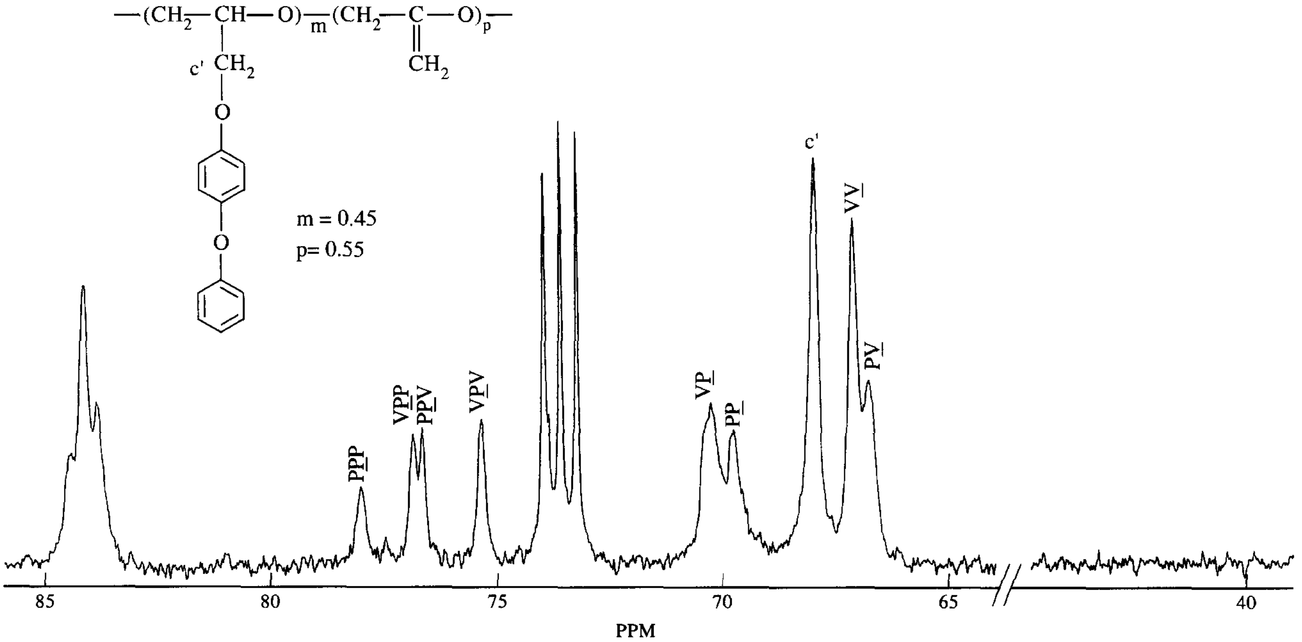

Figure 3 ^{13}C n.m.r. spectrum of poly(oxy-1-*p*-phenoxyphenoxymethyl-ethylene-*co*-oxy-1-methyleneethylene). Comonomer molar composition 45:55.

