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Synthesis of functional polymers by chemical modification of PECH and PECH–PEO with substituted phenolates

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Abstract

To prepare a family of functionalized polymers, we investigated the nucleophilic substitution reaction of poly(epichlorohydrin) (PECH) and its 1:1 copolymer with ethylene oxide (PECH–PEO) with a series of substituted phenolates with electron-withdrawing and electron-donating groups. The basic character of the phenolates involves an undesired dehydrochlorination side-reaction and the subsequent chain scission process. Depending on the characteristics of the substituent directly attached to the phenolate, polymers with different proportions of substituted and vinylic units are obtained. In most cases, the modification is not quantitative and chloromethylated units remain in the final polymer. Similarly, the extent of the cleavage reaction depends on the phenolate. The functional polymers have been structurally characterized by ^{13}C-NMR spectroscopy. Their thermal properties have been evaluated by differential scanning calorimetry and thermogravimetry.

Keywords: Poly(epichlorohydrin); Functionalized polymers; Polymer modification

1. Introduction

Functionalized polymers have been of commercial and scientific interest since the beginning of macromolecular chemistry. Among them, cellulose or rubber were chemically modified to improve their properties [1]. Since Merrifield reported the first solid-phase synthesis of peptides using functionalized polystyrene as a support [2], interest in polymer-supported reagents and catalysts has increased. Their significance lies mainly in the easy work up of the synthetic procedures. Wang [3] also suggested modifying chloromethylated polystyrene by treating it with 4-hydroxybenzyl alcohol. This support has recently been used to synthesize highly complex structures with pharmacological activity by the combinatorial synthesis methodology [4,5]. Similarly, functionalized polymers are useful for other applications like surfactants, controlled release formulations or chromatographic separations [6,7].

Functionalized polymers are prepared either by polymerization or copolymerization of monomers that contain the desired functionality or by chemically modifying preformed polymers. The two methods are in fact complementary, since they both have advantages and disadvantages.

Most of the work on functional polymers has been done with crosslinked polystyrene resins [8]. This is because their polymer backbone is unreactive. This is also a feature of polyether resins, which have unreactive ether linkages in the backbone and could, therefore, substitute polystyrene resins when a greater polarity and flexibility are desired.

In previous papers we attempted the ring-opening polymerization of *p*-functionalized phenylglycidylether derivatives by anionic-coordinative catalysts [9–12]. In most cases, when starting from *p*-functionalized glycidylic monomers we obtained stereoregular polyethers with high molecular weights, although when Lewis basic groups were present in the monomer, very little conversion of polymer was reached due to the deactivation of the catalytic active sites.

The alternative route provided by chemical modification can start from commercial halogenated polyethers such as poly(epichlorohydrin) (PECH) or its copolymer with ethylene oxide (PECH–PEO). Several nucleophiles can smoothly substitute PECH chlorine atoms in the presence of a phase transfer catalyst (PTC) under mild conditions [13]. However, when phenolates were used, degrees of substitution were very low and there was a strong decrease in the inherent viscosity [14]. In early papers [15,16] we studied the reaction of PECH and PECH–PEO with unfunctionalized phenolate in order to ascertain the best reaction conditions that lead to high degrees of substitution and minor chain scission. Similarly, on the basis of the

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end-group analysis by ^{13}C NMR spectroscopy we proposed and confirmed a degradative scission mechanism. This implies dehydrochlorination by phenolate and a subsequent attack of the nucleophile on the vinylic units obtained.

In this paper, we have performed the modification reaction of PECH and PECH–PEO with a series of functionalized phenolates and naphtholates in the conditions already found. The polymers obtained have been structurally characterized by ^{13}C NMR spectroscopy and their thermal properties have been evaluated by differential scanning calorimetry (DSC) and thermogravimetry (TGA).

2. Experimental part

2.1. Materials

Hexane was dried by refluxing over CaH_2 and distilled before use. Tetrahydrofuran (THF) was first distilled over CaH_2 and then over sodium–benzophenone system. Dimethylformamide (DMF) was distilled at reduced pressure over P_2O_5 prior to use.

Poly(epichlorohydrin) (PECH) (Aldrich), with inherent viscosity (η_{inh}) in *N*-methylpyrrolidone (NMP) of 234 ml/g (measured at a concentration of ca. 2 g/l at 30°C) weight average molecular weight ($\overline{M_{\mathrm{w}}}) = 1,144,000$ Da and polydispersity ($\overline{M_{\mathrm{w}}}/\overline{M_{\mathrm{n}}}) = 2.49$ was dried under vacuum and over P_2O_5 at 60°C.

