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Formation of microporous membranes of poly(1,4-butylene succinate) via nonsolvent and thermally induced phase separation

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A B S T R A C T

Microporous membranes of poly(1,4-butylene succinate) (PBS), which is a biodegradable biomass plastic, were prepared from PBS–chloroform solutions via nonsolvent and thermally induced phase separation with a coagulation bath of methanol. The permeation resistance of a membrane prepared from a 10% polymer solution at 25°C was more than 10^{14} m^{-1}. The membrane resistance decreased with increasing pre-incubation temperature. Retention of bacterial cells (0.7ϕ × 2.5 μm) decreased with increasing pre-incubation temperature. Increasing polymer concentration increased the permeation resistance and the retention of the cells. Membranes prepared from the 10% PBS solution pre-incubated at 47.5°C show a permeation resistance of 10^{11} m^{-1} and retention of the bacterial cells of 99%. The PBS membranes will be useful in biosepartion processes as a prefilter that can be disposed by composting after use.

Keywords: Microporous membrane; Poly(1; 4-butylene succinate); Biodegradable plastic; Nonsolvent induced phase separation; Thermally induced phase separation

1. Introduction

Microporous polymer membranes are widely used in microfiltration in many industries, including food and biochemical industries, to separate particles from suspensions [1]. Biodegradable polymers are key materials in green chemistry [2], and biodegradable microporous membranes are attractive in bioseparation processes because they can be composted after use. We have developed biodegradable filtration membranes of poly(L-lactic acid) (PLLA) and poly(ϵ-caprolactone) [3–5]. Recently poly(1,4-butylene succinate) (PBS) has received increased attention as a biodegradable plastics in green chemistry. This polyester is considered to be a biomass plastic because its two monomers, succinic acid and 1,4-butanediol, can be produced from biomass; the former is produced by fermentation as well as by chemical synthesis and the latter can be converted from the acid by hydrogenation [6].

In this study microporous membranes of PBS were formed from PBS–chloroform solutions via the immersion precipitation method and the effect of preparation conditions on the permeation resistance and the retention of bacterial cells were examined.

2. Experimental

2.1. Materials

PBS was purchased from Showa Highpolymer (#1001, Tokyo, Japan). Analytical grade chloroform

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and methanol were used without further purification.

2.2. Phase diagrams

PBS was dissolved in chloroform in a 100 cm^3 flask, sealed with a cork stopper that had been covered with aluminum foil and polytetrafluoroethylene (PTFE) tape. The mixture was first stirred with a PTFE stirring bar. Then a predetermined amount of methanol was added to the solution and then the mixture was stirred and incubated in a water bath at a controlled temperature (15–60°C) to obtain a clear solution. After dissolution, the temperature of the water bath was lowered and kept for a period of 5 min. The cloud point temperature was defined in this study as the temperature at which the solution turned cloudy during the 5 min period, having been clear during the 5 min hold time at a temperature 1°C above the cloud point temperature.

2.3. Membrane formation

PBS was dissolved in chloroform in a 100 cm^3 flask in the same way as in Section 2.2. The mixture was first stirred with a PTFE stirring bar and warmed on the stirrer/hot plate at 25–50°C for 1.5 h. Then the solution was incubated for 5 or 10 min in a water bath at a controlled temperature (25–50°C). The polymer solution was cast on a glass plate with a PTFE frame of 60 × 45 mm. The thickness of the frame was 1 mm. After removing excess polymer solution with the edge of another glass plate the polymer solution on the glass plate was immersed in a coagulation bath of methanol at 25°C and kept there for 30 min. The formed membrane was removed from the glass plate, washed with methanol extensively, and kept in methanol prior to use.

2.4. Scanning electron microscopy (SEM)

The membrane was immersed in liquid nitrogen and then fractured. It was mounted vertically on a sample holder. The surface of the sample was coated with gold–palladium using a sputter coater (JFC-1100E, JEOL, Akishima, Japan). A SEM (JSM-5800, JEOL) with an accelerating voltage of 15 kV was used to examine the membrane cross-sections and surfaces.

2.5. Filtration experiments

A filtration cell (Amicon model 8010, 4.1 cm^2, Millipore, Bedford, MA) was used without its stirrer for dead-end filtration experiments. Water was used to measure the permeation resistance of membranes. The filtration was performed at a transmembrane pressure of 10 kPa and at 25 ± 3°C.

