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Observations on the Anionic Polymerization of Ethylene Oxide by Alkali Metal Naphthalene and Anthracene Complexes

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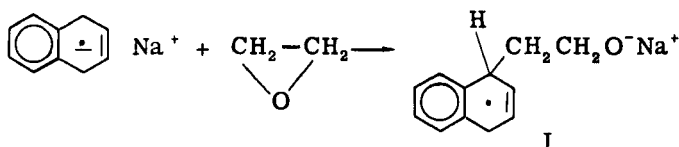
ABSTRACT

The anionic polymerization of ethylene oxide by alkali metal naphthalenes and anthracenes was studied in DMSO and THF to determine the effects of solvent and of polycyclic hydrocarbon, and to obtain information on the mode of initiation. No propagation occurred with lithium naphthalene, and this made it possible to isolate mono- and dihydroxyethyl naphthalene, the species formed on initiation. The molecular weights obtained in the presence of DMSO were about half those obtained in THF, and were proportional to [monomer]/[initiator]. This was explained as being due to differences in initiation; i.e., formation of dimsyl anion as the true initiator in DMSO. The rate of polymerization was first order to monomer, and the molecular weights were found to increase linearly with percent inversion.

INTRODUCTION

The recent report by Kazanskii, Solov'yanov, and Entelis [1] on the kinetics of ethylene oxide polymerization in tetrahydrofuran by alkali metal naphthalene complexes prompts us to report some work that we have carried out on the same subject [2].

Swarc and Richards [3] were the first to study the use of sodium naphthalene as initiator of polymerization of ethylene oxide. They found out that initiation was by direct addition of the monomer to the alkali metal naphthalene:



The radical anions (I) abstract an electron from another alkali metal naphthalene and thus are converted to dianions. Consequently the polymers contained dihydronaphthalene residues.

Kazanskii, Solov'yanov, and Entelis [1] followed the kinetics of the polymerization by dilatometric techniques and found out that there is an initial acceleration, due to the low solubility in THF of alkoxide-type oligomers, which on attaining $\overline{\text{DP}}$ s higher than 15 to 20, pass into solution, and then the reaction becomes first order to monomer. A complicated dependence of the polymerization rate on active center concentration was found due to strong association. The polymerization scheme suggested was one involving association equilibrium and chain propagation via unassociated species.

This complex dependence of rate on the initiator concentration was also found in the polymerization of ethylene oxide in hexamethylphosphoramide [4] by the sodium and potassium alcoholate derivatives of the monomethyl ether of diethylene glycol; with the sodium alcoholate the rate was independent of initiator concentration. More recently Solov'yanov and Kazanskii [5] have shown in the polymerization of ethylene oxide in DMSO at 50 to 75°C initiated by short living polymers of ethylene oxide that the reaction was first order with the potassium alkoxide, but with the sodium the second-order rate constant tended to become larger as the initiator concentration decreased.

In the present work the polymerization of ethylene oxide by alkali metal naphthalene and anthracene was studied in dimethylsulfoxide and compared with that in THF. Conditions were found for isolating the species formed after initiation in order to obtain more evidence concerning the mechanism of initiation by alkali metal naphthalene.

EXPERIMENTAL

Materials

Ethylene oxide gas (Matheson, 99.7% purity) was used. It was dried by passage through a tower of calcium hydride. Dimethylsulfoxide was heated under reflux for 4 hr over calcium hydride and distilled in vacuo under argon. The middle fraction was collected, redistilled, and the middle fraction used. Tetrahydrofuran was dried over benzophenone ketyl [6], and the alkali metal naphthalene and anthracene were prepared as previously described [6].