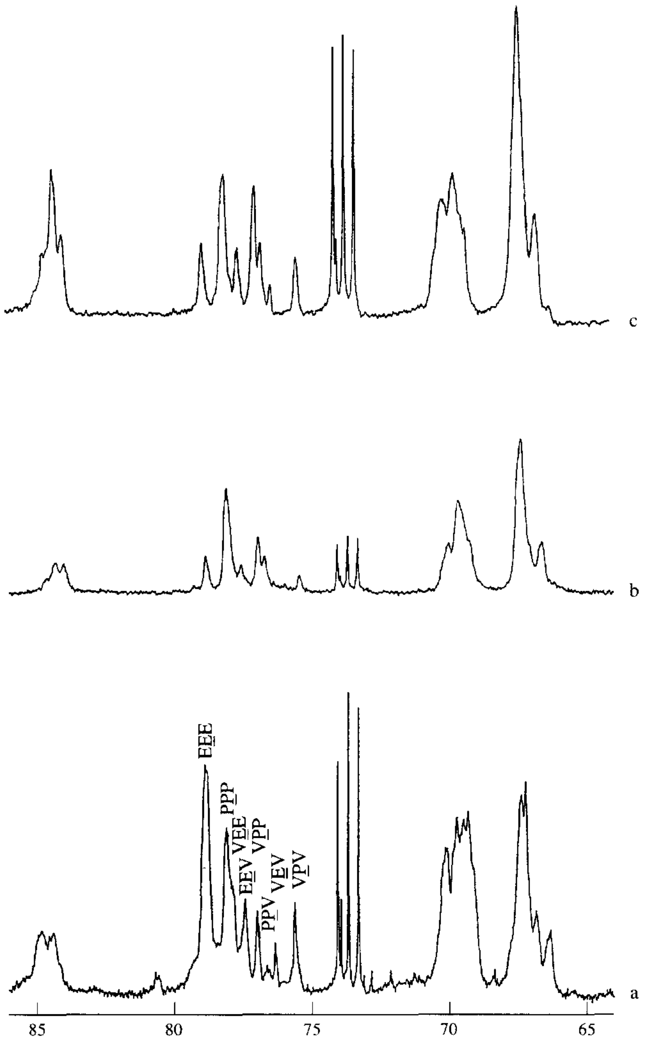

Figure 4 ^{13}C n.m.r. spectra (region between 65 and 85 ppm) of poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethylethylene-*co*-oxy-1-methyleneethylene). Comonomer molar composition: 49:30:21 (a), 18:61:21 (b) and 16:47:37 (c)

among which nine are centred in epichlorohydrin (EEE, EEP, PEE, PEP, EEV, VEE, VEV, PEV and VEP), nine in the vinylether moiety (VVV, VVE, EVV, EVE, PVV, VVP, PVP, PVE and EVP) and nine in phenylglycidylether (PPP, PPE, EPP, EPE, PPV, VPP, VPV, EPV and VPE). It is important to note that the non-symmetry of the environment leads to non-equivalent triads, such as PPE and EPP, so different ^{13}C chemical shifts should be expected.

Furthermore, methylene carbons in the main chain are first expected to be dyad-sensitive. Therefore, there are nine different possibilities (EE, VE, PE, VV, EV, PV, PP, EP and VP) although, depending on the neighbouring groups and the magnetic field used, sensitivities could be higher.

In *Figure 1*, the most split and the best resolved signals between 75 and 80 ppm correspond to the methine carbons in the main chain. The **b** and **b′** signals, which are arise from epichlorohydrin and phenylglycidylether units respectively, each provide nine triads. From the homopolymer spectra we can unmistakably assign the EEE triad (78.7 ppm), which can be split off with resolution enhancement techniques to show stereosequences[12], and the PPP triad (78.1 ppm), which can also be split off at higher resolution[17].

In *Figure 2* it was possible to assign the EEV, VEE and VEV triads by comparing the different intensities of signals in each spectrum. Thus, the signal at 76.3 ppm was assigned to the VEV triad, since its intensity in relation to the other signals increases as the percentage of elimination increases. Both EEV and VEE triads should have the same area for statistical reasons, such as is measured. Although empirical calculations show that the central methine carbon in both triads undergoes the same chemical shift, it was assigned by taking into account the fact that, in the VEE triad, the oxygen in the β position has a stronger deshielding effect because of its higher positive character (mesomeric effect).

Figure 3 shows the region between 75 and 80 ppm of the poly(oxy-1-*p*-phenoxyphenoxymethylethylene-*co*-oxy-1-methyleneethylene) spectrum, where the four triads centred in the substituted unit (PPP, PPV, VPP and VPV) can be observed. From the spectrum of the PPGE homopolymer, PPP was assigned to the signal at 78.1 ppm. On the basis of the shielding caused by the vinylether neighbouring groups, as observed in epichlorohydrin-centred triads, VPV should correspond to the signal at 75.5 ppm. A similar explanation to the one above enabled VPP and PPV triads to be assigned to 77.0 and 76.8 ppm respectively.

In *Figure 4*, 18 different triads of the terpolymer in the region between 75 and 80 ppm, which correspond to the methine carbons **b** and **b′**, should appear. Eight of them are already assigned. Not all expected signals can be clearly distinguished in the spectra because some of them overlap to give broad peaks. Empirical calculations do not distinguish between PPP and PPE or EPP and EPE because the phenoxide or chlorine groups are in a ϵ position, which is too far removed from the methine carbon. The same can be said of the EEP, PEE and PEP triads, which also overlap with the EEE triad, and of the remaining EPV, VPE, PEV and VEP triads which are also overlapped: EPV overlaps with PPV, VPE with VPP, PEV with EEV, and VEP with VEE. This overlapping makes the peaks broader. *Table 1* shows the assignments of all the comonomer sequence triads of the methine and quaternary carbons.

