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Polymerization of Chlorophenyl Glycidyl Ethers. VI.

Chain Transfer Reaction in the Potassium Glycolates-Initiated Anionic Polymerization of p-Chlorophenyl Glycidyl Ether

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Dedicated to Prof. C.I. Simionescu on the occasion of the 60th anniversary of his birthday

SUMMARY

Polymerization of p-chlorophenyl glycidyl ether initiated by potassium glycolates (ethylene, propylene and 2-methyl propylene glycolates) in DMSO containing some 18-crown-6 ether or glycol was investigated. For the reaction system containing the propylene glycolate asymmetrically substituted with a methyl group, relatively high polymerization rates were obtained as compared with those found for the other systems studied, the resultant polymers also having higher molecular weights and comparatively low polydispersities. Aliphatic double bonds were found to be absent in the polymers synthesized, which would suggest that in the anionic polymerization process studied the growing chain is not transferred to the monomer.

INTRODUCTION

The anionic polymerization of oxiranes has been arousing a great interest in recent years. For ethylene oxide polymerization, GEE et al.(1959,1961), and later WOJTECH (1966), used sodium and potassium methoxides in a solution of methanol as catalysts. Methoxides of the alkali metals were also used by LEBEDEV and BARANOV (1966) in the polymerization of phenyl glycidyl ether. SOROKIN et al.(1959,1962) polymerized the aliphatic and aromatic glycidyl ethers using sodium ethoxide and butyl alcohol. BANKS and PETERS (1970) studied the kinetics of polymerization of phenyl glycidyl ether initiated by sodium methoxide in dioxane and DMSO. PRICE et al.(1966,1972), and subsequently BAWN et al.(1969) and BLANCHARD et al.(1972), used potassium tert-butoxide in DMSO for studying the polymerization kinetics of ethylene oxide, phenyl glycidyl ether and other oxiranes.

Works hitherto published on the anionic polymerization of oxiranes in the presence of alcoholates of alkali metals are mainly concerned with polymerization reactions initiated by alcoholates derived from monohydric alcohols. Sodium or potassium alcoholates of trihydric alcohols, and those of alcohols with higher functionalities have also aroused industrial interest as ini-

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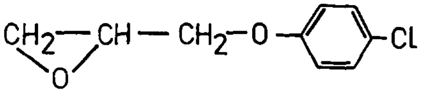
tiators of oxiranes polymerization (GAYLORD, 1963). Polyethers obtained in their presence have a functionality higher than two, and may be hence used, for instance, as the polyol component required for the manufacture of rigid polyurethane foams.
This paper presents the results obtained for the polymerization of p-chlorophenyl glycidyl ether 1.

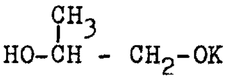


1

Mono-potassium glycolates with different methyl substituents, i.e. ethylene glycolate 2, propylene glycolate 3, and 2-methyl propylene glycolate 4 are employed as polymerization initiators along with DMSO as polymerization solvent.

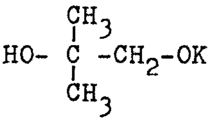
$HO\text{-}CH_2\text{-}CH_2\text{-}OK$

2



$HO\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}OK$

3



$HO\text{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{-}CH_2\text{-}OK$

4

It is the aim of this work to study the influence of the initiator structure and also that of the presence of crown ether or glycol on the course of polymerization of p-chlorophenyl glycidyl ether in DMSO, with particular reference to the growing chain transfer reaction to the monomer.

EXPERIMENTAL

Synthesis of potassium glycolates and preparation of their solutions in DMSO

A suspension of 0.1 mole (3.8 g) of potassium in 200 ml of xylene was prepared under dry argon in a 500 ml four-necked flask fitted with a ground-glass joint stirrer and a dropping funnel, 0.4 mole (22 ml) of anhydrous ethanol being then added dropwise at 20°C. When the whole amount of the potassium had reacted, a mixture of 0.1 mole of glycol with 0.2 mole (12 ml) of ethanol was added and the reaction temperature increased up to 80°C. The above temperature was maintained for one hour and the ethanol distilled off. The white amorphous precipitate of potassium glycolate was filtered, washed with dioxane, then with ether, and finally dried at vacuum.
Potassium glycolates dissolved in DMSO were used as initiators. In order to enhance the solubility of glycolates, equimolar amounts of 18-crown-6 ether or glycol were added to their DMSO solutions. Solubility of the mono-potassium 2-methyl propylene glycolate (4) in DMSO at 25°C and in the presence of the 18-crown-6 ether was found to be equal to 0.5 g/l, the solubilities

of 2 and 3 under the same conditions being equal to 5.7 g/l and 10 g/l, respectively. The glycolates were found to dissolve more readily in DMSO in the presence of the corresponding glycol. Hence, after the addition of glycols, solutions with concentrations of 15 g/l were prepared.

