Investigation of the structure of poly(p-chlorophenyl glycidyl ether) by the ^{13}C n.m.r. technique: tacticity and addition isomerism

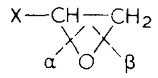
Andrzej Dworak and Zbigniew Jedlinski
Polish Academy of Sciences, Institute of Polymer Chemistry, 41-800 Zabrze, Poland
(Received 22 February 1979)

The *p*-chlorophenyl glycidyl ether was polymerized in the presence of $Al(OiPr)_3$, $ZnCl_2$, $SnCl_4$, BuOK, KOH and by the $Al(OiPr)_3$–$ZnCl_2$ 1:1 initiator system. Analysis of the ^{13}C n.m.r. spectra of the poly(*p*-chlorophenyl glycidyl ethers) obtained has made it possible to determine their tacticity and the content of the head-to-tail and head-to-head linkages in the polymer chain.

INTRODUCTION

The close connection between the mechanism of polymerization and the molecular structure of polyethers has caused considerable attention to be paid to this problem. A number of papers have dealt with the analysis of the tacticity of poly(propylene oxide)[1–9], poly(t-butyloxirane)[10] and poly(methyl glycidyl ether)[11].

However, there is a conspicuous lack of information concerning studies on the problem of addition isomerism, i.e. the determination of the content of the head-to-tail and head-to-head sequences that may be formed in the polymerization of monosubstituted oxiranes in the case of α- and β-ring opening processes taking place:



Price[12,13] has described a method of determining the content of head-to-tail linkages in the poly(propylene oxide) chain by its osonolysis and the subsequent analysis of the structure of chain fragments obtained.

Oguni *et al.*[4] have determined the content of regular linkages in a polymer obtained over hydrolysed triethylaluminium by analysing the ^1H n.m.r. spectrum of poly(propylene oxide) deuterated in the β position. Tani *et al.*[14] have used the same technique for determining the content of regular linkages in the polymer obtained in the presence of $Et_2AlOAlEt_2$. Oguni[3] has given the ^{13}C n.m.r. spectra of poly(propylene oxide) containing irregular linkages, without however attampting to assign a particular structure to the spectral lines observed. We described also the structure of poly(propylene oxide) obtained over various initiator systems[15].

The kinetics of the polymerization of *p*-chlorophenyl glycidyl ether over $Al(OiPr)_3$–$ZnCl_2$ initiator system and the properties of obtained polymers were subjects of our previous studies[16,17]. It was the aim of the present work to determine the structure of poly(*p*-chlorophenylglycidyl ether) as a step indispensable for the further investigation of the polymerization mechanism involved. The poly(*p*-chlorophenylglycidyl ether) was obtained in polymerization reactions carried out using different initiators: $SnCl_4$, $ZnCl_2$, $Al(OiPr)_3$, BuOK, KOH and also the $Al(OiPr)_3$–$ZnCl_2$ 1:1 initiator system. The ^{13}C n.m.r. technique was used chiefly for the analysis of the content of the head-to-tail and head-to-head linkages and also for determining the tacticity of polymers obtained.

EXPERIMENTAL

Polymerization

The details of the polymerization and fractionation procedure have been described previously[16].

^{13}C n.m.r. spectra

The ^{13}C n.m.r. spectra were recorded in DMSO-d_6 or DMSO-d_6–nitrobenzene d_5 (~1:1) solutions at 90°C on a Brucker HX–90 spectrometer. Hexamethyldisiloxane was used as an internal standard. The relaxation times T_1 were determined on a Varian CFT–20 spectrometer by means of the inversion recovery method. The area bounded by the signals was determined using a planimeter. Superimposed signals were separated manually.

RESULTS AND DISCUSSION

The poly(*p*-chlorophenylglycidyl ethers) obtained were found to have different molecular weights and degrees of crystallinity, depending on the kind of polymerization initiator used.

