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# New evidences of the degradation mechanism of poly(oxy-1-chloromethylethylene) with basic reagents: studies with poly(oxy-1-chloromethyl-ethylene-*co*-oxyethylene)

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## Abstract

This is an extension of our previous work on mechanistic studies of the degradation of the main chain during the chemical modification of poly(oxy-1-chloromethylethylene) (PECH) with phenolate to similar studies on the modification of poly(oxy-1-chloromethylethylene-*co*-oxyethylene) (PECH–PEO) with the same reagent. This polymer has been chemically modified with phenolate in the presence of a quaternary ammonium salt, i.e. tetrabutylammonium bromide (TBAB). Several reaction conditions were tested to provide the highest modification degrees with the minimum main-chain cleavage. The substitution of chlorine by phenolate was found to be accompanied by elimination reactions that led to vinylether moieties. The $^{13}$C NMR technique was used to identify the different terminal groups arising from this cleavage. The nature of these groups confirmed that cleavage was caused by nucleophilic attack on the units neighbouring vinylic ones, mainly on the $V\underline{V}$ dyads. The results are consistent with those obtained from the modification reaction of poly(oxy-1-chloromethylethylene) (PECH) with phenolate. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Degradation mechanism; Poly(oxy-1-chloromethyl-ethylene-*co*-oxyethylene); $^{13}$C NMR

## 1. Introduction

Chlorine-containing polymers are suitable starting materials for synthesizing new functional polymers with a wide range of applications. Poly(vinyl chloride) (PVC) [1], poly(chloromethylstyrene) (PCMS) [2], poly(oxy-1-chloromethylethylene) (PECH) [3,4] and its copolymer with ethylene oxide (PECH–PEO) [5] are particularly interesting because they are commercially available and have chlorine atoms which can be nucleophilically substituted. The effectiveness of this kind of process is greater when chlorine is not directly attached to the main chain. Polymers containing chloromethyl units are therefore among the most promising starting materials for synthesizing functional polymers.

In previous papers we studied the chemical modification of PECH with phenolate to find reaction conditions to produce highly modified polymers and reduce side-reactions like backbone degradation. On the basis of the end-groups detected by NMR spectroscopy, we proposed a mechanism to explain the degradative scission of the main chain [6]. Moreover, we accurately characterized the microstructure of the modified polymer, paying particular attention to the comonomer distribution, to see whether the statistics of the modification reaction depend on the chemical microenvironment [7].

This paper aims to modify the 1:1 PECH–PEO copolymer with phenolate to investigate further the degradative scission observed in PECH, since the presence of ethylene oxide units may provide additional information to confirm the postulated mechanism. Moreover, modifying the PECH–PEO copolymer must lead to polymers with a flexible and polar backbone and with lower proportion of aromatic rings than the modified PECH homopolymer. These polymers could be used, when conveniently cross-linked and functionalized, as solid supports for synthesizing compound libraries for biological screening by the combinatorial technique [8] or as polymeric reagents, catalysts or chromatographic stationary phases [2].

## 2. Experimental section

### 2.1. Materials

Hexane was dried by refluxing over $CaH_2$ and distilled

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Table 1
Chemical modification of PECH–PEO with sodium phenolate at 60°C in THF using TBAB as phase-transfer agent

| Exp. | PhONa/Cl ratio (mol) | Time (d) | Yield (%) | Degree of Subs. (%)[a] | Degree of Elim. (%)[a] | $\bar{M}_w$ ($\times 10^{-5}$)[b] | $\bar{M}_w/\bar{M}_w$ est.[c] |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 91 | 40 | 12 | 10.7 | 1.0 |
| 2 | 1 | 4 | 88 | 57 | 17 | 11.2 | 0.9 |
| 3 | 2 | 1 | 98 | 63 | 20 | 11.7 | 1.0 |
| 4 | 2 | 4 | 92 | 74 | 20 | 9.3 | 0.8 |
| 5 | 2 | 7 | 50 | 78 | 12 | 1.5 | 0.1 |
| 6 | 4 | 4 | 64 | 78 | 16 | 6.3 | 0.5 |

[a] Calculated from $^{13}$C NMR in quantitative conditions.

[b] Determined by SEC-MALLS.

