Kinetics of Base-Catalyzed Polymerization of Epoxides in Dimethyl Sulfoxide and Hexamethylphosphoric Triamide

Charles C. Price* and Murali Krishna Akkapeddi[1]

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104. *Received June 15, 1971*

Abstract: The homogeneous polymerization of propylene oxide catalyzed by potassium *tert*-butoxide in DMSO and HMPT gave second-order rate constants for the (*R*,*S*) monomer about double those for (+)-(*R*) (or (−)-(*S*)). The strong steric factors favoring alternate isotactic and syndiotactic placements with *tert*-butylethylene oxide thus also influence propylene oxide to a lesser degree. From studies of molecular weights of poly(ethylene oxide) and poly(propylene oxide) prepared by *tert*-BuOK catalysis in DMSO, relative rates for chain transfer to solvent are about 7×10^{-5} for ethylene oxide and 3×10^{-3} for propylene oxide. The value for PO in DMSO-d_6 ($\sim 1 \times 10^{-3}$) indicates some isotope effect for transfer. Compared to (*R*,*S*)-propylene oxide, the relative rates of polymerization are: ethylene oxide, fivefold; phenyl glycidyl ether, threefold; and *tert*-butylethylene oxide, one-tenth.

Discussion

Kinetics of Propylene Oxide Polymerization. Several earlier investigations have disclosed that base-catalyzed polymerization of epoxides follows second-order kinetics, first order in monomer and first order in base catalyst.[2–8] The preceding paper reports that the base-catalyzed polymerization of *tert*-butylethylene oxide produces a crystalline polymer with an equal number of isotactic and syndiotactic sequences, presumably in regular alternation.[9] If any of the same tendency to incorporate a new monomer of the opposite configuration from the penultimate unit of the growing end held in propylene oxide, then the formation of the sequence *ddd* would proceed at a rate slower than *ddl*. Therefore, a monomer containing only *d* (or *l*) molecules should polymerize at a slower rate. Inspection of the data in Tables I and II shows that this expectation is borne out by experiment in both DMSO and HMPT, the difference in rate being about twofold, *i.e.*, $k_{RS} \simeq 2k_S$. These kinetic data may thus be taken as support for the hypothesis[9] of an alternation of sequence (rather than the alternate possibility of equal blocks of isotactic and syndiotactic sequences[10]).

Table I. Kinetic Data for (*R*,*S*)- and (−)-(*S*)-Propylene Oxide Polymerization by *tert*-BuOK in DMSO-d_6

Temp, °C	[Cat$_0$]	[M$_0$]	$10^4k_2{}^a$ (*R*,*S*)	$10^4k_2{}^a$ (−)-(*S*)
25	0.04	2.87	2.7	1.4
	0.03	2.87	2.2	0.8
	0.02	2.87	2.2	
	0.06	2.05	5.7	
30	0.05	3.1	9.0	3.6
	0.03	2.5	5.6	
40	0.02	2.4	11.3	5.0
	0.04	2.4		4.3
	0.07	2.5	14	
55	0.03	2.5	44	

[a] M^{-1} sec^{-1}.

Table II. Kinetic Data for (*R*,*S*)- and (−)-(*S*)-Propylene Oxide Polymerization by *tert*-BuOK in HMPT

Temp, °C	[Cat$_0$]	[M$_0$]	10^4k_2 (*R*,*S*)	10^4k_2 (−)-(*S*)
14.7	0.077	3.1	2.6	1.4
25	0.077	2.1	14	6.8
	0.046	2.0	8.2	
	0.04	2.5	8.5	5.3
	0.03	2.8	7.3	3.4
	0.017	2.5	7.9	
	0.05[a]	2.87	6.1	
	0.024[b]	1.63	15	
40	0.06	2.9	29	10

[a] Also 0.05 *M* in *tert*-butyl alcohol. [b] Also 0.024 *M* in dicyclohexyl-18-crown-6 (C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 386, 391 (1970)).