Microbial cell suspensions of *Lactobacillus plantarum* NBRC15891^T (0.7ϕ×2.5 μm) were used to examine the retention of bacterial cells by the membranes. The cell sizes were the average values of the sizes of 100 cells measured by optical microscopy. The bacterium was cultured statistically in a modified MRS medium [7] where meat extract was substituted for fish extract. The culture broth after 17 h cultivation at 30°C was diluted 10 times with mainly 0.85% NaCl solution for filtration experiments. The wet cell concentration was 0.5 kg m^{-3}. The cell leakage was monitored with the absorbance at 660 nm of the initial 10 cm^3 permeate. In some experiments, cellulose acetate (CA) membranes (C020A025A, nominal pore size = 0.20 μm, Advantec, Tokyo) were used for comparison.

3. Results and discussion

3.1. Phase diagram of PBS–chloroform–methanol system

In this study chloroform was chosen to prepare microporous membranes of PBS because the solubility index of the solvent (19.0 $MPa^{1/2}$ [8]) is close to that of the polymer (20.3 $MPa^{1/2}$ [9]). We used methanol as a nonsolvent to cause phase separation and to extract residual chloroform because its solubility index (29.7 $MPa^{1/2}$ [8]) differ from that of the polymer. The polymer dissolved in chloroform at least 20% although the dissolution was difficult at high concentrations. The phase diagram of PBS-–chloroform-–methanol system was obtained in a similar way to the method of Witte et al. [10]. At first the cloud point temperatures of 1%, 5%, 10%, and 15% (w/w) PBS solutions in chloroform containing different amounts of methanol were measured (Fig. 1). The cloud point temperatures linearly increased at each polymer concentration. The compositions of phase separation at 10°C, 25°C, 40°C, and 55°C were read from the graph. Then the compositions were plotted on a ternary phase diagram. Fig. 2 shows the ternary phase diagram of PBS–chloroform–methanol system. The left part of each line is one phase region, which increased with temperature.

3.2. Effect of preparation temperature on membrane performance

A PBS membrane that had been prepared from a 10% PBS–chloroform solution prepared at 25°C was almost solids (Figs. 3a and 3b) and water could not permeate the membrane. The membrane resistance

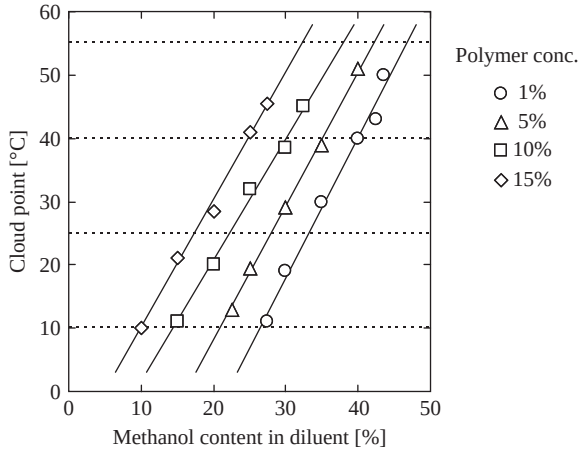

Fig. 1. Phase diagram of PBS-chloroform-methanol system.

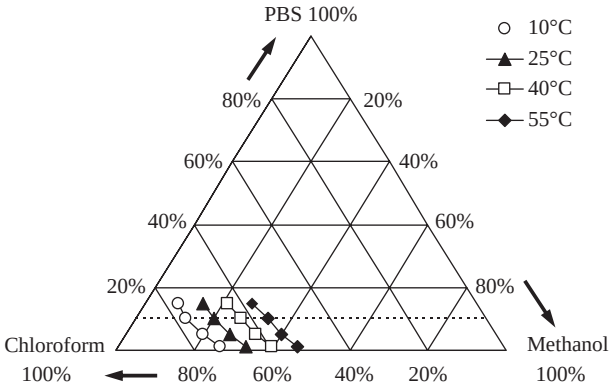

Fig. 2. Ternary phase diagram of PBS–chloroform–methanol system. The broken line shows the composition at a PBS concentration of 10%.

