

Preparation and Properties of Poly(L-lactide)-*block*-poly(trimethylene carbonate) as Biodegradable Thermoplastic Elastomer

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ABSTRACT: Biodegradable ABA triblock copolymers of L-lactide and trimethylene carbonate with given compositions were prepared and chain-extended to produce high molecular weight polymer. The polymers were semicrystalline, and exhibited well microphase-segregated morphology with one crystalline poly(L-lactide) (PLLA) and the other soft and amorphous poly(trimethylene carbonate) (PTMC) block segments. The polymers could be cast into flexible and tough film, reversibly stretchable with elongation up to about 300%. This material may provide a novel thermoplastic elastomer possessing desirable properties including biodegradability, biocompatibility and good mechanical properties including two-phase morphology. Also a preliminary result on the hydrolytic degradation behavior was discussed.

KEY WORDS Poly(L-lactide) (PLLA) / Poly(trimethylene carbonate) (PTMC) / Block Copolymer / Biodegradable / Thermoplastic Elastomer /

Modification of the properties of the brittle biodegradable polyesters such as polylactide (PLA), polyglycolide, and poly(hydroxy alcanoate) has been intensively investigated.^{1,2} Usually a biodegradable or biocompatible rubber is introduced to toughen the materials, so that the modified material remained biodegradable or biocompatible. PLA is one of the most intensively studied biodegradable synthetic polymer that has found significant applicability in the medical and pharmaceutical fields.³ Interest in PLA as a commercial thermoplastic has been increasing, and large-scale production has recently been announced.⁴ Though homo PLLA is limited by its inherent brittleness, its properties can be significantly enhanced and broadened by modification *via* copolymerization, which provides a number of advantages because the architecture and composition of the biomaterials can be tailored to control the material properties (by anionic or coordinated polymerization). In particular, block copolymerization may offer a broader spectrum of mechanical and degradation properties in order to meet the demands of various applications. Blocks with different physical properties, for example, one soft, amorphous and one hard, semicrystalline segment, can be utilized to modulate basic material behavior.^{5,6} For copolymers to be useful as thermoplastic elastomers (TPEs), the controlled synthesis of ABA triblock copolymer is often required. The mechanical properties of the polymer are enhanced by a microphase-separated morphology in which the soft phase gives elasticity and degradation, whereas the rigid phase provides mechanical strength and also acts as a physical crosslinker.

While ABA triblock copolymers containing polylactide segment and low T_g amorphous segment (*e.g.*, polyisobutylene, polydimethyl-siloxane, and polyisoprene) have been reported,^{7–9} these systems have drawback in synthesis using specially prepared telechelic prepolymers and their inherent partial biodegradability. More recently, the synthesis and basic properties on the triblock copolymer systems containing poly(3-hydroxybutyrate), PHB, or poly(1,5-dioxepan-2-one), poly(DXO), middle block has been investigated for the potential utilities as biodegradable thermoplastic elastomers.^{6,10} We were interested in using poly(trimethylene carbonate) (PTMC), a simple aliphatic polycarbonate, as soft and low- T_g segment. PTMC with the reported glass transition temperature of -25°C , is rubbery at room temperature and biodegradable both *in vivo* and *in vitro*, and hence, possesses potential applications in medical and environmental areas.^{11–13}

