Journal of Macromolecular Science, Part A

Anionic Polymerization of Ethylene Oxide by Anhydrous Potassium Hydroxide

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SUMMARY

The heterogeneous anionic polymerization of ethylene oxide in tetrahydrofuran by anhydrous potassium hydroxide, prepared in situ by addition of an equivalent of water to potassium naphthalene, was studied. The effect of time of polymerization, degree of conversion, and monomer and catalyst concentration on the molecular weights was studied. The system was a living one with no chain transfer. The efficiency of the catalyst was low. The polymerization was faster than those previously reported using solid potassium hydroxide due to the high dispersion of the catalyst prepared in this manner. The rate of polymerization increased about threefold by addition of two equivalents of dimethylsulfoxide to the catalyst due to solvation effects.

INTRODUCTION

The polymerization of ethylene oxide by solid potassium hydroxide has been studied for a long time [1-10]. The monomer was usually polymerized without solvent under pressure at relatively high temperature, 100-120°C. The reaction time was long, sometimes several weeks, and the conversions were usually not higher than 50%. These drastic conditions did not permit efficient control of the molecular weights, and the molecular weights

1727

obtained were not high. The potassium hydroxide was used either as pellets or was dried by heating and pulverized. Polymerization of ethylene oxide by alcoholic solutions of potassium alkoxides was also studied [11, 12]. Due to termination by the protic solvents, the molecular weights obtained were low. A detailed study of the polymerization in dimethylsulfoxide (DMSO) was also carried out [13]. The kinetics of the polymerization of ethylene oxide by alkali metal methoxides, prepared in liquid ammonia, in chlorobenzene at 110°C was studied [14].

We have now studied the polymerization of ethylene oxide in tetrahydrofuran catalyzed by solid anhydrous potassium hydroxide prepared in situ by reaction of potassium naphthalene with water. This mode of preparation of the catalyst is simple, and the potassium hydroxide obtained is totally anhydrous and is in the form of a fine crystalline dispersion. The effect of the concentration of reactants and the degree of conversion on the molecular weight of the polymers was studied. The effect of added DMSO on the polymerization was investigated.

EXPERIMENTAL

Materials

Ethylene oxide gas (Matheson), 99.9% purity, was used without further purification. Tetrahydrofuran (THF) was dried as before [15]. DMSO was dried by azeotropic distillation with benzene. Potassium naphthalene solution in THF was prepared as previously described [15]. Argon, 99.98% purity (Matheson), was dried by passing through concentrated sulfuric acid followed by sodium hydroxide pellets. Liquid reagents and solutions were kept under argon and transferred by hypodermic syringes, applying positive argon pressure.

Polymerization and Isolation Procedure

All manipulations were carried out under argon. The polymerizations were run in three-necked flasks fitted with a mechanical stirrer passing through a Teflon seal, a thermometer, and an outlet fitted with a self-sealing rubber cap through which the reagents were introduced with syringes. A calibrated flowmeter was connected to the flask to measure the amount of ethylene gas introduced, and another one was connected to the exit to measure any escaping gas. The flask was dried by flaming in vacuo and cooled under argon.

A solution of potassium naphthalene in THF was introduced followed by an equivalent of water. After that the green color of the potassium naphthalene disappeared, and the desired amount of monomer was added. The reaction mixture was diluted with THF to a constant volume and the reaction mixture was kept at 25°. The polymerization was terminated by addition of acetic acid (1.1 equivalents), and the polymer was precipitated by addition of anhydrous ether, which dissolved naphthalene and dihydronaphthalene. The crude polymer was dissolved in chloroform, filtered from the insoluble potassium acetate, and precipitated by ether. In cases where the polyethylene oxide was a viscous syrup, it was purified from naphthalene by extraction with water and evaporation of the solvent.

The number-average molecular weights ($\overline{M}_n$) of the polyethylene oxides were determined by acetylation with acetic anhydride in pyridine [16], the samples for the determination were further purified by solution in chloroform and precipitation by ether.

