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Studies on the microstructure of poly(phenyl glycidyl ether) using the ^{13}C nuclear magnetic resonance technique

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Microstructural details of poly(phenyl glycidyl ether) (PPGE) and its optically active form obtained by the aluminium isopropoxide (AIP)/$ZnCl_2$ ionic-coordinative initiator were analysed by nuclear magnetic resonance techniques. In order to assign the soluble fraction signals unmistakably, PPGE samples had to be synthesized using various cationic initiator systems. Several modifications were studied in the AIP/$ZnCl_2$ initiator system (such as the use of various zinc salts and the addition of water) and the tacticity and irregularity contents of the polymers were determined.

(Keywords: poly(phenyl glycidyl ether); n.m.r. spectroscopy; microstructure)

INTRODUCTION

Information concerning the microstructure of a polymer is essential for clarifying the polymerization mechanism[1,2]. Moreover, it is common knowledge that microstructure has a great influence on many of the chemical and physical properties of a polymer[3,4].

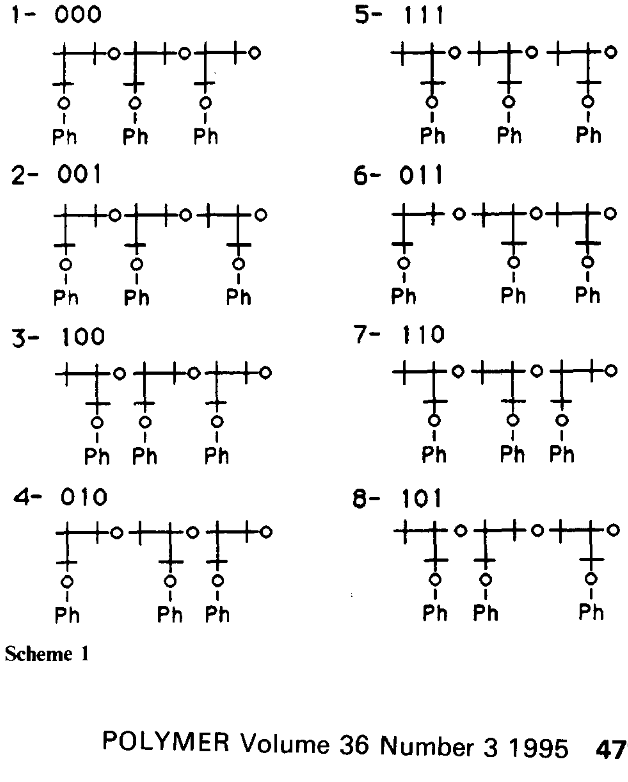
There are a great many studies on tacticity in polyethers, mainly with reference to poly(propylene oxide) (PPO)[5-7], but irregularities and end chain groups have been less frequently studied. In the case of poly(phenyl glycidyl ether) (PPGE) only a few references to ^{1}H nuclear magnetic resonance (n.m.r.) were found[8,9], but some ^{13}C n.m.r. studies have been reported on poly(*p*-chlorophenyl glycidyl ether)[10] and similar compounds[11].

In polyether research by ring-opening polymerization, starting monomers are frequently asymmetrical and polymerization can proceed by attack at either the CH_2-O or the CH-O positions[12]. If both types of ring opening occur in the propagation step, head-to-tail, head-to-head, tail-to-head and tail-to-tail linkages appear in the polymer chain[7,13,14].

In addition to this different regiostructural arrangement there is also a stereochemical consideration. PGE exists in both (*R*) and (*S*) optical forms due to its asymmetric methine carbon. Providing that polymerization results from cleavage of only the CH_2-O bond in the oxirane ring (normal opening), it is possible to generate four different stereochemical triads in the regioregular, head-to-tail (H-T) polymer. However, if in the ring-opening polymerization both C-O bonds are subjected to cleavage, then, in addition to the regioregular triads, three additional regioirregular triads are possible.

Thus, as is well known when both stereosequence and regiosequence are considered, it is possible for sixteen structural triads to exist in PPGE. In principle all of these structural triads (see *Scheme 1*) may be observed by ^{13}C n.m.r. spectroscopy[15-17].

The choice of initiator system plays an important part in the microstructure of the resulting polymer. The ionic-coordination initiator used in this study (aluminium isopropoxide (AIP)/$ZnCl_2$)[18], affords high regioregular polymer chains with variable degrees of stereoregularity. This considerably reduces the number of expected signals in the n.m.r. spectra. Moreover, this initiator leads to two types of polymers which can be separated as a soluble and an insoluble fraction in acetone[19,20]. The two fractions differ notably in their molecular weights and



Scheme 1

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other characteristics, as has been pointed out in a previous paper[21], and these differences should be demonstrable by n.m.r. analysis.

In order to reduce the number of stereoregularity signals in the n.m.r. spectra substantially, a pure isotactic sample of PPGE from the enantiomerically pure (*R*)-phenyl glycidyl ether was prepared. Thus, the unequivocal assignment of the signals in the PPGE spectrum obtained from the racemic monomer was possible.

Using the Teyssié initiator system[22], a well studied ionic-coordinative initiator, a PPGE sample was prepared that was compared with those obtained using AIP/$ZnCl_2$.

Finally, the degree of tacticity and regioregularity content of different PPGE samples obtained using modified initiator systems were quantified and compared.

EXPERIMENTAL

Materials

All solvents and initiators were prepared and purified as described previously[21].

