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# Ring-Chain Equilibrium in the Anionic Polymerization of δ-Valerolactone

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The anionic polymerization of ε-caprolactone with potassium tert-butoxide and lithium tert-butoxide in tetrahydrofuran and toluene provides a thermodynamically controlled, living ring-chain equilibrium system (ITO, HASHIZUKA, and YAMASHITA, 1977; ITO, and YAMASHITA, 1978). As expected from the Jacobson-Stockmayer theory (JACOBSON, and STOCKMAYER, 1950; SEMLYEN, 1976; FLORY,and SEMLYEN, 1966), the product distribution was essentially determined by the entropy term, the lower cyclic oligomers being more favored over the linear polymers with increasing dilution. In order to see the effect of the monomer ring size on the product distribution, the present letter describes the result for the polymerization of δ-valerolactone with lithium tert-butoxide in tetrahydrofuran which resulted in a similar living equilibrium system.

Polymerization, depolymerization, and determination of the product distribution were performed similarly as decribed before (ITO, HASHIZUKA, and YAMASHITA, 1977; ITO, and YAMASHITA, 1978). The cyclic trimer, tetramer, and pentamer were isolated by GPC, and identified by elemental analysis, NMR and mass spectra.

Figure 1 shows the change in product distribution (GPC chromatogram) with polymerization time. Initially polymers were produced, and then, cyclic oligomers increase their proportions while polymers decrease until the equilibrium distribution was attained after about 48 hours. The monomer consumption was rather fast to be almost complete in one hour, and there appeared an maximum for the concentration of the polymers at about one hour.

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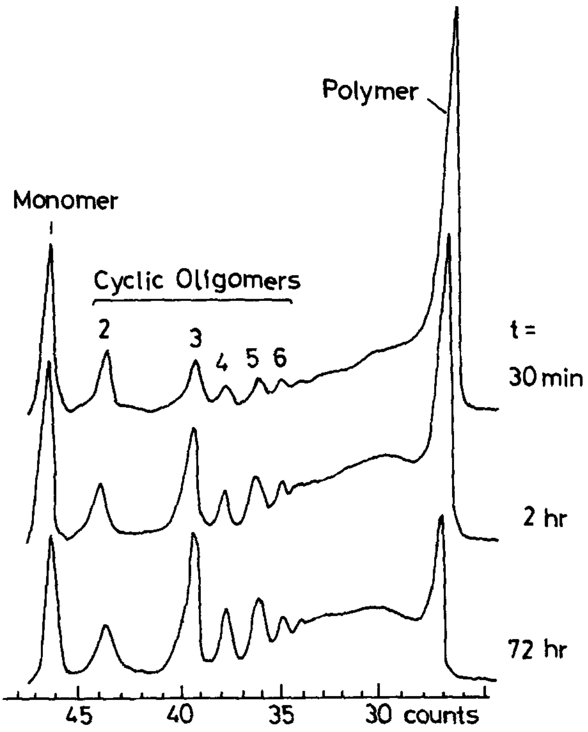
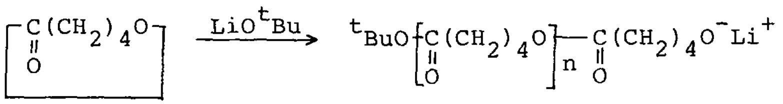


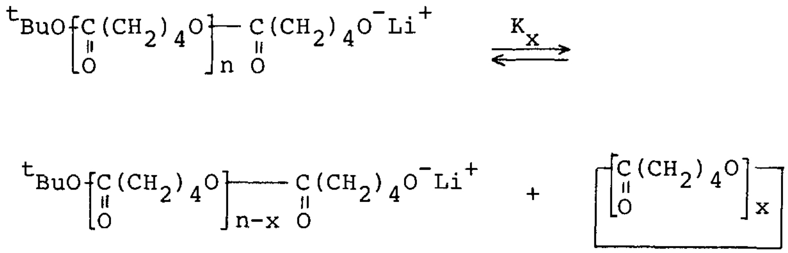
Fig. 1. Change in product distribution (GPC chromatogram) with polymerization time.
$[M]_0 = 0.223\ M$, $[LiO^tBu]_0 = 0.0042\ M$

Therefore, as in the case of ε-caprolactone, the system can be represented by the initial ring-opening polymerization of the monomer, eq. (1), followed by the equilibrium cyclic oligomer formation by back-biting of the living linear polymers, eq. (2):



$$\left[\underset{\underset{O}{\|}}{C}(CH_2)_4O\right] \xrightarrow{LiO^tBu} {}^tBuO\left[\underset{\underset{O}{\|}}{C}(CH_2)_4O\right]_n\!-\underset{\underset{O}{\|}}{C}(CH_2)_4O^-Li^+$$