Polymerization reactions carried out in the presence of the aluminium isopropoxide–zinc chloride 1:1 initiator system were found to give, in addition to the amorphous polymer fraction, a considerable yield of the crystalline polymer fraction of relatively high molecular weight (over 25 000). The other initiators were found to yield amorphous polymers of

0032–3861/80/010093–04$02.00
© 1980 IPC Business Press

low molecular weight (from 3000 to 10 000) and an oligomeric oily fraction (molecular weight below 1000), the latter not having been subjected to n.mr. spectroscopic analyses. Fractionation efficiency, and in particular the absence of low molecular weight oligomers in the amorphous polymer fraction was tested by gel permeation chromatography (g.p.c. solvent–chloroform; columns–Styragel 60 Å + 100 Å).

Discussion of the ^{13}C n.m.r. spectra

Crystalline fraction of the polymers obtained in the presence of Al(OiPr)$_3$–ZnCl$_2$ initiator system. The aliphatic part of the spectrum* of the crystalline polymer fraction was found to consist of three lines: $\delta_1 = 77.3$ ppm, $\delta_2 = 69.0$ ppm and $\delta_3 = 67.1$ ppm.

The line $\delta_1 = 77.3$ ppm was found by the off-resonance decoupling to correspond to the CH group. The assignment of the two lines of two CH$_2$ groups is more difficult owing to the small difference in their chemical shifts. Measurements of the relaxation time T_1 were found to give the following results: $T_1 = 0.27 \pm 0.03$ s for the line $\delta_2 = 69.0$ ppm and $T_1 = 0.31$ s $\pm$ 0.03 s for the line $\delta_3 = 67.1$ ppm, which seems to indicate that the line $\delta_2 = 69.0$ ppm is due to the CH$_2$ group in the polymer chain (decreased mobility).

The spectrum of the crystalline fraction of poly(*p*-chlorophenylglycidyl ether) shown in *Figure 1a* does not exhibit any splitting of signals. A very faint crest of the signal only at $\delta_2 = 69.0$ is to be seen.

The analysis of this ^{13}C n.m.r. spectrum, the high degree of crystallinity of the polymer, and the fact that poly(propylene oxide) polymerized under the same conditions was found to be isotactic[15] enabled us to conclude that the polymer whose spectrum is shown in *Figure 1a* was stereoregular. The weak signal at $\delta = 68.9$ ppm (an intensity of about 20%) was assigned to syndiotactic diads.

Amorphous polymers obtained in the presence of KOH, BuOK (Figure 1b). The ^{13}C n.m.r. spectra of these polymers were found to exhibit a definite splitting of the signal of the CH$_2$ group, a faint but nonetheless distinct doublet being observed at 69.0 ppm and 68.9 ppm. These signals were assigned to iso- and syndiotactic diads in the polymer chain. The ratio of their intensities ($m \cong r \cong 50\%$) shows those polymers are atactic.

Amorphous polymers obtained in the presence of SnCl$_4$, ZnCl$_2$ and Al(OiPr)$_3$ (Figure 1c). The ^{13}C n.m.r. spectra of polymers obtained in the presence of Lewis acid-type initiators, i.e. SnCl$_4$, ZnCl$_2$, and also over Al(OiPr)$_3$ were found to differ basically from those depicted in *Figure 1a* and *1b*, a pronounced splitting of signals due to the CH and CH$_2$ groups being observed. These effects were assigned to the presence of head-to-tail, head-to-head etc. sequences in the polymer chain. The Lewis acid nature of the initiator used, and the fact that poly(propylene oxide) synthesized by us under the same reaction conditions using the same initiator was found to contain a large amount of similar irregular sequences[15] are thought to confirm the above assignment of n.m.r. signals.

Determination of the content of regular (head-to-tail) sequences in the chain

In order to determine quantitatively the content of regular linkages (head-to-tail) in the investigated polymers, it was found necessary to assign the signals observed in the ^{13}C n.m.r. spectra (*Figure 1c*), i.e. two lines due to the CH group, four lines due to the CH$_2$ group in the polymer chain and two lines of the CH$_2$ side group to various possible isomers, corresponding to different addition directions, that may be present in the polymer chain.

The splitting of the signal due to the CH group into two lines is though to confirm the supposition that these two lines correspond to those CH groups in the polymer chain whose respective neighbourhoods differ markedly from one another; the regular linkages CH$_2$–O–CH– (line 1 at $\delta_1 = 77.8$ ppm) and the irregular linkages CH–O–CH (line 2 at $\delta_2 = 77.0$ ppm). The content of the regular linkages in the polymer chain is thus equal to the relative intensity of the line 1 (*Table 1*).