Polymerization Procedure

The polymerization was carried out in three-necked flasks fitted with a high-speed stirrer, a thermometer, a self-sealing rubber cap through which the reagents were added with syringes, an Anschutz fitted with a Teflon stirring gland, and a three-way stopcock which permitted joining the apparatus either to an oil pump or to argon. The Teflon stirring gland permitted stirring under vacuum. The apparatus was joined to a vacuum line, dried while stirring by flaming in vacuo, and flushed with argon. This procedure was repeated twice. The solvent was introduced, the required amount of ethylene oxide, measured by a flowmeter, was bubbled at 0°C and the initiator solution was added at the required temperature. The reaction mixture was neutralized with acetic acid and added dropwise to a large volume of ether. The precipitated polymer was filtered, dissolved in chloroform, filtered from insoluble alkali metal acetate, and reprecipitated by ether. The mixture was cooled to -20°C and the polyethylene oxide was filtered and dried. In cases where low oily polymer was formed, the ether filtrate was concentrated to recover all the polymer. In the polymerization carried out in the presence of DMSO, the solvent was evaporated in vacuo (3 Torr) up to 60°C, and the residue was crystallized. In the kinetic runs aliquot portions were removed by syringes, transferred to closed vessels and weighed, and the polymerizations were terminated as usual. The \bar{M}_n 's of the polyethylene oxides were determined by acetylation of the hydroxyl end groups by acetic anhydride-pyridine [7] and also from intrinsic viscosities measured on aqueous solutions of the polymers. The following equation [8] was used for calculating the molecular weights:

$$[\eta] = 0.02 + 33 \times 10^{-5} \bar{M}_n^{0.72}$$

Monohydroxyethyl dihydronaphthalene

One equivalent of ethylene oxide was bubbled under argon into a solution of 2 equivalents of lithium naphthalene (50 ml, 1 N) at -18°C with stirring. The reaction mixture changed from green to deep red and, after a short stirring, the mixture was neutralized with an equivalent of hydrochloric acid, the THF was driven off in vacuo, and the residue was extracted with chloroform. The chloroform was extracted with water, dried, and distilled. After a forerun of naphthalene, the monohydroxyethyl dihydronaphthalene was collected at $190^{\circ}\text{C}/22$ Torrs.

Analysis: Calculated for $\text{C}_{12}\text{H}_{14}\text{O}$: C, 82.8; H, 8.0. Found: C, 82.8; H, 7.5.

Dihydroxyethyl dihydronaphthalene

This was carried out as before, only using double the amount of ethylene oxide. After addition of the ethylene oxide, the reaction mixture was stirred for an hour at 0°C until the red color of the mixture disappeared. The mixture was neutralized as before, extracted with chloroform, filtered, and the product was collected at 160 to $180^{\circ}\text{C}/3$ Torrs; it solidified on standing, mp about 40°C .

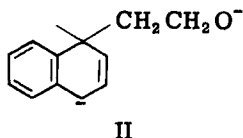
Analysis: Calculated for $\text{C}_{14}\text{H}_{18}\text{O}_2$: C, 77.0; H, 8.2. Found: C, 76.4; H, 8.0.

RESULTS AND DISCUSSION

Previous work on the anionic polymerization of ethylene oxide by butyl lithium has shown that after the initiation step, no propagation occurs [2, 9]. This was also confirmed in the polymerization initiated by lithium naphthalene [1, 2]. This inactivity of the Li-metal in epoxide polymerization has been explained as being due to extremely strong association of active centers [1]. We have now utilized this fact to isolate the species formed at the initiation and thus obtain confirmation of the accepted mechanism of Richards and Szwarc in which initiation was suggested to take place by direct addition of the monomer to the alkali metal naphthalene. This mechanism was supported by spectral evidence which showed the presence of dihydronaphthalene residues in the polymers.

Experiments were carried out at 30°C for 8 hr using [ethylene oxide]/[lithium naphthalene] = 35 in THF as well as in DMSO but no polymer was formed, showing that even in DMSO the association of the Li alkoxides was still strong enough not to allow polymerization. In THF a white precipitate was formed on addition of the initiator, but in DMSO the reaction was homogeneous.

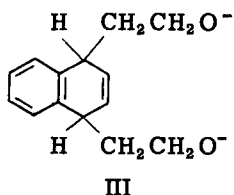
Now the reaction between 1 mole of ethylene oxide and 2 moles of lithium naphthalene is expected to give the colored carbanion (II) or its 1,2-isomer:



In fact, on passing 1 mole of ethylene oxide into a solution of 2 equivalents of lithium naphthalene in THF, the color of the reaction mixture changed from green (the color of the alkali metal naphthalene) to red, the color of the carbanion (II), and monohydroxyethyl dihydronaphthalene was isolated from the mixture.