Poly(oxy-1-chloromethylethylene-*co*-oxyethylene) 1:1 copolymer (PECH–PEO) (Zeon Chemicals Inc.), with inherent viscosity in NMP 280 ml/g (measured at a concentration of ca. 2 g/l at 30°C), weight average molecular weight 940,000 Da and polydispersity 2.40, was dried under vacuum and over P_2O_5 at 60°C.

Tetrabutylammonium bromide (TBAB) (synthesis grade, Aldrich), which was used as a solid–liquid phase transfer agent was dried over P_2O_5 under vacuum at room temperature.

Sodium hydride (60% dispersion in mineral oil, Aldrich) and 3-*t*-butyl-4-hydroxy-5-methylphenyl sulphide (Santonox®) (Aldrich) were used without previous purification.

Dry phenol (Probus) was prepared by fractional distillation. 4-Benzyloxyphenol, 4-hydroxybenzonitrile, 2,6-dimethylphenol, 4-phenoxyphenol, methyl 4-hydroxybenzoate, 4-chlorophenol, 4-hydroxybenzophenone (Fluka) and 4-*t*-butylphenol, 4-hydroxyacetophenone, 4-methylphenol, 1- and 2-naphthol and 4-[2–(phenylisopropyl)]phenol (Aldrich) were dried over P_2O_5 under vacuum prior to use. 4-Nitrophenol (Aldrich) was purified by recrystallization in aqueous HCl 0.5 N. 4-Dodecylphenol and 4-dodecyloxyphenol were synthesized as previously described [9].

Sodium phenolates 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. The precipitated phenolates were filtered off under argon and washed several times with a mixture of hexane and THF. Finally sodium phenolates were dried in the vacuum and stored in schlenck flasks under inert atmosphere.

2.2. General procedure for modification of poly(epichlorohydrin) with sodium phenolates

PECH (0.273 g, 2.95 mmol) was dissolved in anhydrous THF (15 ml) and a solution of sodium phenolate (2.95 mmol) and dry TBAB (0.951 g, 2.95 mmol) in anhydrous THF (15 ml) was added under an inert atmosphere. The reaction mixture was stirred at 60°C for 1 day in the dark. The polymer solution was then precipitated into water. The resulting polymer was purified by reprecipitating twice from THF into water. 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 for 48 h. The yield was calculated from the recovered polymer taking into account the degrees of substitution and elimination determined from ^{13}C NMR spectroscopy. Results are shown in Table 1.

2.3. General procedure for modification of poly(oxy-1-chloromethylethylene-co-oxyethylene) with sodium phenolates

PECH–PEO (0.214 g, 1.57 mmol) was dissolved in anhydrous THF (25 ml) and a solution of sodium phenolate (3.14 mmol) and dry TBAB (1.014 g, 3.14 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. 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 for 48 h. The yield was calculated from the recovered polymer taking into account the degrees of substitution and elimination determined from ^{13}C NMR spectroscopy. Results are shown in Table 2.

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 a solvent. They were recorded under quantitative conditions, i.e. with the sequence inverse gated decoupling and using a delay time of 3 s. The resolution was enhanced by using an LB = 2, *zero-filling* and the Lorentz–Gaussian transformation technique [17], with factors of GF = 0.1 and GFS = 0.05. Substitution and elimination degrees were determined by integrating ^{13}C NMR signals.

Chlorine content was determined using 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 on a SEC-MALLS system, made up of a

Table 1
Chemical features of the polymers obtained by chemical modification of PECH with substituted phenolates at 1 and 4 days of reaction time