In order to make the assignment of the four lines due to the CH$_2$ group it was necessary to undertake the analysis of longer sequences that may be present in the polymer chain as a result of irregular addition[18]

As shown in *Figure 2*, eight kinds of such three-unit sequences may be present in the chain and four of them may be differentiated by spectroscopy: 000 + 111, 001 + 011, 110 + 100, 010 + 101. The assignment of the regular triads 000 + 111 to the line 6 in spectrum 1c may be done straightforwardly by comparison of that spectrum with the spectrum 1b Noting that[19,20]

$$[001] = [100],\ [011] = [110]$$

and therefore

$$[001 + 011] = [110 + 100]$$

(square brackets denote the participation on the chain structure of sequences contained within them i.e. the relative intensity of corresponding n.m.r. signals) one can assign the signal of the triad pairs 001 + 011 and 110 + 100 to the lines 3 and 4 in spectrum 1c, which show equal intensities (*Table 1*).

This makes it possible to assign the CH$_2$ group signals in the following manner:

line 3 $\delta_3 = 70.4$ ppm – triads 011 + 001
line 4 $\delta_4 = 70.0$ ppm – triads 110 + 100
line 5 $\delta_5 = 69.4$ ppm – triads 010 + 101
line 6 $\delta_6 = 69.0$ ppm – triads 000 + 111

The assignment of the lines 3 and 4 may be opposite to that one made above but, in view of their intensities being the same that is of no consequence in further considerations. The above assignment satisfies the necessary quantitative relations betwee the signal intensities J of the CH and CH$_2$ groups:

$$J_1 = J_6 + J_3, \qquad J_2 = J_5 + J_4$$

The content of irregular additions determined from the intensities of CH$_2$ signals agrees well with that calculated from the CH group signal intensities, which yield an additional support for the correctness of the analysis of the spectra. The data listed in *Table 1* comprise average values computed from the signal intensities of the CH and CH$_2$ groups.

These values may be compared with the results obtained by Oguni *et al.*[8] and Tani *et al.*[14], who found 62% of regular linkages in their ^{1}H n.m.r. studies of deuterated poly(propylene oxide) obtained over hydrolysed triethyl aluminium, and

---

* Signals due to aromatic carbon atoms are the same for all polymers and do not give any information on their microstructure, and hence will not be discussed in the present work