The sharp color changes observed in the reaction and the fastness of the reaction of ethylene oxide with lithium naphthalene suggested that even with potassium naphthalene it would be possible to stop the reaction at the initiation stage, provided that only 1 mole of ethylene oxide is bubbled into 2 moles of the potassium naphthalene. In fact, on neutralizing the red reaction mixture and working up, we obtained similar results as with lithium naphthalene, and essentially the monohydroxyethyl derivative of dihydronaphthalene was isolated and no polymeric product.

To obtain the dihydroxyethyl derivative of dihydronaphthalene, reaction was carried out using a 1:1 ratio of monomer to lithium naphthalene. The red color of the solution that was first formed slowly disappeared due to the formation of the colorless dialkoxide (III) or its 1,2-isomer, and the dihydroxyethyl derivative of dihydronaphthalene was isolated. This same reaction could not be carried out with potassium naphthalene since polymer formation occurred.



The UV spectrum of the dihydroxyethyl dihydronaphthalene in ethanol had a λ_{max} at 265 $m\mu$ which was similar to the polyethylene oxides obtained by polymerization with sodium naphthalene (λ_{max} 262 $m\mu$ and a shoulder at 272 $m\mu$). Polyethylene oxide was found to adsorb naphthalene and dihydronaphthalene strongly as seen from UV spectrum. Repeated purification by recrystallization from chloroform-ether did not help, and only by passing steam into the material was

it possible to purify the polyethylene oxide from adsorbed hydrocarbon. The IR spectra of monohydroxyethyl naphthalene and of dihydroxyethyl naphthalene showed absorptions at 1024, 3350^{-1} (OH), 2920, 3030 (aromatic CH), 1512, 1600 (aromatic and conjugated double bond), 765, 780, and 800 (aromatic ring). The NMR spectrum of the dihydroxyethyl dihydronaphthalene showed peaks at 7.2 ppm (aromatic protons), 5.9 ppm (vinyl protons of 1,4-dihydronaphthalene) and 6.4 ppm (vinyl protons of the 1,2-isomer). The ratio of the peak areas showed that the ratio of the 1,4- to the 1,2-isomers was 4 to 1.

Experiments were carried out to determine the general effect of solvent and type of alkali metal polycyclic hydrocarbon on the polymerization. In THF, the temperature rose on addition of potassium naphthalene to ethylene oxide, the color changed to dark red and in a short time it disappeared, and a heavy white precipitate was formed which slowly disappeared on continuing the reaction and stirring. The reactions in the presence of DMSO or a mixture of DMSO-THF (1:1) were homogeneous from the start and more exothermic. The time for complete initiation, as observed from the color changes, was much shorter in the case of DMSO (few minutes) than in the case of THF. The molecular weights in the presence of THF were higher than those in DMSO. In THF they were close to $2[\text{monomer}]/[\text{initiator}]$ (2M/C), according to the mechanism of Richards and Szwarc [3], while in DMSO they were close to half this value (Table 1).

The rate of polymerization by potassium naphthalene in DMSO was studied together with the dependence of molecular weight on percent conversion (Table 2). After 3 min the color of the initiator disappeared completely. The reaction was first order in monomer [5] as seen from the linear plot of $\ln[\text{ethylene oxide}]_0/[\text{ethylene oxide}]_t$ vs time (Fig. 1). The pseudo-first-order rate constant calculated from the slope was $2.45 \times 10^{-4} \text{ sec}^{-1}$. The molecular weights increased linearly with increasing conversion (Fig. 2). Both of the lines depicting $\log[\text{ethylene oxide}]_0/[\text{ethylene oxide}]_t$ vs time and molecular weight vs conversion extrapolate to zero, showing that initiation is fast relative to propagation.

For comparison the polymerization in THF initiated by potassium naphthalene was found to be much slower with a pseudo-first-order rate constant of $2.4 \times 10^{-6} \text{ sec}^{-1}$ (for M/C = 45.5 under otherwise comparable conditions).