The different intensities of the triads discussed above can be compared in *Figure 4*. The comparison between spectra *a* and *b* shows an appreciable increase in the degree of modification of the polymer in *b*, since the PPP triad rises and EEE diminishes. When comparing spectra *b* and *c* (they both have the same degree of modification but the latter has a greater degree of elimination) the intensity of the VPP, PPV and VPV triads can be seen to increase quite considerably.

Up to now, no mention of the quaternary carbon signal in the vinylether units, **b**″, has been made. In the homopolymer, this signal appears at 157.2 ppm (VVV) and, as expected, has a low intensity. When PECH is modified with phenolates, this signal is split due to the comonomer sequence, giving signals between 157 and 160 ppm. The quaternary carbon of the aromatic ring appears in the same region, thus preventing the sequence triads from being analysed accurately (see *Figure 5a*). However, in the spectra of poly(oxy-1-chloromethylethylene-*co*-oxy-1-methylene-ethylene) there is a signal other than the VVV signal further downfield, which was assigned to the EVE triad. By taking into account the evolution of the intensity of both signals with the comonomer ratio (the peak at 157.2 increases with the vinylic moiety ratio), VVE and EVV triads overlap with the VVV signal (see *Figure 5b–d* and *Table 1*).

It is difficult to obtain additional information from methylene carbons in the main chain in the terpolymer spectra, since overlapped signals appear. In *Figure 4* broad peaks at about 70 ppm (**a** and **a**′) and 66 ppm (**a**″ overlapped with **c**′) can be observed, in which sequence sensitivity cannot be well appreciated. Nevertheless, a careful study of the line intensities made from spectra of poly(oxy-1-chloromethylethylene-*co*-oxy-1-methyleneethylene) (see *Figure 2*) indicates that the region between 65 and 72 ppm (**a** and **a**″) shows sequence effects and tacticity mixed together. Signal **a** is split into two main resonances. The one at higher field appears as a doublet. Because of its high intensity and chemical shift, it was assigned to the EE dyad, which is split because of its tacticity in the same way as for the homopolymer. Tacticity dyads were assigned according to the literature[12] (see *Table 2*). Signals at 70.1 and 70.3 ppm should correspond to the VE dyad, since its area increases with the elimination ratio. Nevertheless, this signal shows an additional splitting when the ratio of elimination increases, giving in *Figure 2b* and *c* triad sensitivity. Both VEV and VEE triads were assigned by comparing their relative areas and comonomer composition.

Furthermore, signal **a**″ (between 66 and 68 ppm) has two main resonances. One of them is the dyad VV at lower field, assigned in accordance with the homopolymer model shift, and whose area increases with the elimination ratio. The other signal corresponds to the EV dyad, and was assigned in the same manner as before. Both signals seem to suggest that the sensitivity is higher.

Finally, methylene pendant carbons must be taken into account. In *Figure 1*, at 43.6 ppm there is a wide-shaped peak, which corresponds to the chloromethylated group (**c**), in which fine structure due to different sequences is not resolved. Peaks corresponding to the carbons **c**′ and **a**″ (between 66 and 68 ppm) overlap partially, as mentioned above, and a broad signal appears. The methylene carbon from the vinylether unit (**c**″) shows a broad resonance between 83 and 85 ppm, which may be split by different comonomer sequences. In *Figure 2*, the greater simplicity of the polymer (it only contains V and E units) allows this signal to be analysed further. As can be seen, two main resonances appear. The one at higher field was assigned to the VV dyad because of its chemical shift and the fact that its intensity increases with the ratio of elimination. The other one corresponds to the EV dyad.

By integrating the methine carbon triads (**b**) and methylene carbon dyads (**a**) of the poly(oxy-1-chloromethyl-ethylene-*co*-oxy-1-methyleneethylene) spectra (*Figure 2*), Bernouillian statistics for the elimination reaction has been fitted, since calculated probabilities and relative integrations, collected in *Table 3*, are in good agreement.