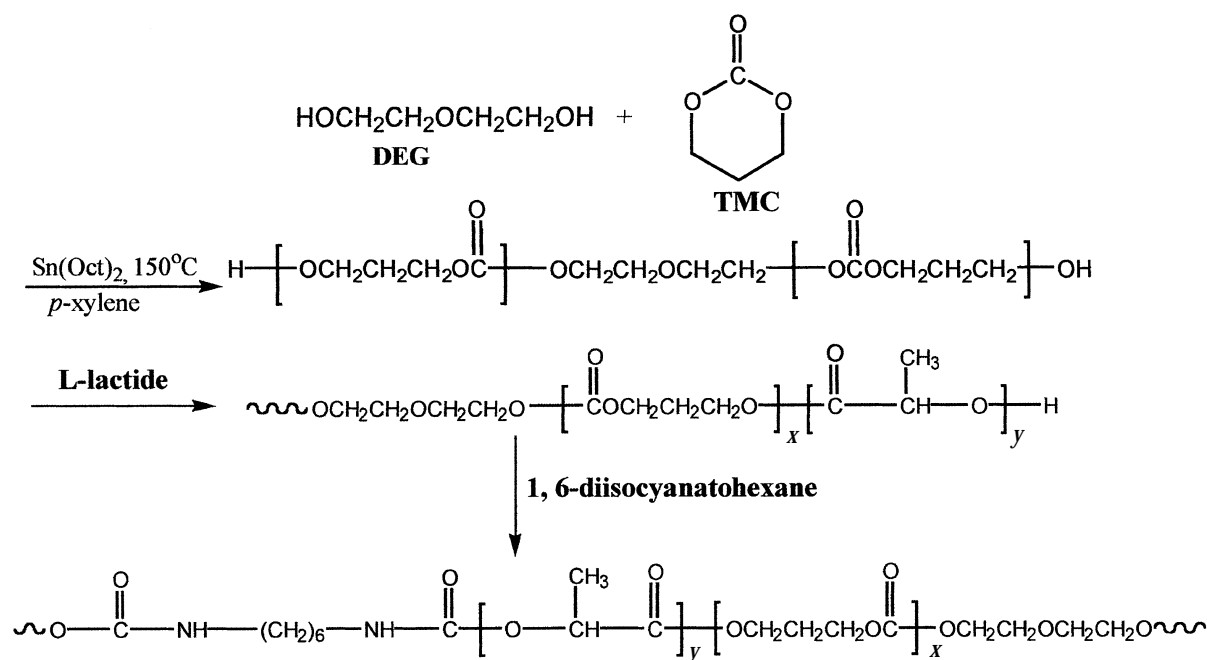
Here we report the preparation and chain extension of P(LLA-*b*-TMC-*b*-LLA) triblock copolymers. Also the basic tensile properties as thermoplastic elastomer along with the phase-separated morphology will be discussed.

EXPERIMENTAL

Chemicals and Measurements

L-Lactide was purified by recrystallization twice from dry ethyl acetate and dried in vacuum at room temperature. Trimethylene carbonate (TMC) was purchased from Behringer Ingelheim and purified by sublimation. Diethylene glycol, hexamethylene diiso-

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Scheme 1.

cyanate (HMDI) and stannous octoate was purchased from Aldrich Co. and used as received. *p*-Xylene was dried over calcium hydride (CaH₂) for 24 h prior to distillation.

Infrared spectra were obtained on a Unicam 1000 FT-IR spectrometer. ¹H NMR spectra were taken on a Varian Unity Inova 500 MHz Spectrometer using CDCl₃ as the solvent. Thermal analysis was carried out on a Perkin–Elmer DSC/TGA7 Series thermal analysis system. The molecular weight data were obtained by gel permeation chromatography (GPC, Waters) using chloroform as the eluent at a flow rate of 1 mL min⁻¹. Polystyrene standards were used to calibrate the molecular weight. Tensile test was carried out using Instron model 5565, and the film morphology was observed by Optical Microscope (Samwon Scientific Ind. Co. LTD, Korea) model CSB-HA3.

*Synthesis and Chain Extension of Triblock Copolymer; Poly(LLA-*b*-TMC-*b*-LLA)*

i) Triblock copolymers were prepared by sequential ring-opening polymerization of trimethylene carbonate and L-lactide in the presence of diethylene glycol as the typical polymerization procedure was described previously;¹⁴ All glassware was flame-dried prior to use. The desired amounts of TMC (3 g, 29.4 mmol), diethylene glycol (13 μL, 0.5 mol% of TMC) and catalyst (Sn(oct)₂, 0.2 mol% of total monomer) were weighed into a 3-necked round flask under a nitrogen atmosphere inside a drybox. The flask was fitted with a magnetic stirrer and condenser. *p*-Xylene (15 mL) was transferred to a flask using a syringe. The homoge-

neous mixture was stirred for 24 h at 140°C and a small amount was sampled for analysis. The second monomer, L-lactide (4.23 g, 29.4 mmol), was charged into the reaction flask and stirred for additional 36 h to obtain a viscous polymer solution. The polymer formed was isolated by precipitation into a large amount of methanol/hexane, purified by reprecipitation from chloroform solution, washed, and finally dried in vacuum to obtain white and bulky powder.

ii) The block copolymer (1 g), above prepared, was dissolved in 30 mL of dry toluene and heated to about 130°C to distilled off residual moisture inside as an azeotropic mixture. Then, a predetermined amount of HMDI, the chain-extending agent, was added by using microsyringe, and the reaction mixture was stirred for 4 h before precipitation into an excess amount of methanol. The resulting powder was filtered, washed, and dried in vacuum at 50°C. To prepare film sample, the polymer was dissolved in chloroform, cast on a glass Petri-dish, solidified in air, and dried thoroughly *in vacuo* at 40°C.