[c] $\bar{M}_w$ est. calculated from the molecular weight of the starting PECH–PEO and the degrees of substitution and elimination when it is assumed that no cleavage or crosslinking occurs.

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), used as a phase transfer agent, was dried over $P_2O_5$ under vacuum at room temperature. Dry phenol (Probus) was prepared by fractional distillation. 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.

Sodium phenolate was prepared in a Schlenk flask by dropwise addition of a solution of phenol in THF over a suspension of pure NaH in anhydrous hexane under argon. Phenolate was filtered off under argon and washed several times with a mixture of hexane and THF. The solvent was eliminated under vacuum and the sodium phenolate was stored in a Schlenk flask under an inert atmosphere.

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

Poly(oxyethylene-*co*-oxy-1-methyleneethylene) 1:1 copolymer was synthesized from PECH–PEO and sodium methoxide following a previously described procedure [7].

### 2.2. Substitution reaction of poly(oxy-1-chloromethylethylene-co-oxyethylene) with sodium phenolate

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 inert atmosphere. The reaction mixture was stirred at 60°C for 4 days in the dark. The polymer solution was then precipitated into water. The resulting polymer was purified by reprecipitating twice from THF into water, and a small amount of 3-*t*-butyl-4-hydroxy-5-methylphenyl sulphide was added, 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% (determined by quantitative $^{13}$C NMR spectroscopy). $\bar{M}_w = 1\,120\,000$ Da.

The modification process was repeated at different reaction times and with several proportions of phenolate/active chlorine. The results are shown in Table 1.

### 2.3. Kinetic studies

#### 2.3.1. Elimination of PECH and PECH–PEO with sodium methoxide

Dry PECH (1.00 g, 10.8 mmol) and PECH–PEO (1.00 g, 7.3 mmol) were dissolved in two Schlenk flasks in anhydrous THF (50 mL). Equimolar solutions of sodium methoxide in 25 mL of THF were added with conventional inert handling techniques. The mixture was magnetically stirred and kept at 60°C. Samples were taken through a syringe at predetermined times. The polymer samples were precipitated into water, dried under vacuum and analysed by quantitative $^{13}$C NMR spectroscopy.

#### 2.3.2. Substitution of PECH–PEO with sodium phenolate in presence of TBAB

PECH–PEO (12.3 mg, 0.09 mmol) were dissolved in anhydrous deuterated THF in a septum valve sealed NMR tube. 29.0 mg of TBAB (0.09 mmol) and 10.5 mg of sodium phenolate (0.09 mmol) were then added under inert anhydrous conditions. The evolution of the reaction was followed by recording $^{13}$C NMR spectra at different times with the tube maintained at 60°C.

### 2.4. Degradation essays of poly(oxyethylene-co-oxy-1-methyleneethylene)

#### 2.4.1. Degradation with TBAB

Poly(oxyethylene-*co*-oxy-1-methyleneethylene) (0.5 g, 5 mmol) and 1.62 g of TBAB (5 mmol) were dissolved in 25 mL of anhydrous THF. The mixture was heated at 60°C until a notable decrease in the viscosity was observed (10 days). A sample of this mixture was dried under vacuum and analysed by $^{13}$C NMR.

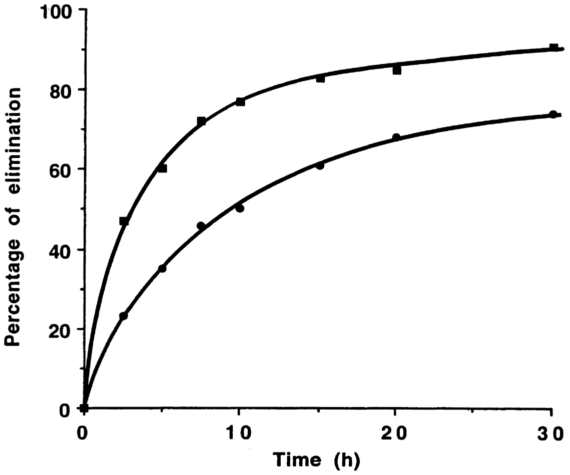


Fig. 1. Evolution of eliminated units against reaction time in the treatment of PECH (●) and PECH–PEO (■) with sodium methoxide at 60°C in THF.