From spectra collected in *Figure 4b* and *c*, single integrations of the methine carbon triads (**b**) are difficult

Table 1 Assignment of comonomer triad sequences of methine carbons centred in the epichlorohydrin (**b**) and phenylglycidylether (**b**′) units, and quaternary carbons centred in the vinylether unit (**b**″) in the ^{13}C n.m.r. spectra of poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethyl-ethylene-*co*-oxy-1-methyleneethylene)

b		**b**′		**b**″	
δ (ppm)	Sequence	δ (ppm)	Sequence	δ (ppm)	Sequence
78.6	EEE EEP PEE PEP	78.1	PPP PPE EPP EPE	159.0	PVP
77.8	VEE VEP	77.0	VPP VPE	158.5	VVE EVV EVE
77.3	EEV PEV	76.8	PPV EPV	157.2	VVV
76.3	VEV	75.6	VPV	—	VVP PVV EVP PVE

to obtain. However, four broad non-resolved signals including several overlapped triads could be integrated either directly or by using deconvolution procedures (*Table 3*). Hence, the probabilities of these four groups were calculated by Bernouillian statistics. The good agreement observed among calculated probabilities and relative integration also corroborates Bernouillian statistics in the case of the substitution process.

Therefore, the environment of an ECH unit does not seem to affect its ability to experience substitution or elimination, which must be due to the longer distance of the chlorine atom to the main chain. It should be noted that in polymers like poly(vinyl chloride), where the chlorine atom is closer to the main chain, an important effect of the environment on the substitution reaction has been reported[18].

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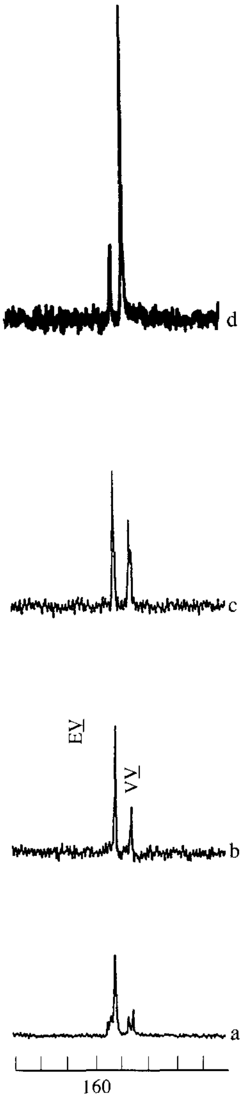

Figure 5 ^{13}C n.m.r. spectra (region between 140 and 180 ppm) of poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethylethylene-*co*-oxy-1-methyleneethylene), comonomer composition: 16:46:38 (a) and poly(oxy-1-chloromethylethylene-*co*-oxy-1-methyleneethylene), comonomer molar composition: 80:20 (b), 60:40 (c) and 25:75 (d)

Table 2 Assignment of dyad and triad sequences of methylene carbon in the main chain centred in the epichlorohydrin (**a**), phenylglycidylether (**a′**) and vinylether (**a″**) units in the ^{13}C n.m.r. spectra of poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethylethylene-*co*-oxy-1-methyleneethylene)

a		**a′**		**a″**	
δ (ppm)	Sequence	δ (ppm)	Sequence	δ (ppm)	Sequence
69.4	m-$\mathrm{E\underline{E}}$	70.2	$\mathrm{V\underline{P}}$	67.3	$\mathrm{V\underline{V}}$
69.1	r-$\mathrm{E\underline{E}}$	69.8	$\mathrm{P\underline{P}}$	66.5	$\mathrm{E\underline{V}V}$
70.3	$\mathrm{V\underline{E}V}$	—	$\mathrm{E\underline{P}}$	66.4	$\mathrm{E\underline{V}E}$
70.1	$\mathrm{V\underline{E}E}$			66.7	$\mathrm{P\underline{V}}$
—	$\mathrm{P\underline{E}}$				

Table 3 Analysis of ^{13}C NMR spectra triad sequences for poly(oxy-1-chloromethylethylene-*co*-oxy-1-methyleneethylene) and poly(oxy-1-chloromethylethylene-*co*-oxy-1-phenoxymethy-ethylene-*co*-oxy-1-methyleneethylene) by Bernouillian statistics