RESULTS AND DISCUSSION

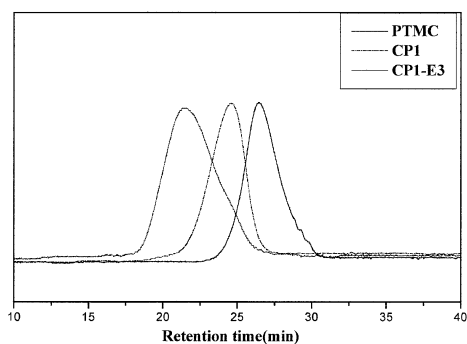
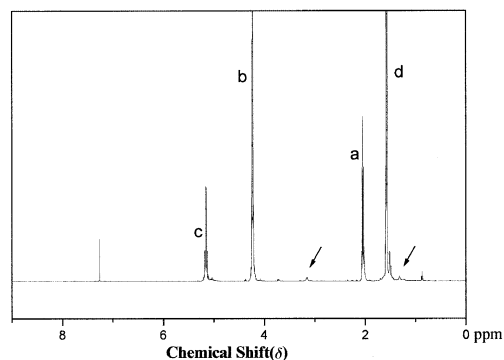
Synthesis of Triblock Copolymers and Their Chain-Extension

As described in our previous communication,¹⁴ block copolymers were prepared by sequential ring-opening polymerization of TMC and L-LA in the presence of small amount of diethyleneglycol (the whole reaction scheme including chain-extension is shown above), and the structure and basic thermal properties

Table I. Characteristics of P(LLA-*b*-TMC-*b*-LLA) Triblock Copolymers

	Yield ^a %		GPC			DSC		TMC Content ^b
			M_n	M_w	M_w/M_n	T_m peak, °C	ΔH_m J g ⁻¹	
CP1	75	PTMC	6600	8700	1.32	139.4	16.4	43%
		Copolymer	14200	21000	1.48		(28.8) ^c	
CP2	80	PTMC	8500	11700	1.38	162.8	24.3	48%
		Copolymer	25200	43000	1.71		(46.7) ^c	

^aTotal copolymer yield. ^bTMC unit wt% in copolymer determined by ¹H NMR. ^cCalculated value based on PLA block weight.


Figure 1. GPC chromatograms of PTMC prepolymer, triblock copolymer, and the chain-extended sample.

Figure 2. A typical ¹H NMR spectrum of chain-extended triblock copolymer.

have been characterized by spectroscopy and thermal analysis. The characteristics of the prepared copolymers are shown in Table I. The molecular weight of the synthesized copolymers were M_n 14000 and 25000, respectively, controllable by the amount of diethyleneglycol to a certain range. Attempts for the synthesis of much higher molecular weight materials were not successful and it seemed to be limited in our given polymerization reaction conditions. The resulting polymers could be cast into flexible films, though the sample was too weak to show a viable mechanical strength.

On the other hand, it is expected that the final triblock copolymers possess hydroxyl groups at both chain ends, which can be utilized for the chain extension process (or coupling reaction) to improve the molecular weight of as-polymerized materials. In this case, the chain-extended polymers should have multi-block chain structure, at least in part. Table II shows the results of chain extension for the copolymer **CP1** using several different amount of diisocyanate compound (HMDI for this study). The chain-extended copolymer using HMDI with [NCO]/[OH] ratio of 4 provided better result, giving 2.5–3 times of increase in the average molecular weight. Here, [OH] is the end-hydroxyl concentration of triblock copolymer theoretically calculated from the M_n value by GPC. When the amount of HMDI was raised further, an additional increase in the molecular weight, however, was not observed. Instead, some amount of insoluble gel (3–4