### 2.4.2. Degradation with sodium phenolate

Poly(oxyethylene-*co*-oxy-1-methyleneethylene) (0.5 g, 5 mmol), 1.62 g of TBAB (5 mmol) and 0.58 g of sodium phenolate (5 mmol) were dissolved in 25 mL of anhydrous THF and the mixture was heated at 60°C. After 10 days the polymer was solvent-dried and analysed by $^{13}$C NMR.

### 2.5. 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 a solvent. The degrees of substitution and elimination were determined by integrating $^{13}$C NMR signals under quantitative conditions i.e. with inverse gated decoupling sequence and a delay time of 3 s. Resolution was enhanced by using an LB = 2, *zero-filling* and the Lorentz–Gaussian transformation technique [9], with GF = 0.1 and GFS = 0.05.

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

Weight average molecular weights and polydispersities were determined with a SEC-MALLS system, made up of an HPLC Waters 510 pump, three serial columns (Shodex K-80M, PLgel 5μ MIXED-D and PLgel 3μ MIXED-E) and one precolumn (Shodex K-800 P). Two detectors were placed after the columns, a laser-light scattering detector (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 a solvent (MALLINCKRODT ChromAR HPLC), flux of 1.0 mL/min, helium as degasser and ca. $3 \times 10^{-4}$ g of sample injected via a 100 μL loop.

## 3. Results and discussion

The modification of PECH with phenolate was first reported by Nishikubo and co., [10] but degrees of modification were low and the polymeric main chain was usually considerably degraded. Results are better when the procedure uses hydroxide-free sodium phenolate and strictly anhydrous conditions [6]. However, a dehydrochlorination side-reaction leading to vinylether units takes place to a non-negligible extent. Moreover, there is a degradative chain-scission involving these vinylic units. A degradation mechanism has been proposed. In view of these previous results, our present study attempted to confirm this degradative chain-scission mechanism by $^{13}$C NMR spectroscopy end-group analysis of the products obtained in some specially designed experiments. $^{1}$H NMR spectroscopy gave no additional information because of the overlapping and poor resolution of signals corresponding to end-groups and main chain protons. Also, PECH–PEO 1:1 copolymer has been chemically modified with phenolate to obtain highly modified polymers with minor degradation.

Our studies of the modification of PECH [11] and PECH–PEO [5] with aliphatic carboxylates concluded that the PECH–PEO main chain does not degrade as much as the PECH main chain, although the degrees of substitution were generally lower. This was attributed to the more compact random coil of PECH–PEO, which contains the more flexible ethylene oxide units.

To achieve high degrees of substitution with minimum chain scission, several essays of modification of PECH–PEO with sodium phenolate were performed in different reaction conditions (see Table 1). All experiments were done in the presence of TBAB as the phase transfer agent in THF at 60°C and in the absence of moisture, as it was established with PECH [6]. Degrees of modification were fairly good, particularly when the phenolate/chlorine ratio was 2:1 and the reaction time was 1–4 days. Longer reaction times or nucleophile/chlorine ratios above 2:1 do not increase the extent of modification significantly, but degradation becomes more significant. The extension in which the polymer degradation occurs is estimated as a factor ($\bar{M}_w/\bar{M}_w$ est.) that includes the molecular weight of the starting PECH–PEO and the degrees of substitution and elimination. In this factor $\bar{M}_w$ est. is obtained from these data by assuming that no degradation (or branching) takes place.

By comparing these results with those from modifying PECH, [6] we may conclude that the copolymer leads to functionalized polymers with lower degrees of substitution and elimination, when the phenolate/chlorine ratio is 1:1, either at one or four days (exp. 1 and 2). This could be understood on the basis of a more compact random coil, which is expected for PECH–PEO, and that reduces the accessibility of the phenolate to the chloromethylgroups and to the backbone hydrogens. When the proportion of phenolate is higher (ratio 2:1, exp.3 and 4), substitution