Exp.	Reactive	1 day					4 days				
		Sust. (%)	Elim. (%)	Yield (%)	$\overline{M_w}$ (10^{-5})	$\overline{M_w}/\overline{M_w}$ est.	Sust. (%)	Elim. (%)	Yield (%)	$\overline{M_w}$ (10^{-5})	$\overline{M_w}/\overline{M_w}$ est.
1	C_6H_5ONa	49	22	98	13.1	0.94	60	21	98	12.0	0.81
2	4-ClC_6H_4ONa	16	4	98	12.6	0.97	68	21	92	16.2	0.89
3	4-$O_2NC_6H_4ONa$	[b]	[b]	97	[a]	–	[b]	[b]	98	[a]	–
4	4-$MeCOC_6H_4ONa$	43	4	98	16.7	1.01	82	10	88	[a]	–
5	4-$C_6H_5COC_6H_4ONa$	28	~0	91	16.8	0.98	59	8	94	[a]	–
6	4-$MeOCOC_6H_4ONa$	20	2	97	13.6	0.96	36	0	90	[a]	–
7	4-NCC_6H_4ONa	31	3	95	14.5	1.00	82	11	86	[a]	–
8	1-naphtONa	52	10	84	11.4	0.64	64	13	76	10.6	0.56
9	2-naphtONa	46	5	58	7.8	0.45	64	18	47	4.8	0.26
10	4-MeC_6H_4ONa	49	25	93	10.9	0.85	58	29	72	7.8	0.70
11	4-DodecylC_6H_4ONa	37	20	69	15.6	0.75	44	27	64	15.4	0.68
12	4-*t*-BuC_6H_4ONa	29	21	99	10.4	0.71	51	24	85	4.6	0.26
13	4-$[C_6H_5C(CH_3)_2]C_6H_4ONa$	36	20	96	[a]	–	69	22	69	9.3	0.28
14	2,6-dimethylC_6H_4ONa	50	21	83	11.7	0.74	49	20	75	6.9	0.40
15	4-$BnOC_6H_4ONa$	32	19	96	[a]	–	43	26	99	[a]	–
16	4-DodecyloxyC_6H_4ONa	20	18	82	[a]	–	28	20	79	[a]	–
17	4-$C_6H_5OC_6H_4ONa$	45	55	34	[a]	–					

[a] Not soluble in THF.
[b] Not soluble in all common deuterated solvents.

HPLC Waters 510 pump, three columns (Shodex K-80M, PLgel 5μ MIXED-D and PLgel 3μ MIXED-E) and one precolumn (Shodex K-800P). 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 (MALLINCRODT ChromAR HPLC), flux of 1.0 ml/min, helium as a degasser and 3×10^{-4} g of sample injected via a 100-μl loop.

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyser. The calorimeter was calibrated using an Indium standard (heat flow calibration) and an Indium–Lead–Zinc standard (temperature calibration). The sample of polymer of about 5 mg of known weight was put into an aluminium pan and heated at a heating rate of 20°C/min in N_2 atmosphere.

Thermogravimetric analyses were carried out on a Perkin–Elmer TGA-7 system in N_2 at a heating rate of 10°C/min up to 600°C.

3. Results and discussion

As mentioned in Section 1, functionalized polymers have been synthesized by chemically modifying chloromethylated polyethers (commercial PECH and PECH–PEO) with functionalized phenolates. The advantage of the resulting polymers is that they have greater flexibility and polarity because there are two oxygen atoms in the substituted unit. Moreover, the oxygen directly attached to the aromatic ring improve its reactivity towards the electrophilic substitution reaction. The large number of commercial functionalized phenols makes this kind of modified resin highly versatile.

Previous studies [15,16] led us to the appropriate reaction conditions, when phenolate acts as a nucleophile, if a high modification degree with minor degradation is desired. We proved that the conditions recommended for undegraded polymers are strictly anhydrous, hydroxide-free phenolate, a minimum nucleophile/chlorine ratio and short reaction times. In fact, the degree of modification seems to reach a *plateau* and longer reaction times or higher proportions of nucleophiles do not increase it. In fact, they cause a higher degradation of the main chain, since nucleophiles are the species responsible for the degradation process, which takes place by their attack on the vinylic units formed by dehydrochlorination.