was calculated to be more than 1.7×10^{14} m^{-1} at a transmembrane pressure of 10 kPa. The solid structure of the membrane is thought to be due to delayed demixing by slow intrusion of methanol to the PBS solution at 25°C. The increase the temperature would accelerate the diffusion of methanol in PBS solution. However, an open methanol bath at a high temperature is hazardous because of the low boiling point (64.7°C) and high flammability. Thus we mixed the thermally induced phase separation method [11,12] to the nonsolvent-induced phase separation. The polymer solution was cast at a high temperature and the solution on the plate was immersed in a nonsolvent bath at a room temperature (25°C). In this method the polymer solution would initially allow methanol diffuse without phase separation at a high temperature and then instantaneous phase separation and rapid solidification of polymer would occur as the temperature decreases (Fig. 3).

A PBS membrane prepared from a 10% PBS–chloroform solution prepared at 50°C was microporous (Figs. 3c and 3d) and had a permeation resistance of 4×10^{10} m^{-1}. The microporous structure, which shows a condensed particle layer suggests that a solid–liquid phase separation was occurred at the conditions. Fig. 4 demonstrates the effect of membrane solution preparation temperature on membrane performance for temperatures ranging from 42.5°C to 50°C. The membrane resistance, R_m, was calculated by the following equation:

$$R_m = \frac{\Delta P}{\mu J}, \quad (1)$$

where ΔP, μ, and J are transmembrane pressure, viscosity of permeate, and permeation flux, respectively. The viscosity of water at 25°C was 0.89 mPa s [13].

The effect of casting solution temperature on structure and performance is attributed to the changes in rates of chloroform extraction and influx of methanol into the polymer solution during the immersion in the quench bath. The bacterial cell retention was more than 99% for membranes prepared with a 45–47.5°C solution and decreased with the increasing dissolution temperature. Thus, we set the dissolution temperature at 47.5°C for our subsequent experiments.

3.3. Effect of incubation time on membrane performance

The incubation time also affected the membrane performance. The permeation resistance decreased to half without decreasing the retention of bacterial cells when the incubation time of solutions was changed from 5 to 10 min.

A similar phenomenon where the incubation (aging) time of the polymer solution after dissolution affects the membrane properties was reported by Lin et al. [14]. In the preparation of poly(vinylidene fluoride) membranes the longer the aging time the smaller the globules in the formed membrane. In their study the polymer (dope) solution was dissolved at 50–110°C, cooled to 25°C, and then aged for 0–80 d. They think the structure change was attributed to the nuclei formed during aging although they did not examine the effect of the structural change on the permeation properties of the membranes. Won et al. also showed the effect of aging time of the polymer solution on the membrane morphology in the preparation of polysulfone membrane from a clear solution in a mixed solvent of *N*-methyl-2-pyrrolidone and ethyl acetate [15]. The skin layer of the membrane became porous prepared after aging the solution for 1–2 d at room temperature while the membrane prepared without aging

