

High Activity of Rare Earth Tetrahydroborates for Ring-Opening Polymerization of ω -Pentadecalactone

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ABSTRACT: Ring-opening polymerization of ω -pentadecalactone (PDL) by tetrahydroborate complexes of rare earth metals, $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ ($\text{Ln} = \text{La}$ (1), Nd (2), Y (3)), was studied. These complexes showed high activity for PDL polymerization in THF at 60°C. Among the complexes 1–3, the neodymium complex 2 was most active. The obtained poly(PDL) was demonstrated to be hydroxy-telechelic by ¹H-NMR and MALDI-TOF MS spectroscopy.

Biodegradation of the poly(PDL) in compost at 60°C was investigated, where 18% weight loss of the samples was observed after 280 days. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2098–2103, 2011

Key words: ring-opening polymerization; ω -pentadecalactone; hydroxy-telechelic polymer; rare earth metal tetrahydroborate complexes

INTRODUCTION

Ring-opening polymerization (ROP) of cyclic esters is a major synthetic route to aliphatic polyesters as well as polycondensation. Polymerizabilities of cyclic ester monomers are strongly dependent on the monomer ring-size. Small- and medium-size (di)lactones (4, 6, and 7-membered) can relatively easily be polymerized because of their large ring-strains. Many catalysts and/or initiators have been developed for the ROP of this class of cyclic ester monomers.^{1–6} On the other hand, ROP of macrolactones such as 16-membered ω -pentadecalactone (PDL) has been less explored. The polymers of macrolactones such as poly(PDL) show similar physical properties with those of low-density polyethylene,⁷ and are potentially biodegradable.

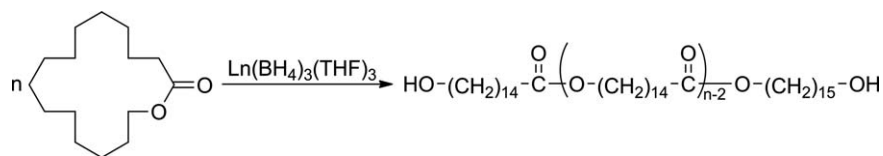
Kobayashi and coworkers^{8,9} first reported the ability of some lipases to promote ROP of macrolactones such as ω -undecalactone, ω -dodecalactone, and PDL, which stimulate study of enzymatic catalysts for the polymerization of macrolactones. Since Gross and coworkers^{10,11} found that excellent catalytic activity of Novozyme-435 (Lipase-B from *Candida antarctica*)

for polymerization of PDL to produce poly(PDL) with high molecular weight ($M_n \sim 86 \times 10^3$ g/mol), most of high-molecular weight poly(PDL)s have been synthesized by enzymatic catalysts.^{12–18} In contrast to nonenzymatic catalysts, enzymatic catalysts tend to show higher activities for ROP of larger lactones.¹⁹ Anionic polymerization of PDL by KO^tBu has also been reported to produce poly(PDL) with M_n of $\sim 10^5$.²⁰ Another example of nonenzymatic catalysts for PDL polymerization is yttrium isopropoxide, $\text{Y}(\text{O}^i\text{Pr})_3$, which achieved controlled polymerization of PDL.²¹

On the other hand, tetrahydroborate complexes of rare earth metals, $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ ($\text{Ln} =$ rare earth metals), have recently been reported to catalyze ROP of cyclic esters such as lactide, ϵ -caprolactone, and δ -valerolactone.^{22–27} Those complexes are characteristic of ability to produce hydroxy-telechelic polyesters due to the reduction of carbonyl group by hydroborate functionality. Hydroxy-telechelic polymers are important for the synthesis of some advanced polymers such as triblock copolymers^{28,29} and polyurethanes.^{30–33} In this system, the ROP of six-membered lactone, δ -valerolactone, was significantly slower in comparison with that of seven-membered ϵ -caprolactone.²⁷ This encouraged us to study ROP of larger lactones by rare earth tetrahydroborates. In this study, we chose commercially available PDL as a representative macrolactone and studied catalytic activity of $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ for the ROP of PDL (Scheme 1).