RESULTS

The potassium hydroxide initiator was obtained by addition of 1 equivalent of water to potassium naphthalene in THF. Experiments in which 1.5, 2, or 3 equivalents of water were added did not lead to polymerization of the ethylene oxide under the conditions investigated.

The effect of time of polymerization was studied. Two series of experiments were carried out, one in THF (Table 1) and the other in THF in the presence of two equivalents of DMSO to the initiator (Table 2), at the same [monomer]/[initiator] ratio (M/C) = 10.

It is seen that the degree of conversion increased with time. In THF after 6 hr the conversion was only 0.3% and became 90% after 54 hr. A strong acceleration in rate was observed after about 17 hr (Fig. 1). In the presence of DMSO the polymerization was faster and after 20 hr the conversion was 79%. The $\overline{M}_n$ of the polymers increased with time, parallel to the increase in the degree of conversion. Thus, while the polymer obtained after 17 hr in the case of THF had $\overline{M}_n$ = 2140, that obtained after 54 hr had $\overline{M}n$ = 10,000. The polymers having low molecular weights (less than 1000) were viscous, while the higher polymers were solid. In the presence of DMSO the $\overline{M}_n$ values were not much different at the high conversions from those obtained in THF.

Assuming that the polymerization was of the "living" type and no transfer reactions occurred, it was possible from the $\overline{DP}_n$ obtained and the per cent

Table 1. Effect of Polymerization Time[a]

Time (hr)	Conversion (%)	$\overline{M}_n$	Catalyst efficiency (%)	Polymer mp (°C)
6	0.3	1,020	1.0	–
17	4.7	2,140	1.0	45.0
24	14.7	5,750	1.1	–
43	73.5	8,950	3.6	60.5
48	82.0	9,250	3.8	61.0
54	90.0	10,020	3.9	62.0

[a]Experimental conditions: solvent, THF; ethylene oxide, 4.85 mole/1; potassium hydroxide, 0.485 mole/1; M/C = 10; temperature, 25°.

Table 2. Effect of DMSO on Conversion[a]

Time (hr)	Conversion (%)	$\overline{M}_n$	Catalyst efficiency (%)	Polymer mp (°C)
5	2	450	2.0	—
11	27	4,600	2.4	57.5
15	50	6,650	2.9	59.5
18	70	11,980	2.7	62.5
20	79	9,600	3.3	62.0

[a]Experimental conditons: DMSO (2 equiv) was added to potassium naphthalene in THF followed by water (1 equiv). Potassium hydroxide concentration, 0.485 mole/1; ethylene oxide concentration, 4.85 mole/1; M/C = 10; temperature, 25°.
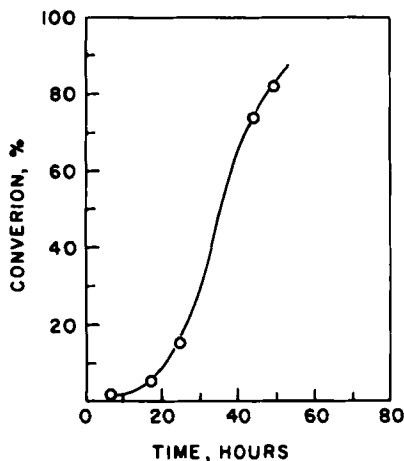
Fig. 1. Dependence of conversion on time of polymerization (polymerization in THF).

conversion to calculate the per cent or the amount of initiator that participated in the polymerization by using the equation, $X = (Y \times M/C)/\overline{DP}_n$, where X is the fraction per cent of the catalyst that initiated polymerization, Y is the monomer conversion, and M/C is the initial ratio of monomer to catalyst. The efficiency of the catalyst thus calculated was low and increased with the time of polymerization and the degree of conversion.