(1)



$$ {}^{t}\mathrm{BuO}\!\left[\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}(\mathrm{CH_2})_4\mathrm{O}\right]_{n}\!\!-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}(\mathrm{CH_2})_4\mathrm{O}^{-}\mathrm{Li}^{+} \overset{K_x}{\rightleftarrows} {}^{t}\mathrm{BuO}\!\left[\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}(\mathrm{CH_2})_4\mathrm{O}\right]_{n-x}\!\!-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}(\mathrm{CH_2})_4\mathrm{O}^{-}\mathrm{Li}^{+} + \left[\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}(\mathrm{CH_2})_4\mathrm{O}\right]_{x} $$

(2)

As expected for the equilibrium system, the concentration of each product at equilibrium was found to be influenced exclusively by the concentration of the total monomer units present, not influenced by the history of the experiments including polymerization, depolymerization, and two-stage monomer charge. The molar cyclization equilibrium constant, $K_x$, was determined from the limitting equilibrium concentration of the corresponding cyclic oligomer, in the same manner as before (ITO, HASHIZUKA, and YAMASHITA, 1977). The result is given in Table 1, together with that of ε-caprolactone.

Table 1. Molar cyclization equilibrium constant, $K_x$ at 0°C, and the corresponding free energy and entropy change.

| | δ-Valerolactone | | | ε-Caprolactone | | |
|---|---|---|---|---|---|---|
| | $K_x \times 10^2$ | $\Delta G^\circ$ | $\Delta S$ | $K_x \times 10^2$ | $\Delta G^\circ$ | $\Delta S$ |
| x | M | kJ/mol | J/mol·deg | M | kJ/mol | J/mol·deg |
| 2 | 0.60 | 11.6 | – | 6.50 | 6.19 | -22.6 |
| 3 | 2.77 | 8.15 | -29.8 | 1.07 | 10.3 | -37.6 |
| 4 | 0.80 | 9.20 | -40.1 | 0.98 | 10.5 | -38.5 |
| 5 | 0.66 | 11.4 | -41.6 | 0.60 | 11.6 | -42.6 |
| 6 | 0.42 | 12.4 | -44.3 | 0.34 | 12.9 | -47.2 |

Figure 2 shows the log-log plots, indicating that $K_x$ decreases in proportion to -2.5 power of the ring size, x, in accord with the Jacobson-Stockmayer theory, with an exception of the dimer. As compared with ε-caprolactone, δ-valerolactone oligomers gave almost the same $K_x$ values except for dimer and trimer. Since the

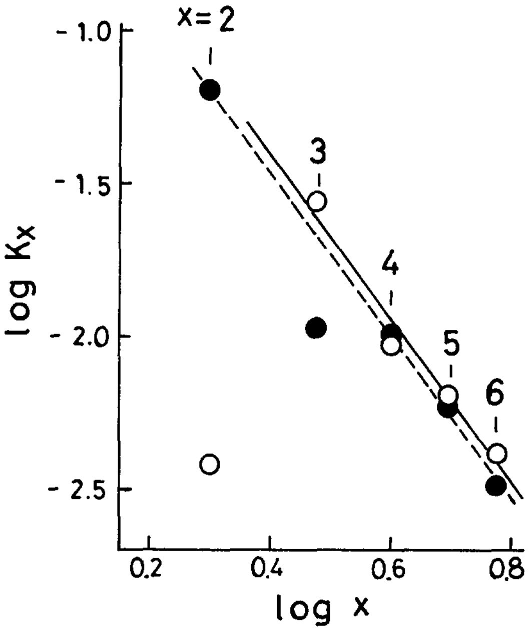


Fig. 2. Log-log plots of molar cyclization constant ($K_x$) against ring size (x) for δ-valerolactone (○) and ε-caprolactone (●). The slopes of the straight lines are -2.5

δ-valerolactone case accords with the Jacobson-Stockmeyer theory except the dimer, it is concluded that the polymerization-depolymerization equilibrium involved is essentially determined by the entropy difference among the cyclic oligomers of $x \geq 3$ and the linear polymers. The corresponding free energy and entropy changes were calculated by $-RT \underline{\ln} K_x = \Delta G^\circ = -T \cdot \Delta S$, by neglecting the enthalpy change, and listed in Table 1. As to the deviation of the dimer, it was thought that the enthalpy of δ-valerolactone dimer could not be neglected, suggesting some ring strain of the twelve membered ring. This point as well as the deviation of ε-caprolactone trimer remain to be further investigated to examine the conformation and the strain, if any, of large ring compounds.

## SUMMARY

The anionic polymerization of δ-valerolactone in tetrahydrofuran with lithium *tert*-butoxide was found to give a living ring-chain equilibrium system, in which the cyclic oligomers are produced by back-biting degradation from the initially formed linear polymers. The molar cyclization equilibrium constant for the trimer through hexamer decreased in proportion to -2.5 power of the ring size, in accord with the Jacobson-Stockmayer theory.

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