

# Low-temperature formation of $\alpha$ -alumina from various polyhydroxoaluminum–hydroxy acid composite gels

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## Abstract

Low-temperature  $\alpha$ -alumina formation was attempted using various polyhydroxoaluminum (PHA)–hydroxy acid composite gels, which were prepared from PHA solutions containing different amounts of hydroxy acids, such as lactic acid, glycolic acid, malic acid, citric acid or mandelic acid. The composite gels began to transform into  $\alpha$ -alumina when heated at lower temperatures of around 500 °C and the  $\alpha$ -alumina fraction of the heat-treated products increased with increasing temperature. The  $\alpha$ -alumina fraction was also dependent on both the type and amount of hydroxy acid additive. Among the composite gels studied, significant low-temperature  $\alpha$ -alumina formation was observed for the PHA–mandelic acid, PHA–citric acid and PHA–lactic acid series. Low-temperature  $\alpha$ -alumina formation was further promoted by employing a two-step heat-treatment method. The interaction between the functional groups of PHA and hydroxy acid and the seeding effect appear to play important roles in the course of the gelation and calcination processes for low-temperature  $\alpha$ -alumina formation.

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## 1. Introduction

Alumina is an advanced ceramic that has a wide range of applications in various industrial areas.  $\alpha$ -Alumina (corundum) is a thermodynamically stable polymorph of  $\text{Al}_2\text{O}_3$ . In general, the preparation of  $\alpha$ -alumina powders requires calcination of alumina precursors, such as aluminum hydroxides or hydrated aluminas, at temperatures above 1100 °C to allow transformation into  $\alpha$ -alumina, along with the intermediate formation of metastable transition aluminas at lower temperatures [1,2]. Calcination at such high temperatures inevitably induces unwanted crystal growth and particle coarsening, which makes it difficult to synthesize  $\alpha$ -alumina powders with fine primary particles [3,4]. Therefore, lowering the temperature of  $\alpha$ -alumina formation has been a subject of interest to many researchers, because the synthesis of nanosized  $\alpha$ -alumina powders with controlled morphology

could be attained by reduction of the  $\alpha$ -transformation temperature. Many approaches, such as sol–gel and solution processes [5–12], have been attempted in order to reduce the  $\alpha$ -transformation temperature and synthesize fine  $\alpha$ -alumina powders. However, most of these approaches still require temperatures above 800 °C to form  $\alpha$ -alumina. Mechanochemical treatment [2,4,13,14] and the introduction of seeds [7,15–17] or  $\text{AlF}_3$  [18–20] also accelerate the  $\alpha$ -transformation of alumina.

Concentrated polyhydroxoaluminum (PHA) solutions prepared by the Al metal dissolution method have such features as a high OH/Al ratio and a high content of the highly polymerized Keggin  $\text{Al}_{13}$  ion ( $[\text{Al}_{13}\text{O}_4(\text{OH})_{12}(\text{H}_2\text{O})_{24}]^{7+}$ ) species [21]. We have reported a sol–gel process using PHA solutions as a starting material for the preparation of transition aluminas [22–24]. Transition aluminas with controlled polymorph and pore properties have been prepared using PHA composite gels containing organic additives such as polyethylene glycol and quaternary ammonium ions [22–24]. The interaction of additives with PHA ions to modulate the gel structure is a key factor in controlling the polymorph and pore

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properties. We also reported that the addition of lactic acid (LA) to PHA solution formed a PHA–LA composite gel with a low LA content (3–10 mass%) that began to transform directly into  $\alpha$ -alumina upon heat-treatment at low temperatures of around 500 °C [25]. This low-temperature transformation into  $\alpha$ -alumina is remarkable, although the transformation is only completed after heat-treatment at ca. 1100 °C.

In the present study, various hydroxy acids, including LA, were used as additives for the preparation of PHA composite gel alumina precursors to yield  $\alpha$ -alumina at low-temperatures. The hydroxy acid molecule contains both –OH and –COOH functional groups. The interaction between the OH groups in PHA ions and the functional groups of the hydroxy acid molecules may modulate the PHA gel structure. In addition, the ability of the hydroxy acids to form complexes with aluminum may also lead to the modulation of the gel structure. Thus, the aim of this study is to systematically investigate the effects of hydroxy acid species and their content on low-temperature  $\alpha$ -alumina formation from various PHA–hydroxy acid composite gels. A two-step heat-treatment method is also employed to promote low-temperature  $\alpha$ -alumina formation from the composite gels.