From Table 1 it can be seen that the acceleration in rate observed is due to an increase in the amount of catalyst which initiated polymerization. It can also be seen that from about 73 to 90% conversion, the amount of catalyst which initiated polymerization remained approximately constant. In the case of added DMSO (Table 2) a similar picture was observed but here from as low a conversion as 27% the amount of catalyst that participated in the initiation remained approximately constant.

From the data of Table 1, first-order plots for the disappearance of monomer were drawn (Fig. 2). It is observed that two linear regions exist having two different rate constants, the passing from one to the other being continuous. The observed rate constant for the first (slow) stage in THF was $k_{obs}\ 1 = 6.4 \times 10^{-7}\ sec^{-1}$ and for the second (fast) one was $k_{obs}\ 2 = 2.0 \times 10^{-5}\ sec^{-1}$. The polymerization was faster in the presence of two equivalents of DMSO and $k_{obs}\ 2$ was $4.7 \times 10^{-5}\ sec^{-1}$.
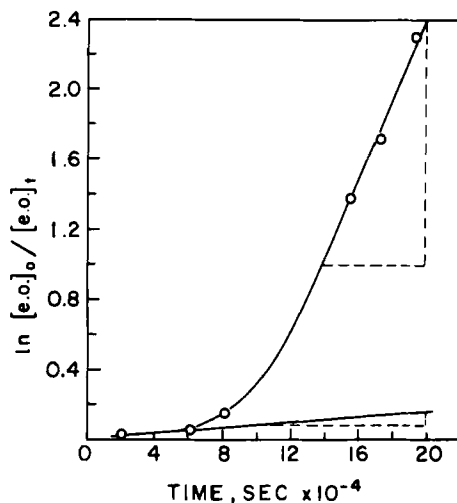
Fig. 2. First-order plot of the disappearance of monomer vs. time (polymerization in THF).

Effect of Monomer Concentration

This was studied in THF solution at three catalyst concentrations (Table 3). The polymerizations were carried out for 60 hr, and the yields were about 85-97%. The number-average molecular weights $\overline{M}_n$ increased (not linearly) with increasing monomer concentration, and were much higher than those calculated from the M/C ratios. To compare the $\overline{M}_n$ values more accurately, corrected $\overline{M}_n$ values were estimated from Fig. 3 on the basis of the same conversion (97%). The per cent of the catalyst participating in initiation increased with increasing monomer concentration. The efficiency of the initiator was higher at the lower catalyst concentrations.

The slope of the lines depicting the dependence of $\overline{M}_n$ on monomer concentration decreased with increasing initiator concentration, showing that the effect of increasing $\overline{M}_n$ with monomer concentration is less pronounced at the high initiator concentrations. The slope of the lines depicting $\overline{M}_n$ vs. monomer is also greater at the low monomer concentrations, showing that the change in $\overline{M}_n$ at these concentrations is more pronounced.

Experiments were carried out in which the monomer was added in two portions, the second one being added after 60 hr, i.e., approximately after complete conversion of the former. The $\overline{M}_n$ values obtained were similar to those obtained when all the monomer was added in one portion.

Table 3. Effect of Monomer Concentration[a]

[e.o.] (mole/1)	[Catalyst] (mole/1)	Conversion (%)	$\overline{M}_n$	$\overline{M}_n$ (corrected)[b]	Catalyst efficiency (%)	Polymer mp (°C)
2.42	0.242	79	4,950	5,300	6.1	58.0
4.84	0.242	96	14,600	14,670	6.0	64.0
7.26	0.242	92	18,570	18,870	6.5	64.5
10.90	0.242	95	20,700	20,900	8.8	65.0
4.84	0.727	84	9,500	9,960	2.6	61.0
7.27	0.727	87	12,700	13,150	3.0	62.0
14.54	0.727	91	17,920	18,350	4.4	64.5
4.84	0.970	97	9,420	9,420	2.3	61.5
9.70	0.970	83	11,500	12,400	3.2	63.0
19.40	0.970	90	14,150	14,550	5.5	64.0
4.84[c]	0.242	88	13,200	13,700	5.9	63.5
14.54[c]	0.727	93	18,770	18,950	4.2	64.5