wt%) was found to be formed in the reaction mixture, which is probably resulted from the crosslinking side reaction observed in the well-known urethane chemistry. Figure 1 shows the change in GPC chromatograms of PTMC prepolymer, triblock copolymer, and the chain-extended sample. First, a shift of distribution curve toward high molecular weight and unimodal distribution profile of both PTMC prepolymer and the corresponding copolymer suggested well formation of triblock copolymers from this synthesis. After chain extension, the distribution shifted further to higher molecular weight, though the molecular weight distribution became rather broader. In the similar manner, block copolymer **CP2** was chain-extended by reacting with HMDI ([NCO]/[OH] = 4), and a considerably high molecular weight polymer could be obtained with M_n 52000, and M_w 135000, respectively. The chain-extended polymers (CP1-E3 and CP2-E) were used to cast films to study the morphology and basic tensile properties described below.

A typical ¹H NMR spectrum of block copolymer after chain-extension is shown in Figure 2. The methine (c) and methyl protons (d) of the PLA block are shown at 5.17 and 1.5 ppm, and methylene protons (a, b) are shown at 2.06 and 4.24 ppm, respectively. Also methylene protons of HMDI moiety were observed at 3.13 and 1.34 ppm, respectively, to assure the incorporation of the unit in the copolymer structure. Monomer com-

Table II. Result of Chain-Extension Using Several Different Amount of Diisocyanate Compound (HMDI)

[NCO]/[OH] ^a	Yield %	GPC			DSC		
		M_n	M_w	M_w/M_n	T_g °C	T_m peak, °C	ΔH_m J g ⁻¹
CP1		14200	21000	1.48	-8.2	139.4	16.4
CP1-E1	2	20900	34200	1.63	-4.5	139.6	16.2
CP1-E2	3	26000	48500	1.82	-2.1	131.0	15.3
CP1-E3	4	31800	59200	1.86	-1.8	130.0	13.1
CP1-E4	5	27300	51300	1.88	-2.7	129.5	12.3

^a[OH] in the ratio was theoretically calculated based on M_n of copolymer.

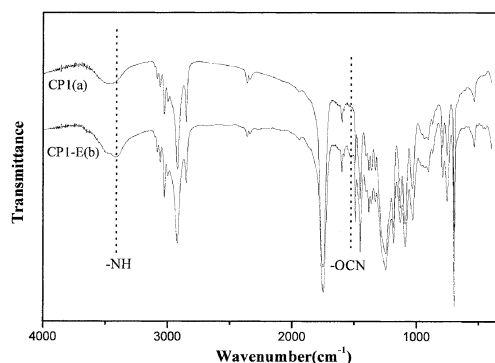


Figure 3. FT-IR spectra of triblock copolymer (a) and the chain-extended sample (b).

position of the copolymer was determined from the integration ratio between proton signals **c** and **a** (as the results are included in Table I).

Figure 3 depicts the FT-IR spectra of triblock copolymer and the chain-extended one. Copolymer (CP1, a) has a strong C=O stretching band at 1752 cm^{-1} , and at 1185 and 1248 cm^{-1} of the C–C–O and O–C–O asymmetric stretching of the ester and the carbonate groups of the copolymer, respectively. From the chain-extended products (CP1-E, b), additional characteristic absorption bands corresponding to NH stretching at 3420 cm^{-1} , and OCN at 1510 cm^{-1} of urethane group were observed to identify the structures.

Thermal Properties

The thermal stability was measured by thermogravimetry in nitrogen. The triblock copolymers were stable to about 250°C , with the decomposition onset shifting toward higher temperature after chain-extension due to the much improved molecular weight of copolymer sample (Figure 4).

The glass transition and melting behavior of the materials were analyzed by low temperature differential scanning calorimetry. Typical thermograms (CP2) are shown in Figure 5 and the thermal properties of block copolymer CP2 and its chain-extended polymer CP2-E (both powder and cast film) are summarized in Table III. The first heating scan (CP2) showed glass transition at around -11°C and PLLA melting endotherm

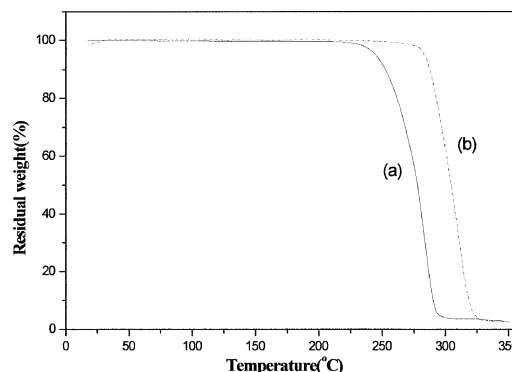


Figure 4. TGA thermograms of block copolymer (CP2, a) and the chain-extended one (CP2-E, b).