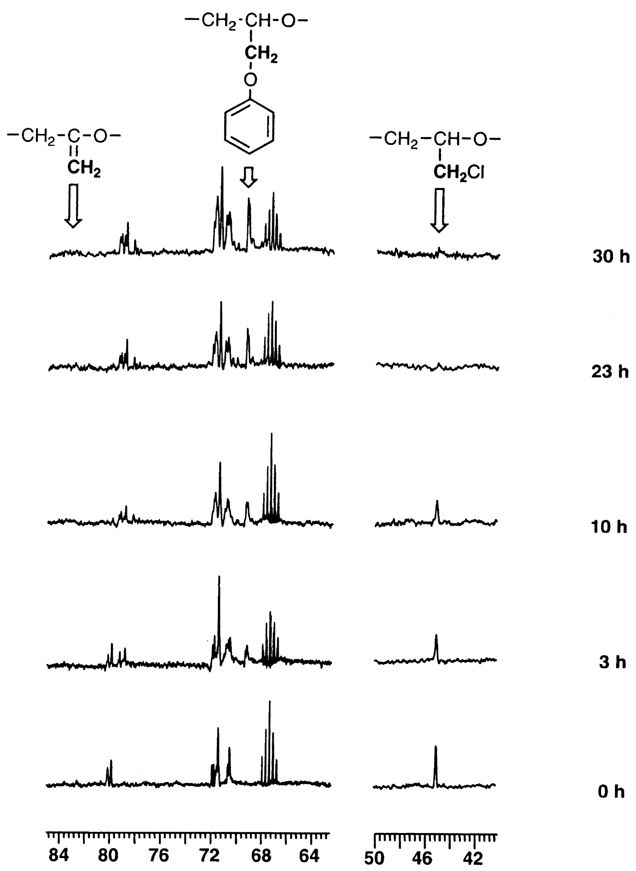


Fig. 2. Region between 42 and 84 ppm of the $^{13}$C NMR spectra of a mixture of PECH–PEO copolymer, sodium phenolate and TBAB at 60°C in deuterated THF recorded at prefixed reaction times.

degrees are higher, but elimination increases only slightly, which seems to indicate that the access of the phenolate to the backbone hydrogens is more hindered than to the chloromethyl carbon.

To test the behaviour of both homo- and copolymer towards elimination, we made a kinetic study by $^{13}$C NMR spectroscopy, using sodium methoxide as a basic reagent to avoid the competitive substitution process. Fig. 1 plots the percentage of eliminated units against reaction time. It must be pointed out that substitution by methoxide was not detected in either of the cases. As can be seen, the copolymer PECH–PEO is eliminated faster and to a higher extent than the PECH homopolymer. These results can be explained by the different sizes of phenolate and methoxide and their different behaviour as reagents. In the first case, tetrabutylammonium phenolate produces more substitution than elimination because of its nucleophilicity and volume. So, with PECH, as substitution takes place, the random coil expands, thus facilitating further substitution and elimination. With copolymer, the 50% of unmodifiable ethylene oxide units limit this uncoiling. When methoxide is used, the rigidity of the backbone increases as the elimination progresses. With the copolymer, the flexible oxyethylene units limit the rigidity of the backbone, and facilitate the progress of the elimination reaction. On the other hand, with the homopolymer, the occurrence of consecutive oxyvinylidene units produces a rigid, poorly soluble polymer and limit elimination.

To investigate the kinetics of the modification of PECH–PEO copolymer with phenolate, a $^{13}$C NMR study was made in deuterated THF as a solvent. Fig. 2 shows spectra recorded at different times. These results show that the substitution process is fast and extensive and that elimination is considerably slower and smaller. The low proportion and poor resolution of the eliminated unit signals make it difficult to quantify the competitive processes accurately.

The overall composition of tetrapolymer obtained in this modification procedure was evaluated by quantitative $^{13}$C NMR spectroscopy (see Fig. 3). If we take into account that the initial polymer has a PECH–PEO molar ratio of 1:1, the comonomer percentages can be calculated from the integration of signals $\mathbf{c}''$ (CH$_2$ in the vinylether units) at 84 ppm,