The observation of a 2:1 preference for (*R*,*S*)- over (*S*)-propylene oxide polymerization offers a reasonable explanation for an anomalous observation on the isotactic sequence lengths in base-catalyzed poly((*S*)-propylene oxide). It has been shown that the (−)-(*S*)-propylene oxide prepared from optically pure (+)-(*S*)-propylene glycol is usually contaminated with about 10% (+)-(*R*) isomer.[11] The polymer prepared from this monomer, according to its melting point, had isotactic sequence lengths of 20 or more,[12] rather than about ten as expected for a random distribution of the 10% of (+)-(*R*) isomer. If there is indeed a rate factor favoring alternating sequences by 2:1, then the 10% of (+)-(*R*) isomer will be depleted at a more rapid relative rate than the (−)-(*S*). The unreacted remaining monomer will thus increase in optical purity and give isotactic sequences of increasing length.

We have no explanation for the disturbingly erratic rate "constants" obtained for polymerization of propylene oxide in DMSO (the kinetics for PGE, *e.g.*, were much more reproducible). While the values at 25° in Table I are in reasonable accord with earlier reports[2]

---

(1) From the doctoral dissertation of M. K. Akkapeddi, 1971.

(2) C. C. Price and D. D. Carmelite, *J. Amer. Chem. Soc.*, **88**, 4039 (1966).

(3) E. C. Steiner, R. R. Pelletier, and R. O. Trucks, *ibid.*, **86**, 4678 (1964).

(4) G. Gee, W. C. E. Higginson, K. J. Taylor, and M. W. Trenholme, *J. Chem. Soc.*, 4298 (1961).

(5) C. C. Price and H. Fukutani, *J. Polym. Sci.*, **6**, 2653 (1968).

(6) C. E. H. Bawn, A. Ledwith, and N. McFarlane, *Polymers*, **10**, 653 (1969).

(7) G. Ezra and A. Zilkha, *J. Polym. Sci., Part A-1*, **8**, 1343 (1970).

(8) P. Banks and R. H. Peters, *ibid., Part A-1*, **8**, 2595 (1970).

(9) C. C. Price, M. K. Akkapeddi, B. T. DeBona, and B. C. Furie, *J. Amer. Chem. Soc.*, **94**, 3961 (1972).

(10) H. Tani and N. Oguni, *Polym. Lett.*, **7**, 803 (1969).

(11) B. Franzus and J. H. Surridge, *J. Org. Chem.*, **31**, 4286 (1966).

(12) C. C. Price and A. L. Tumolo, *J. Polym. Sci., Part A-1*, **5**, 175 (1967).

of 2.5 × 10^{-4} M^{-1} $\sec^{-1}$ and the activation energy derived from the data in Table I of 17.2 kcal/mol^{-1} also is in reasonable accord with earlier reports[4] of 17.8 kcal mol^{-1}, we do not place high confidence in the accuracy of our values ($k = 1.15 \times 10^9 \exp^{-17.2/RT}$).

We have chosen to report rate constants for the reaction after a "steady" rate has been achieved, rather than the more rapid initial rate reported elsewhere.[6] There are two obvious factors which would lead to a more rapid initial rate: (1) the more rapid initial reaction of unchelated *tert*-butoxide ion to monomer, compared to a slower rate for the growing chain where the ion pair may be further stabilized by ether chelation, and (2) the generation of hydroxyl groups by chain transfer to monomer and/or solvent, which would stabilize the alkoxide ion by hydrogen bonding.

The data in Table II for polymerization of propylene oxide in HMPT show this solvent to give rates faster than in DMSO by a factor of about threefold. Since it also gives reaction mixtures which remain homogeneous as polymer forms, it is a superior solvent for the reaction. The major reason for the enhanced rate is a lower activation energy of 16.3 kcal mol^{-1} ($k = 7.3 \times 10^8 \exp^{-16.3/RT}$).

Kinetics for Other Epoxides. The rate of polymerization for ethylene oxide in HMPT was about fourfold greater than for propylene oxide ($k = 2.75 \times 10^7 \exp^{-13.3/RT}$) and that for *tert*-butylethylene oxide about one-tenth ($k = 2.0 \times 10^8 \exp^{-17.1/RT}$), as summarized in Table III.