Polymerization of p-chlorophenyl glycidyl ether

The reaction flask was fitted with a magnetic stirrer and a three way stopcock and was heated under vacuum, purged with argon and thermostated at 25°C, whereupon the reagents were introduced. Course of the polymerization reaction was followed by monitoring the changes in the content of epoxide groups in samples taken at various times from the reaction mixture. When the reaction had been completed, the reaction mixture was neutralized with dilute hydrochloric acid, the polymer being precipitated with methanol.

Analytical methods

Number average molecular weights ($\overline{M}_n$) of the polymers were determined at 80°C in chlorobenzene using the KNAUER Vapor Pressure Osmometer.

Molecular weight distributions (MWDs) of the polymers obtained were determined by gel permeation chromatography using the ALC/GPC 202 chromatograph (Waters Associates, Inc.), the polystyrene equivalent molecular weight scale being used throughout. A set of 7 columns, each 1.20 m long, packed with crosslinked polystyrene gels (STYRAGEL) having the following pore sizes: 60 Å, 100 Å, 250 Å, 500 Å, 10^3 Å, 10^4 Å and 10^5 Å, was used. The GPC analyses were performed at 20°C in chloroform using a differential refractometer as column eluate detector. The calibration dependence, determined for the above set of columns in chloroform using narrow MWD polystyrene and poly(propylene glycol) standards supplied by Waters Associates, was found to be linear over the whole working range of retention volumes at GPC solvent flow rate of 1 cm^3/min.

It was hence possible to determine the polydispersity of polymer samples studied (the shape of their chromatograms was approximately Gaussian) using the relation derived by BLY (1969,1972):

$$(\overline{M}_w/\overline{M}_n)_P/W_P = (\overline{M}_w/\overline{M}_n)_{PS}/W_{PS}$$

where: $\overline{M}_w$ is the weight-average molecular weight
$\overline{M}_n$ is the number-average molecular weight
W - chromatogram width, as determined by the distance between the point of intersection with the chromatogram baseline of the tangents drawn at chromatogram peak inflection points
P, PS - are the indices referring respectively to the polydispersities of the polymer studied and the polystyrene standard of known average molecular weights.

Determination of the $\overline{M}_w/\overline{M}_n$ ratio for polymer samples whose chromatograms had a shape different from that of a Gaussian curve required a suitable digitalization of chromatograms and the performance of computations using a standard procedure (CAZES, 1966).

Determination of epoxide group content.

A 0.2 - 0.7 g sample was taken from the reaction mixture and dissolved in 10 ml of a 0.2 N solution of hydrochloric acid in dioxane, the whole being then allowed to stand for one hour at room temperature. The solution was then titrated with 0.1 N KOH using phenolphthalein as indicator, a blank determination being run simultaneously.

Determination of hydroxyl number (I_{OH}).

Between 2 and 3 grams of the polymer were dissloved in 25 ml of 1 N solution of phthalic anhydride in pyridine, the flask containing that solution being placed on a steam bath for 2 hours. The flask was then cooled down, and 25 ml of 1.1 N NaOH and 1 ml of a 1% solution of phenolphthalein in pyridine were added and the resultant mixture titrated with 0.5 N KOH, a blank test being run at the same time.

Determination of double bond content.

Between 2 and 3 grams of the polymer were dissloved in 10 ml of 2-chloroethanol saturated with sodium nitrate, and then 20 ml of a 0.15 M solution of mercury diacetate were added and the whole allowed to stand for 2 hours in the dark. 25 ml of a 2.0 M solution of sodium chloride were added to the above mixture which was subsequently titrated with a 0.1 N KOH solution in methanol, a blank test being run at the same time.

DISCUSSION

The studies of the polymerization of p-chlorophenyl glycidyl ether initiated by several potassium glycolates showed these reactions to be of first order with respect to the instantaneous concentration of the monomer. The above finding is well borne out by the straight line relations found when plotting $\ln[M]_o/[M]_t$ against polymerization time (figure 1).

First-order reaction rate constants (k_1), determined from the linear relation for the various initiator systems used, are listed in table 1. Polymerization rate may be thus seen to be higher in the case of systems containing the crown ether than that found for glycol-containing systems, polymerization rate being also found to depend on the nature of glycolate used. However, both in the presence of glycol or crown ether, polymerization rate is highest when a propylene glycolate having an asymmetric structure, e.g. 3, is used as initiator. Polymers obtained in the presence of propylene glycol also had relatively high molecular weights and low polydispersity, as illustrated in figure 2, showing the normalized chromatograms of polymers obtained when using different initiators.