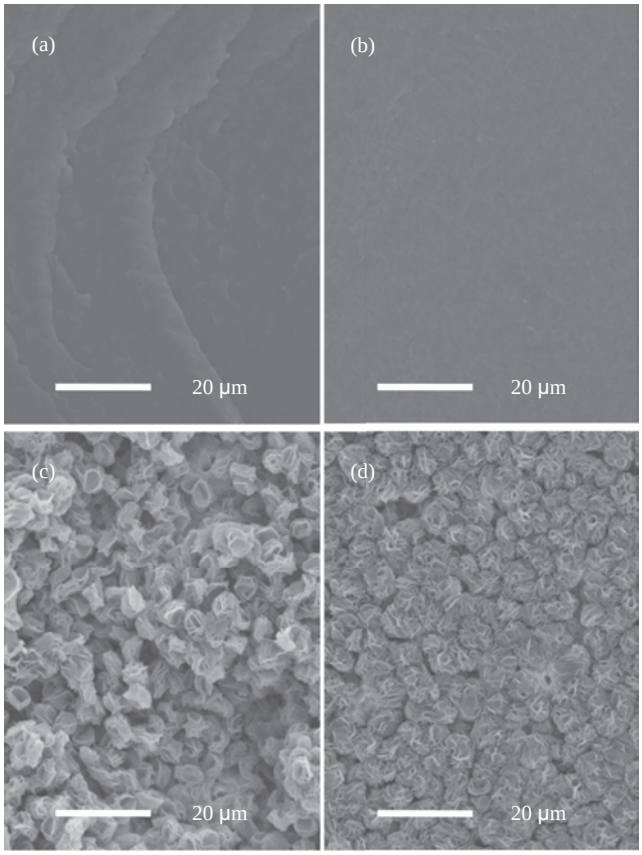

Fig. 3. SEM photographs of cross-sections (a, c) and top surface (b, d) of PBS membranes. Polymer conc. = 10%. Dissolution temperature: (a, b) 25°C and (c, d) 50°C.

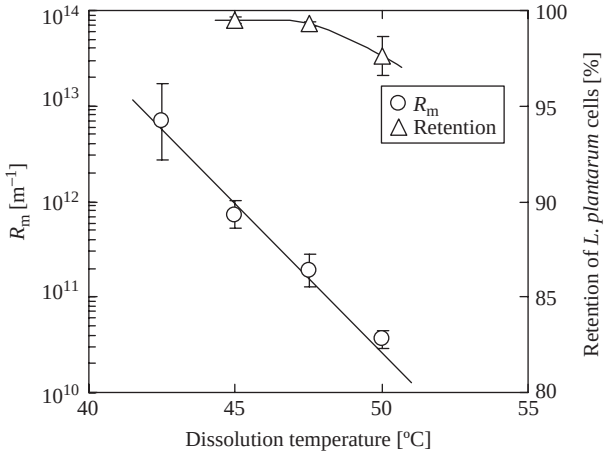

Fig. 4. Effect of dissolution temperature on permeation resistance (R_m) and retention of *L. plantarum* cells of PBS membranes. Polymer conc. = 10%. The polymer solutions were incubated for 5 min in a water bath at each temperature before casting.

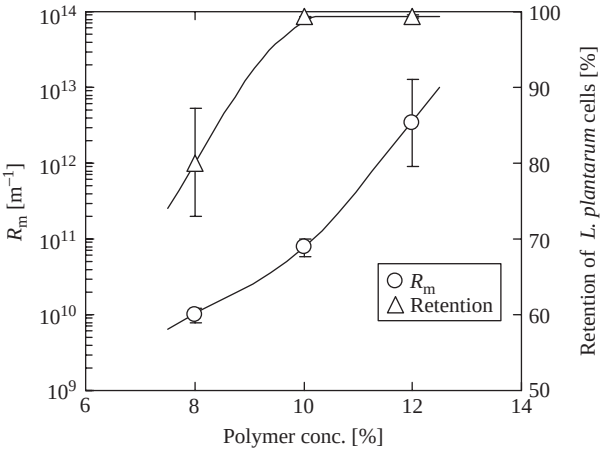

Fig. 5. Effect of polymer concentration on permeation resistance (R_m) and retention of *L. plantarum* cells of PBS membranes. Dissolution temperature = 47.5°C. The polymer solution incubated for 10 min in a water bath at 47.5°C before casting.

had a defect-free skin layer. The permeability was increased by the aging. They think that the structure change is explained by the nodule and nodule aggregates' formation during aging. In our study some change such as formation of small nuclei would occur in the polymer solution in the incubation although the incubation time and temperature were different from those in the above studies.

3.4. Effect of polymer concentration on membrane performance

Increasing the polymer concentration in the casting solution increased the permeation resistance and bacterial cell retention (Fig. 5). The casting solutions of higher concentrations formed dense structures because of the higher volume fraction of the polymer in the solution and the delayed demixing at coagulation. The membrane prepared from 10% solution showed good performance in permeability and cell retention.

