Anionic Polymerization of Ethylene Oxide in Dimethyl Sulphoxide

C. E. H. BAWN, A. LEDWITH and N. MCFARLANE*

The polymerization of ethylene oxide has been investigated in anhydrous DMSO using potassium tert-butoxide as initiator. At low conversion the polymerization obeys the rate expression

$$R_p = k_p\,[\textit{ethylene oxide}]\,[\mathrm{K^{+-}OBu^t}]$$

where $k_p = 0{\cdot}10 \pm 0{\cdot}03$ *litre* $\mathrm{mole^{-1}\ sec^{-1}}$, $\Delta H^{\ddagger}_p = 6{\cdot}4$ *kcal* $\mathrm{mole^{-1}}$, *and* $\Delta S^{\ddagger}_p = -41$ *cal* $\mathrm{mole^{-1}\ deg^{-1}}$, *at 25°C. Values of* k_p *obtained are thought to represent propagation by free alkoxide ion, and are much greater than previously reported values. At 25°C polyethylene oxide is only slightly soluble in DMSO and hence the polymerizations develop the characteristics of colloidal systems as conversion and molecular weight increase. Raising the temperature to 50°C or addition of 1,2-dimethoxy ethane helps to maintain homogeneity in the reaction mixtures. Molecular weights increase with increasing [monomer] and decreasing [catalyst].*

DURING the past few years the use of dipolar aprotic solvents for base-catalysed reactions has increased enormously[1,2]. Dimethyl sulphoxide (DMSO) is the most useful of the dipolar aprotic solvents and shows a marked ability to solvate cations (especially K^+) whilst leaving anions essentially unsolvated[2,3]. As a consequence nucleophilic reactivity of anions is greater in solvents such as DMSO and this effect has been utilized for many kinetic studies as well as synthetic purposes[1,3,4].

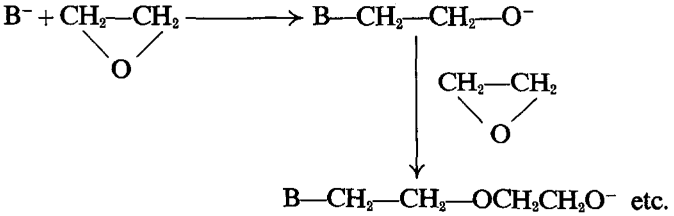
There is a special interest[5] in the use of metal alkoxides in DMSO because of a rapid proton transfer leading to equilibria of the type

$$\mathrm{K^{+-}OBu^t + CH_3SOCH_3 \overset{K}{\rightleftharpoons} K^{+-}CH_2SOCH_3 + Bu^tOH}$$

Methyl sulphinyl carbanion ($\mathrm{CH_3SOCH_2^-}$) has been given the trivial name dimsyl ion[6] and is involved in the majority of base-catalysed reactions in DMSO, in spite of the fact that the equilibrium lies far to the left ($K = 1{\cdot}5 \times 10^{-7}$).

Alkali metal derivatives of DMSO can be synthesized in several different ways[5,6] although ion-pair dissociation constants of the various metal–dimsyl derivatives in DMSO vary markedly as the metal cation changes[7]. However, with potassium as gegenion both alkoxide and dimsyl ions are completely dissociated in DMSO at salt concentrations less than 10^{-1}M.

Polymerization of oxiranes occurs readily under the influence of strong bases in both protic and aprotic solvents[8,9], propagation involving stepwise growth of alkoxide ions, e.g. for ethylene oxide:



$$\mathrm{B^- + CH_2{-}CH_2(O) \longrightarrow B{-}CH_2{-}CH_2{-}O^- \xrightarrow{CH_2{-}CH_2(O)} B{-}CH_2{-}CH_2{-}OCH_2CH_2O^-}\ \text{etc.}$$

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*Present address: Shell Research Ltd, Woodstock Agricultural Research Centre, Sittingbourne, Kent.

Several preliminary communications have described anionic polymerizations in DMSO[10–12] and this paper gives details of the polymerization of ethylene oxide initiated by potassium tert-butoxide.