## 2. Experimental

A PHA solution containing 23.6 mass%  $\text{Al}_2\text{O}_3$  with an OH/Al ratio of 2.51 was prepared by dissolving Al metal in an HCl solution, as previously reported [21,26]. LA, glycolic acid (GA), malic acid (MIA), citric acid (CA) or mandelic acid (MnA) was used as hydroxy acid additives. Each hydroxy acid was added to the PHA solution and stirred for 30 min to obtain PHA–hydroxy acid mixed solutions. The amount of each hydroxy acid was varied from 0 to 10 mass%, based on the mass of  $\text{Al}_2\text{O}_3$  obtained from the PHA solution. The mixed solutions were then held at 60 °C for 2 days to obtain PHA–hydroxy acid composite gels (PHA–HA(*x*), where HA represents the hydroxy acid and *x* indicates the amount of HA).

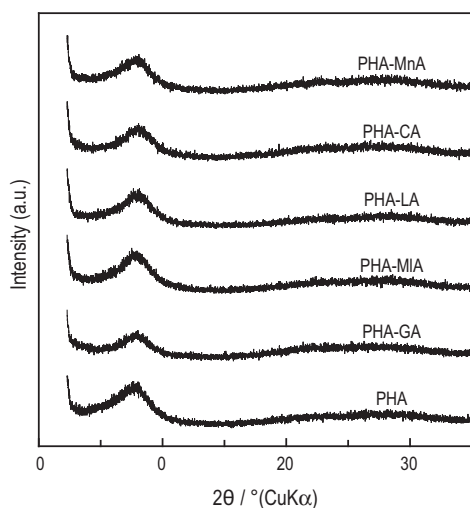


Fig. 1. XRD patterns of PHA and various PHA–hydroxy acid (5.0 mass%) composite gels.

The PHA–hydroxy acid composite gels were heat-treated at 400–1000 °C for 3 h in air using a heating rate of 1.5 °C/min. A two-step heat-treatment method was also employed. The composite gels and their heat-treated products were ground using an agate mortar and pestle, and passed through a 325 mesh (45  $\mu\text{m}$ ) sieve prior to characterization.

Powder X-ray diffraction (XRD) patterns of the composite gels and their heat-treated products were obtained using Cu K $\alpha$  monochromated radiation. The mass fraction of  $\alpha$ -alumina in the heat-treated products was estimated from the relative intensity of the (104) reflection of  $\alpha$ -alumina. The morphology of the heat-treated products was examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

## 3. Results and discussion

### 3.1. Low-temperature formation of $\alpha$ -alumina from PHA–hydroxy acid composite gels

Fig. 1 shows XRD patterns of PHA–hydroxy acid composite gels. The content of hydroxy acid was 5.0 mass%, which was the optimum amount for low-temperature  $\alpha$ -transformation in the PHA–LA composite gel system according to the previous study [25]. The PHA gel and PHA–hydroxy acid composite gels had broad reflection peaks at approximately  $2\theta = 8^\circ$ , which is ascribable to a loosely stacked structure consisting of highly polymerized planar PHA ions [24,25]. The effect of hydroxy acids on the peak shift can be classified into two groups; one group exhibits a slight shift to higher angles (PHA–MnA, PHA–LA and PHA–CA composite gels), while the other group has almost no shift (PHA–MIA and PHA–GA composite gels). The former group shows that the gel structure is modified to tighten the loosely stacked sequences, while the latter group shows little potential for modulation of the PHA gel structure. These results suggest that each hydroxy acid has a modulation effect on the loosely stacked structure of the composite gels, even for a small addition of 5.0 mass%. In the previous study of the PHA–LA composite gel system [25], when the LA content of the PHA–LA composite gels was increased above 10 mass%, the peak around  $2\theta = 8^\circ$  was significantly shifted to the lower angle side; however, such a large amount of additive was not effective for low-temperature  $\alpha$ -alumina formation.