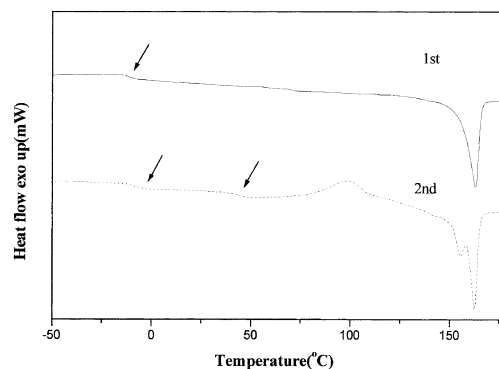
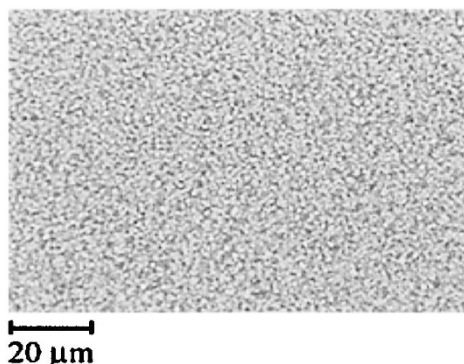


Figure 5. Typical DSC thermograms of triblock copolymer, CP2.

with the peak temperature of 163°C , (and the following cooling scan showed a broad and weak crystallization exothermic transition at $110\text{--}80^\circ\text{C}$). The second heating scan of the same sample showed two separate glass transitions at *ca.* -9°C (corresponding to PTMC block), and at *ca.* 47°C (PLLA block), and also an exothermic transition at $90\text{--}110^\circ\text{C}$ due to the cold crystallization, which is followed by melting transition again with peak temperature of 162°C . The lower glass transition of PTMC block appeared at somewhat higher temperature than that of pure PTMC, which is probably resulted from the influence of high T_g PLLA block segment, and/or sorts of partial phase mixing between two polymers. Anyhow the glass transition temperature, observed at two different positions, and a rel-

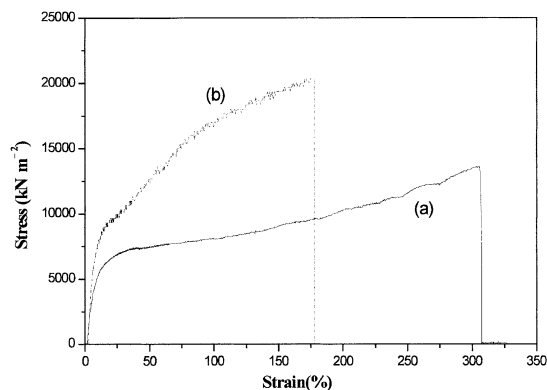
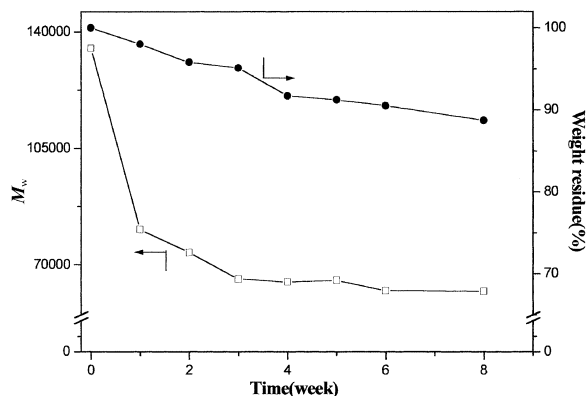
Table III. Thermal Properties of High M.W. Block Copolymer, Chain-Extended