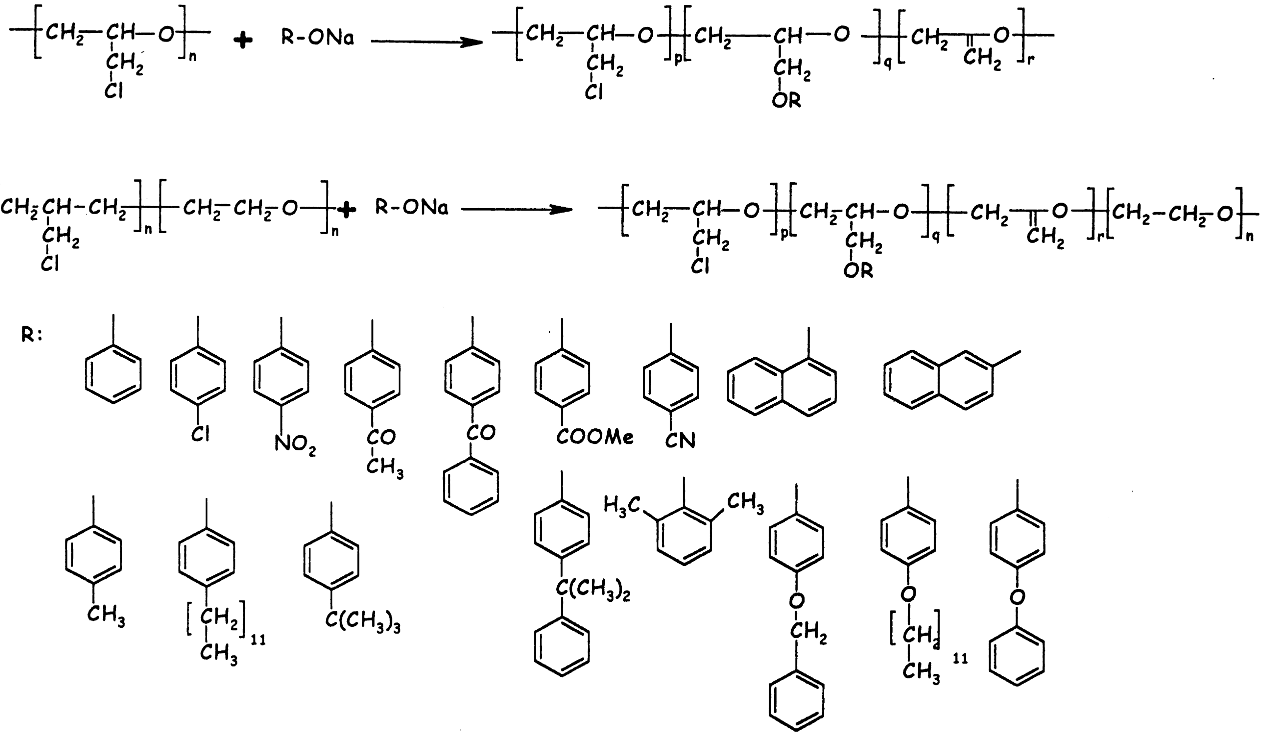
However, there are some differences between PECH and PECH–PEO polymers in the modification by phenolate. Generally, the copolymer leads to polymers with lower degrees of modification when the phenolate/chlorine ratio is 1:1, although better results are obtained with a ratio of 2:1. In all conditions, the copolymer leads to lower degrees of elimination and a minor extent of the main-chain scission reaction. With PECH–PEO, therefore, a nucleophile/chlorine ratio of 2:1 does not significantly degrade the polymer.

Scheme 1 shows the different phenolates used and the structural units from the modification of PECH and PECH–PEO. The basic character of the phenolates led to a dehydrochlorination side-reaction and so vinylic units are present in the polymer chain. Therefore, since the chemical modification is generally incomplete, a terpolymer is originated with PECH and a tetrapolymer with PECH–PEO. This makes it difficult to assign the different signals of the ^{13}C NMR spectra of the synthesized polymers. It must be mentioned that the overall ter- or tetra-polymer composition was evaluated by quantitative ^{13}C NMR spectroscopy (see Figs. 1 and 2). The integration of signals c$''$ (CH_2 in the vinylic units) at 84 ppm, b + b$'$ (methine carbons in the main chain) at 75–79 ppm and c (chloromethyl group) at

Table 2
Chemical features and DSC data of the polymers obtained by chemical modification of PECH–PEO with substituted phenolates at 4 days reaction time