Fig. 2 shows XRD patterns of heat-treated products obtained from PHA–hydroxy acid (5.0 mass%) composite gels. After heat treatment above 500 °C (Fig. 2(a)), all of the PHA–hydroxy acid composite gels, except for the PHA–MnA system, partially crystallized into  $\alpha$ -alumina, while the PHA gel formed only  $\gamma$ -alumina. This unusual crystallization behavior of the composite gels, i.e., the formation of  $\alpha$ -alumina at considerably low temperatures, resembles the thermal decomposition route of diaspor ( $\alpha$ - $\text{AlOOH}$ ), which directly leads to  $\alpha$ -alumina [3]. A similar phenomenon has been reported by several researchers in the case of sol–gel-derived precursors from  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  or aluminum alkoxide as a starting material [5–9]. Kamiya and co-workers [6–8] reported that alumina gels prepared under carefully controlled reaction conditions transformed into

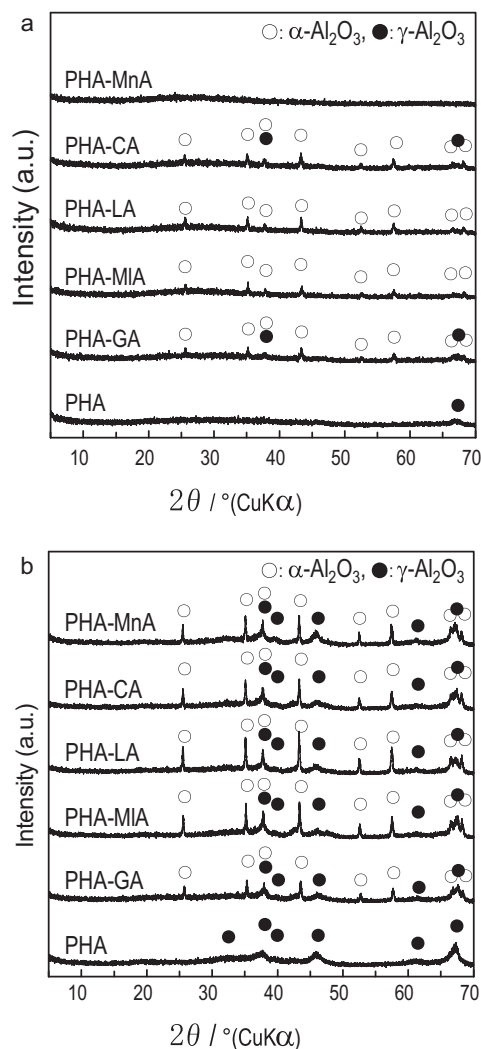


Fig. 2. XRD patterns of products obtained from PHA and various PHA–hydroxy acid (5.0 mass%) composite gels after heat treatment at (a) 500 °C and (b) 800 °C.

$\alpha$ -alumina at temperatures as low as ca. 500 °C and concluded that direct transformation into  $\alpha$ -alumina at such low temperatures was probably caused by the partial formation of a diasporic-like structure during the sol–gel process. In the present PHA–hydroxy acid composite gel system, it is plausible that a similar diasporic-like structure forms, although the mechanism remains to be solved.

The  $\alpha$ -alumina peaks became sharper for heat treatment at 800 °C (Fig. 2(b)), accompanied by an increase in the intensity of peaks assignable to  $\gamma$ -alumina. In contrast, the transformation of the PHA gel without an additive into  $\alpha$ -alumina occurred at 1000 °C, which is in agreement with the previously reported crystallization behavior [25].

Fig. 3 shows the mass fraction of  $\alpha$ -alumina obtained from the various composite gels containing 5.0 mass% hydroxy acid treated at different temperatures.  $\alpha$ -Alumina formation from the composite gels began at around 500 °C. For PHA–LA series, the  $\alpha$ -fraction was significantly increased at heat treatment temperatures up to 600 °C and then became saturated at 800 °C, followed by a further increase for heat treatment

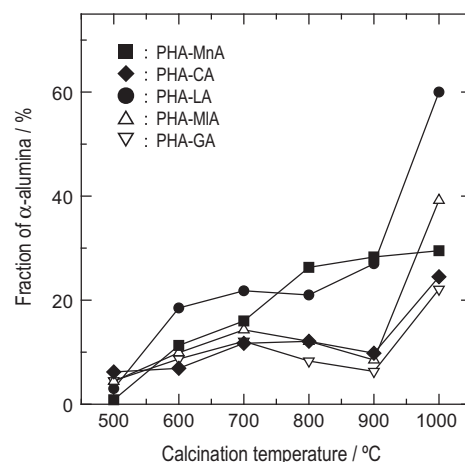


Fig. 3. Fraction of  $\alpha$ -alumina in products formed from various PHA–hydroxy acid (5.0 mass%) composite gels vs. heat treatment temperature.