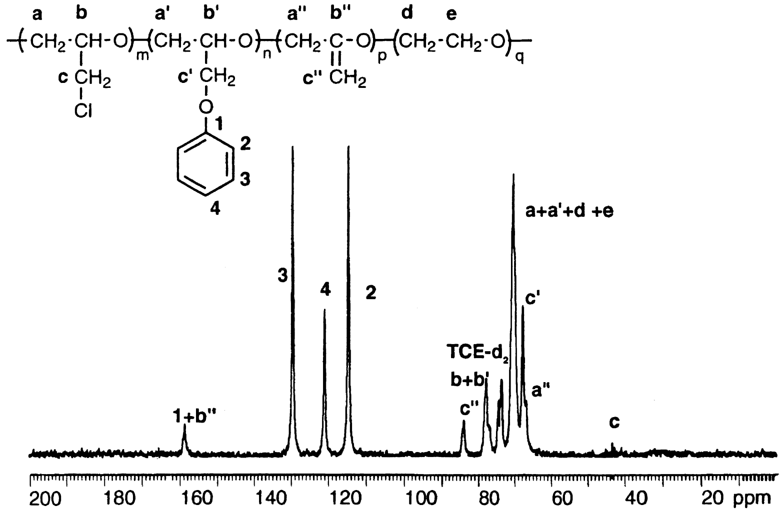
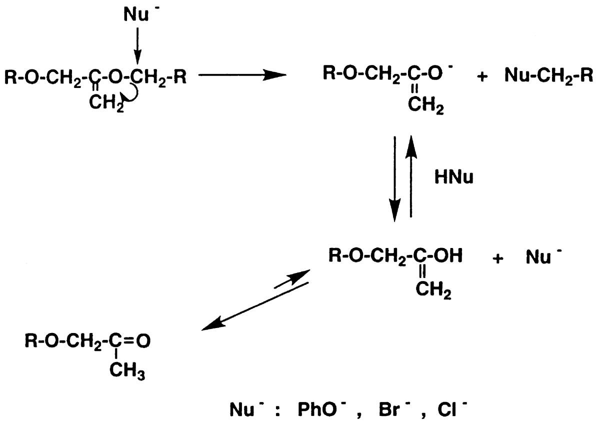


Fig. 3. $^{13}$C NMR spectrum recorded in deuterated tetrachloroethane of a polymer obtained from the chemical modification of PECH–PEO with phenolate.



Scheme 1.

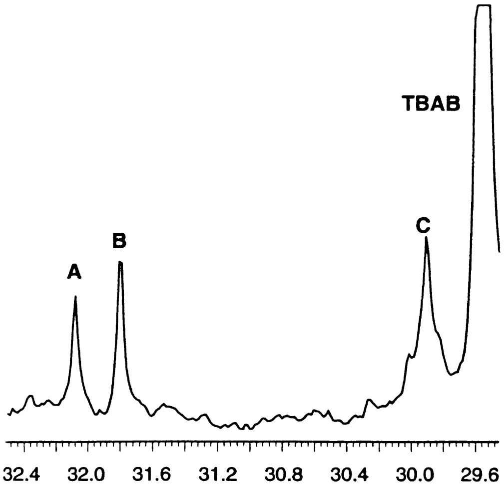
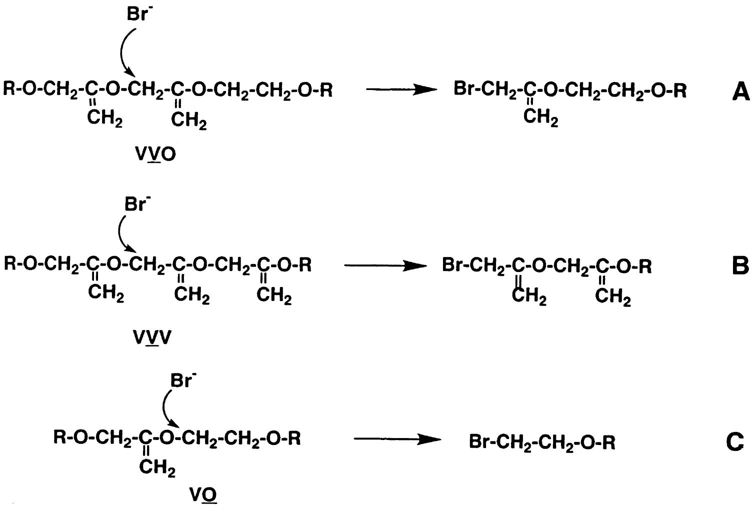


Fig. 4. Region between 29.6 and 32.4 ppm of the $^{13}$C NMR spectrum recorded in deuterated tetrachloroethane of the totally dehydrochlorinated PECH–PEO treated at 60°C with TBAB in THF for 10 days.