[a]Experimental conditions as in Table 1. Reaction time, 60 hr.
[b]The $\overline{M}_n$ values were corrected on the basis of the same conversion (97%) estimated from Fig. 3.
[c]The monomer was added in two equal portions, the second portion being added 60 hr after the first. Total time of polymerization, 120 hr.
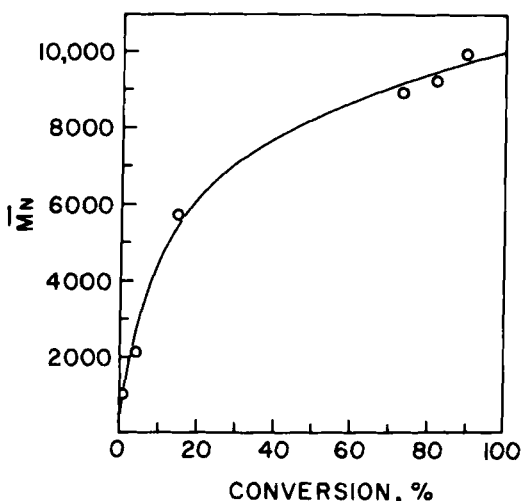
Fig. 3. Dependence of the number-average molecular weight on per cent conversion (polymerization in THF).

Effect of Initiator Concentration

This was investigated using a high and a low monomer concentration (Table 4). The molecular weights increased with decreasing initiator concentration but not linearly. The dependence of $\overline{M}_n$ on $1/[C]$ was much more pronounced at the higher monomer concentrations (Fig. 4). The efficiency of the initiator decreased with increasing initiator concentration, and it was between 2 to 6%. However, the absolute amount of initiator molecules that initiated polymerization increased with increasing initiator concentration.

DISCUSSION

The present polymerization of ethylene oxide was initiated by potassium hydroxide formed by the reaction of water with potassium naphthalene. Monomer was introduced only after the intense color of the potassium naphthalene disappeared completely, so that the latter cannot be the effective initiator. The fact that addition of 1.5 to 2 equivalents of water to the potassium naphthalene did not lead to potassium hydroxide, which could initiate polymerization, indicates that anhydrous potassium hydroxide is the effective catalyst, and its effect is completely destroyed in the presence of water.

Table 4. Effect of Initiator Concentration[a]

[KOH] (mole/1)	M/C	Conversion (%)	$\bar{M}_n$	$\bar{M}_n$ (corrected)[b]	Catalyst efficiency (%)	Polymer mp (°C)
			Series A			
0.242	20.0	96	14,600	14,650	6.0	64
0.484	10.0	85	11,030	11,520	3.4	62
0.727	6.7	84	9,500	9,970	2.6	61
0.970	5.0	97	9,420	9,420	2.3	61
			Series B			
0.242	40	91	30,400	31,100	5.4	66
0.324	30	88	21,150	21,600	5.4	65
0.484	20	93	15,400	15,580	5.2	64.5
0.970	10	93	11,510	11,650	3.8	63

[a]Experimental conditions as in Table 1. [Monomer] in Series A, 4.85 mole/1; in Series B, 9.70 mole/1; reaction time, 60 hr.
[b]The $\bar{M}_n$ values were corrected on the basis of the same conversion (97%) estimated from Fig. 3.
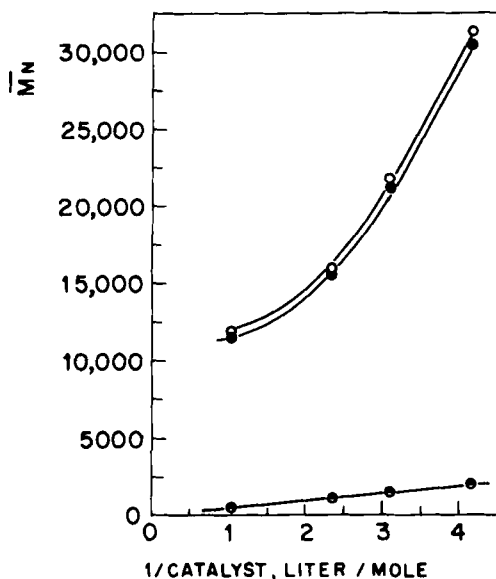
Fig. 4. Dependence of the number-average molecular weight on the reciprocal of the catalyst concentration (polymerization in THF; [monomer], 9.70 mole/1). (⊖)Calculated from M/C. (●) Experimentally found. (○) Corrected on the basis of 97% conversion.