EXPERIMENTAL

Materials

Dimethyl sulphoxide—Dimethyl sulphoxide (Guest Industries Ltd, industrial grade) was distilled in an all glass apparatus under nitrogen at reduced pressure. The first fraction, of boiling point up to 106°C at 18–20 mm Hg, was discarded. The middle fraction (b.pt 106°C–107°C at 18–20 mm Hg) was retained and stirred over freshly powdered barium oxide for two days. The supernatant liquid was decanted on to freshly powdered barium oxide and distilled at a controlling reduced pressure (6–7 mm) under dry nitrogen using a five foot column packed with Fenske helices. The fractions collected had a boiling point of 65°–66°C at 6 mm Hg, and were stored in sealed vessels containing fresh barium oxide. As required these vessels were joined to flasks via the break-seal and attached to the vacuum line. After breaking the seal of the original flask, by means of a metal-in-glass breaker used in conjunction with a magnet, and degassing by the usual freezing–melting technique, molecular distillation under high vacuum conditions was carried out. The receiver was cooled in liquid nitrogen and the flask containing the dimethyl sulphoxide was warmed in warm water (60°–70°C). The final pure dimethyl sulphoxide was used as required, and was never opened to air.

Various other purification techniques were tried. Distillation from the initiator to be used, potassium tert-butoxide, was one such process. Another was employing calcium hydride as the drying agent. Both of these techniques failed to improve upon the purity of the dimethyl sulphoxide. The former may possibly introduce tert-butanol into the system, while the latter contains calcium carbide as an impurity which will react with any water present forming acetylene. As dimethyl sulphoxide is one of the best known solvents for acetylene this might seriously affect an anionic polymerization reaction.

Potassium tert-butoxide—Crude potassium tert-butoxide (*ca.* 25 g) was pumped for about 24 hours under high vacuum conditions while at a temperature of 80°–90°C maintained by a water bath. This removed all the tert-butyl alcohol except that associated with the alkoxide as alcohol of crystallization. The bulk of this product was retained in a stoppered vessel until needed.

As required portions of the potassium tert-butoxide (*ca.* 3–4 g) were sublimed in a vacuum sublimation apparatus at 160°C under high vacuum conditions. The cold finger was maintained at 0°C by means of ice-water. The pure product was stored in sealed glass phials under vacuum until required.

Ethylene oxide—Ethylene oxide (B.D.H. Laboratory reagent) was distilled, under high vacuum at 0°C, after degassing, on to calcium hydride in a flask fitted with a greased vacuum tap. This stock solution was retained in the refrigerator and as required aliquots were distilled from this flask under high vacuum at 0°C.

Solvents—All solvents and other reagents were analytical reagent grade materials used without further purification.

Kinetic measurements

Polymerization was followed by conventional dilatometry. Reaction rates were rather high for this technique and so special procedures were necessary to eliminate zero time errors consequent on the rapid initiation reactions.

Initiator solutions of potassium tert-butoxide were prepared from stock solutions in sealed thin walled, glass phials. The initiator concentration was estimated by breaking representative phials into water for estimation by titration with standard acid. Suitable glass phials of initiator solution were carefully placed into ordinary Pyrex test tubes having a sharp glass 'spike' protruding from the base inwards. Calibrated capillary stems were then glass welded to the test tube and the complete dilatometer filled with the requisite solvent–monomer mixture by distillation under high vacuum. When the dilatometer was filled, sealed and removed from the vacuum line, it was allowed to reach temperature equilibrium in a suitable constant temperature bath. The reaction was started by vibrating the dilatometer stem with a Vibro stirrer which after a few seconds vibration ruptured the glass phial containing the initiator against the inverted spike, whereupon the vibration was continued for a further short period so as to improve mixing.

Polymerizations were allowed to go to completion after which the polyethylene oxide was recovered by precipitation into cold ether.

Molecular weights

Intrinsic viscosities, $[\eta]$, were measured in water at 30°C and molecular weights were estimated from the expression[13]

$$[\eta] = 1{\cdot}25 \times 10^{-4} M^{0{\cdot}78}$$

RESULTS

The polymerization of ethylene oxide in DMSO was studied at 25°C and 50°C and the results are shown in *Tables 1* and *2*. Although initial rates showed a linear dependence in both [potassium tert-butoxide] and [ethylene oxide] each kinetic run (at 25°C) gave values of $\{R_p/[\mathrm{M}]_t\}$ which fell steadily with time to a final constant value (see *Figure 1*). This decay was not observed at 50°C and even at 25°C the decay was eliminated by adding 1,2-dimethoxy ethane to the reaction mixture (*Figure 1*).

Physically it was observed that runs at 25°C were accompanied by increasing light scatter by the reaction mixtures and eventually the polymer precipitated. At 50°C apparently the polymer remained soluble throughout.