above 900 °C. The PHA–MnA series showed a significant increase in the  $\alpha$ -fraction when treated at up to 800 °C, which then became saturated above 800 °C. In contrast, an increase in the fraction of  $\alpha$ -alumina for the PHA–CA, PHA–MIA and PHA–GA series was observed with increasing heat treatment temperature up to 700 °C, which it then decreased up to 900 °C, but showed a steep increase with further treatment at 1000 °C. The decrease in the  $\alpha$ -fraction around 800 °C is probably due to a change in the crystallization mechanism. In the PHA–CA, PHA–MIA and PHA–GA series, low-temperature  $\alpha$ -transformation begins at around 500 °C and the  $\alpha$ -fraction increases during heat treatment up to 700 °C. For calcination temperatures of 800 °C or higher, the soaking time in the temperature range below 700 °C, which plays an important role for  $\alpha$ -alumina nucleation, was shortened because a fixed heating rate of 1.5 °C/min was employed. Therefore, these conditions were unfavorable for low-temperature  $\alpha$ -transformation, because the full nucleation process was incomplete, and the formation of  $\gamma$ -alumina became dominant. Our previous study [25] showed that the formation of  $\alpha$ -alumina was promoted to a greater extent for a slower heating rate of 1.0 °C/min, while it was retarded at faster heating rates ( $\geq 3$  °C/min). Therefore, the  $\alpha$ -fraction tends to decrease in the temperature range 800–900 °C. However, the  $\alpha$ -fraction in the PHA–LA and PHA–MnA series, which gave relatively high  $\alpha$ -fractions at 700 °C, increased with increasing temperature, even above 800 °C. In these cases, the  $\alpha$ -alumina particles that are formed in the lower temperature range can effectively act as seeds for  $\alpha$ -transformation [26] above 800 °C.

Fig. 4 shows the  $\alpha$ -alumina fraction of the products obtained from different PHA–hydroxy acid composite gels at 800 °C, as a function of the hydroxy acid content. The hydroxy acid content in the figure was expressed in mol percent rather than mass percent, for ease of chemical comparison among the hydroxy acids. The  $\alpha$ -alumina fraction was dependent on both the type and the amount of hydroxy acid. In all cases, the  $\alpha$ -fraction was first increased with increasing content of hydroxy acid up to a maximum value, and then decreased with further increase in the hydroxy acid content. The content to give the

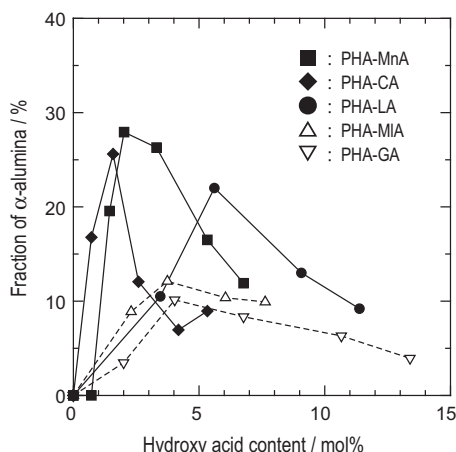


Fig. 4. Fraction of  $\alpha$ -alumina in products formed from various PHA-hydroxy acid composite gels at 800 °C vs. hydroxy acid content.

maximum  $\alpha$ -fraction changed depending on the type of hydroxy acid; however, the optimum additive content was distributed in a relatively narrow range below 6 mol%. Among the composite gels in the present study, low-temperature  $\alpha$ -transformation was most significant for the PHA-MnA, -CA and -LA series; the maximum  $\alpha$ -fraction of 28% was obtained for the composite gel containing 2.0 mol% MnA.