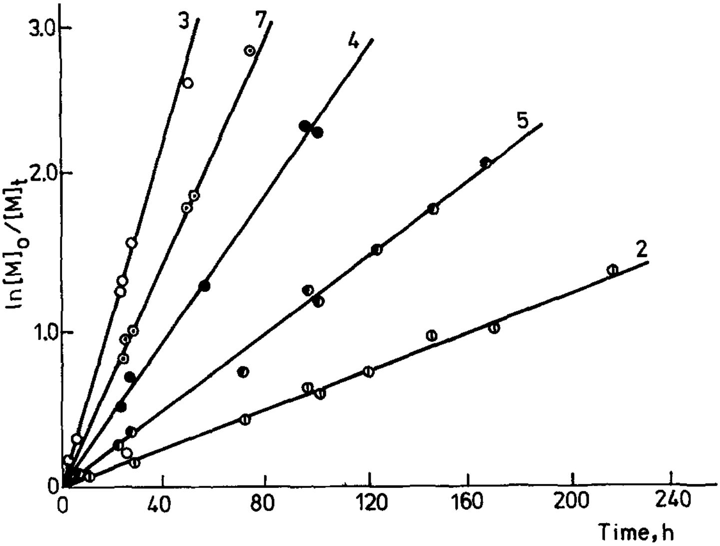


Figure 1. First-order rate plots obtained for the polymerization of p-chlorophenyl glycidyl ether initiated by various potassium glycolates in DMSO at 25^{o}C. Numbers correspond to those in tables 1 and 2.

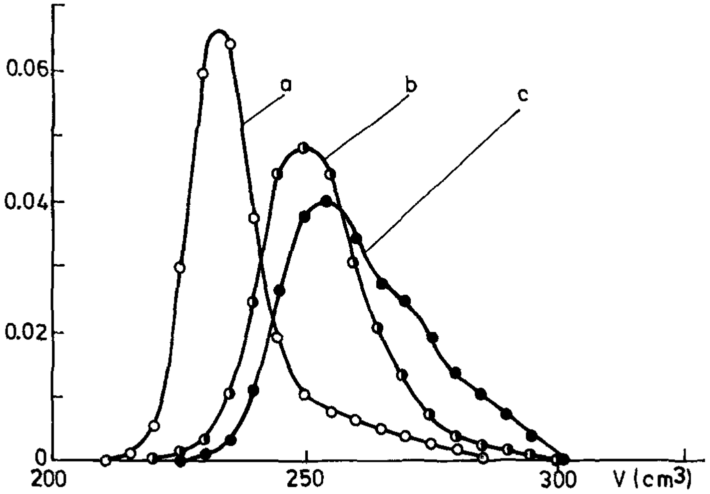


Figure 2. Normalized chromatograms of three poly(p-chlorophenyl glycidyl ether) samples obtained in the presence of a) 3 and propylene glycol; b) 4 and 2-methyl propylene glycol; c) 2 and ethylene glycol

Table 1.
Influence of potassium glycolate used on the polymerization of p-chlorophenyl glycidyl ether at 25°C

Exp. no.	Initial monomer concentration	Potassium glycolate used	Potassium glycolate concentration (mole/l)	Glycol concentration (mole/l)	18-crown-6 concentration (mole/l)	$k_1 x 10^5$ (s^{-1})	$\overline{M}_n$ (VPO)	$\overline{M}_w/\overline{M}_n$ (GPC)
1	2.11	2	0.035	-	0.035	0.99	2600	1.55
2	1.81	2	0.042	0.042	-	0.18	880	2.74
3	1.93	3	0.036	-	0.035	1.58	3400	1.40
4	1.63	3	0.035	0.033	-	0.66	2900	1.55
5	1.79	4	0.039	0.035	-	0.35	1000	2.02

Table 2.
Properties of some poly(p-chlorophenyl glycidyl ethers) obtained at 25°C.
Ethylene $[\text{glycolate}]_o/[\text{crown}]_o = 1$

Exp. no.	Initial monomer concentration	Ethylene glycolate concentration (mole/l)	Reaction time (hr)	Reaction yield (%)	$\overline{M}_n$ (VPO)	I_{OH}	Polymer softening range (°C)
6	1.94	0.030	192	82.4	2700	40.6	55-68
1	2.11	0.035	74	93.7	2600	41.5	63-76
7	1.79	0.040	74	84.8	2600		57-64
8	1.92	0.051	48	94.2	2700		
9	1.84	0.062	50	91.0	2850	40.4	61-66
10	1.81	0.065	46	83.4	2950	38.5	

The MWD curve of the polymer obtained in the presence of 3 may be seen to feature a much greater amount of high-molecular weight fractions than the MWD curves of polymers obtained using other initiators. It was found for the ethylene glycolate initiated polymerization that molecular weights of polymers obtained were independent on the initial concentration of the glycolate in the reaction mixture (table 2). The absence of such a dependence indicates clearly that, in the systems investigated, the chain transfer reactions proceed at a much faster rate than the polymerization initiation reaction. In the papers referred to in the introductory part of the present paper, and concerning the polymerization of oxiranes initiated by alcoholates of alkali metals in DMSO solution, three types of growing polymer chain transfer reactions had been considered, and namely those involving the chain transfer to the solvent, to the monomer, and to the alcohol.