DISCUSSION

Polymerization of ethylene oxide in DMSO occurs readily using solutions of potassium tert-butoxide as initiator. Initial reaction rates were given by the expression

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = R_p = k_p [\mathrm{M}] [\mathrm{K}^{+-}\mathrm{OBu}^t]$$

where [M] represents the initial concentration of ethylene oxide. Molecular weights of the polymers increased with increasing [monomer] and with decreasing [KOBu^t]. At very low conversion, when the systems were truly homogeneous, it is likely that the degrees of polymerization approximate to

Table 1. Polymerization of ethylene oxide by potassium tert-butoxide in dimethyl sulphoxide at 25°C

Concentration, mole l^{-1} Monomer	$10^3\times$ Initiator	*Initial rates* ($10^3\times R_p$) *mole* l^{-1} sec^{-1}	*Initial rate coefficient* ($10^2\times k_p$) *l. mole*$^{-1}$ sec^{-1}	*Molecular weights*[13]	*% yield*
5·50	12·2	8·35	12·4	11 480	89
4·25	12·2	6·20	12·0	8 510	75
3·22	11·6	2·32	6·2	8 700	89
2·55	12·1	2·64	8·6	7 240	66
1·70	12·2	1·36	6·6	6 630	100
0·84	12·6	0·91	8·0	4 320	21
4·23	15·30	7·55	11·7	8 130	85
4·38	9·34	4·48	11·0	14 130	85
4·08	5·66	3·19	13·7	18 840	83
3·95	5·27	2·06	9·9	13 120	74
4·31	2·19	1·22	12·8	33 100	77
4·06	1·88	0·48	6·3	22 400	86
4·31	0·48	0·26	12·6	45 000	76
1·73	12·4	0·24	1·1*	6 500	100
1·58	7·75	0·20	1·6	(containing $3{\cdot}78\times10^{-2}$ mole l^{-1} Bu^{t}OH)	
1·58	7·75	0·42	3·4	(containing $1{\cdot}62\times10^{-2}$ mole l^{-1} Bu^{t}OH)	

*Containing dimethoxyethane 20% v/v of the total solution.

Table 2. Polymerization of ethylene oxide by potassium tert-butoxide in dimethyl sulphoxide at 50°C

Concentration, mole l^{-1} Monomer	$10^3\times$ Initiator	*Initial rates* ($10^3\times R_p$) *mole* l^{-1} sec^{-1}	*Initial rate coefficient* ($10^2\times k_p$) *l mole*$^{-1}$ sec^{-1}	*Molecular weights*[13]	*% yield*
3·14	9·61	6·84	23	10 350	58
3·43	7·81	6·51	24	15 850	69
3·40	5·07	2·74	16	20 400	90
3·40	2·40	1·35	17	23 130	74
3·45	1·36	0·99	21	30 900	70
4·81	7·30	7·50	22	26 300	63
2·42	7·60	5·00	27	12 300	86
1·54	7·90	3·65	30	8 610	80
0·82	7·70	2·29	36	5 930	55

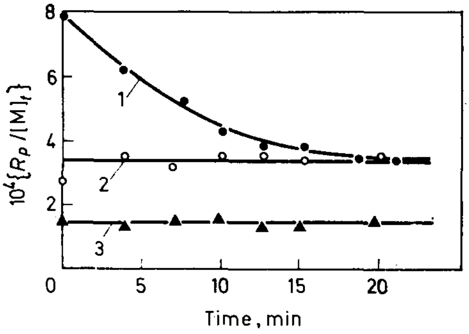


Figure 1—Values of $\{R_p/[M]_t\}$ versus time. Curve 1: monomer concentration 1·70 mole l^{-1}, initiator concentration $12{\cdot}2\times10^{-3}$ mole l^{-1}, temperature 25°C and respectively for curve 2: 1·73, $12{\cdot}4\times10^{-3}$, 25°C, in presence of 20% v/v dimethoxy ethane; curve 3: 1·54, $7{\cdot}90\times10^{-3}$, 50°C

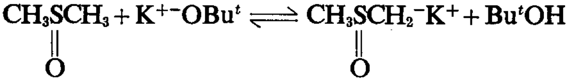
the ratio [monomer used]/[catalyst] but difficulties encountered in recovering all the polymer made it impossible to test this prediction adequately.

Development of micelles and eventual precipitation of polymer was evident from a physical examination of the systems during polymerization, and from the fall in values of $(R_p/[\mathrm{M}])_t$ with time. This effect was most marked at 25°C and was readily relieved either by raising the temperature to 50°C or by addition of 20 vol.% 1,2-dimethoxy ethane—a good solvent for polyethylene oxide (*Figure 1*). DMSO undergoes a phase transition between 35°–45°C and clearly becomes a much better solvent for polyethylene oxide above this transition temperature[4].

Table 1 also shows that small amounts of added tert-butanol have a pronounced effect on the rate of propagation. Chemical analysis of the lower molecular weight polymers established that sulphur was present in low concentration (< 0·4 per cent) and this would arise from initiation and transfer reactions involving DMSO. Experimentally the sulphur analysis was subject to large errors and hence it is not practicable to attempt correlation between sulphur content and degree of polymerization.

