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Anionic Ring-Opening Polymerization of Macrocyclic Esters

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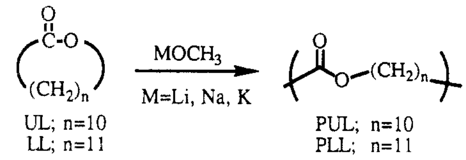
Ring-opening polymerization of lactones is one of the typical polymerization modes which afford polyesters. It is also well-known that 4, 6, and 7-membered lactones undergo ring-opening polymerization with various initiators.[1,2] Although many attempts have been made to correlate ring-opening polymerizability of lactones with some factors such as ring strain, hydrolysis rate, or their basicities, any clear correlation has not yet been found. However, some generalization can be made as follows: (1) An increase in the strain in the ring increases the ring-opening polymerizability. (2) Alkyl or aryl substituents on the lactones decrease their polymerizabilities. (3) As the equilibrium constant in alkaline hydrolysis increases, the polymerizability increases. Therefore, unsubstituted macrocyclic esters having small ring strain will be regarded as low-polymerizable monomers. The polymerization of macrocyclic esters, such as bis(ethylene isophthalate)[3] and trisalicylide,[4] has been reported. However, they are so-called lactides and do not belong to the category of lactones. There is only one report which deals with polymerization of macrocyclic esters, but polymerization behaviors have not been described in detail.[5] In this paper, anionic ring-opening polymerization of 12- and 13-membered macrocyclic esters is described with comparison to that of ϵ-caprolactone (CL).



12-Membered lactone, oxacyclododecan-2-one (undecanoic ω-lactone, UL), was used after distillation under reduced pressure. 13-Membered lactone, oxacyclotridecan-2-one (λ-laurolactone, LL), was prepared in 47% yield by the reaction of cyclododecanone with *m*-CPBA in dichloromethane.[6]

The polymerization was carried out in bulk with metal methoxide as anionic initiators under a nitrogen atmosphere. The molecular weights of the obtained polymers were estimated by GPC (eluent, THF) after calibration with standard polystyrenes. The results are summarized in Table 1.

In runs 1–4, the effect of temperature on the polymerization of LL was examined using sodium methoxide. From these results, polymerization at 120 °C was found to be the optimum condition. The yield of the resulting polymer decreased to recover the monomer in 70% yield when the reaction was carried out at 150 °C, which might indicate the existence of a ceiling temperature at above 150 °C. When the polymerization of LL was carried out at 120 °C with lithium methoxide or potassium methoxide, corresponding polymers were obtained in good yields. Similarly, polymerization of UL also gave the corresponding polymer in high yield under reaction conditions similar to those of LL. These results indicate that ring-opening polymerization of 12- and 13-membered cyclic esters proceeds easily and that the effect of countercations on the yields and molecular weights of the obtained polymers is negligible in these conditions. Other initiators such as methyllithium, butyllithium, and diethylzinc were not found to be effective for the polymerization of UL or LL.

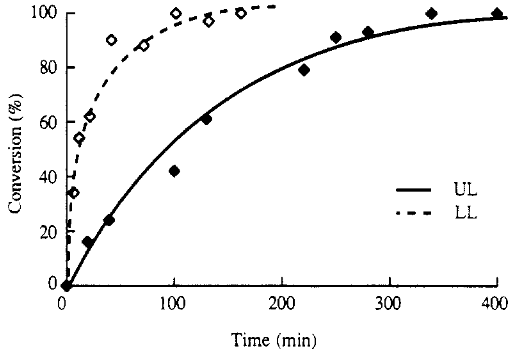


Figure 1. Time–conversion curves of the polymerization of UL and LL in THF at 0 °C.

Table 1. Polymerization of LL and UL in Bulk

run	lactone	initiator[a]	temp (°C)	yield (%)[b]	$\bar{M}_n$[b,c]	$\bar{M}_w$[b,c]
1	LL	$NaOCH_3$	150	23	7200	9400
2	LL	$NaOCH_3$	120	77	6100	12000
3	LL	$NaOCH_3$	90	57	7300	8800
4	LL	$NaOCH_3$	rt	1	13700	16000
5	LL	$LiOCH_3$	120	77	11000	16000
6	LL	$KOCH_3$	120	82	8900	14000
7	UL	$LiOCH_3$	120	94	7600	9400
8	UL	$NaOCH_3$	120	89	7300	8900
9	UL	$KOCH_3$	120	90	6000	8000

[a] 6 mol % initiator was employed. [b] Methanol-insoluble part. [c] Estimated by GPC (solvent, THF; PSt standards).

Table 2. Polymerization of UL with $NaOCH_3$ in THF[a]

run	temp (°C)	time (h)	conv (%)[b]	yield (%)[c]	$\bar{M}_n$[c,d]	$\bar{M}_w$[c,d]
1	120	2	100	75	7600	8700
2	100	2	99	81	5200	7500
3	90	4	99	75	5500	7500
4	50	4	99	81	3400	5000

[a] $NaOCH_3$ (6 mol %); conc of UL, 1 mmol/1 mL of THF. [b] Determined by GC. [c] Methanol-insoluble part. [d] Estimated by GPC (solvent, THF, PSt standards).

To obtain more detailed information about the polymerization behavior of macrocyclic esters, solution polymerization of LL in THF was examined. The reaction was carried out in a sealed tube using sodium methoxide as the initiator at 50–120 °C. The results are shown in Table 2.