Figure	Comonomer ratio^a (mol%)	Sequence	Probability (calc., %)	Integration (%)	Deconvoluted (%)
Figure 2a	E = 90	$E\underline{E}E$	81	83	
	V = 10	$V\underline{E}E$	9	9	
		$E\underline{E}V$	9	8	
		$V\underline{E}V$	1	—	
Figure 2b	E = 80	$E\underline{E}E$	64	65	
	V = 20	$V\underline{E}E$	16	16	
		$E\underline{E}V$	16	15	
		$V\underline{E}V$	4	4	
Figure 2c	E = 62	$E\underline{E}E$	38	40	
	V = 38	$V\underline{E}E$	24	24	
		$E\underline{E}V$	24	24	
		$V\underline{E}V$	14	12	
Figure 4b	E = 18	$E\underline{E}E + E\underline{E}P + P\underline{E}E + P\underline{E}P$	14	11	11
	P = 61	$P\underline{P}P + P\underline{P}E + E\underline{P}P + E\underline{P}E + V\underline{E}E + V\underline{E}P + E\underline{E}V + P\underline{E}V$	56	52	52
	V = 21	$V\underline{P}P + V\underline{P}E + P\underline{P}V + E\underline{P}V + V\underline{E}V$	27	33	31
		$V\underline{P}V$	3	4	6
Figure 4c	E = 16	$E\underline{E}E + E\underline{E}P + P\underline{E}E + P\underline{E}P$	10	12	13
	P = 47	$P\underline{P}P + P\underline{P}E + E\underline{P}P + E\underline{P}E + V\underline{E}E + V\underline{E}P + E\underline{E}V + P\underline{E}V$	42	44	44
	V = 37	$V\underline{P}P + V\underline{P}E + P\underline{P}V + E\underline{P}V + V\underline{E}V$	38	34	34
		$V\underline{P}V$	10	10	9

^{a}Calculated from ^{13}C n.m.r. spectra in quantitative conditions and checked by chlorine elemental analysis. E = epichlorohydrin unit, P = phenylglycidylether unit and V = vinylether unit

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REFERENCES

1. Ronda, J. C., Serra, A., Mantecón, A. and Cádiz, V., *Reactive and Functional Polymers*, 1995, **28**, 1.
2. Ronda, J. C., Serra, A. and Cádiz, V., *Macromol. Chem. Phys.*, 1997, **198**, 2917.
3. Ronda, J. C., Serra, A. and Cádiz, V., *Macromol. Chem. Phys.*, 1997, **198**, 2935.
4. Ronda, J. C., Serra, A. and Cádiz, V., *Macromol. Chem. Phys.*, in press.
5. Reina, J. A., Cádiz, V., Mantecón, A. and Serra, A., *Angew. Makromol. Chem.*, 1993, **209**, 95.
6. Galià, M., Mantecón, A., Cádiz, V. and Serra, A., *J. Polym. Sci., Polym. Chem. Ed.*, 1994, **32**, 829.
7. Nuyken, O., Latterman, G., Dannhorn, W. and Vogel, R., *Makromol. Chem.*, 1992, **193**, 1057.
8. Piercourt, S., Lacoudre, N., Le Borgne, A., Spassky, N., Friedrich, C. and Noël, C., *Makromol. Chem.*, 1992, **193**, 705.
9. Pugh, C. and Percec, V., *ACS Symp. Ser.*, 1988, **364**, 97.
10. Nishikubo, T., Iizawa, T., Mizutani, Y. and Okawara, M., *Makromol. Chem., Rapid Commun.*, 1982, **3**, 617.
11. Nishikubo, T., Iizawa, T., Sugawara, Y. and Shimokawa, T., *J. Polym. Sci., Polym. Chem. Ed.*, 1986, **24**, 1097.
12. Cheng, H. N. and Smith, D. A., *J. Appl. Polym. Sci.*, 1987, **34**, 909.
13. Ronda, J. C., Serra, A., Mantecón, A. and Cádiz, V., *Acta Polym.*, 1996, **47**, 269.
14. Ferrige, A. G. and Lindon, J. C., *J. Magn. Reson.*, 1978, **31**, 337.
15. Cheng, H. N. and Smith, D. A., *Makromol. Chem.*, 1990, **192**, 267.
16. Reina, J. A., Serra, A., Mantecón, A. and Cádiz, V., *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 941.
17. Ronda, J. C., Serra, A., Mantecón, A. and Cádiz, V., *Polymer*, 1995, **36**, 471.
18. Millán, J. L., Martínez, G., Mijangos, C. and Gómez-Elvira, J. M., *Makromol. Chem. Macromol. Symp.*, 1989, **29**, 185.