Exp.	Reactive	Sust. (%)	Elim. (%)	Yield (%)	$\overline{M_w}$ (10^{-5})	$\overline{M_w}/\overline{M_w}$ est.	T_g (°C)	T_m (°C)
1	C_6H_5ONa	74	20	92	9.3	0.8	−21	–
2	4-ClC_6H_4ONa	74	14	81	[a]	–	−17	–
3	4-$MeCOC_6H_4ONa$	55	5	82	[a]	–	−16	–
4	4-$C_6H_5COC_6H_4ONa$	39	5	93	[a]	–	−11	–
5	4-$MeOCOC_6H_4ONa$	34	8	99	[a]	–	−24	–
6	4-NCC_6H_4ONa	42	6	91	[a]	–	−27	–
7	1-naphtONa	76	16	88	[a]	–	1	–
8	2-naphtONa	68	14	77	[a]	–	−2	–
9	4-MeC_6H_4ONa	66	28	79	10.2	0.95	−25	–
10	4-DodecylC_6H_4ONa	60	22	96	[a]	–	−5	19/45
11	4-*t*-BuC_6H_4ONa	70	28	86	[a]	–	−15	–
12	4-$[C_6H_5C(CH_3)_2]C_6H_4ONa$	60	28	91	[a]	–	−33	–
13	2,6-dimethylC_6H_4ONa	76	20	91	[a]	–	−20	–
14	4-$BnOC_6H_4ONa$	51	~0	97	[a]	–	−38	120
15	4-DodecyloxyC_6H_4ONa	68	0	38	[a]	–	−5	48/57

[a] Not soluble in THF.



Scheme 1.

43 ppm enables the comonomer percentage to be calculated with an initial PECH–PEO comonomer ratio of 1:1.

Table 1 summarizes the results from the chemical modification of PECH with 17 different phenolates after 1 or 4 days. The extent to which the polymer is degraded is estimated as a factor that compares the molecular weights of the starting and modified polymers. The degrees of modification and elimination are, therefore, used to calculate an estimated average molecular weight of the modified polymer in ideal conditions, i.e. without cleavage or crosslinking, and this is compared to the one obtained experimentally.

From the point of view of their reactivity, the phenolates can be divided into two groups: those with electron-withdrawing substituents (exp. 2–7) and those with electron-donating substituents (exp. 8–17). Unsubstituted phenolate (exp. 1) is tested as standard.

As can be seen in the former group, the degrees of modification and elimination achieved after 1 day are lower than with unfunctionalized phenolate, although the yields of the recovered polymer are similar. When the reaction time is increased to 4 days the degrees of modification are higher. These results can be explained by the electron-withdrawing ability of the substituent, which reduces both the nucleophilicity and basicity of the phenolate. As expected from the characteristics of these phenolates and the degradation mechanism, which requires an active nucleophile and the formation of vinylic units, the factor $\overline{M_w}/\overline{M_w}$ est. is about one. This seems to indicate that no degradation occurs.

The polymers prepared after 4 days, which contain a higher percentage of modified units, were, except for the 4-chlorophenol derivative, insoluble in THF. Therefore, the molecular weights could not be determined. However, the high yields of recovered polymer indicate that the degradation is not extensive. It must be mentioned that in the modification with 4-nitrophenol (exp. 3), the percentages of substitution and elimination could not be determined, because of the insolubility of the polymer obtained in deuterated conventional solvents. On the other hand, the unexpected decrease in the degree of elimination at longer reaction time in exp. 6 (4-carboxymethylphenolate) can be explained by the fact that the vinylic units disappear in the degradation process. Similarly, this degradation is consistent with the smaller quantity of polymer recovered.

We must not forget that the active species in the substitution reaction is tetrabutylammonium phenolate, a nacked anion, formed by the interchange between solid sodium phenolate and tetrabutylammonium bromide. The concentration of the active species, therefore, depends not only on the initial phenolate/chlorine ratio, but on the solubility of both phenolates and on the extent to which the interchange takes place. Therefore, the rationalization of the results is not easy.

When we compare these results with those from the polymerization of functional glycidylic monomers [10] we can see that modification is the best way to obtain functionalized polymers when methylketone or cyano groups are attached to the aromatic ring. This is because these groups passivate the ionic coordinative initiator used in the polymerization. However, the polymers obtained by the two methods are

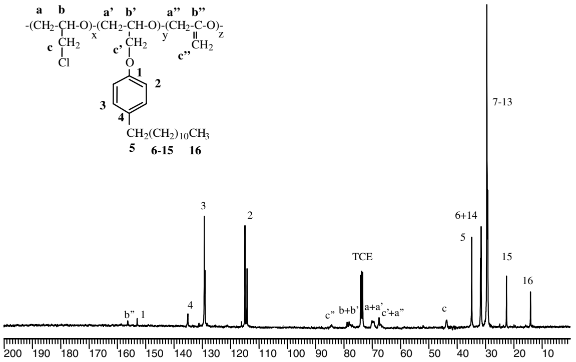


Fig. 1. ^{13}C NMR spectrum of the polymer obtained by chemical modification of PECH with 4-dodecylphenolate in deuterated 1,1,2,2-tetrachloroethane.

slightly different. For example, the stereoregularity of the main chain is highly isotactic in those polymers obtained via polymerization, while it is atactic for those obtained via modification. Similarly, modification leads to a copolymer with chlorinated and vinylic units, which may affect some of their final applications negatively.