In all cases, monomer was completely consumed to afford poly(LL) in good yields. Small amounts of cyclic oligomers formed by a backbiting reaction as well as linear oligomers could be detected in the methanol-soluble part. In the case of the polymerization of ϵ-caprolactone in THF, monomer was first converted to linear polymer, and subsequently the formation of cyclic oligomers was observed, resulting in a considerable decrease of the molecular weight by a backbiting reaction from the polymer.[7] On the other hand, it should be noted that the decrease of molecular weight resulting from a backbiting reaction may be negligible in the polymerization of LL compared with ϵ-caprolactone.

Time–conversion curves of the polymerization of LL and UL using sodium methoxide at 0 °C in THF are shown in Figure 1. Conversion of monomer was monitored by

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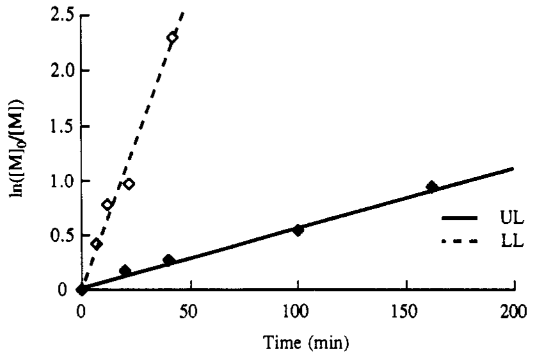

Figure 2. First-order propagation rate plots of the polymerization of UL and LL in THF at 0 °C.

Table 3. First-Order Propagation Rate Constants at 0 °C, Ring Strain Energy of Corresponding Cyclic Hydrocarbons,[a] and $^{13}C-^{1}H$ Spin-Spin Coupling Constants[b] of UL, LL, and CL

monomer	k_p (s^{-1})[c]	ring strain energy per CH_2 (kcal)	$J(^{13}C-^{1}H)$ (Hz)
UL	2.2×10^{-3}	0.6	144.5
LL	1.5×10^{-2}	0.6	147.4
CL	1.2×10^{-1}	1.1	154.8

[a] See ref 7. [b] Measured in $CDCl_3$. [c] Conditions: conc of monomer, 1 mmol/1 mL of THF; $NaOCH_3$, 6 mol %; 0 °C.

GC using hexadecane as an internal standard. LL was consumed completely within 200 min after charging the monomer to the solution containing the initiator. On the other hand, it took 400 min for consumption of UL. First-order rate plots of the polymerization of LL and UL are illustrated in Figure 2, assuming that propagation rates may be proportional to monomer concentration.

As shown in Figure 2, a linear relationship could be observed between the reaction time and $\ln([M]_0/[M])$ at the initial stage of polymerization. From the integrated rate equation, k_p(LL) and k_p(UL) at 0 °C were calculated and the results are summarized in Table 3 together with k_p of ϵ-caprolactone, k_p(CL), determined in the same manner. Table 3 also shows the ring strain energy of corresponding 7-, 12-, and 13-membered cyclic hydrocarbons per methylene unit[7] and $^{13}C-^{1}H$ spin-spin coupling constants of methylene groups attached to oxygen. The larger propagation rate of CL compared with those of UL and LL might be explained by its large ring strain energy. The larger propagation rate of LL than that of UL could not be interpreted by the ring strain energy of the corresponding cyclic hydrocarbon, since there is no significant difference in ring strain energy between 12- and 13-membered cyclic hydrocarbons. It has been known that $^{13}C-^{1}H$ spin-spin coupling constants, $J(^{13}C-^{1}H)$, are correlated to the s-character of carbon atomic orbitals and that an increase in $J(^{13}C-^{1}H)$ indicates an increase in the s-character.[8] The order of increase in the value of $J(^{13}C-^{1}H)$ was found to be UL < LL < CL as shown in Table 3, which agreed well with the order of propagation rates of the monomers. The difference in propagation rates of LL and UL might arise from the difference in the s-character of methylene carbon.

In summary, we have examined the ring-opening polymerization of macrocyclic esters in comparison with CL. It is concluded that macrocyclic esters considered as low-polymerizable monomers easily undergo ring-opening polymerization by common anionic initiators. The propagation rates of macrocyclic esters were found to increase with an increase in the s-character of the methylene carbon.

References and Notes

(1) Johns, D. B.; Lenz, R. W.; Luick, A. *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science Publishers: London, Great Britain, 1984; Vol. 1, Chapter 7, p 461.

(2) Jerome R.; Teyssie, Ph. *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, Great Britain, 1989; Vol. 3, Part 1, Chapter 34, p 501.

(3) Yoda, K.; Kimoto, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1687.

(4) Hall, H. K., Jr.; Schneider, A. K. *J. Am. Chem. Soc.* **1958**, *80*, 6409.

(5) Koleske, J. V.; Lundberg, R. D. *J. Polym. Sci., Polym.* **1972**, *10*, 323.

(6) Fouque, E.; Rousseau, G. *Synthesis* **1989**, 661.

(7) Gerenberg, A.; Liebraun, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

(8) (a) Shoolery, J. N. *J. Chem. Phys.* **1959**, *31*, 1427. (b) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870. (c) Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1969**, *31*, 768.