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Scheme 1 Ring-opening polymerization of ω -pentadecalactone by rare earth tetrahydroborates.

EXPERIMENTAL AND METHODS

General

All the manipulations were carried out under an atmosphere of pure and dry nitrogen, using standard Schlenk techniques. $^1\text{H-NMR}$ spectra were recorded on a JEOL JNM-LA400 spectrometer (400 MHz). Chemical shifts of $^1\text{H-NMR}$ were calibrated using residual chloroform ($\delta = 7.26$ ppm) in chloroform-*d*. Molecular weights of the polymers were determined by gel permeation chromatography (GPC). The GPC measurements were carried out on a Waters 150 CV high-speed liquid chromatograph equipped with a differential refractometer, using ODCB as eluent at 135°C . The GPC columns were calibrated with standard polystyrenes. The measurement of MALDI-TOF MS was made using SHIMADZU AXIMA-CFR plus at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. The spectra were recorded in positive-ion mode using 2,5-dihydroxybenzoic acid as a matrix.

Materials

Tetrahydrofuran was distilled from Na-benzophenone under argon prior to use. Toluene was purified by distillation from Na-benzophenone. Tetrahydroborate complexes of rare earth metals, $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ ($\text{Ln} = \text{La}$ (**1**), Nd (**2**), Y (**3**)), were prepared according to literature.^{22,24,27,34-36} ω -Pentadecalactone (Aldrich)

was distilled under reduced pressure from calcium hydride.

Polymerization of ω -pentadecanolactone by $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$

ω -Pentadecanolactone was added to THF solution of rare earth tetrahydroborate complex at a 60°C to start polymerization. The resulting solution was stirred for a given time. The polymerization was quenched by addition of aq. HCl or methanol. The mixture was poured into an excess amount of methanol to precipitate the polymer, which was collected by centrifugation, washed with methanol, and then dried *in vacuo* overnight.

Degradation by a compost

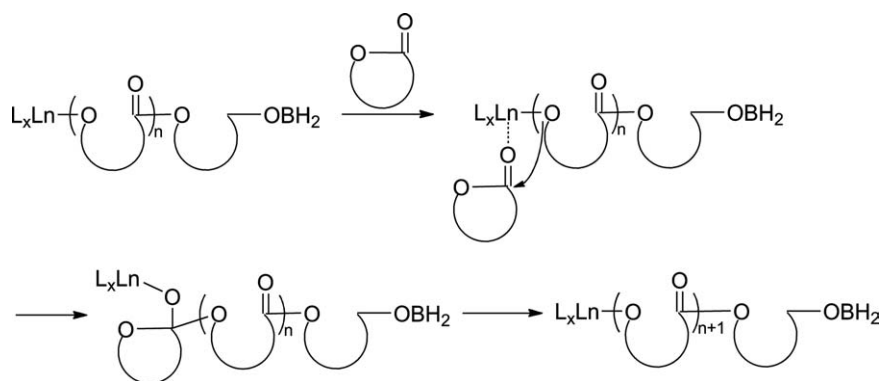
Commercially available effective microorganism (EM) fermented solution (30 mL) containing *Rhodospirillum*, *Rhodopseudomonas*, *Pseudomonas*, *Micrococcus*, *Bacillus*, *Lactobacillus*, *Streptococcus*, *Saccharomyces*, *Aspergillus*, *Penicillium*, etc. and theriaca syrup (40 mL) were added to 2000 mL of water, and this solution was sprayed on the mixture of rice hulls (5 kg) and rice bran (15 kg). Resulting material was wrapped with a polyethylene film and then dried in the shade for 1 day. The content of water was evaluated by the weight loss of the samples after heating them to 200°C . The samples were sealed in polyethylene mesh, and it was hold in the resulting compost for a fixed time. The evaluation of