The second group of substituted phenolates are those with electron-donating groups attached to the aromatic ring (exp. 8–17 in Table 1). Although their higher nucleophilicity and basicity were expected to be reflected in higher degrees of substitution and elimination, this did not happen in all cases. This is because nucleophilicity and basicity are only two of the factors affecting substitution and elimination reactions. Other important factors that can differ strongly from one phenolate to another are the steric hindrance of the phenolate oxygen, the ability to lead to a less compact random coil, the inherent solubility of sodium phenolate and the stability of tetrabutylammonium phenolate. The degrees of elimination observed are generally rather high. The exceptions are the two naphtholates (exps. 8 and 9) which have moderate degrees of elimination. This is explained by the fact that vinylic units disappear in the degradation process and, therefore, this observation seems to be related to the great factor of degradation determined. However, the substitution percentage is higher, since a decrease in molecular weight makes it easier to attack the active sites in the polymer.

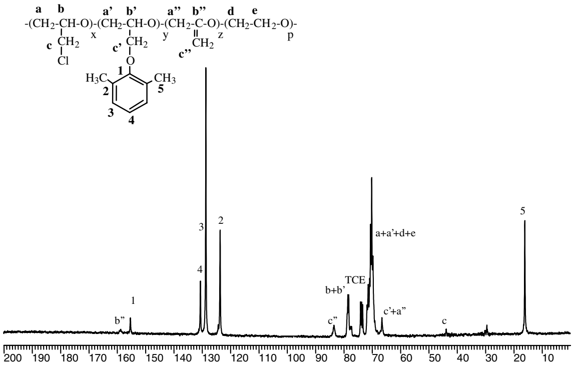


Fig. 2. ^{13}C NMR spectrum of the polymer obtained by chemical modification of PECH–PEO with 2,6-dimethylphenolate in deuterated 1,1,2,2-tetrachloroethane.

In general, longer reaction times lead to higher degrees of substitution except in exp. 14, where a *plateau* is reached after 1 day, possibly due to the high steric hindrance of the methyl groups in the *ortho* positions. Similarly, longer reaction times lead to greater elimination and degradation, thus decreasing the yields of the recovered polymer.

It must be pointed out that in exp. 17, using 4-phenoxyphenolate as a reagent led to a completely chlorine-free PECH derivative. This reaction was, therefore, performed only at 1 day. The insolubility of this polymer in THF prevented determination of its molecular weight, but the low percentage of recovered polymer (only 34%) hints at a high degradation.

These results are similar to those from the polymerization of the corresponding glycidylic monomers with electron-donating groups [9], although the polymers have structural differences their applications may be different.

From previous results from the chemical modification of PECH–PEO with phenolate [16] and the results from the modification of PECH with substituted phenolates discussed above, we choose the suitable conditions for achieving high degrees of substitution with minor chain scission in the chemical modification of PECH–PEO. The recommended reaction time in this case is, therefore, 4 days and the best nucleophile/chlorine ratio is 2:1. Results are shown in Table 2.

In this case 4-nitrophenolate has not been tested because of the high insolubility of its PECH derivatives. The degrees of the substitution achieved in these conditions are fairly good. The degree of elimination is higher for phenolates with electron-donating groups as we also saw in PECH. The insolubility of most polymers in THF prevents determination of their molecular weights and so we cannot know the extent to which degradation has taken place. Since the yields are generally high, degradation must generally be low, except for exps. 15 and 16 where the strong nucleophilicity of the phenolate may lead to a higher degradation, as suggested from the lower yields. Exp. 3 produced a slightly crosslinked polymer, which means that its ^{13}C NMR spectrum must be recorded in a gel state. This crosslinking can be explained by the acidity of the protons of the methylketone group, which can lead to an aldol condensation in a basic medium in a low proportion. This undesired reaction did not take place in PECH modification, although less phenolate was used.