(*S*(+))-epichlorohydrin (99%) was supplied by Fluka and used without further purification. All the organic compounds were supplied by Fluka or Aldrich and used without previous purification.

Synthesis of (R)-phenylglycidylether.

Phenol (5.65 g, 0.06 mol) and (*S*(+))-epichlorohydrin (5.60 g, 0.06 mol) were added to a 50 ml three-necked round-bottomed flask fitted with a mechanical stirrer, reflux condenser and $CaCl_2$ tube. A 30% NaOH solution (2.40 g NaOH, 0.06 mol) was added dropwise, ensuring that the temperature did not exceed 50°C. After the addition, the temperature was kept at 50°C for 3 h.

The reaction mixture was extracted with ethylic ether and the ethereal solution was washed several times with 1% NaOH solution until no phenol traces were detected. After washing with water and drying ($MgSO_4$), the ethereal solution was concentrated to obtain a yellowish oil. Vacuum distillation in the presence of CaH_2 afforded a colourless liquid (6.20 g, 68%): b.p. 70–73°C (1 ~ 2 mm Hg).

Chiral purity was determined by examining the ^1H n.m.r. spectra in the presence of the chiral shift reagent, tris[3-(heptafluoropropyl hydroxymethylene)-(+)-camphorato]europium (III) [$Eu(hfc)_3$][23]. Assay conditions showed that 0.6 molar equivalents of $Eu(hfc)_3$ per mole of PGE was the optimal ratio for the determination. In this manner, we found that the synthesized (*R*)-PGE had a chiral purity of 97±2%.

Polymerization

PGE was polymerized with the AIP initiator system alone and associated with various zinc salts ($ZnCl_2$, $ZnBr_2$, ZnI_2 and $Zn(AcO)_2$) in different monomer/initiator and Zn/Al ratios. The diethylether of the diethylene glycol was used as solvent. Polymerization, polymer fractionation and characterization were carried out following the previously described procedure[21].

The polymerization and preparation of the Teyssié catalyst were carried out according to the reported procedure[24].

Measurement of n.m.r. spectrum

^{13}C n.m.r. spectra were recorded at 75.4 MHz in a Varian Gemini 300 spectrometer with proton noise decoupling. Samples were prepared as 10–20% (w/v) solutions in $CDCl_3$, tetrachloroethane-d_2 (TCE-d_2), C_6D_6, acetone-d_6 and pyridine-d_5. Those used in quantitative measurements were also filtered and degassed with helium. Spectra were recorded at 30°C, with a flip angle of 45° and the number of transients ranging from 40 000 to 200 000 with a delay time between sampling pulses equal to 10 times the longest carbon T_1 for internal chain units in quantitative experiments. The central peak of $CDCl_3$ and TCE-d_2 was taken as a reference and the chemical shifts are given in ppm from tetramethylsilane (TMS) using the appropriate shift conversions. The distortionless enhancement by polarization transfer (d.e.p.t.) multiple pulse sequences include the compensated 180° pulse. The ^{13}C spin-lattice relaxation times were recorded with the standard 180°-τ-90° inversion recovery sequence. Peak area ratios were determined using a planimeter, or manually if necessary.

RESULTS AND DISCUSSION

The ^{13}C n.m.r. spectra of both the soluble and insoluble PPGE fractions were found to consist mainly of four aromatic signals and three groups of aliphatic signals. Moreover, numerous low intensity signals were observed in the soluble polymer fraction spectrum (*Figure 1*). The aromatic signals were assigned using empirical data. These signals did not show any splitting due to the polymer tacticity and no further studies were made. The aliphatic part of the spectrum shows three signals centred at 78.1, 69.8 and 67.8 ppm. The signal at lower field was found by d.e.p.t. experiments to correspond to the methine carbon (peak a in *Figure 1*). Assigning the two CH_2 groups was more difficult because of the minor difference in their chemical shifts. Measurements of the relaxation times were found to give the following results: $T_1 = 0.15$ s for the signal at 69.8 ppm, and $T_1 = 0.17$ s for the signal at 67.8 ppm, which seems to indicate that the signal at 69.8 ppm (peak b in *Figure 1*) is due to the methylene carbon in the polymer chain on the basis of its lower mobility[25]. These assignments coincide with those reported by Dworak and Jedlinski for poly(*p*-chlorophenyl glycidyl ether)[10].

Determination of tacticity

As far as the multiplicity of signals is concerned, as can be seen in *Figure 2*, the methine carbon shows three peaks due to a clear triad sensitivity, where the heterotactic (*mr*) and (*rm*) triads appear as a single signal because of their close chemical shifts. The intensity of these triads changes noticeably when soluble and insoluble fractions are compared. The higher methine signal of the soluble and insoluble fraction spectra (*Figures 2a* and *b*) coincides with the single signal in the spectrum of the pure isotactic PPGE sample (peak c in *Figure 2*). Thus we can conclude that the signal at 78.3 ppm corresponds to the isotactic triad and consequently the signal at 78.0 ppm is attributed to the syndiotactic triad.

The main chain methylene carbon appears as two signals which correspond at least to a diad sensitivity.