TABLE I
Polymerization of PDL Catalyzed by $\text{Ln}(\text{BH}_4)_3(\text{THF})_3^{\text{a}}$

| Run | Cat. | [PDL] ₀ (mol/L) | [PDL] ₀ /[Ln] (mol/mol) | Temp. ($^\circ\text{C}$) | Time (min) | Yield (%) | M_n^{b} (kg/mol) | M_w/M_n^{b} |
|-----|------------------------------------|----------------------------|------------------------------------|----------------------------|------------|-----------|---------------------------|----------------------|
| 1 | 1 | 2.76 | 150 | 60 | 1 | 24 | 14 | 2.8 |
| 2 | 2 | 2.76 | 150 | 60 | 1 | 83 | 21 | 2.2 |
| 3 | 3 | 2.76 | 150 | 60 | 1 | 66 | 11 | 1.9 |
| 4 | 1 | 2.76 | 150 | r.t. | 150 | <1 | – | – |
| 5 | 1 | 2.76 | 150 | 40 | 150 | <1 | – | – |
| 6 | 1 | 0.55 | 150 | 60 | 150 | 17 | – | – |
| 7 | 2 | 1.36 | 50 | 60 | 5 | 25 | 0.8 | 1.0 |
| 8 | 2 | 1.36 | 50 | 60 | 30 | 44 | 1.9 | 1.2 |
| 9 | 2 | 1.36 | 50 | 60 | 50 | 65 | 2.2 | 1.4 |
| 10 | 2 | 1.36 | 50 | 60 | 240 | >99 | 5.7 | 1.7 |
| 11 | 2 | 1.36 | 600 | 60 | 480 | 87 | 39 | 1.7 |
| 12 | $\text{Nd}(\text{O}^i\text{Pr})_3$ | 1.36 | 300 | 60 | 240 | >99 | 35 | 1.6 |

^a Polymerization was carried out in THF.

^b Determined by GPC in *o*-dichlorobenzene calibrated with standard polystyrenes.



Scheme 2 Possible propagation in the ring-opening polymerization of ω -pentadecalactone by rare earth tetrahydroborates.

the biodegradation was carried out by measuring the weight loss with a compost.

RESULTS AND DISCUSSION

Tetrahydroborate complexes of rare earth metals, $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ ($\text{Ln} = \text{La}$ (1), Nd (2), Y (3)), were prepared according to literature from the reaction of LnCl_3 or $\text{LnCl}_3(\text{THF})_3$ with three equivalents of NaBH_4 in THF.^{22,24,34-36} ROP of PDL by the rare earth complexes 1–3 were performed in THF typically at 60°C. The results are summarized in Table I. At high PDL concentration of 2.76 M, the complexes 1–3 were found to show high activity for the PDL polymerization (runs 1–3, respectively). Among the three complexes 1–3, the neodymium complex 2 was most active (run 2), and poly(PDL) with M_n of 21,000 was obtained in 83% yield within a minute. This is in sharp contrast to the fact that the tetrahydroborate complex of larger rare earth metal show

higher catalytic activity in the ROP of D,L-lactide and δ -valerolactone.²⁷ The ROP of cyclic esters by rare earth tetrahydroborates has been considered to proceed in coordination-insertion mechanism (Scheme 2).^{22,24,25,37} Larger atom size of catalyst metal center should decrease steric crowding at the reaction site, which could accelerate coordination step and also could slower ring-opening step. PDL is low in ring-strain in comparison with those of D,L-lactide and δ -valerolactone, which could make the latter step important. The relative activity of 1–3 observed here might come from a delicate balance of these factors. The examples of the reported catalysts for the polymerization of PDL are summarized in Table II. Catalyst activities were calculated as shown in Table II for rough comparison, although they may not be the best presentation of catalytic activity. The activities of enzyme catalysts are rather low in units of g/g h, although they should be high in units of kg/mol h due to their high molecular weight. The neodymium