A threshold concentration of potassium hydroxide was necessary for polymerization, and this may be connected at least in part with the heterogeneous nature of the initiator. The same applies to the low efficiency of the initiator. Monomer molecules add easier to growing chains than to insoluble initiator.

It was seen that the per cent of initiator that participated in the polymerization increased initially with time of polymerization, and there was also an increase in the molecular weights, indicating that new chains and propagation were occurring simultaneously at the early stages of the polymerization initiation. At the latter stages of polymerization, the amount of catalyst which initiated polymerization, as calculated from the molecular weights, did not increase further, while the molecular weights continued to increase, indicating that at these stages of the polymerization essentially propagation occurred but not initiation.

Since the polymerization is of the "living" type, the rate equation for these latter stages of the polymerization will be (provided that the reaction is first-order to the catalyst which initiated polymerization) $-d[e.o.]/dt = k_p[Co][e.o.]$

or in its integrated form $\ln[e.o.]_0/[e.o.]_t = k_p[C_0]t$, where k_p is the propagation rate constant and C_0 is the concentration of the growing ends which is equivalent to the average initiator concentration which participated in the polymerization at the high reaction times.

The k_{obs} values found from the slope of $\ln[e.o.]_0/[e.o.]_t$ vs. t (Fig. 2) are therefore equal to k_p $[C_0]$. Now in the case of THF, $C_0 = 18.2 \times 10^{-3}$ mole/1 (calculated from $\overline{DP}_n$ and per cent conversion) and therefore $k_p = 1.05 \times 10^{-3}$ 1 $mole^{-1}$ sec^{-1}, as calculated from $k_{obs}2$. In the case of THF + 2 equiv DMSO, $C_0 = 14.0 \times 10^{-3}$ mole/1 and since $k_{obs} 2 = 4.7 \times 10^{-5}$ sec^{-1}, therefore $k_p = 3.35 \times 10^{-3}$ liter $mole^{-1}$ sec^{-1}, which is about three times larger than that obtained in the absence of DMSO.

These values may be compared with those found in the homogeneous polymerization of ethylene oxide by sodium methoxide and ethoxide in dioxane at 30° where k_p was 2.95×10^{-5} and 7.2×10^{-5} liter $mole^{-1}$ sec^{-1}, respectively [17].

The increase in rate observed in the presence of 2 equiv of DMSO cannot be due to an increase in the bulk dielectric constant of polymerization medium since the amounts of DMSO added were small, but solvation effects should be important. DMSO, being a Lewis base, can effectively solvate the potassium cations. This can increase the rate of both initiation and propagation. Comparison of the per cent initiator that participated in the polymerization in the case of THF + 2 equiv DMSO with that in the presence of THF alone showed that less KOH participated in initiation in the former so that the increase in the rate of propagation is the more dominant effect of the solvation.

Although the initiation is heterogeneous, there is direct although not linear dependence of the molecular weights on the monomer concentration and inverse dependence on the initiatior concentration. Increasing the monomer concentration at constant initiator concentration (Table 3) shows that initially there is a relatively large increase in molecular weight with increase of monomer concentration but afterwards the increase is much smaller. This may be due to the fact that increasing the monomer concentration increases not only the length of the growing chains but also introduces more initiator molecules into the reaction. Likewise, increasing the catalyst concentration (Table 4) decreases the slope of the dependence of $\overline{M}_n$ vs. monomer due to the same reason, i.e., more catalyst initiates polymerization with increasing catalyst concentration.