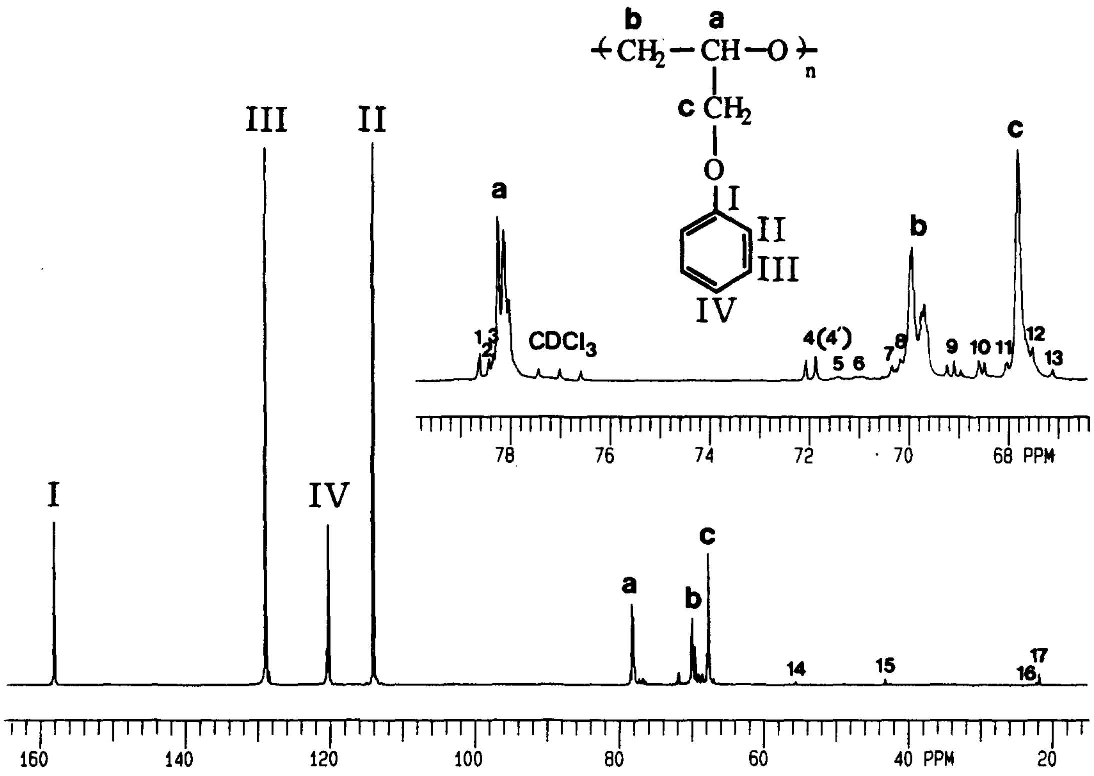


Figure 1 ^{13}C n.m.r. spectrum of the PPGE soluble fraction ($CDCl_3$)

The peak at 69.9 ppm is attributable to the isotactic diad using the same arguments as above. The syndiotactic signal shows an additional splitting, which is especially well defined for the soluble fraction, indicating a clear tetrad sensitivity. This higher sensitivity of the syndiotactic diad has already been reported[7,26] for PPO and PBO (poly(butylene oxide)) where the four possible tetrads appear as two signals *rm* (*mrm*+*rrm*) and *rr* (*rrm*+*mrr*). In our case, three signals (or four under some recording conditions) can be observed. These tetrads could be assigned according to their structural sequence and because for isotactic sequences they are more deshielded.

In the case of the pendent chain methylene carbon (peak c in *Figure 2*) we expected up to four signals as triad sensitivity. However, only one signal was observed, confirming its lower sensitivity to tacticity. This behaviour coincides with that observed for polyepichlorohydrin[27] and polyglycidol[28] and contrasts with that of PPO[7,26] and poly(methyl glycidyl ether)[11] where the expected splitting was observed. All the aforementioned tacticity assignments are shown in *Figure 3*.

From the quantification of the ^{13}C n.m.r. signals corresponding to the methine and methylene carbons in the polymeric chain, the degree of tacticity of the insoluble and soluble PPGE samples was determined. The different diad and triad areas were calculated by integrating these signals in the spectra recorded under quantitative conditions.

The degree of tacticity, as a percentage of isotactic diads, was calculated from the methine carbon (i, h, s) and methylene carbon (I, S) signals (*Figure 3*) and concordant values were obtained in all cases.

In *Table 1* the results of different samples of soluble and insoluble PPGE fractions are shown. As is well known[12,29], the initiator complex usually possesses two