TABLE II
Comparison of PDL Polymerization by Various Catalysts (or Initiators)

| Cat. | [PDL] ₀ (mol/L) | [PDL] ₀ /[cat] | | Temp (°C) | Time (min) | Yield (%) | Activity | | M_n (kg/mol) | M_w/M_n | Ref. |
|-----------------------------------|-------------------------------|---------------------------|------|--------------|---------------|------------------|-----------------------|--------------------|-------------------|-----------|-----------|
| | | mol/mol | g/g | | | | kg/mol h ^a | g/g h ^b | | | |
| 1 | 2.76 ^c | 150 | 90 | 60 | 1 | 24 | 520 | 1300 | 14 | 2.8 | This work |
| 2 | 2.76 ^c | 150 | 89 | 60 | 1 | 83 | 1800 | 4400 | 21 | 2.2 | This work |
| 3 | 2.76 ^c | 150 | 103 | 60 | 1 | 66 | 1400 | 4100 | 11 | 1.9 | This work |
| KO ^t Bu | 2.20 ^c | 523 | 1120 | 35 | 45 | 75 | 130 | 1100 | 92 | 2.1 | 20 |
| Y(O ⁱ Pr) ₃ | 3.82 ^d | 65 | 59 | 60 | 10 | 100 ^e | 94 | 350 | 6.4 | – | 21 |
| Y(O ⁱ Pr) ₃ | 3.82 ^d | 400 | 361 | 100 | 5 | 70 ^e | 810 | 3000 | 25 | 1.5 | 21 |
| Lipase P | 3.82 ^d | | 3.67 | 60 | 240 | 35 ^e | | 0.32 | 2.6 | 1.8 | 8 |
| Lipase P | 3.82 ^d | | 3.67 | 75 | 14,400 | 100 ^e | | 0.02 | 6.4 | 1.8 | 8 |
| Novozyme-435 | 2.2 ^f | | 10 | 70 | 120 | 90 | | 4.5 | 86 | 2.4 | 11 |
| Novozyme-435 | 1.5 ^f | | 10 | 90 | 2 | 41 | | 123 | | | 11 |

^a In kg(polymer)/mol(catalyst) h.

^b In g(polymer)/g(catalyst) h.

^c Solution polymerization in THF.

^d Bulk polymerization.

^e Conversion.

^f Polymerization in toluene.

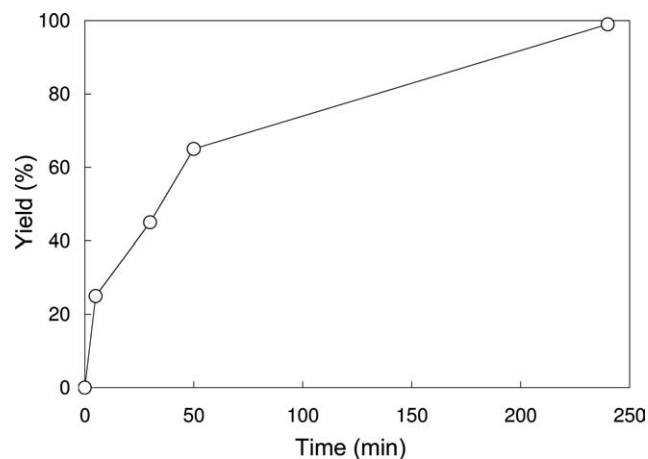


Figure 1 Plots of yield versus time for the polymerization of PDL catalyzed by $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ (**2**) at $[\text{M}]_0 = 1.36$ mol/L and $[\text{M}]_0/[\text{I}]_0 = 50$.

complex **2** can be regarded as one of the most active catalysts for the polymerization of PDL. The yttrium complex **3** is also considerably more active than $\text{Y}(\text{O}^i\text{Pr})_3$ at 60°C .

No polymerization of PDL by **1** was observed at 40°C or lower (runs 4 and 5). The ΔH_p° and ΔS_p° values for PDL polymerization have been estimated to be 3 kJ mol^{-1} and $23 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.³⁸ Because both the ΔH_p° and ΔS_p° values are positive in PDL polymerization, higher polymerization temperature is thermodynamically more favorable. The polymerization of PDL became slower at lower concentration of PDL (run 6).