In their paper on the polymerization of ethylene oxide and propylene oxide PRICE and AKKAPEDDI (1972) demonstrated that, as a result of the polymer chain transfer to DMSO, sulphur is to be found in the polymer backbone, thus:

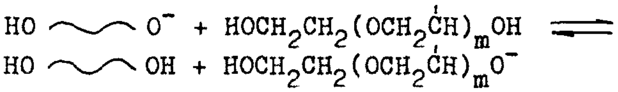
$$\sim O^- + CH_3SOCH_3 \rightleftharpoons \sim OH + CH_3SOCH_2^- \xrightarrow{\text{monomer}} CH_3SOCH_2 \sim\!\sim\!\sim O^-$$

These authors did not consider, however, the possibility of such a reaction in the polymerization of phenyl glycidyl ether and its homologues, which was in agreement with the earlier paper of BANKS and PETERS (1970), who had found no trace of sulphur in polymers of phenyl glycidyl ether obtained in DMSO and in the presence of sodium methoxide. Double bonds were found to be formed in polymers of phenyl glycidyl ether as a result of chain transfer to the monomer, as reported by BANKS and PETERS (1970), PRICE et al.(1968,1972) and SOROKIN et al.(1971):

$$\sim O^- + \underset{\diagdown O \diagup}{CH_2-CH}-CH_2OC_6H_5 \longrightarrow \sim OH + \underset{|\ O^-}{CH_2}CH=CHOC_6H_5$$

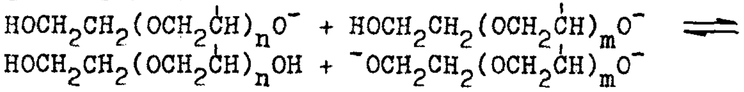
However, no aliphatic double bonds were found in the polymers obtained in the present work. The numerical values of iodine numbers determined for individual polymer samples ranged between -0.2 and + 0.2, which is within limits of experimental error of the iodine number determination technique used. The same finding had been reported by EZRA and ZILKHA (1970) who had employed potassium naphtalene in DMSO to initiate the polymerization of phenyl glycidyl ether.

Among the possible chain transfer reactions considered, that involving the participation of glycol would therefore seem to be the only one taking place in the case of the polymerization system studied. The reaction scheme is the following:



$$HO\sim\sim O^- + HOCH_2CH_2(OCH_2\overset{|}{C}H)_mOH \rightleftharpoons HO\sim\sim OH + HOCH_2CH_2(OCH_2\overset{|}{C}H)_mO^-$$

where m may assume any value between zero and infinity. The above reaction scheme could be extended further by considering also the probable reactions involving two growing polymer chains:



$$HOCH_2CH_2(OCH_2\overset{|}{C}H)_nO^- + HOCH_2CH_2(OCH_2\overset{|}{C}H)_mO^- \rightleftharpoons HOCH_2CH_2(OCH_2\overset{|}{C}H)_nOH + {}^-OCH_2CH_2(OCH_2\overset{|}{C}H)_mO^-$$

The above listed reactions of growing polymer chains result in a lowering of the number average molecular weight of polymers obtained, their polydispersity being hence increased. According to our experimental results, the extent of these reactions was shown to depend on the initiator nature. The above findings, and also the different polymerization rates determined for the various initiator systems used in the present work, would seem to indicate that the inductive and steric effects, due to the methyl substituents of glycolates as well as glycols, are most probably responsible for the phenomena observed. Both those effects may have an influence on such properties of glycolates and glycols in DMSO solution as for instance, the degree of dissociation of glycolates, the tendency to form molecular aggregates, or on the different reactivity of end groups in polymerization processes. It would hence appear reasonable to suppose that the course of polymerization of p-chlorophenyl glycidyl ether is determined by the above mentioned properties of glycolates and glycols in DMSO solution, the said properties depending on the number of methyl substituents present in the initiator employed.

In the case of the asymmetrically substituted propylene glycolate, the ratio of the rate of chain transfer to the rate of the initiation step was considerably smaller than that determined for the other initiator systems belonging to the homologous series of potassium glycolates investigated.

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