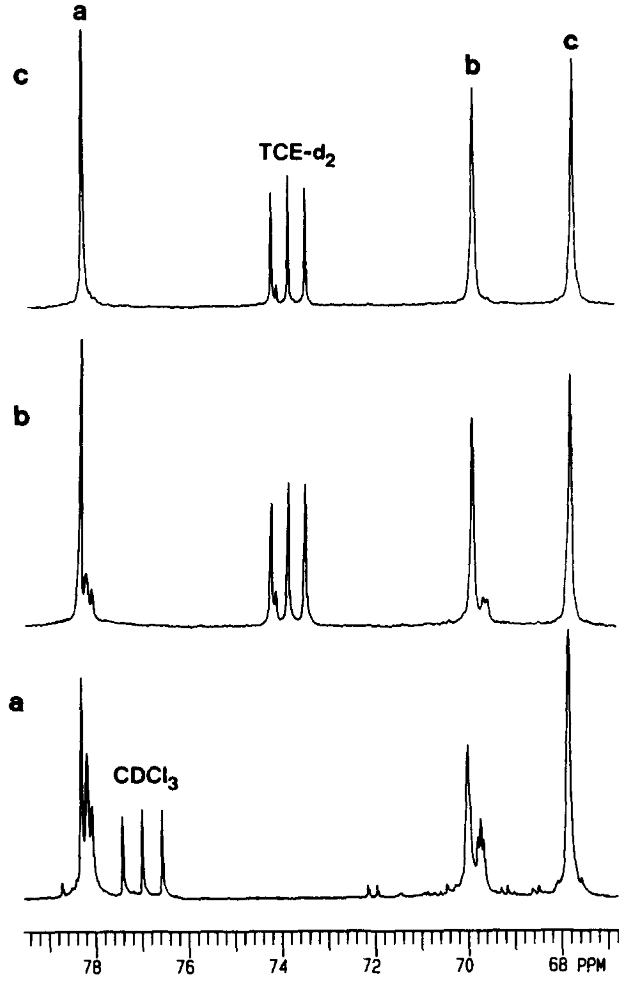
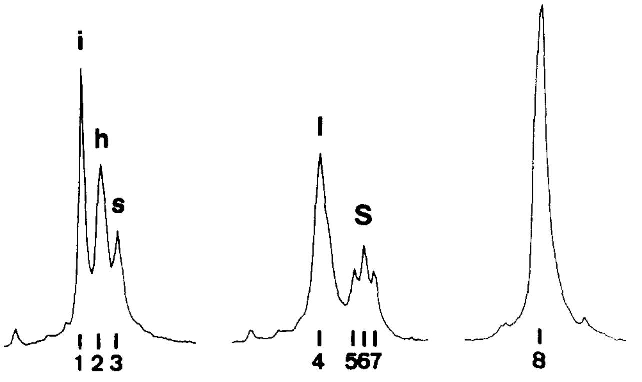


Figure 2 ^{13}C n.m.r. spectra of PPGE (region between 79 and 67 ppm): (a) soluble fraction; (b) insoluble fraction; (c) optically pure PPGE



Peak	δ (ppm)	DEPT	Tacticity
1	78.26	CH	mm
2	78.14	"	mr + rm
3	78.04	"	rr
4	69.96	CH_2	m
5	69.76	"	r(mrm)
6	69.70	"	r(mrr + rrm)
7	69.63	"	r(rr)
8	67.82	CH_2	---

Figure 3 Assignments of the main chain PPGE carbons in the ^{13}C n.m.r. spectrum of soluble fraction in $CDCl_3$

types of active sites, those with stereoselectivity, leading to a high-molecular-weight isotactic polymer, and those without stereoselectivity, leading to a low-molecular-weight atactic polymer.

From the results it can be concluded that all soluble fraction samples are not completely atactic. Moreover, the first experiment in *Table 1*, where different Zn/Al ratios were used (range 0.2–1.2), seems to indicate that the structure of the corresponding active sites in the initiator complex does not depend on the ratio Zn/Al. This behaviour implies that the zinc chloride proportion in the medium only has an effect on the number of active species and therefore on the polymerization rate and on the final conversion, as has been reported in a previous study[21].

On comparing the experiments made with different halides (experiments 1, 2 and 3), it is possible to prove that the tacticity of the polymer is similar for all of them, in spite of their coordinative ability as the Lewis acid decreases from chloride to iodide and steric hindrance increases. On the other hand, when zinc acetate is used (experiment 4) the polymer obtained is practically atactic. This fact could be explained because of its poor coordination ability with the oxiranic oxygen, due to the presence of its own oxygens.

It seems that the presence of water in the initiator system does not affect the structure of the active sites,

Table 1 Percentage of isotactic diads for soluble and insoluble PPGE fractions obtained using different initiator systems

			Area (%)[a]					
				Methine		Methylene		
Experiment	Initiator system	Fraction	i	h	s	l	S	Isotactic diads[b] (%)
1	AIP/$ZnCl_2$ Mon./init. = 100/1 Zn/Al = 0.2 to 1.2	Sol.	36.8	42.2	21.1	58.3	41.7	58.0
2	AIP/$ZnBr_2$ Mon./init. = 100/1 Zn/Al = 0.5	Sol.	35.5	44.9	19.5	59.7	40.3	58.8
3	AIP/ZnI_2 Mon./init. = 100/1 Zn/Al = 0.5	Sol.	38.5	42.8	18.7	60.4	39.6	60.0
4	AIP/$Zn(AcO)_2$ Mon./init. = 100/1 Zn/Al = 0.5	Sol.	28.4	45.6	26.1	52.7	47.3	51.9
5	$[(i\text{-PrO})_2AlO]_2Zn$ Mon./init. = 100/1 Zn/Al = 0.5	Sol.	31.9	45.5	22.9	55.5	44.5	55.1
6	AIP/$ZnCl_2$/H_2O 100/1, Zn/Al: 0.5 H_2O/Al = 1.0	Sol.	36.5	42.7	20.8	59.0	41.0	58.5
7	AIP/$ZnCl_2$ Pure (*R*)-PGE 100/1, Zn/Al: 0.5	Insol.	93.2	4.6	2.2	96.5	3.5	96.0
8	AIP/$ZnCl_2$ Mon./init. 100/1 Zn/Al = 0.2–1.2	Insol.	65.0	21.9	14.2	77.7	22.3	78.2
9	AIP/$ZnCl_2$ Mon./init. 200/1 Zn/Cl = 0.5	Insol.	69.2	20.2	10.5	81.4	18.6	80.4
10	$[(i\text{-PrO})_2AlO]_2Zn$ Mon./init. = 100/1 Zn/Al = 0.5	Insol.	58.5	27.2	14.3	73.6	26.4	72.8

[a] Average values from several experiments
[b] Average values from methinic carbon $(i+\frac{1}{2}h)$ and of methylenic carbon (l)

since the polymer obtained has a similar degree of tacticity (experiment 6). This indicates that water only modifies the competitive polymerization mechanisms and therefore varies the final degree of conversion of the different fractions. This behaviour matches the observed evolution of the experimental conversion values[21].