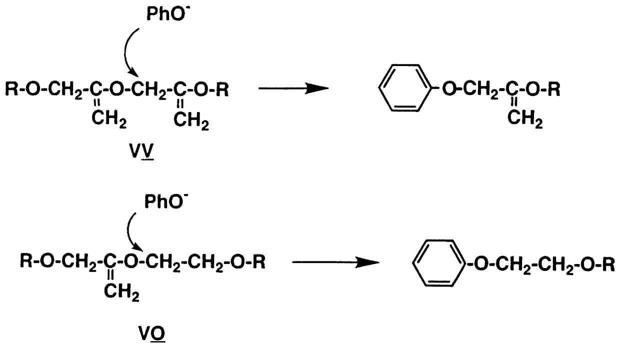
b + b′ (methine carbons in the main chain) at 78–79 ppm and **c** (chloromethyl group) at 43 ppm. Chlorine elemental analyses results were in agreement with the comonomer composition determined by quantitative $^{13}$C NMR spectroscopy. The pattern of the aliphatic zone of this spectrum is complex because of the comonomer sequence of the four different structural units, whose complete assignment has recently been reported [12].

In previous studies [6], we proposed a mechanistic explanation for the degradative scission of the main chain in the reaction of PECH with nucleophiles. This mechanism must contribute to the degradation of PECH–PEO in similar conditions, but structural differences could provide further information on this (see Scheme 1). It is noticeable, that degradative main chain scission in PECH–PEO takes place to a lesser extent. This degradation, according to our mechanistic explanation, takes place mostly by allylic attack of the nucleophile on the methylene carbon in an oxymethyleneethylene–oxymethyleneethylene dyad (V$\underline{\text{V}}$) and the 50% of ethylene oxide units (O) lead to a lower percentage of these dyads and, consequently, to a smaller chain-scission process. Moreover, the occurrence of 50% of ethylene oxide non-eliminable units diminishes the percentage of elimination, thus preventing a strong degradative scission of the chain. Unlike PECH, therefore, a nucleophile/chlorine ratio of 2:1 does not degrade the polymer further until after four days (exp. 3 and 4). Longer reaction times (7 days, exp. 5), however lead to a greater degradation with only a slight increase in the degree of substitution. A higher nucleophile/chlorine ratio (exp.6) is not advisable since lead to highly degraded polymers in poorer yields without a significant improvement in the degree of substitution.

In the degradation of PECH, there are three different nucleophiles in the reaction medium, namely: phenolate, bromide from TBAB and chloride formed by the substitution/elimination of the polymer. The $^{13}$C NMR spectra of some modified polymers (exp. 5 and 6) show two small



Scheme 2.



Scheme 3.

signals at 29.4 and 205 ppm. These are attributable to the methylketone end-group produced in the degradation. Phenolate terminal groups, also produced in the chain scission, could not be detected, because of the overlap with the signals from the carbons of the substituted unit. Similarly, chlorine end-groups overlap with chloromethyl structural units. Bromine terminal groups, which are also expected to form, should undergo fast substitution because of their ability as a leaving group. Signals from brominated terminal groups should therefore be much less intense than signals from the methyl ketone groups, and none have been detected.

To prove the mechanism proposed for the degradative chain scission of the main chain [6] with PECH–PEO, poly(oxyethylene-*co*-oxy-1-methyleneethylene) 1:1 was prepared by treating commercial PECH–PEO with a high proportion of anhydrous sodium methoxide. This led to a completely dehydrochlorinated polymer. This polymer was reacted with TBAB in THF as a solvent for 10 days. The $^{13}$C NMR spectrum of the oligomeric product obtained (see Fig. 4) showed three different $CH_2$ Br end-group signals at 32.1, 31.8 and 29.9 ppm (**A**, **B** and **C**, respectively). According to the proposed mechanism, the expected brominated end-groups for this oligomeric product were $Br–CH_2–C(=CH_2)–O–$ and $Br–CH_2–CH_2–O–$. These were originated by bromide attack on the V*V* and V*O* sequences, respectively. The fact that there are three signals indicates that one of them is split by the effect of the neighbouring unit (see Scheme 2). From empirical calculations and the chemical shifts observed with the poly(oxy-1-methyleneethylene) reacted in the same conditions [6] we assigned the signals at 32.1 and 31.8 ppm to the attack on the V*V* dyad and the signal at 29.9 ppm to the attack on the V*O* dyad. Since the signal at 31.8 ppm coincides exactly with the signal obtained with the totally eliminated PECH, this was attributed to the attack on the V*V*V sequence (structure **B** in Scheme 2), while the signal at 32.1 ppm was assigned to the attack on the V*V*O triad (structure **A** in Scheme 2). The signal at 29.9 ppm can therefore be assigned to the attack on the oxyethylene unit of the V*O* dyad (structure **C** in Scheme 2). Moreover, this chemical shift is very close to those described for some 2-bromoethylethers [13]. This signal could also be split by the different neighbouring units. However, the great intensity of the close TBAB signal prevents a more accurate analysis of this zone.

