Polymerization of Chlorophenyl Glycidyl Ethers. VI.

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

Zbigniew Jedliński, Andrej Stolarzewicz, Pawel Szewczyk and Ryszard Tymczyński
Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze, Poland

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 BARANOVA (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-
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.

\[
\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{Cl}
\]

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.

\[
\begin{align*}
\text{HO-CH}_2-\text{CH}_2-\text{OK} & \quad \text{HO-CH} = \text{CH}_2-\text{OK} & \quad \text{HO-C-CH}_2-\text{OK} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

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