Because the PDL polymerization by **2** at $[\text{PDL}]_0$ of 2.76 mol/L was too fast to be monitored, time-dependence of the PDL polymerization with **2** was recorded at lower PDL concentration ($[\text{PDL}]_0$ of 1.36 mol/L). To characterize polymer structure, $[\text{PDL}]_0/[\text{Ln}] = 50$ was adopted (runs 7–10). The time-yield plot is shown in Figure 1. The polymer yield

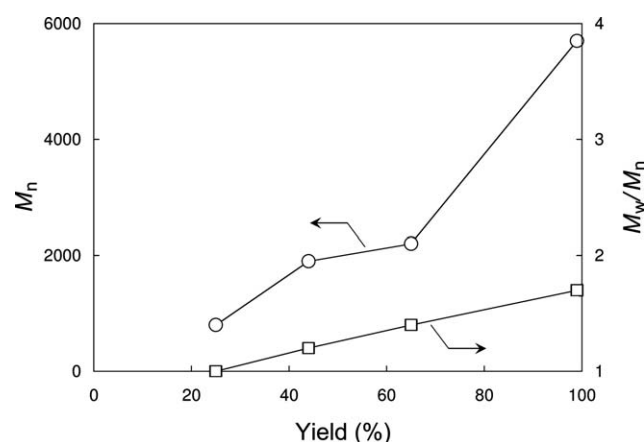


Figure 2 Plots of M_n (○) and M_w/M_n (□) versus yield for the polymerization of PDL catalyzed by $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ at $[\text{M}]_0/[\text{I}]_0 = 300$.

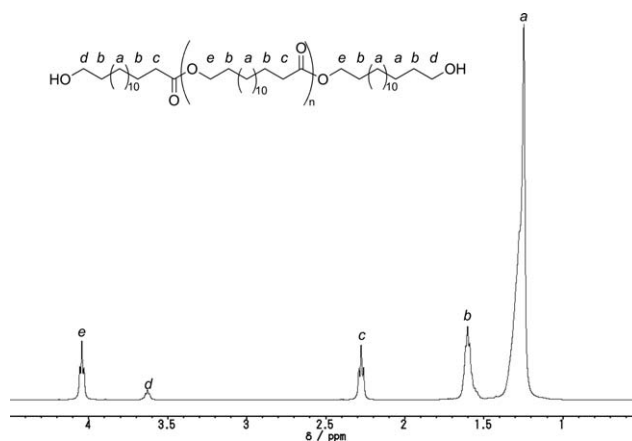


Figure 3 $^1\text{H-NMR}$ spectrum of poly(PDL) obtained in run 10.

increased with time without induction period. The absence of induction period contributed to higher activity of **2** than that of $\text{Y}(\text{O}^i\text{Pr})_3$, which has been reported to show an induction period in PDL polymerization.²¹ This could come from the difference in aggregation of the rare earth metals complexes: mononuclear structure of the tetrahydroborates^{35,36,39} versus aggregated structure of the alkoxides.^{40–45} Figure 2 shows the dependence of the molecular weights and the molecular weight distributions of the resulting polymers on the polymer yield. The molecular weight of the resulting poly(PDL) gradually increased with the polymer yield. Although the M_w/M_n values were gradually increasing, they remained rather low (below 1.7). Thus, the polymerization system could be somewhat controlled. Large M_w/M_n values of the PDLs synthesized at higher concentration might be due to high propagation rate relative to initiation rate.

The $^1\text{H-NMR}$ spectrum of the poly(PDL) (run 10) is shown in Figure 3. In addition to the signals from the repeating units (*a*, *b*, *c*, and *e*), the peak assignable to the α -protons to the terminal hydroxy group (*d*) appeared at 3.63 ppm. No peaks assignable to other terminal groups were observed. Assuming the hydroxy-telechelic structure, $\text{H}\{\text{O}(\text{CH}_2)_{14}\text{CO}\}_n\text{O}(\text{CH}_2)_{15}\text{OH}$, the M_n of the poly(PDL) was calculated to be 2800 from the $^1\text{H-NMR}$ peak intensity. The number of polymer chains produced by one Nd complex was

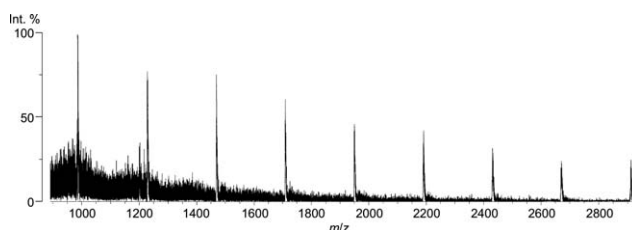


Figure 4 MALDI-TOF mass spectrum of the sample obtained in run 10 (time = 240 min).