The main step in our degradation mechanism is the nucleophilic attack on the methylene carbon directly attached to the vinylic unit. This mechanism has been clearly verified for both homo- and copolymer only when the nucleophile is a bromide anion. In the modification process, phenolate seems to be the nucleophile that is responsible for the chain scission mechanism. To confirm our mechanism, the completely dehydrochlorinated PECH–PEO was heated at 60°C in THF in the presence of equimolecular amounts of phenolate and TBAB for 10 days. In our postulated mechanism the phenolate group can attack either on the ethylene or vinylic unit, and so lead to two different final groups (see Scheme 3). The $^{13}$C NMR spectrum of the product showed signals in the aromatic region corresponding to the phenylether end-groups, which indicates that the phenolate has attacked the backbone. Moreover, in addition to the expected signals, in the region corresponding to the backbone carbons there were resonances at 77.2 ppm (**c**$^*$) and 67.6 ppm (**a**$^*$). Empirical calculations

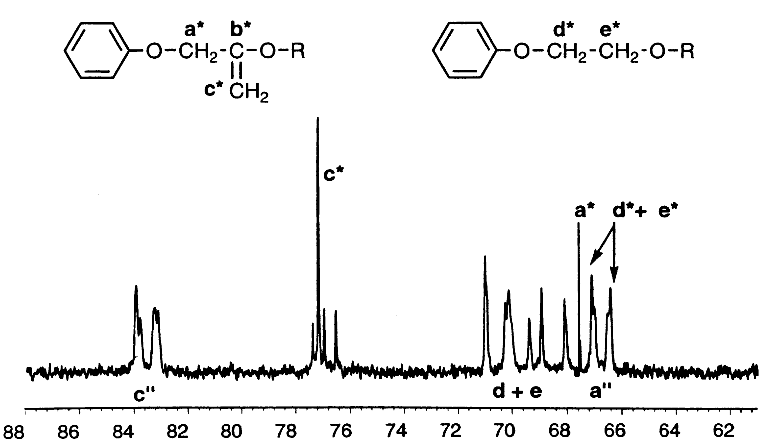


Fig. 5. Region between 62 and 88 ppm of the $^{13}$C NMR spectrum recorded in $CDCl_3$ of the totally dehydrochlorinated PECH–PEO treated with sodium phenolate and TBAB in THF for 10 days.

and a comparison with a model compound [13] attribute these to the attack on the vinylic unit (see Fig. 5). At the region between 66 and 67 ppm there were two new signals which partially overlapped with the **a**″ methylene carbon in the main chain. These signals are attributed to the final group that originated from the attack by phenolate on the ethylene unit.

Finally, the intensity of the assigned end-group signals seems to confirm that in the modification of the PECH–PEO copolymer, the scission of the main chain is also most probably caused by the attack of phenolate on the methylene carbon of a V$\underline{V}$ dyad, i.e. by a nucleophilic attack on an allylic position.

To sum up, our degradation mechanism for the modification of PECH with nucleophiles is confirmed on the basis of the reaction of poly(oxyethylene-*co*-oxy-1-methyleneethylene) 1:1 copolymer with phenolate and/or TBAB. Moreover, by extending this mechanism to the modification of PECH–PEO we assigned the bromide and phenolate final groups that originated in the degradative scission of the backbone, and whose relative intensities indicate that the most favoured attack takes place on the V$\underline{V}$ dyad. There is less degradation in PECH–PEO than in PECH. This is probably because there are fewer V$\underline{V}$ dyads.

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