Table III. Kinetic Data for Polymerization of Ethylene Oxide and *tert*-Butylethylene Oxide by *tert*-BuOK in HMPT

Monomer	Temp, °C	[Cat$_0$]	[M$_0$]	10^4k_2, M^{-1} sec^{-1}
EO	40	0.01	2.3	114
		0.008	3.4	138
	60	0.007	2.6	510
tert-BuEO	40	0.053	2.4	2.4
	45	0.077	3.1	4.1
	60	0.037	1.3	13

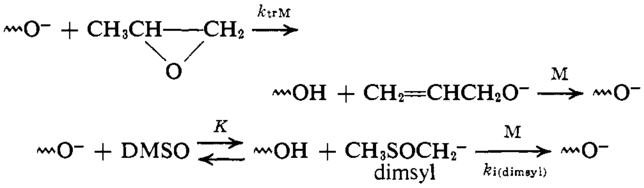
Our value for the rate of ethylene oxide polymerization in HMPT is about 40-fold less than that reported in DMSO by Bawn, Ledwith, and McFarlane.[6] They did choose to report initial rates rather than "steady-state" rates so there will be the factor of the influence of hydroxyl groups generated by transfer. Their assertion that the discrepancy may be due to hydroxylic impurities in our solvents seems unlikely, since our molecular weights are in reasonable agreement with theirs (39,000 *vs.* 45,000). We, of course, used a direct measurement for monomer rather than a dilatometric procedure in DMSO, but in HMPT our dilatometric measurements gave rates differing from DMSO by only threefold. Undoubtedly, however, the most important reason for the differences in rate is the large difference in catalyst concentration. We used much higher concentrations, which according to the data of Figueruelo and Worsfold[13] would lead to greater association of alkoxides and to lower rate constants. Our catalyst concentrations (and rates) correspond to those of Figueruelo and Worsfold at their highest catalyst concentration.

The rates of polymerization for phenyl glycidyl ethers, summarized in Table IV, indicate an activation energy of 14.7 kcal mol^{-1} ($k = 5.4 \times 10^7 \exp^{-14.7/RT}$). The threefold greater rate for PGE compared to propylene oxide as well as the relative rates for substituted phenyl glycidyl ethers are all in accord with copolymerization ratios reported earlier.[14] The data of Ezra and Zilkha for PGE rates in DMSO, however, differ from ours by a factor of about tenfold. They chose to use a very low monomer–catalyst ratio, which would mean they did measure a significant amount of chain initiation and developed a very small amount of hydroxyl (by chain transfer) relative to alkoxide ions.

Table IV. Kinetic Data for Polymerization of Phenyl Glycidyl Ethers by *tert*-BuOK in DMSO-d_6

M	Temp, °C	[Cat$_0$]	[M$_0$]	10^4k_2, M^{-1} sec^{-1}
PGE	24	0.02	3.0	7.2
	30	0.016	3.0	12
		0.06	3.0	13
		0.08	3.1	14
		0.11	3.3	14.5
	40	0.025	3.0	26
		0.038	3.0	25
		0.053	3.0	28
p-Cl	24	0.018	2.7	9.7
p-CH$_3$	25	0.067	2.5	3.8
2,6-(CH$_3$)$_2$	25	0.06	3.0	3.6
p-CH$_3$O	35	0.16	3.3	16.5

Chain Transfer to DMSO. Earlier data[15] had indicated a value for chain transfer of growing polymer chains to propylene oxide monomer, $k_p/k_{tr} \simeq 50$. In the unreactive polar solvent HMPT, our data indicate



$$\sim\!O^- + CH_3CH\!-\!CH_2(O) \xrightarrow{k_{trM}} \sim\!OH + CH_2\!=\!CHCH_2O^- \xrightarrow{M} \sim\!O^-$$

$$\sim\!O^- + DMSO \overset{K}{\rightleftarrows} \sim\!OH + \underset{\text{dimsyl}}{CH_3SOCH_2^-} \xrightarrow[k_{i(dimsyl)}]{M} \sim\!O^-$$

$k_p/k_{tr} = 70$, in reasonable agreement with that obtained earlier in bulk.

In order to take into account the factors of chain transfer and catalyst–monomer ratio on the degree of polymerization, we suggest the use of the following equation

$$\frac{1}{DP} = \frac{1}{DP_0} + \frac{\alpha}{1+\alpha} + \frac{\beta K[\mathrm{DMSO}]}{1+\alpha} \tag{1}$$

in which $\alpha = k_{tr(M)}/k_p$ and $\beta = k_{i(dimsyl)}/k_p$. This relationship is derived by the assumption that

$$DP = \frac{\text{monomer molecules reacted}}{[\mathrm{cat}_0] + P_t} \tag{2}$$

where P_t is the number of new polymer chains initiated. It will consist of (1) the number of alcohol groups formed by transfer to monomer and (2) the number of

---

(13) J. E. Figueruelo and D. J. Worsfold, *Eur. Polym. J.*, **4**, 439 (1968).