Experiments were carried out using potassium biphenyl, monopotassium anthracene, and dipotassium anthracene as initiators of polymerization. While with potassium biphenyl the initiation was fast, similar to that found with potassium naphthalene, that with the anthracene derivatives was slower. Here the blue-green color of the catalyst passed over to red, which remained to the end. The

TABLE 1. Molecular Weight Dependence on Solvent^a

Ethylene oxide (moles/liter)	Potassium naphthalene (mole/liter)	M/C	THF (ml)	DMSO (ml)	Reaction time (hr)	Conversion (%)	$[\eta]$ (dl/g)	\bar{M}_n	Calculated \bar{M}_n^b
6.0	0.100	60	25	25	48	84	0.100	2050	4440
6.0	0.100	60	49.5	0.5	48	87	0.114	2570	4600
6.0	0.045	135	50	-	48	89	0.268	9870	10,400
6.0	0.025	240	1	50	4.5	97	0.216	7120	20,380
5.15	0.040	129	25	25	8	68	0.178	5300	7700
7.0	0.200	35	50	-	2	90	-	2900	2770
7.0	0.200	35	50	-	1.5	73	-	2520	2250

^aExperimental conditions: The polymerizations were carried out in THF or THF-DMSO mixtures using potassium naphthalene at 30°C.

^bCalculated according to 2M/C, and taking into account the percent conversion.

TABLE 2. Kinetics of Polymerization by Potassium Naphthalene in DMSO^a

Time (sec $\times 10^{-3}$)	Conversion (%)	$[\eta]$ (dl/g)	\bar{M}_n	Calculated \bar{M}_n^b
1.08	32.0	0.120	2800	4030
1.68	46.4	0.150	4020	5840
2.52	54.3	0.177	5220	6840
3.36	62.1	0.189	5780	7820
6.06	77.2	0.204	6520	9720
11.04	93.7	0.232	7930	11800
22.60	97.4	0.245	8630	12250

^aExperimental conditions: Ethylene oxide, 6.0 moles/liter; K-naphthalene, 2.1×10^{-2} mole/liter; M/C = 286; temp, 30°; solvent, DMSO (196 ml) and THF (4 ml).

^bCalculated according to M/C and taking into account the percent conversion.

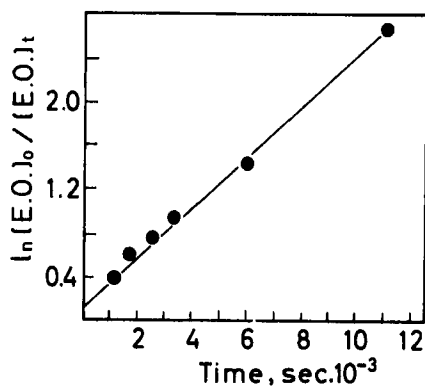


FIG. 1. Polymerization of ethylene oxide by potassium naphthalene in DMSO.

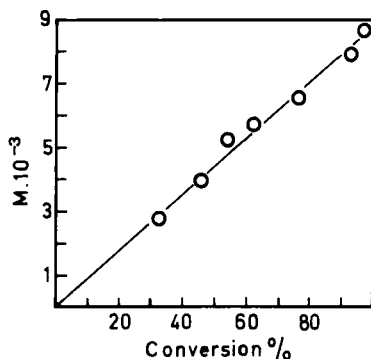


FIG. 2. Polymerization of ethylene oxide by potassium naphthalene in DMSO. Plot of \bar{M}_n vs percent conversion.

reactions in THF in this case gave low yields, and it was difficult to pass from the insoluble low oligomer alkoxides formed at the start to homogeneous conditions. In the presence of DMSO, the precipitate first formed dissolved and higher yields were obtained (Table 3). The slow initiation (the color of the initiator disappeared completely after 53 min, Table 4) means that propagation is starting before initiation is completed. That is why the average molecular weights obtained at low conversion (Table 4) were higher than those calculated from M/C , but after 50% conversion there was fair agreement with the calculated values. The slow initiation also leads to autoacceleration, which can be observed from extrapolations depicting molecular weight vs percent conversion (Fig. 3).