As far as the study of the tacticity of the insoluble fractions is concerned, also shown in *Table 1*, it must be pointed out that the spectra were recorded in the gel state (polymer swollen in tetrachloroethane-d_2) and for that reason very accurate quantitative measurements could not be obtained.

As can be seen in experiment 7, it was possible to obtain a polymer with a higher percentage of isotactic diads (96%) in the insoluble fraction, when the enantiomeric pure monomer was polymerized.

From the analysis of the results in experiments 8 and 9, we can confirm that the insoluble fraction is basically isotactic, with a degree of tacticity similar to the one previously reported for PPO[6] and poly(*p*-chlorophenyl glycidyl ether)[10] using the same initiator system. Moreover, from experiment 8 it can be deduced that the stereoselective active sites show the same Zn/Al ratio independence observed for the non-stereoselective ones.

When the catalyst described by Teyssié is used (experiments 5 and 10) a comparatively lower degree of tacticity for both fractions can be observed. This can be attributed to the faster polymerization rate, which may have repercussions on the selectivity of the polymerization.

All these results confirm that the insoluble fraction is highly isotactic and the soluble fraction is nearly atactic, as can be expected for an ionic-coordinative mechanism.

Determining the irregularity content

As has already been noted, the soluble fraction spectrum (*Figure 1*) shows a great number of small signals that, considering to its low molecular weight, we can expect to correspond mainly to the end chain groups. Also, as the coordinative polymerization mechanism can produce a certain percentage of irregular linkages, the appearance of the corresponding signals may be considered. Before assigning the different signals it was necessary to distinguish between the former and the latter type of signals.

The small signals that appear below 60 ppm (signals 14–17 in *Figure 1*) present a much greater shielding than those of the main chain (60–80 ppm) and can clearly be attributed to end chain groups. However, in the region where main chain carbons appear, irregularity signals can also be expected, together with some other end chain group signals.

In order to assign the resonances produced by various end-groups we examined PPGE samples with number-average molecular weights of 3200 and 800 (*Figure 4*). Since both fractions are synthesized by the same initiator, irregular linkage content must be similar in both samples and only those signals due to end-groups must undergo a relative intensity increase when molecular weight decreases. By comparing the spectra shown in *Figure 4* we can observe that in the oligomeric fraction spectrum (*Figure 4a*) the signals numbered 1, 2, 3, 4, 7, 8, 9, 10, 11, 12 and 13 increase fourfold with respect to the higher molecular weight fraction (*Figure 4b*). However, signals 5 and 6 do not behave in the same fashion, which seems to indicate that they correspond to irregular linkages. To confirm this first assignment, relaxation times were measured.

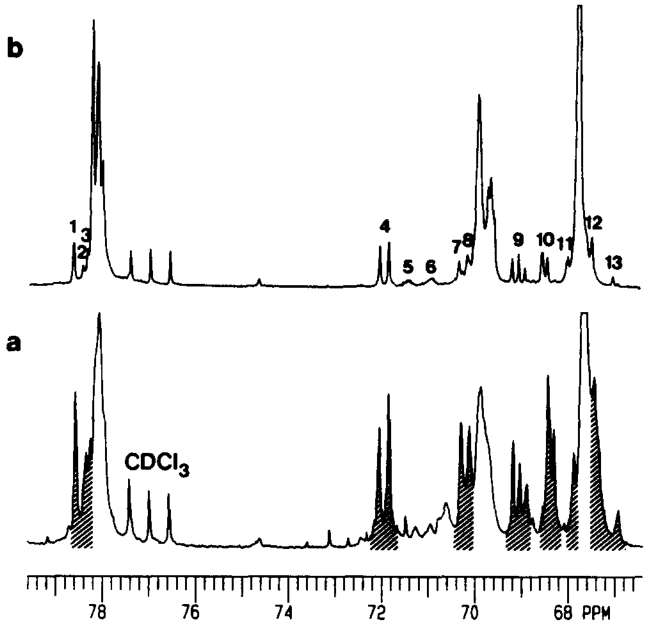


Figure 4 ^{13}C n.m.r. spectra (region between 65 and 80 ppm) of two PPGE samples of different molecular weight: (a) $\bar{M}_n = 800$; (b) $\bar{M}_n = 3200$

Table 2 Chemical shifts (δ), d.e.p.t. experiments, relaxation times (T_1) and assignments for aliphatic carbons in the ^{13}C n.m.r. spectrum of PPGE soluble fraction.