(14) C. C. Price, Y. Atarashi, and R. Yamamoto, *J. Polym. Sci.*, **7**, 569 (1969).

(15) C. C. Price and L. E. St. Pierre, *J. Amer. Chem. Soc.*, **78**, 3432 (1956).

new polymer chains formed by transfer to DMSO. The latter processes must be integrated over the course of the polymerization

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = k_p[M_t][cat_0] + k_{tr(M)}[M_t][cat_0] \quad (3)$$

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_{tr(M)}[M_t][cat_0] + k_{i(dimsyl)}[dimsyl][M_t] \quad (4)$$

By substituting for [dimsyl], K[DMSO][cat$_0$], the ratio of eq 4 to eq 3 gives

$$-\frac{\mathrm{d}P}{\mathrm{d}M} = \frac{k_{tr(M)}}{k_p + k_{tr(M)}} + \frac{k_{i(dimsyl)}K[DMSO]}{k_p + k_{tr(M)}} \quad (5)$$

Transposing dM and integrating gives

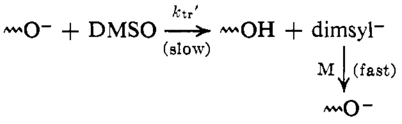
$$P_t = \frac{\alpha}{1+\alpha}[M_0 - M_t] + \frac{\beta K[DMSO]}{1+\alpha}[M_0 - M_t] \quad (6)$$

Substituting eq 6 in eq 2 leads to eq 1.

Application of eq 1 to the earlier data[2] on molecular weight of poly(propylene oxide) in DMSO leads to $\beta_{PO}K \simeq 2.5 \times 10^{-3}$. Multiplying by $k_p(2.5 \times 10^{-4})$ gives $Kk_{i(dimsyl)} \simeq 6 \times 10^{-7}\ M^{-1}\ sec^{-1}$ (for PO).

The data for the overall degree of polymerization of PO in DMSO-d_6 of 34 also can be analyzed for chain transfer to deuterated solvent. This value for $\beta K \simeq 1 \times 10^{-3}$ indicates an isotope effect for the hydrogen abstraction from DMSO.

One interpretation of this apparent isotope effect would be that the assumption of proton equilibration between alkoxide and DMSO being rapid compared to reaction of dimsyl ion with propylene oxide is not correct. If we make the alternate assumption that the



$$\begin{tikzcd} \sim O^- + DMSO \arrow[r, "k_{tr}'", "(slow)"'] & \sim OH + dimsyl^- \arrow[d, "M"', "(fast)"] \\ & \sim O^- \end{tikzcd}$$

proton transfer step is rate controlling, then the last term in eq 1 is modified to

$$\frac{\beta'}{1+\alpha}\frac{[DMSO]}{[M_0]}\ln\frac{[M_0]}{[M_t]}$$

where $\beta' = k_{tr}'/k_p$. For purposes of calculation, $[M_t]$ can be assumed to be 1% of $[M_0]$, since polymer formed after 99% conversion will be of such low molecular weight as to be discarded in work-up. Since $[M_0]$ was about 4 M, this modified eq 1 will give values for β' comparable to values for βK from eq 1.

The data for chain transfer for ethylene oxide in DMSO, estimated from the molecular weight of poly(ethylene oxide) formed in DMSO at a monomer: catalyst ratio of 2000, which gave a polymer of DP = 900 (rather than the calculated 2000 for no chain transfer) gave $\beta_{EO}K \simeq 7 \times 10^{-5}$. Using our extrapolated k_p at 25° (3×10^{-3}), this gives $Kk_{i(dimsyl)} \simeq 2.3 \times 10^{-7}$ M^{-1} sec^{-1} (for EO).

The value for K has been variously reported as 1.5×10^{-7}, 1.5×10^{-4}, and 0.6×10^{-4}.[16] Using the value of $K = 10^{-4}$ gives a value of $k_{i(dimsyl)} \simeq 2.3 \times 10^{-3}$ M^{-1} sec^{-1}, very close to the value of k_p for EO. Similar analysis of the data for propylene oxides gives for this system $k_{i(dimsyl)} = 6 \times 10^{-3}$ M^{-1} sec^{-1}, about 25-fold greater than k_p.