	DSC(1st)			DSC(2nd)					
	T_g °C	T_m peak, °C	ΔH_m J g ⁻¹	T_{g1} °C	T_{g2} °C	T_m peak, °C	ΔH_m J g ⁻¹	T_c peak, °C	ΔH_c J g ⁻¹
CP2	-11.1	162.8	24.3	-8.9	47.1	162.0	16.6	89.0	-9.1
CP2-E (powder)	-9.9	159.0	18.9	-7.2	38.0	159.3	14.8	106.0	-8.2
CP2-E (cast film)	-10.3	158.7	15.6	-8.4	36.5	158.9	14.5	100.6	-8.0


Figure 6. Optical micrograph of the cast polymer film (CP2-E).

atively high crystallinity of the sample must suggest the phase-separated morphology of the block copolymers. The melting enthalpy (ΔH_m) of the PLLA in triblock copolymer (CP2) was calculated to be 24.3 J g⁻¹. Based on the PLLA content in the copolymer of 52 wt%, the enthalpy can be expressed as 46.7 J g⁻¹-PLLA. This high value means not only high crystallinity of the resulting copolymer, but the crystallization of PLLA block is not hindered much by the PTMC block. (Also this result is obviously compared to the amorphous nature of random copolymer with similar monomer composition.¹⁵) The degree of crystallinity was calculated to be *ca.* 50% based on the theoretical pure PLLA,¹⁶ which is in the almost same ranges compared to those of homo PLLAs prepared by normal solution polymerization.¹⁷ This high crystallinity might be resulted from phase-segregated morphology of the prepared block copolymer, which enhances the crystallization of PLLA block by flexible and mobile PTMC segments with low T_g . The chain-extended samples in both powder and film forms showed similar thermal properties, except a little decreases in melting temperature and the enthalpy values compared to those of sample before chain-extension. For the polymer sample CP1, the melting point and the crystallinity was relatively low, presumably due to the lower molecular weight of the material.

The suggested phase-separated morphology was observed by optical microscopy of the cast film. A rep-


Figure 7. Stress-strain curve from Instron measurement; (a) CP1-E3, (b) CP2-E.

Figure 8. Weight and molar mass change of the cast films in saline phosphate buffer of pH 7.4 (polymer sample: CP2-E).

representative picture is shown in Figure 6. The interconnected, two-phase morphology comprising crystalline PLLA domain and amorphous PTMC-rich domain is apparent, and the domain size (width) was estimated to be about 1–2 μm. It is interesting that both the prepared ABA triblock copolymer and the chain-extended one possess one crystalline block and another rubbery block component, forming well phase-separated morphology. So, this material can exhibit behavior as a thermoplastic elastomer like other conventional TPEs known.

The tensile properties were measured by Instron, and a typical stress-strain curves are shown in Figure 7. The original translucent film was elongated to about 200–

300%, variable by the different sample thickness and measurement condition. As the sample elongated, the film became opaque gradually by the condensed crystalline region, presumably accompanied by induced-crystallization. When the force to stretched film was released, the sample contracted back toward initial state.

A preliminary degradation experiment of the cast film (about 30 μm thick) was carried out in pH7.4 buffer saline solution at 40°C. As the dipping time elapsed, the molecular weight dropped rapidly within a week to about half of original molecular weight, and then seemed to be leveled with a little decrease thereafter. The mass loss, however, was small with about 5 wt% in 2–3 wk, and additional 5–7 wt% within the time period of 8 wk. The results were plotted in Figure 8. It was expected that the block copolymer comprising with relatively hydrophobic monomers possess resistance to hydrolytic degradation. However, the chain-extended samples contains urethane linkage, which is more labile to the hydrolysis, so that the decreases in the molecular weight within a few weeks seems to be resulted from the preferable hydrolytic chain scission of the urethane bond. As an evident from the IR analysis, the sample after 4 wk did not show the characteristic absorption bands assignable to urethane linking groups.

To summarize, ABA triblock copolymers of L-lactide and trimethylene carbonate with given compositions were prepared and chain-extended to produce high molecular weight polymer, forming elastomeric tough film. The polymers were partially crystalline and exhibited well phase-segregated morphology. This material may provide a novel thermoplastic elastomer possessing desirable properties including biodegradability, biocompatibility and good mechanical properties including elasticity. A preliminary result on the hydrolytic degradation behavior was also elucidated.

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