Resonance	δ (ppm)	D.e.p.t.	T_1 ($\pm 2\%$)	Assignment
1	78.67	CH	0.361	EG
2	78.47	CH	0.413	EG
3	78.32	CH	0.387	EG
a	78.26	CH	0.257	Main chain
a	78.14	CH	0.262	Main chain
a	78.04	CH	0.254	Main chain
4(4′)	72.07	$CH_2 + CH$	[a]	EG
4	71.89	CH_2	0.242	EG
5	71.32	CH_2	0.183	I
6	70.88	CH_2	0.165	I
7	70.39	CH_2	[a]	EG
8	70.21	CH_2	[a]	EG
b	69.96	CH_2	0.161	Main chain
b	69.76	CH_2	[a]	Main chain
b	69.70	CH_2	0.153	Main chain
b	69.63	CH_2	0.145	Main chain
9	69.24	CH	0.317	EG
9	69.10	CH	0.467	EG
9	68.97	CH	[a]	EG
10	68.60	CH_2	0.319	EG
10	68.48	CH_2	0.260	EG
11	68.04	CH_2	[a]	EG
c	67.82	CH_2	0.174	Main chain
12	67.53	CH_2	[a]	EG
13	67.11	CH_2	[a]	EG
14	56.57	CH	[a]	EG
15	43.33	CH_2	[a]	EG
16	22.60	CH_3	[a]	EG
17	21.98	CH_3	[a]	EG
17′	21.89	CH_3	[a]	EG

EG, end chain group; I, irregularity

[a] Owing to its low intensity, it was not possible to calculate the exact values for T_1; however, it could be observed qualitatively that relaxation times are higher than obtained for the main chain

The d.e.p.t. results and the relaxation time values for the signals that appear between 80 and 65 ppm, are shown in *Table 2*. As can be seen, signals 5 and 6 (methylene carbons) present a relaxation time which is very close to that obtained for the main chain methylene carbon. The rest of the small signals have higher relaxation times, which correspond to the higher mobility of the final groups. Thus, signals 5 and 6 can be attributed to methylene irregular chain linkages.

The end chain group signals were also assigned but this will be considered in a future paper.

As far as the different regiosequences due to the two directions of ring-opening are concerned, we can expect four different triads, one regular and three irregular. Since H–H, H–T and T–T linkages present different separations between their asymmetric centres it can be expected that three different, well separated signals will appear in the ^{13}C n.m.r. spectrum for each methylene and methine chain carbon. In addition, this separation should be greater than that caused by the different stereosequences.

In order to assign the small signals that correspond to irregular sequences in the soluble fraction spectrum, we proceeded to the analysis of a PPGE sample obtained with AIP alone. This cationic initiator affords low-molecular-weight polymers with a high irregularity content.

When the aliphatic region was examined, four main methine signals at 78.1, 77.9, 77.6 and 77.4 ppm and four methylene signals at 71.4, 70.9, 70.3 and 69.8 ppm were observed. All these signals, which are partially overlapped by other signals due to end chain groups, correspond to the main chain carbons of the four triads. On the other hand, the methylene carbon of the pendent chain does not show any splitting.

By comparing these signals to the regular spectrum sample obtained with AIP/$ZnCl_2$, we can deduce that the signals at 78.1 and 69.8 correspond unmistakably to the H–T regular sequence. The assignment of the other signals requires a more detailed study. An empirical estimation of the chemical shifts taking the different sequences of the four triads into account, following Grant and Paul rules, leads to an assignment which basically depends on the magnitude of the conformational gamma gauche effect, which is not well known. In fact, in some triad sequences this difference only depends on the influence of an additional δ-carbon, therefore it can be expected that their chemical shifts only differ by 0.1–0.3 ppm. However, the differences observed in the chemical shifts of the four triads range from 0.5 to 1 ppm. This confirms that conformational effects are very important and make this empirical assignment unreliable.

As the intensities of the different methine and methylene carbon signals are closely related to the probabilities of the two ring-opening modes, a study of the statistical distribution of the regular and irregular linkages can help in the assignment of these signals. In order to elucidate the statistical triad sequence distribution for this polymer, it is necessary to know all the triad signal areas to a high degree of accuracy. Unfortunately, when this method is applied to low-molecular-weight samples, as in this case, these signals very often appear partially overlapped with the end chain groups, making accurate measurements difficult.

Since the chemical shifts of the final groups are greatly affected by the nature of the solvent, the same irregular PPGE sample was recorded in several deuterated solvents (chloroform, acetone, pyridine, benzene and TCE). The comparison of these spectra showed that, with the exception of those recorded in the halogenated solvents, a suitable separation and delimitation of the areas bounded by the signals is achieved. The best results were obtained from the spectra recorded in acetone, which showed only a noteworthy overlapping with one signal attributed to the hydroxylated end-group carbons. According to the results obtained from these experiments, the measurements were made mainly from the spectra recorded in acetone as solvent with the addition of an appropriate amount of trichloroacetylisocyanate (TAI) (*Figure 5*). As TAI reacts with the hydroxylic group, this produces a considerable deshielding of the troublesome carbon signals[30]. The approximate average area values obtained from the manually deconvoluted peaks (shaded area in *Figure 5*) are shown in *Table 3*.

The application of the Bernouillian statistical model[31] implies that the sequence areas [010+101], [100+110], [001+011] should be the same and smaller than the sequence area [000+111]. However, this is not in agreement with the above experimental data. As can be seen, one of the irregular triads presents a higher intensity and for this reason it can be concluded that this model cannot be applied.