Chain Transfer to PGE Monomer. Data on the variation of molecular weight for the polymerization of PGE analogs in bulk with *tert*-BuOK is summarized in Table V. These data make possible an estimate of the relative rates of propagation to transfer for these monomers, varying from 21 to 165. For propylene oxide under comparable conditions, $k_p/k_{tr} \simeq 50$.[17] The value we report here in Table V for PGE of 75, based on earlier data,[8] is in excellent agreement with that of 73 reported by Banks and Peters for sodium methoxide catalysis[18] and conflicts with the statement of Ezra and Zilkha that PGE does not chain transfer to monomer.[19]

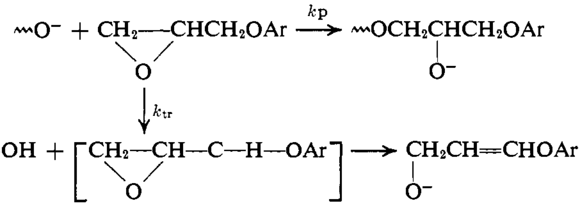
Table V. Effect of *tert*-BuOK Concentration on Molecular Weight of Poly(PGE) in Bulk

Subst	$[M_0]/[cat_0]$	$\bar{M}_n{}^a$	DP	$k_p/k_{tr}{}^b$	10^6k_{tr}
H	100	6,450	43	75	1.0
p-Cl	25	1,670			
	50	4,425			
	100	5,540	30	49	2.0
p-Me	25	4,110			
	50	5,650			
	80	8,600			
	150	11,900	73	110	0.35
p-MeO	25	3,930			
	40	5,925			
	63	10,400			
	88	13,750	76	165	0.33
2,6-Me$_2$	50	2,500			
	100	3,500			
	200	3,850	22	21	1.7

[a] By Mechrolab Vapor Osmometer. [b] From $1/DP = [cat]_0/[M_0] + \alpha/(1+\alpha)$; $\alpha = k_{tr}/k_p$.

The rate data for the substituted phenyl glycidyl ethers (Table IV) can be combined with data for chain transfer to monomer in these ethers to give information on the rates for transfer, included in Table V.

The values for k_p, plotted against Hammett σ constants, give $\rho_p = 0.55$ while those for k_{tr} give $\rho_{tr} = 1.52$. Since the transfer reaction would develop anionic character at the carbon attached to the aryl ether oxygen while propagation would place anionic character more remote from the aryl group, it is reasonable for the transfer reaction to be more sensitive to the electrical character of substituents in the ring, as indicated by the larger ρ value.



Experimental Section

Dimethyl-d_6 sulfoxide was dried by refluxing over anhydrous barium oxide at 7 mm for 3 hr and then distilled, bp 63° (7 mm). It was kept in sealed ampoules under dry nitrogen. **Hexamethyl-**

---

[16] A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1963); E. C. Steiner and J. M. Gilbert, *J. Amer. Chem. Soc.*, **85**, 3054 (1963); C. D. Ritchie and R. E. Uschold, *ibid.*, **89**, 2960 (1967).

[17] C. C. Price and L. E. St. Pierre, *ibid.*, **78**, 3432 (1956).

[18] P. Banks and R. H. Peters, *J. Polym. Sci., Part A-1*, **8**, 2595 (1970).

[19] G. Ezra and A. Zilkha, *ibid., Part A-1*, **8**, 1343 (1970).

phosphoric triamide (HMPT) was dried by refluxing over calcium hydride powder at 0.6 mm for 6 hr and then distilled, bp 65° (0.6 mm). It was further dried by distillation from its blue sodium solution. **Potassium *tert*-butoxide** was sublimed at 220° (0.6 mm) and dissolved in either solvent above in a drybox under nitrogen.