To sum up, it is extremely difficult to correlate all these results because of the many factors and side reactions in the modification processes. In general, modification is a simpler method for obtaining functionalized polymers than polymerization or copolymerization, especially from the practical point of view. However, both routes are not comparable in this case, since the obtained polymers have strong structural differences. These differences are more important when the nucleophiles have a strong basic character.

In earlier studies that used aliphatic [18] or aromatic

Table 3
DSC data of the polymers obtained by chemical modification of PECH with substituted phenolates

Exp.	Reactive	1 day					4 days				
		Sust. (%)	Elim. (%)	$\overline{M_w}$ real/$\overline{M_w}$ est.	T_g (°C)	T_m (°C)	Sust. (%)	Elim. (%)	$\overline{M_w}$ real/$\overline{M_w}$ est.	T_g (°C)	T_m (°C)
1	C_6H_5ONa	49	22	0.94	1	–	60	21	0.81	1	–
2	4-ClC_6H_4ONa	16	4	0.97	−19	–	68	21	0.89	10	–
3	4-$MeCOC_6H_4ONa$	43	4	1.01	10	–	82	10	[a]	19	–
4	4-$C_6H_5COC_6H_4ONa$	28	~0	0.98	16	–	59	8	[a]	42	–
5	4-$MeOOCC_6H_4ONa$	20	2	0.96	1	–	36	0	[a]	−2	162
6	4-NCC_6H_4ONa	31	3	1.00	10	–	82	11	[a]	48	–
7	1-naphtONa	52	10	0.64	39	–	64	13	0.56	43	–
8	2-naphtONa	46	5	0.45	25	–	64	18	0.26	36	–
9	4-MeC_6H_4ONa	49	25	0.85	−2	–	58	29	0.70	1	–
10	4-DodecylC_6H_4ONa	37	20	0.75	−5	16/59	44	27	0.68	−5	16/54
11	4-*t*-BuC_6H_4ONa	29	21	0.71	−9	–	51	24	0.26	−9	–
12	4-$(C_6H_5Me_2)CC_6H_4ONa$	36	20	[a]	−5	–	69	22	0.28	−9	–
13	2,6-dimethylC_6H_3ONa	50	21	0.74	5	–	49	20	0.40	4	–
14	4-$BnOC_6H_4ONa$	32	19	[a]	−8	99	43	26	[a]	4	75/93
15	4-DodecyloxyC_6H_4ONa	20	18	[a]	20	39/77	28	20	[a]	20	42/77
16	4-$C_6H_5OC_6H_4ONa$	45	55	[a]	5	–					

[a] Not soluble in THF.

[19,20] carboxylates as nucleophiles, elimination did not compete to a significant extent and there was not a lot of degradation. It was, therefore, easier to compare modification and polymerization and modification is certainly the recommended method.

The structural characterization of the synthesized polymers was performed by ^{13}C NMR spectroscopy. As mentioned above, modifying PECH and PECH–PEO with phenolates led to copolymers with three or four different structural units, respectively. For example, Figs. 1 and 2 show two ^{13}C NMR spectra of modified polymers. In both spectra high intensity signals in the aromatic zone confirm that substitution has taken place. Also in both cases, main chain signals of the modified unit can be recognized (a′, b′ and c′). The presence of signals at 43.6 ppm corresponding to chloromethyl group (c) indicates that modification is not complete, and the signals at 84 ppm (CH_2 in the vinylether unit, c″), prove that the elimination reaction occurs. Signals in the 65–80 ppm region are due to the carbons in the main chain. The splitting of the resonances associated to these carbons may be attributed to the comonomer sequences and to tacticity. A complete analysis of these fine structures can potentially provide information about polymer composition while the influence of neighbouring units on the modification process has already been reported [21,22].

The thermal characterization of the modified polymers was made by DSC and TGA to determine their glass transition temperatures (T_gs) and thermal stabilities. Table 3 shows the results obtained by DSC for the modified polymers. We can see, it collects glass transition temperatures and some melting temperatures, since some polymers show melting endotherms.