Evidence for the absence of transfer reactions in the present polymerization was obtained from the following considerations: Pepper [18] has shown that for living polymerizations the reciprocal of the degree of polymerization is directly proportional to the reciprocal of the degree of conversion, y, according to the equation:

$$1/\overline{DP}_n = (C_0/M_0) \cdot 1/y + k_{tr}/k_p + k_{tr}$$

where C_0 and M_0 are the starting catalyst and monomer concentrations, resepctively, and k_{tr} and k_p are the transfer and propagation rate constants. The last term of the equation takes account of any transfer reactions occurring during the polymerization. The slope of the line gives the ratio, C_0/M_0, and its intercept the value of $k_{tr}/k_p + k_{tr}$.

In cases where the initiation process is rapid and there are no transfer reactions, the plot of $1/\overline{DP}_n$ vs. $1/y$ should be linear. In cases where the initiation is slow and both propagation and initiation are occurring simultaneously, the dependence will not be linear.

To find the behavior of the present polymerization, we plotted $1/\overline{DP}_n$ vs. $1/y$ (Fig. 5). The plots were not very clear but it could be seen that for both series of experiments, in the presence of THF and THF + DMSO, two linear regions having different slopes are obtained, the turning point being at $1/y = 1.36$, i.e., a conversion of about 73% in the case of THF, and at $1/y = 2.0$, i.e., a conversion of about 50% in the case of THF + DMSO.
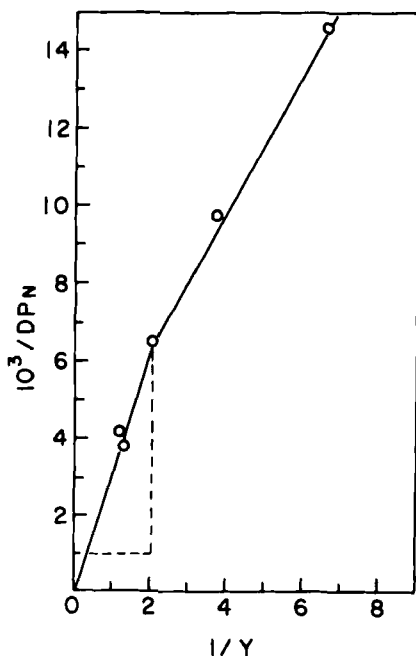
Fig. 5. Dependence of $1/\overline{DP}_n$ on 1/conversion (1/Y) (complete conversion taken as 1) (polymerization in THF + 2 equiv DMSO).

Therefore, in the first stage of the reaction there is both initiation and propagation due to slow initiation. Extrapolation of the second line goes to zero, and therefore $k_{tr} = 0$, i.e., there is no transfer to monomer or to solvent. The slope of this line is $C_0/M_0 = 3.3 \times 10^{-3}$, and since $M_0 = 4.85$ mole/1, then $C_0 = 19.0 \times 10^{-3}$ mole/1, and C_0 is the initiator concentration which participated in the reaction. This value compares favorably with C_0 calculated from $\overline{DP}_n$ which was $18.2 \times 10^{-3} \pm 1.4$ mole/1 for the experiments (Table 1) (THF) for which the slope of the line was drawn. C_0 in the case of THF + 2 equiv DMSO was 14.0×10^{-3} mole/1, obtained experimentally, and from the slope of Fig. 5 it was 16.0×10^{-3} mole/1, which is also in good agreement.

In conclusion, it was seen that the potassium hydroxide formed in situ by addition of water to a solution of potassium naphthalene in THF was more active as an initiator of polymerization of ethylene oxide than solid potassium hydroxide previously used, notwithstanding the heterogeneous nature of the polymerization. Addition of only two equivalents of DMSO to the catalyst was found to increase the rate of polymerization threefold.

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