If the first-order Markov statistics model is considered[32], a general method proposed by Price predicts the percentage of the different triads as a function of two parameters: $P_{\alpha/\beta}$, the probability that an α-opening is followed by a β-opening; and $P_{\beta/\alpha}$, the probability that a β-opening is followed by an α-opening. These equations are strictly valid only for infinite chains but according to Price they can be applied to chains of relative finite length[32]. In our case, due to the low polymerization degree, the calculated results must be considered only as

Table 3 Intensities of CH and CH_2 triad signals in the ^{13}C n.m.r. spectrum of PPGE obtained with AIP alone

	Peak			
	a_1, b_4	a_2, b_2	a_3, b_1	a_4, b_3
Area (%)	36–38	26–27	18–19	17–18

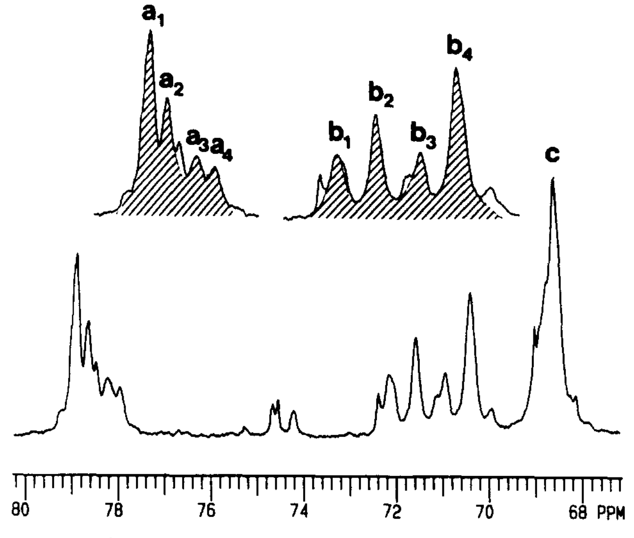


Figure 5 ^{13}C n.m.r. spectrum (region between 65 and 80 ppm) of PPGE obtained with AIP alone, recorded in deuterated acetone in presence of TAI (triad signals are shaded)

Table 4 ^{13}C n.m.r. triad signal intensities calculated by applying Markov statistics to the PPGE obtained with AIP alone

Percentage of triads				Irregular linkages content (%)	Ring-opening probabilities		β-opening (%)
000+111	010+101	100+110	001+011		$P_{\alpha/\beta}$	$P_{\beta/\alpha}$	
37.0	26.0	18.5	18.5	44.5	0.87	0.30	74

Table 5 Chemical shifts and assignments of regular and irregular triad signals from the ^{13}C n.m.r. spectrum of PPGE obtained with AIP alone (recorded in $CDCl_3$)

Methine carbons			Methylene carbons		
Peak	δ (ppm)	Triad assignment	Peak	δ (ppm)	Triad assignment
a_1	78.1	[000+111]	b_1	71.4	[001+011]
a_2	77.9	[010+101]	b_2	70.9	[010+101]
a_3	77.6	[001+011]	b_3	70.3	[100+110]
a_4	77.4	[100+110]	b_4	69.8	[000+111]

an approximation that may be useful only when they match the experimental data.

The application of these equations to different values of $P_{\alpha/\beta}$ and $P_{\beta/\alpha}$ allows us to prove that for $P_{\alpha/\beta}=0.87$ and $P_{\beta/\alpha}=0.30$ the percentages obtained are very close to the experimental values. This fact confirms that first-order Markov statistics describe the distribution of the irregular sequences in this irregular polymer. *Table 4* shows the values calculated from this model, which closely coincide with those reported by Dworak and Jedlinski for the poly(*p*-chlorophenyl glycidyl ether) obtained with only AIP as initiator[33].

On comparing these results with the above experimental data, it can be proved that signals a_1 and b_4 in *Figure 5* correspond to the methine and methylene carbons of the [000+111] triad and signals a_2 and b_2 correspond to the same carbons in the [010+101] triad. The assignment of the other triads can be proposed taking into account that [100+110] sequences undergo an additional γ-carbon influence in relation to [001+011] sequences, and therefore the latter should be expected to appear more shielded. All these assignments are summarized in *Table 5*.

Although, as has already been mentioned, the different area percentages coincide with those reported by Jedlinsky and colleagues, their methylene carbon triad assignment does not coincide with that in the present study. This fact cannot be attributed only to the effect of the aromatic ring substitution. Several experiments carried out in order to clarify these differences showed that when the PPGE(AIP) spectrum was recorded in deuterated dimethyl sulfoxide (DMSO) (the solvent they used), a different ratio of the areas bounded by the signals is obtained as a result of the overlapping of one methylene carbon signal corresponding to the hydroxylic end chain and one triad signal. In addition, the lower resolution of the n.m.r. device they used may have contributed to this incorrect assignment. In contrast, the ratio between the signals of the different triads for the methine carbon does not seem to depend on the solvent used.

Figure 6 shows two representative PPGE samples with different degrees of regularity. From the analysis of these spectra it can be seen that the irregular methine carbon signals (not plotted) are included in the stereoregular triad signals of the main regular chain. In the methylene region, signals 5 and 6 are due to the [001+011] and [010+101] irregular triad methylene carbons. The signal corresponding to the sequence [100+110], which should appear at 70.3 ppm, must be included in the end chain group signals.

Once the different triads were assigned, their areas were calculated to find the percentage of irregularities in both samples. These results are shown in *Table 6* (experiments 3 and 10).