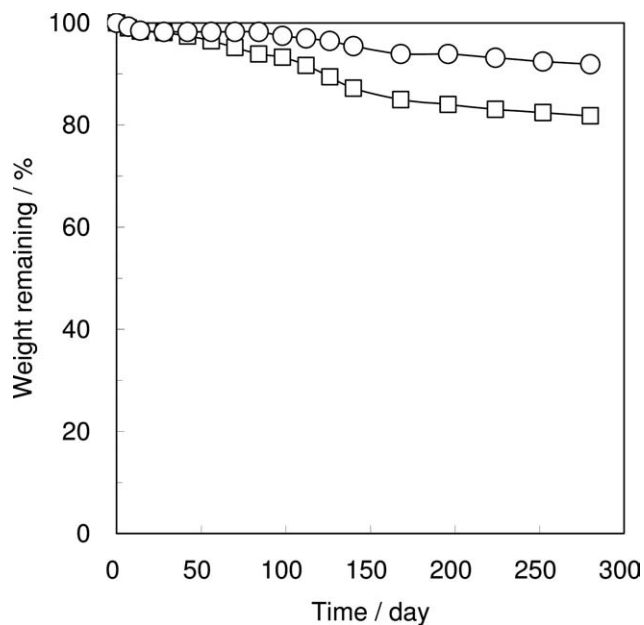


Figure 5 Degradation of poly(PDL) obtained with **2** (○) and $\text{Nd}(\text{O}^i\text{Pr})_3$ (□) in compost at 60°C.

estimated to be 4.2, indicating that all the tetrahydroborate moiety in **2** should initiate the polymerization accompanied with some chain transfer. Figure 4 shows MALDI-TOF MS spectrum of the obtained poly(PDL) (run10). The observed peaks are in good agreement with the calculated values for the hydroxy-telechelic structure, e.g., m/z (obs.) = 988.5 versus m/z (th.) = 987.9 for $\text{H}\{\text{O}(\text{CH}_2)_{14}\text{CO}\}_3\text{O}(\text{CH}_2)_{15}\text{OH} + \text{Na}^+$. These results support the formation of hydroxy-telechelic poly(PDL).²² We assume that the mechanism of the PDL polymerization by the rare earth tetrahydroborates should be similar to that of the CL polymerization.^{22,24,25}

Heise and coworkers¹⁴ has recently reported hydrolytic and enzymatic (Lipase PS) degradation study of poly(PDL) and other polymacrolactones, in which no degradation was observed. We studied biodegradation of poly(PDL) in compost at 60°C. Two poly(PDL) samples with relatively high molecular weights were prepared for this purpose, one is hydroxy-telechelic poly(PDL) prepared by the ROP of PDL using **2** (Table I, run 11). The other poly(PDL) sample was synthesized by using $\text{Nd}(\text{O}^i\text{Pr})_3$ instead of **2** (Table I, run 12), which should have one hydroxy and one isopropyl ester end groups.^{21,44,45} The results are shown in Figure 5. Both of the samples showed slow degradation, 18% weight loss was observed after 280 days. This is in sharp contrast to the compost degradation of poly(L-lactide), which was completely degraded within 42 days under similar conditions.³³ Low degradability of poly(PDL) could be attributed to its high hydrophobicity and crystallinity.¹⁴ The terminal groups seem to have a

little effect on the degradability of the poly(PDL)s, although the mechanism is not clear yet.

CONCLUSIONS

Tris(tetrahydroborate) complexes of rare earth metals, $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ ($\text{Ln} = \text{La}$ (**1**), Nd (**2**), Y (**3**)), were demonstrated to be highly active catalyst/initiator for the ROP of a macrolactone PDL. The neodymium complex **2** was found to be one of the most active catalyst for PDL polymerization. The obtained poly(PDL)s were revealed to be hydroxy-telechelic by ¹H-NMR and MALDI-TOF MS spectroscopy. They showed slow degradation in compost at 60°C.

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