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Irregular sequence distribution statistics in poly(*p*-chlorophenyl glycidyl ethers)

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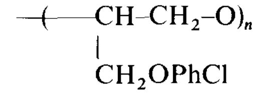
Irregular sequences (head-to-head, tail-to-tail) always occur in polyether chains formed by the opening of the oxirane ring both in the α and β positions during polymerization. These sequences also influence the microstructure of the polyether chains and hence the properties of the resultant polymer. Knowledge of the number and distribution of the sequences makes it possible to draw conclusions as to the actual chain structure and the polymerization mechanism leading to its formation.

Information concerning this aspect of polyether structure is based upon analysis of the products of the decomposition of polyethers by ozonolysis[1,2] or by the action of butyllithium[3] and on the results of n.m.r. studies[4–8]. The sequence distribution of irregular linkages has not been previously described.

A method of interpreting the ^{13}C n.m.r. spectra of poly(*p*-chlorophenyl glycidyl ethers)



$$\left(\underset{\displaystyle CH_2OPhCl}{CH}-CH_2-O\right)_n$$

containing irregular linkages was proposed in our previous work[8]: it made possible the determination of the number of different addition triads in the structure of the polyether chain, and also the number of irregular linkages (head-to-head, tail-to-tail) in a number of polyethers prepared using various initiator systems (*Table* 1).

The distribution of regular and irregular linkages can be determined from a knowledge of the relative numbers of the different triads along the polymer chain. Bernoulli statistics may be used to describe this distribution, assuming that the probability of α (or β) ring-opening at a given reaction stage does not depend on the direction of ring-opening in the preceding stage of the reaction[9].

It follows from calculations involving Bernouli statistics that the number of triad sequences, 010+101, 110+100, 011+001 must be equal in all cases. This, however, contradicts the experimental data, where it was found that [010+101]>[110+100]=[001+011] (*Table* 1). Consequently, Bernoulli statistics cannot be used to describe the distribution of irregular chain sequences in the polyethers studied.

A general method due to Price[10] may be used to calculate the number of individual triads, when first-order Markov statistics apply.

Table 1 Content of irregular linkages and ring-opening probabilities in poly(*p*-chlorophenyl glycidyl ethers). Polymerization conditions: solvent, 1,2-dichlorobenzene; monomer concentration, 4.25 mol l^{-1}; initiator concentration, 1.8×10^{-2} mol l^{-1}, temperature 90°C

	Initiator	Percentage of triads 000 + 111	 010 + 101	 110 + 100	 001 + 011	Irregular linkages content %	Ring-opening probabilities $p_{\alpha/\beta}$	 $p_{\beta/\alpha}$	Percentage participation of opening
	$ZnCl_2$	41	22	18	19	41	0.82	0.21	75
	Al $OiPr_3$	36	25	19	20	44	0.81	0.31	72
	$SnCl_4$	28	27	22	23	49	0.12	0.38	65
$Al(OiPr)_3$ + $ZnCl_2$ +	Zn:Al = 2	58	15	14	13	28	0.92	0.16	85
	Zn:Al = 0.5	74	9.5	8.5	8	18	0.95	0.10	90
	Zn:Al = 0.25	59	15	13	13	28	0.90	0.17	84

Designation of triads: $0 = O-\underset{\displaystyle CH_2OPhCl}{CH}-CH_2$ $1 = O-CH_2-\underset{\displaystyle CH_2OPhCl}{CH}$

$p_{\alpha/\beta}$ = probability that α opening is followed by β opening
$p_{\beta/\alpha}$ = probability that β opening is followed by α opening

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The following relations are then obtained:

$$[000+111]=\frac{p_{\beta/\alpha}(1-p_{\alpha/\beta})^2+p_{\alpha/\beta}(1-p_{\beta/\alpha})^2}{p_{\alpha/\beta}+p_{\beta/\alpha}}$$

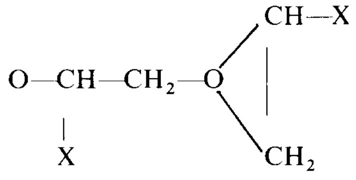
$$[010+101]=p_{\alpha/\beta}p_{\beta/\alpha}$$

$$[011+001]=[100+110]=\frac{p_{\alpha/\beta}p_{\beta/\alpha}(2-p_{\alpha/\beta}-p_{\beta/\alpha})}{p_{\alpha/\beta}+p_{\beta/\alpha}}$$

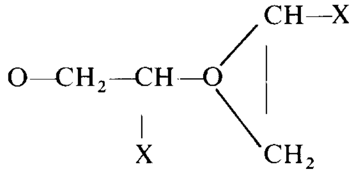
which indicate the numbers of the different triads as a function of two parameters: $p_{\alpha/\beta}$, the probability that an α operning is followed by a β opening; and $p_{\beta/\alpha}$, the probability that β opening is followed by an α opening.

From these equations both parameters $p_{\alpha/\beta}$ and $p_{\beta/\alpha}$ may be calculated and the shares of α and β opening during the polymerization may be estimated*.

The applicability of first order Markov statistics for describing the distribution of irregular sequences in the polyether chains studied indicates the dependence of the opening of oxirane ring in a given reaction step on the direction of that opening in the preceding reaction step. To explain this we have to consider the fact that the structure of the gorwing chain end depends upon the direction of oxirane ring opening leading to its formation:



(I)



This proof of the applicability of first order Markov stastitics allows to conclude that the probability for the oxirane ring opening in a given direction (e.g., β) depends on the structure of the growing chain end. For an attack of the terminal unit (I), formed as a result of β opening, the probability of β opening is different from that obtained for the attack of the terminal unit (II), produced in an α ring opening process. Investigations of the dependence of polymer structure on the type of initiator system used is the subject of a seperate publication[11].

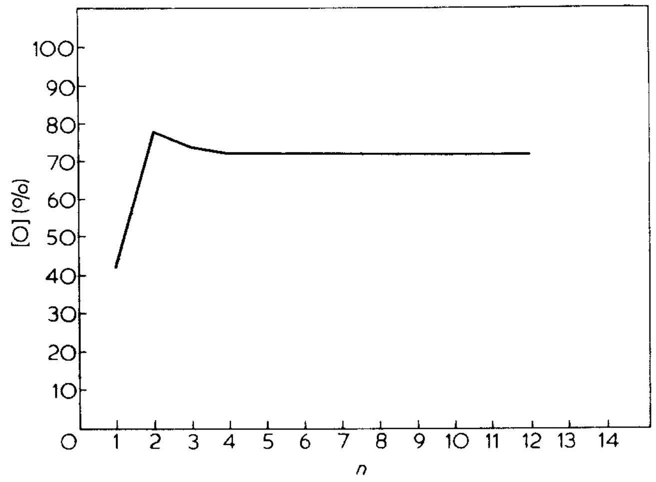


Figure 1 Dependence of polymer composition (content of 'normal' units [O]) on the degree of polymerization *n*. Calculated for the $p_{\alpha/\beta}$ = 0,81; $p_{\beta/\alpha}$ = 0.31

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* This is strictly valid only for infinite chains, but according to Price[10], the possibility of applying these equations to chains of finite length, i.e. those having more than ~20 recurring units, is justifiable.