The fact that the molecular weights obtained in the presence of DMSO were close to those calculated from M/C , while those obtained in THF were close to $2M/C$, indicates clearly that there is a difference in the mechanism of polymerization. In THF the mechanism of initiation is, as suggested by Richards and Szwarc [3], that of direct addition of ethylene oxide to the alkali metal naphthalene. This in the end leads to the formation of dianions, which account for $\overline{DP} = 2M/C$. The fact that the molecular weights obtained in DMSO were close to M/C indicates that propagation is by monoanions and not by dianions, i.e., a different mode of initiation is occurring. This may be due to possible interaction of the alkali metal naphthalene or anthracene with the DMSO to form a new type of initiator. In fact, we have shown in the polymerization of phenylglycidyl ether by potassium naphthalene in DMSO [10] that such an interaction occurs, leading to the formation of dimethyl anion, $^-\text{CH}_2\text{SOCH}_3$, which is the real

TABLE 3. Polymerization by Potassium Biphenyl, Monopotassium Anthracene, and Dipotassium Anthracene^a

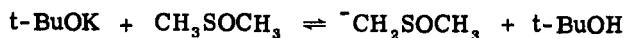
Initiator	Initiator (mole/liter)	THF (ml)	DMSO (ml)	M/C	Yield (%)
Potassium biphenyl	0.16	50	-	37.5	100
Monopotassium anthracene	0.16	50	-	37.5	21
Monopotassium anthracene	0.16	50	-	37.5	27
Monopotassium anthracene	0.06	50	-	100	5
Monopotassium anthracene	0.16	40	10	37.5	76
Monopotassium anthracene	0.06	40	10	100	53
Dipotassium anthracene	0.08	50	-	37.5 ^b	73
Dipotassium anthracene	0.03	50	-	100 ^b	9
Dipotassium anthracene	0.01	45	5	300 ^b	31 ^c

^aExperimental conditions: Ethylene oxide, 6.0 moles/liter, was used; temp, 30°; time, 24 hr.

^bM/C calculated according to the potassium in the initiator.

^cReaction time, 12 days.

initiator. Other work on anionic polymerizations by strong bases in DMSO has also indicated the formation of dimsyl anions which initiate polymerization. Thus Ledwith, Bawn, and McFarlane [11] have shown in the polymerization of ethylene oxide in DMSO by potassium tert-butoxide that the real initiator is the dimsyl anion formed in the equilibrium reaction:



and the polymers accordingly contained sulfur.

TABLE 4. Polymerization by Monopotassium Anthracene in DMSO.^a
Dependence of Molecular Weight on Percent Conversion

Conversion (%)	$[\eta]$ (dl/g)	\bar{M}_n	Calculated \bar{M}_n^b
16.2	0.150	4,020	2,040
31.1	0.183	5,510	3,910
44.0	0.192	5,940	5,540
47.7	0.205	6,580	6,010
56.7	0.227	7,750	7,140
67.8	0.243	8,530	8,530
83.0	0.264	9,710	10,400
92.7	0.281	10,590	11,700

^aExperimental conditions: Ethylene oxide, 6.0 mole/liter; initiator, 2.1×10^{-2} mole/liter; $M/C = 286$; temp, 30° ; solvent, DMSO (188 ml) and THF (12 ml).

^bCalculated according to M/C and taking into account the percent conversion.

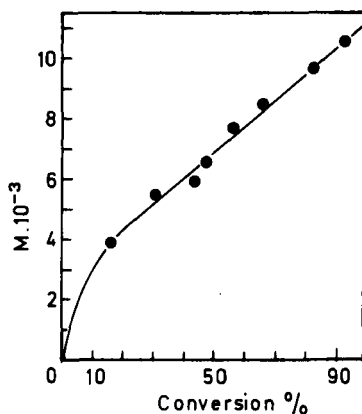


FIG. 3. Polymerization of ethylene oxide by monopotassium anthracene in DMSO. Plot of \bar{M}_n vs percent conversion, $M/C = 286$.

In the present case the formation of the dimsyl anions can be either by interaction of the initiator with the DMSO or of carbanion intermediates of the polycyclic hydrocarbons formed by addition of ethylene oxide, i.e., after initiation. In fact, some of the polyethylene oxides showed the presence of dihydroanthracene residues in their spectrum.

The fact that the molecular weights obtained with potassium naphthalene in DMSO increased linearly with percent conversion indicates that the system is a living one with no termination or transfer to solvent [5].

The polymerizations in DMSO were much faster than those in THF. This may be due to the high dielectric constant of DMSO ($\epsilon = 46.4$) [12] which can increase the rate of both the initiation and propagation. The high polarity of the solvent permits good solvation of the cation, and thus promotes the nucleophilicity of the base [13, 14].

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