The reactions involved may be summarized as follows:

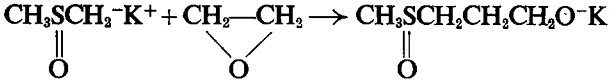
1. *Pre-initiation*



$$\mathrm{CH_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{CH_3} + \mathrm{K^{+-}OBu^t} \rightleftharpoons \mathrm{CH_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{CH_2^-K^+} + \mathrm{Bu^tOH}$$

The equilibrium constant for this reaction is $1{\cdot}5 \pm 0{\cdot}5 \times 10^{-7}$, and the equilibrium is quickly established[5].

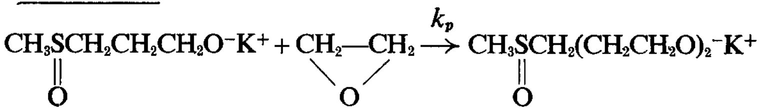
2. *Initiation*



$$\mathrm{CH_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{CH_2^-K^+} + \underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{CH_2{-}CH_2}} \rightarrow \mathrm{CH_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{CH_2CH_2CH_2O^-K^+}$$

This reaction is assumed to be fast compared with propagation*.

3. *Propagation*



$$\mathrm{CH_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{CH_2CH_2CH_2O^-K^+} + \underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{CH_2{-}CH_2}} \xrightarrow{k_p} \mathrm{CH_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{CH_2(CH_2CH_2O)_2^-K^+}$$

followed by successive monomer additions which are assumed to be kinetically indistinguishable and have the same rate constant k_p:

at 25°C, $k_p = 0{\cdot}10 \pm 0{\cdot}03$ l. mole^{-1} sec^{-1}
at 50°C, $k_p = 0{\cdot}25 \pm 0{\cdot}08$ l. mole^{-1} sec^{-1}

According to this reaction sequence there would be one molecule of ^{t}BuOH formed for each initiating dimsyl ion. Alcohols in DMSO are known to solvate alkoxide ions strongly via hydrogen bonding and therefore each propagating primary alkoxide ion will be associated with at least one alcohol

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*Even though the dimsyl ion is present in such low concentration, previous work[5] involving addition to benzophenone shows that it is orders of magnitude more reactive than the tert-butoxide ion.

molecule. Initially this would be tert-butanol, formed in the initiation reaction but proton transfer between alcohol and alkoxide ion will be rapid and the end result will be random growth of two polymer molecules per anionic unit, e.g.

$$\sim\!\sim CH_2CH_2O^- \ldots HOR \rightleftharpoons \sim\!\sim CH_2CH_2\text{—}OH \ldots O^-R$$

Transfer to DMSO is also possible, i.e.

$$\sim\!\sim CH_2CH_2O^- + CH_3SOCH_3 \rightleftharpoons \sim\!\sim CH_2CH_2OH + CH_3SOCH_2^-$$

but the molecular weight data show that this reaction is not very important.

In DMSO the propagating potassium alkoxide ion pair is completely dissociated[7] and as a consequence the propagation reaction is very fast. It is interesting to compare the present value of k_p at 25°C with that determined by Gee, Higginson and Merrall[9] for the polymerization of ethylene oxide by free ions in methanol–dioxan mixture (approximately 10^{-4} l. mole^{-1} sec^{-1} at 30°C).

At 25°C in DMSO the transition state parameters for polymerization of ethylene oxide are $\Delta H^{\star} = 6{\cdot}4$ kcal mole^{-1}, $\Delta S^{\star} = -41$ cal mole^{-1} deg^{-1}. Clearly the high values of k_p observed are a consequence of the low value of $\Delta H^{\star}$ (cf. $\Delta H^{\star}$ for propagation in methanol–dioxan[9] is 17·2 kcal mole^{-1}).

Overall DMSO provides a medium for polymerization in which the propagating alkoxide is comparatively unsolvated whereas the transition state for propagation (charge dispersed) is highly solvated[3]. This has the effect of lowering $\Delta H^{\star}$ and increasing $\Delta S^{\star}$. Introduction of hydrogen bonding substrates such as alcohols (or water) would destroy the favourable solvation characteristics described above.

Recently Price and his collaborators[12] have reported values of rates of polymerization for epoxides in DMSO which are substantially less than those reported here. Furthermore these lower rates were obtained using *higher* initiator concentrations than used here and it is likely that the large discrepancies arise either from heterogeneity of initiator phase in the work of Price *et al.* or perhaps the presence of hydroxylic impurities—the latter now shown to have a marked effect on reaction rates.

Donnan Laboratories,
University of Liverpool

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