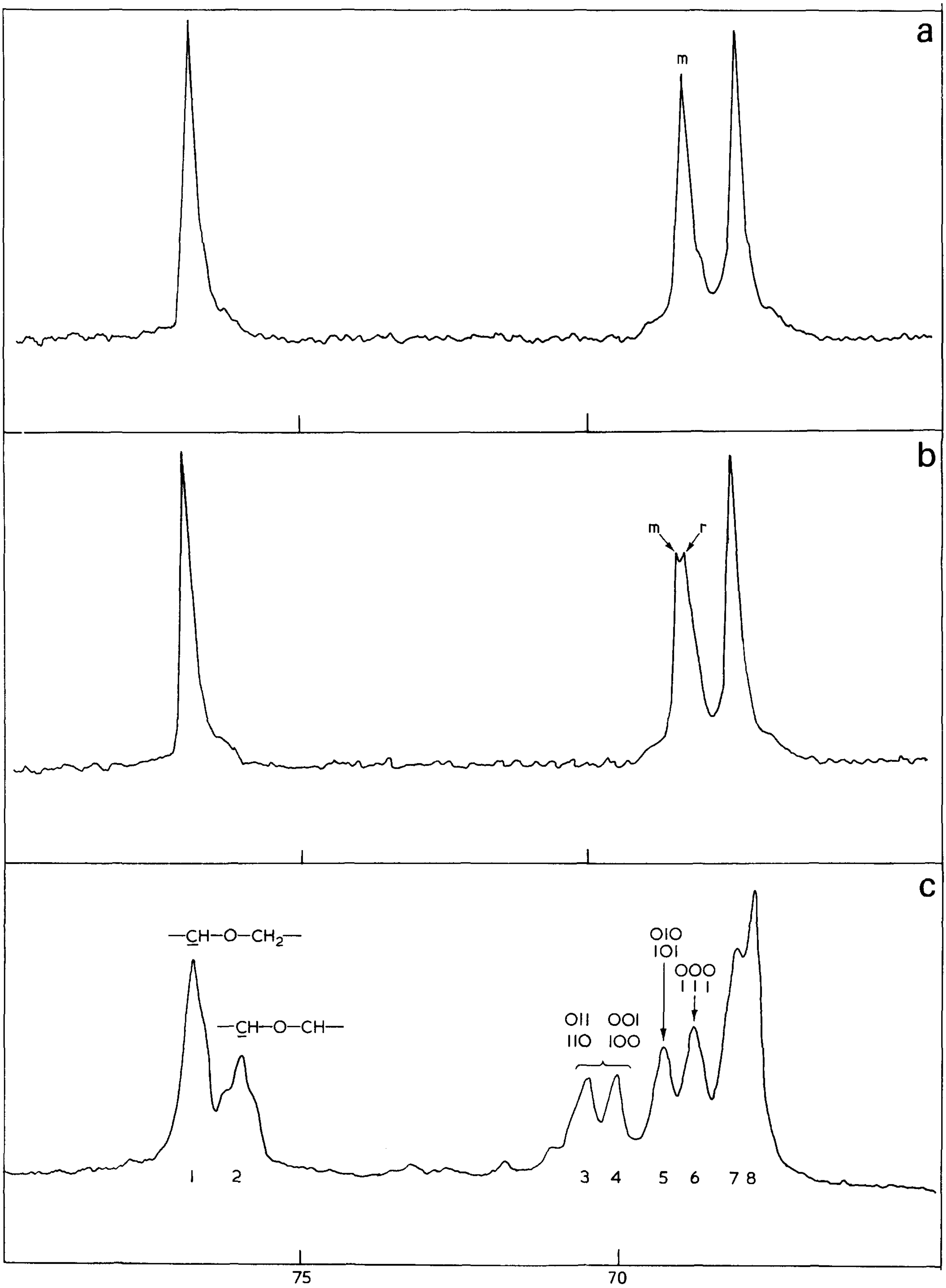


Figure 1 ^{13}C n.m.r. spectra of poly(p-chlorophenylglycidyl ether) (aliphatic part) (a) initiator system Al(OiPr)$_3$/ZnCl$_2$ (1:1) (b) initiators KOH, BuOK (c) initiators Al(OiPr)$_3$, ZnCl$_2$, SnCl$_4$

Table 1 Intensities of the CH and CH_2 groups signals in the ^{13}C n.m.r. spectra and the content of the regular (head-to-tail) linkages in poly(*p*-chlorophenylglycidyl ether)

	Intensity (%)*						
	CH		CH_2				Content of head-to-tail linkages (%)
Initiator	J_1	J_2	J_3	J_4	J_5	J_6	
$ZnCl_2$	61	39	18	19	22	41	60
$Al(OiPr)_3$	58	42	21	19	25	36	57
$SnCl_4$	54	46	23	22	27	28	52

* Accuracy ± 2% (approx), averaged values for at least 3 samples

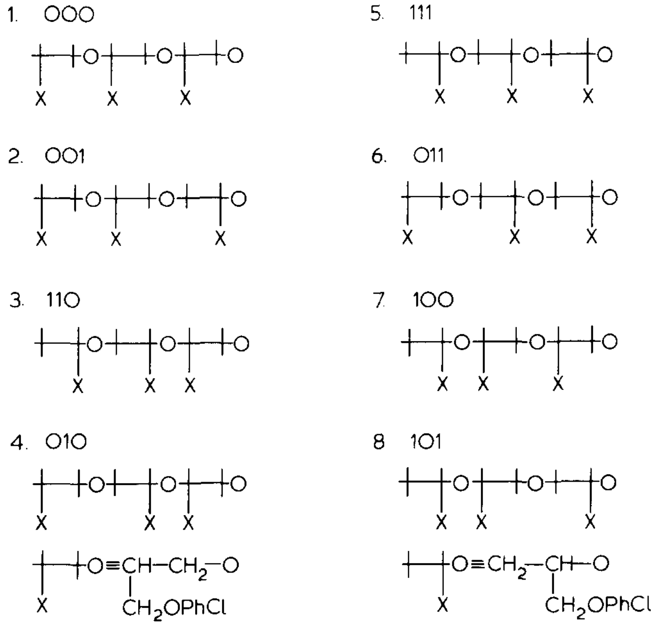


Figure 2 Triads formed in poly(*p*-chlorophenylglycidyl ether) due to different oxirane ring opening direction