The intensities of the three irregular triads are very

Table 6 Irregular linkages content of several PPGE soluble samples obtained with different initiator systems

Experiment	Initiator system	Calculated percentage of triads		β-opening (%)	Irregular linkages content (%)
		[000+111]	[001+011] [010+101]		
1	AIP/$ZnCl_2$ Zn/Al=0.2	90.6	3.1	96.6	6.7
2	AIP/$ZnCl_2$ Zn/Al=0.4	94.4	1.9	98.1	3.8
3	AIP/$ZnCl_2$ Zn/Al=0.5	95.9	1.4	98.6	2.8
4	AIP/$ZnCl_2$ Zn/Al=0.6	96.2	1.2	98.7	2.6
5	AIP/$ZnCl_2$ Zn/Al=0.8	96.8	1.1	98.9	2.2
6	AIP/$ZnCl_2$ Zn/Al=1.0	96.8	1.1	98.9	2.2
7	AIP/$ZnCl_2$ Zn/Al=1.2	96.8	1.2	98.9	2.3
8	AIP/$ZnBr_2$ Zn/Al=0.5	95.6	1.5	98.5	3.0
9	AIP/ZnI_2 Zn/Al=0.5	94.7	1.7	98.2	3.5
10	AIP/$Zn(AcO)_2$ Zn/Al=0.5	90.6	3.1	96.6	6.7
11	AIP/$ZnCl_2/H_2O$ H_2O/Al=1.0 Zn/Al=0.5	95.9	1.4	98.6	2.8
12	Teyssié catalyst	96.0	1.3	98.7	2.6

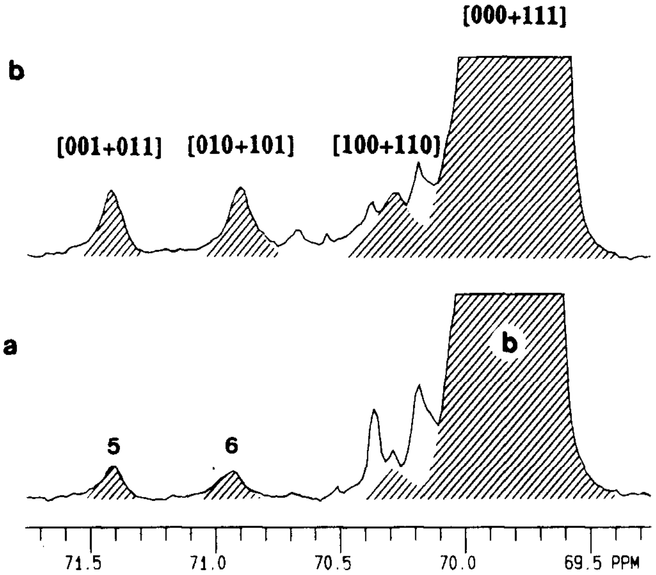


Figure 6 ^{13}C n.m.r. spectra (region between 69 and 72 ppm) of PPGE soluble fraction in $CDCl_3$: (a) prepared with AIP/$ZnCl_2$ (monomer/initiator = 100/1, Zn/Al = 0.5); (b) prepared with AIP/$Zn(AcO)_2$ (monomer/initiator = 100/1, Zn/Al = 0.5)

close, due to the fact that in polymers with high regioregularity the ratio $P_{\alpha/\beta}$ is about 1 and $P_{\beta/\alpha}$ is about 0. This produces an apparent approximation to the Bernouillian statistics.

By comparing the methylene carbon areas of the irregular triads, [001 + 011] and [010 + 101], with the regular triad [000 + 111], the degree of regularity of the soluble PPGE fractions may be straightforwardly calculated. The results show that in most experiments the polymer attains a degree of regularity which is higher than 98%.

As can be seen in *Table 6*, experiments 1 to 7, which were carried out with different Zn/Al ratios, show an increase in the degree of regularity with the Zn/Al ratio up to 0.5–0.8. From this point it remains practically constant. This behaviour can be explained by the presence of a low-molecular-weight fraction formed by a cationic mechanism due to the excess of AIP in the reaction medium. This seems to be confirmed by the analysis of the oligomeric fractions, which show a similar behaviour when compared with Zn/Al ratio but a higher irregular linkage content (8–20%).

When different zinc salts were used (experiments 3, 8, 9 and 10) it was observed that a decrease in the coordinative ability leads to a gradual decrease in the regularity of the chain. The presence of water (experiment 11) has no influence on the regioregularity of the polymer.

The use of the Teyssié catalyst (experiment 12) leads to polymers with degrees of regioregularity that are similar to those synthesized using our initiator system. In contrast to the degree of tacticity, which undergoes a decrease due to the higher polymerization rate, the regioregularity does not seem to be affected.

We would like to point out that the irregular linkage percentage is notably lower than that reported by Jedlinsky for the poly(*p*-chlorophenyl glycidyl ether) obtained using the same initiator system. This difference appears to be due to the polymerization solvent. Jedlinsky and coworkers use *o*-dichlorobenzene or dioxane with poor coordination ability in comparison with the ethereal solvent used in the present study. This coordination ability is shown by the formation of a stable adduct with zinc chloride. Taking this into account we can expect this solvent to be a part of the initiator system, increasing its stability and probably the stereoselectivity of the opening attack on the least substituted site in the oxirane ring, due to its enhanced steric hindrance. Studies on catalyst composition and structure that coincide with this theory will be the subject of a separate publication.

Irregularity signals were not detected in the n.m.r. spectrum of the PPGE insoluble fraction, so the regioregularity reached is practically 100%.

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