(*R*,*S*)-Propylene oxide was dried by refluxing over calcium hydride for 6 hr and distillation, bp 34.5°. **(−)-(*S*)-Propylene oxide,** $[\alpha]_D$ −11.8° (neat), was prepared from (+)-(*S*)-lactic acid[9] and **(+)-(*R*)-propylene oxide,** $[\alpha]_D$ 10.95° from (−)-(*R*) propylene glycol prepared by fermentation.[20] **Ethylene oxide** was dried by passing through columns of drierite and calcium hydride and was condensed on a vacuum line into calibrated tubes. ***tert*-Butylethylene oxide** was prepared from *tert*-butylethylene as described elsewhere.[9] **Phenyl glycidyl ether** was dried by refluxing at 4 mm over calcium hydride and distilled, bp 99° (4 mm). The substituted analogs were prepared as described elsewhere.[9,21]

Polymerizations in DMSO-d_6. Monomer and catalyst solutions were transferred in a drybox to nmr tubes (7 cm longer than usual). These were cooled in liquid N_2, sealed, and kept in a constant temperature bath. The conversion of propylene oxide to polymer was estimated by comparing the nmr integrals near δ 2.7 ppm (monomer methylene and methine) with those near δ 3.4 (polymer methylene and methine). For phenyl glycidyl ether, the epoxide methylene peaks near δ 2.7 were compared to the polymer multiplet developing near δ 3.8. The results were plotted graphically as a pseudo-first-order reaction. In almost every case there was a rapid initial reaction (for 10–20% conversion) and then very satisfactory straight lines from which the pseudo-first-order constant k_1' could be estimated. We suspect that the initial decrease is due to development of alcohol groups by chain transfer to monomer and solvent. This factor suggests the rate constants we report are not for truly "aprotic" DMSO. Representative data are summarized in Tables I and IV.

Polymerizations in HMPT. The reaction rates in HMPT were measured dilatometrically on about 3 ml of reaction mixture. The dilatometer was thoroughly dried at 180° for several hours. By means of a ground glass joint, it could be connected through an oblique-bore vacuum stopcock to a vacuum line. After injecting the catalyst solution *via* a long hypodermic needle in a nitrogen-filled drybox, the dilatometer flask was attached to the vacuum line, cooled in liquid N_2, and degassed. A known amount of monomer was then distilled in from another calibrated tube of the vacuum system. The dilatometer was again cooled in liquid N_2, degassed, and sealed with a flame. After warming to melt the contents, they were shaken to ensure mixing and placed in a constant temperature bath. The level in the capillary was read from time to time with a cathetometer from which the extent of reaction could be estimated. Again pseudo-first-order plots gave excellent straight lines, with much less (or sometimes no more) rapid initial reaction as was the rule in DMSO. Results are summarized in Tables II and III.

Chain Transfer. A. Ethylene Oxide. A solution of resublimed *tert*-BuOK in dry DMSO was placed in a thick-walled tube fitted with an oblique-bore stopcock and dry monomer was distilled in from a vacuum line. After 2 weeks at room temperature, the contents were dissolved in benzene and the polymer, precipitated by pouring into a large excess of dry ether, was obtained in quantitative yield. Molecular weights were determined in water using the relation (see Table VI)[22]

$$[\eta] = 6.4 \times 10^{-5}\bar{M}_v^{0.82}$$

B. **Propylene oxide** (3.5 ml, 50 mmol) in DMSO-d_6 (6 ml) containing 34 mg (0.33 mmol) of *tert*-BuOK was sealed under dry N_2 and kept at 25° for 5 days. The viscous reaction mixture, which had separated into two layers, was extracted with cyclohexane. Evaporation left the polymer which gave its number average molecular weight by vapor osmometer, $\bar{M}_n$ = 2000, *DP* = 34.5.

Table VI

$10^2[\text{cat}_0]$	$[M_0]$	$[\eta]$	$\bar{M}_v$	*DP*	$[M_0]/[\text{cat}_0]$
3.85	7.7	0.112	9,000	205	200
0.385	7.7	0.375	39,000	900	2000

C. **Propylene oxide** (5.8 g, 100 mmol) in 20 ml of HMPT containing 74 mg (0.66 mmol) of *tert*-BuOK was polymerized at 25° for 1 week. Unlike in DMSO, this reaction mixture remained homogeneous. After neutralization with solid CO_2, the polymer was extracted with cyclohexane and its molecular weight measured by vapor osmometer, $\bar{M}_n$ = 2800, *DP* = 48.

---

(20) P. A. Levene and A. Walti, *J. Biol. Chem.*, **68**, 415 (1926).

(21) C. C. Price and L. Brecker, *J. Polym. Sci., Part A-1*, 7, 575 (1969).

(22) F. E. Bailey and R. W. Callard, *J. Appl. Polym. Sci.*, 1, 56 (1959).