Fig. 6 shows the microporous structures of a PBS membrane prepared by casting a 10% PBS solution cast on a glass plate after preheated at 47.5°C for 10 min and then immersing the solution into a methanol bath at 25°C. The internal structure (Fig. 6b) differed from that prepared with a preheating at 50°C (Fig. 3c). The internal components of the former were more connected and the pores were narrower than that of the latter. That would be the reason why the retention of *L. plantarum* cells was higher. The internal pores would be formed by liquid–liquid phase separation [12] although further studies are necessary to clarify the mechanism. On the other hand the surfaces of the both

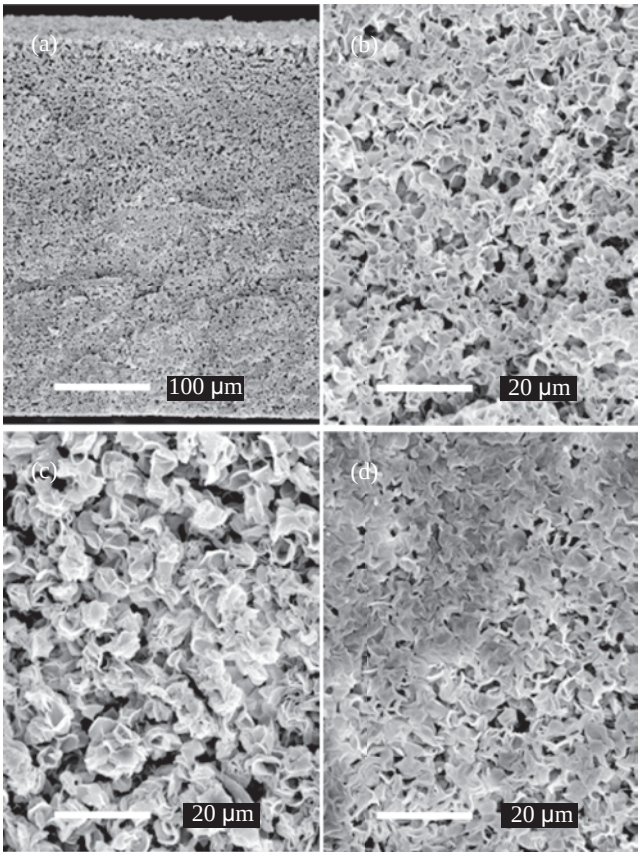

Fig. 6. SEM photographs of cross-sections and top and bottom surfaces of PBS membranes. Polymer conc. = 10%; dissolution temperature = 47.5°C. (a) Cross-section overview, (b) cross-section at middle part, (c) top surface, (d) bottom surface.

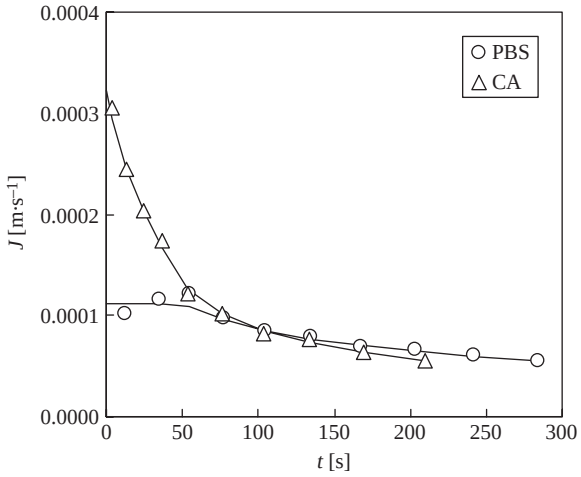

Fig. 7. Permeation flux in filtration of *L. plantarum* suspension in 3% NaCl solution with PBS and CA membranes. J and t denote permeation flux and filtration time, respectively.

membranes were similar and composed of particles (Figs. 6c and 3c). The effect of the rough surface of the membrane will be discussed later.

3.5. Filtration characteristics of PBS membrane

Fig. 7 shows the permeation fluxes in filtration of *L. plantarum* cell suspension with PBS and CA membranes. The suspension contains 3% NaCl in the experiment because we would like to apply the biodegradable membranes to the process for filtration of seawater and liquid foods containing salts in the future. The PBS membrane was prepared with preheating a PBS solution at 47.5°C for 10 min. The initial permeation flux with the PBS membrane was lower than that with the CA membrane. The CA membrane has a nominal pore size of 0.20 μm and its permeation resistance measured in this study was 4.5×10^{10} m^{-1} which is one half of that of the PBS membrane (9.5×10^{10} m^{-1}) used in the filtration shown in Fig. 7. The initial permeate flux J_0 can be estimated by the following equation:

$$J_0 = \frac{\Delta P}{\mu R_m}. \tag{2}$$

The viscosity of 3% NaCl solution was estimated to be 9.3 mPa s from the viscosity of water at 25°C and that the viscosity of water increase 8% by addition of 5% NaCl at 20°C [16]. The calculated initial permeation flux were 1.1×10^{-4} m s^{-1} and 2.3×10^{-4} m s^{-1} for PBS and CA membranes, respectively. The experimental and calculated flux agreed well for PBS membrane while the experimental flux was 40% higher than the calculate value for the CA membrane. The disagreement would be due to the difficulty in measurement of initial flux (8 s for 1 cm^3 of permeate). The permeation flux decreased rapidly after the filtration started in the filtration with the CA membrane while the decrease in flux was slow with the PBS membrane.

It is known that the permeation resistance increases linearly to the permeate volume in cake filtration [17]. In filtration of dilute suspensions the permeation flux follows Eq. (3) in cake filtration.

$$\frac{1}{J} = \frac{\mu(R_m + \alpha C v)}{\Delta P}, \tag{3}$$

where α, C, and v are specific resistance of cake, particle concentration, and permeate volume per unit filtration area.

Fig. 8 shows the plots of $1/J$ vs. v for the filtration in Fig. 7. The value of $1/J$ increased linearly for the CA membrane except the initial part ($v < 0.01$ m). The slope

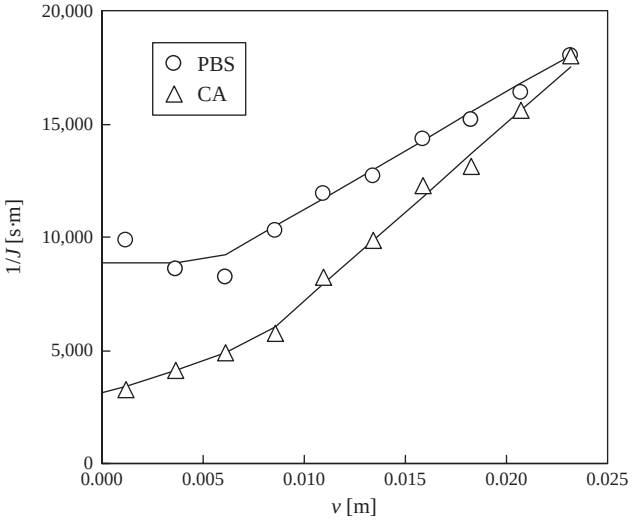

Fig. 8. $1/J$ vs v plot for filtration of *L. plantarum* suspension in 3% NaCl solution with PBS and CA membranes. J and v denote permeation flux and permeate volume per unit filtration area, respectively.

of the graph corresponds to $\frac{\mu\alpha C}{\Delta P}$. On the other hand the value of $1/J$ increased slowly in the filtration with the PBS membrane compared to that with the CA membrane. The slow increase means the apparent value of α decreased.

The decrease in apparent specific resistance would be due to the rough top surface of the PBS membrane (Fig. 6c). The particles dispersed near the top surface of the membrane instead of building a dense cake layer. The PBS membrane acted as a depth filter membrane [5] in the initial stage although the permeation flux was lower than the CA membrane due to the higher membrane resistance. The membrane resistance could be reduced by decreasing the thickness of a PBS solution layer in membrane preparation. However, further effort will be necessary to optimize the preparation conditions for the preparation because the mass and heat transfer would be different in the thinner layer.

4. Conclusions

Microporous membranes of biodegradable PBS were developed in this study by combination of non-solvent and thermally induced phase separation methods. The temperature and polymer concentration in preparation significantly affected the membrane resistance and retention of bacteria. PBS membranes would be useful in filtration process in food and biochemical industries to reduce industrial wastes because the membrane after use is compostable.

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Symbols

C	particle concentration [kg m^{-3}]
J	permeation flux [$m \cdot s^{-1}$]
J_0	initial permeation flux [$m \cdot s^{-1}$]
R_m	membrane resistance [m^{-1}]
t	time [s]
v	permeate volume per unit filtration area [m]
α	specific resistance of cake [m kg^{-1}]
ΔP	transmembrane pressure [Pa]
μ	viscosity of permeate [Pa s]

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