with those of Price *et al.*[12,13] who found, on the basis of their gas chromatographic studies of osonolysis products, the content of regular linkages equalled 76% or 65% using $AlEt_3/H_2O$ or $ZnEt_2/H_2O$ respectively as initiators for the polymerization of propylene oxide.

The results presented herein confirm the close dependence of the structure of poly(*p*-chlorophenyl glycidyl ether) on the initiator system used. The use of potassium butylate and potassium hydroxide as initiators was found to lead to the formation of practically atactic polymers containing exclusively the head-to-tail regular sequences in the chain. On the other hand, polymers obtained in the presence of aluminium isopropoxide and in the presence of Lewis acid initiators ($ZnCl_2$, $SnCl_4$) were found to have a considerable amount of irregular head-to-head sequences, which means that ring opening takes place both in the α and β positions. The ring opening process and subsequently the polymerization in the presence of aluminium isopropoxide and zinc chloride alone were found found to differ from those taking place in the presence of the initiator system aluminium isopropoxide–zinc chloride 1:1. In the latter case crystalline isotactic polymers usually obtained in ionic-coordinative polymerization were found to be formed.

ACKNOWLEDGEMENT

The authors are indebted to Dr F. Keller (University of Leipzig, GDR) for some of the ^{13}C n.m.r. spectra used in this work.

REFERENCES

1 Schaefer, J. *Macromolecules* (1969) **2**, 533
2 Schaefer, J. *Macromolecules* (1972) **5**, 590
3 Oguni, N., Lee, K., Tani, H. *Macromolecules* (1972) **5**, 819
4 Oguni, N., Maeda, S., Tani, H. *Macromolecules* (1973) **6**, 459
5 Hirano, T., Pham, H. K., Tsuruta, T. *Makromol. Chem.* (1972) **153**, 331
6 Lapeyre, W., Cheradame, H., Spassky, N., Sigwalt, P. *J. Chim. Phys. Phys.-Chim. Biol.* (1973) **70**, 838
7 Uryu, T., Shimazu, H., Matsuzaki, K. *J. Polym. Sci. (Polym. Lett. Edn)* (1973) **11**, 275
8 Oguni, N., Watanabe, S., Tani, H. *Polym. J.* (1973) **4**, 664
9 Aggarwal, S. L., Marker, L. F *ACS Symposia Ser.* (1974) **6**, 38
10 Sato, A., Tsuneo, H., Tsuruta, T. *Makromol. Chem.* (1977) **178**, 609
11 Spassky, N., Pourdjavadi, A., Sigwalt, P. *Europ. Polym. J.* (1977) **13**, 467
12 Price, C. C., Spector, R. *J. Am. Chem. Soc.* (1965) **87**, 2069
13 Price, C. C., Spector, R., Tumulo, A. *J. Polym. Sci. (A)*(1967) **5**, 407
14 Tani, H., Oguni, N., Watanabe, S. *J. Polym. Sci. (A)* (1968) **6**, 577
15 Jedliński, Z., Dworak, A., Bero, M. *Makromol. Chem.* (1979) **180**, 949
16 Jedlinski, Z., Bero, M., Dworak, A., Piechowiak, E. *Acta Polymerica* (1979), **30**, 249
17 Jedlinski, Z. *Vysokomol. Soed.* Plenary and Main Lectures of the IUPAC-Symposium, Tashkent 1978
18 Elgert, K. -F., Ritter, W. *Makromol. Chem.* (1977) **178**, 2827
19 Price, F. C. *J. Chem. Phys.* (1962) **37**, 209
20 Bovey, F. A. *Pure Appl. Chem.* (1967) **15**, 349