In general, random copolymers have glass transition temperatures at an intermediate value between the T_g values of the corresponding homopolymers. These can be evaluated by the Fox equation [23]. The polymers we synthesized from PECH present three different structural units that correspond to three homopolymers. The T_g values of the PECH homopolymer and the atactic poly(phenylglycidylether) [24] homopolymer are −22 and 2°C, respectively. The poly(oxy-1-methyleneethylene) homopolymer, on the other hand, is a crystalline solid without T_g but with a melting endotherm at 109°C, followed by an exotherm due to a sigmatropization process. Moreover, functional groups on the phenol must also influence T_g. Similarly, if the modified polymers are to some extent degraded, the oligomers will act as plasticizers and lower the T_g. It is, therefore, difficult to predict or even to rationalize the T_g values obtained for each polymer. However, if we compare the T_g values for the polymers obtained at 1 or 4 days, we may conclude that, as in general, increasing the substitution degree leads to a parallel increase in T_g if there is no extensive degradation. This can be attributed to the rigidity introduced by the aromatic moieties. Similarly, the study by DSC of modified PECH with phenolate in different conditions confirms that elimination degrees do not influence the T_g values.

In general, the polymers obtained are amorphous, although in some cases there are one or two melting endotherms, which indicates their ability to crystallize. In exps. 10 and 15, where the polymer contains long aliphatic lateral chains, two different melting endotherms appear, probably due to the crystallization of the main and side chains. The polymers obtained in exp. 5 (4 days) and 14, since no long aliphatic side chain exist, show only one melting endotherm and therefore crystallize only the main chain. The coexistence of crystalline and amorphous regions should, in theory, produce an increase in the T_g, since the crystallites act as physical crosslinking points.

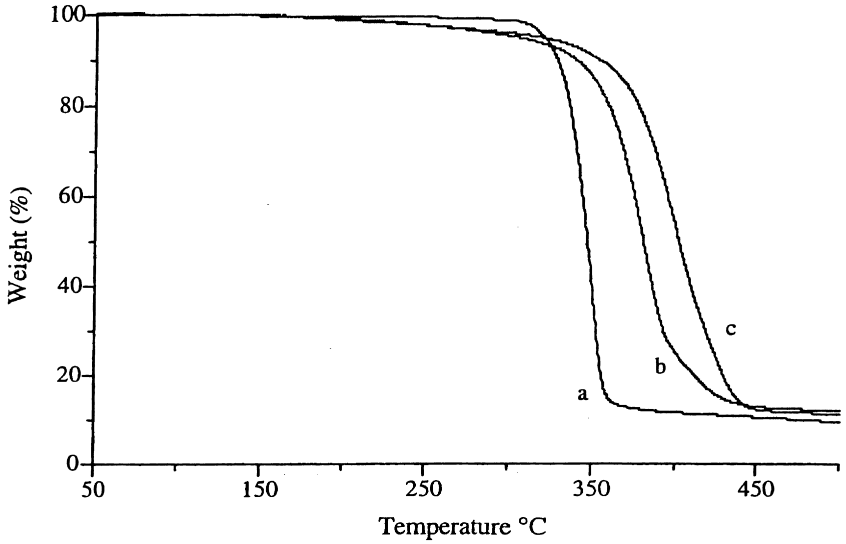


Fig. 3. TGA curves of commercial PECH (a) and its 1-naphtholate modified at 1 day (b) and 4 days (c).

Table 2 shows the DSC data for the polymers obtained by modifying PECH–PEO with several phenolates. The T_g values are generally much lower than with modified PECH, due to the 50% of flexible oxyethylene units present. Three polymers show melting endotherms: those from exps. 10 and 15, which contain long aliphatic lateral chains that can crystallize the one from exp. 14, as with PECH derivatives.

The thermogravimetries of starting PECH and PECH–PEO are very close and similar. This suggests that thermal degradation takes place mainly on the epichlorohydrin units. As an example Fig. 3 shows that the modified polymers have similar or even slightly lower onset temperatures than the starting polymer. However, temperatures for the maximum rate of degradation and char yields are generally higher. Similarly, increasing the substitution percentages leads to higher thermal stabilities.

There are some exceptions to this general trend, however. Several polymers present two peaks in the derivative of the curve, which indicates two different degradative mechanisms. This behaviour is observed in the polymers with bulky substituents, e.g. dodecyl, dodecyloxy, benzyloxy or 2-phenylisopropyl.

The polymers with a low factor $\overline{M_w}/\overline{M_w}$ est. show a weak loss of weight at temperatures under 150°C. This may be due to the volatilization of the oligomeric fractions.

From TGA studies we may conclude that the polymers obtained do not show higher thermal stability than PECH or PECH–PEO, although the char yields, because of aromatic groups in the structural units are generally higher.

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