Hydroxy acid molecules in composite gels can interact with PHA ions through their functional groups, combining the clustered domains of planar PHA ions to modulate the gel structure, which is favorable for low-temperature  $\alpha$ -transformation in respect of the  $\text{Al}^{3+}$  environment, i.e., enrichment of octahedral  $\text{Al}^{3+}$  content. Interaction depends on both the type and amount of the hydroxy acids. On the basis of the present results, the PHA-MnA (2.0 mol%) gel was determined to be the best precursor for low-temperature  $\alpha$ -alumina formation under the experimental conditions employed.

### 3.2. Effect of two-step heat-treatment for the low-temperature $\alpha$ -transformation

In order to promote low-temperature  $\alpha$ -alumina formation, a two-step heat-treatment method was applied to the PHA-MnA (2.0 mol%) composite gel. The first step involved heating the composite gel between 400 and 700 °C for 1 h, followed by a second step of continuous heating at 800 °C for 3 h.

Table 1 shows the fraction of  $\alpha$ -alumina obtained using the two-step heat-treatment on the PHA-MnA (2.0 mol%) com-

posite gel. The  $\alpha$ -fraction obtained from the two-step heat-treatment method was increased over that for the one-step heat-treatment at 800 °C, regardless of the first-step heat-treatment temperature. This result also implies that the soak time in the temperature range below 700 °C is a key factor for the promotion of low-temperature  $\alpha$ -transformation. The  $\alpha$ -fraction of PHA-MnA (2.0 mol%)-500/800 and PHA-MnA (2.0 mol%)-600/800 samples was over 50 mass%.

An  $\alpha$ -fraction of 58 mass% was obtained by the two-step heat treatment (500/800 °C), which is more than twice that obtained by the one-step heat treatment at 800 °C. Low-temperature  $\alpha$ -alumina formation began at around 500 °C.  $\alpha$ -Alumina particles formed at the first-treatment temperatures above 500 °C probably act as seeds to promote  $\alpha$ -transformation during the second-step heat-treatment. The difference in the  $\alpha$ -fraction between the one-step and the two-step heat treatments decreased when the first-step treatment temperature was 700 °C, probably due to a decrease in the seeding effect.

Fig. 5 shows SEM and TEM micrographs of the products obtained from the PHA-MnA (2.0 mol%) composite gel at 800 °C, with or without a first-step heat treatment. Aggregates of plate-like crystallites less than ca. 200 nm in size were observed. The plate-like crystallites correspond to  $\alpha$ -alumina. In the case of products having a lower  $\alpha$ -alumina fraction (for example, PHA-MnA (2.0 mol%)-800 in Fig. 5(a)), plate-like  $\alpha$ -alumina crystallites were observed in a matrix of nanosized transitional alumina particles. The frequency of appearance of the plate-like crystallites increased as the  $\alpha$ -alumina fraction increased (for example PHA-MnA (2.0 mol%)-500/800 in Fig. 5(b)), although the size of the crystallites in each product was almost unchanged. Fig. 5(c) shows a TEM micrograph of PHA-MnA (2.0 mol%)-500/800, which also indicates that the powder mainly consisted of two types of different morphology particles; large (100–200 nm) plate-like crystallites of  $\alpha$ -alumina and fine (around 10 nm) particles of  $\gamma$ -alumina.

The present results indicate that PHA-hydroxy acid composite gels, especially the PHA-MnA, PHA-CA and PHA-LA composite gels, have potential as precursors for the low-temperature formation of  $\alpha$ -alumina powders. Although further increase in the  $\alpha$ -fraction and the lowering of aggregation remain to be overcome, the knowledge obtained here may extend the potential of the PHA sol-gel process to the fabrication of  $\alpha$ -alumina nanopowders that can be applied to the production of nanocrystalline alumina ceramics or alumina nanocomposites at lower sintering temperatures.

Table 1  
Fraction of  $\alpha$ -alumina of the products obtained from PHA-MnA(2.0 mol%) composite gel by the two-step heat-treatment method.

Sample	Calcination temperature (°C)		Fraction of $\alpha$ -alumina (mass%)
	First-step	Second-step	
PHA-MnA(2.0 mol%)-800	—	800	27.9
PHA-MnA(2.0 mol%)-400/800	400	800	34.7
PHA-MnA(2.0 mol%)-500/800	500	800	58.4
PHA-MnA(2.0 mol%)-600/800	600	800	51.5
PHA-MnA(2.0 mol%)-700/800	700	800	36.4

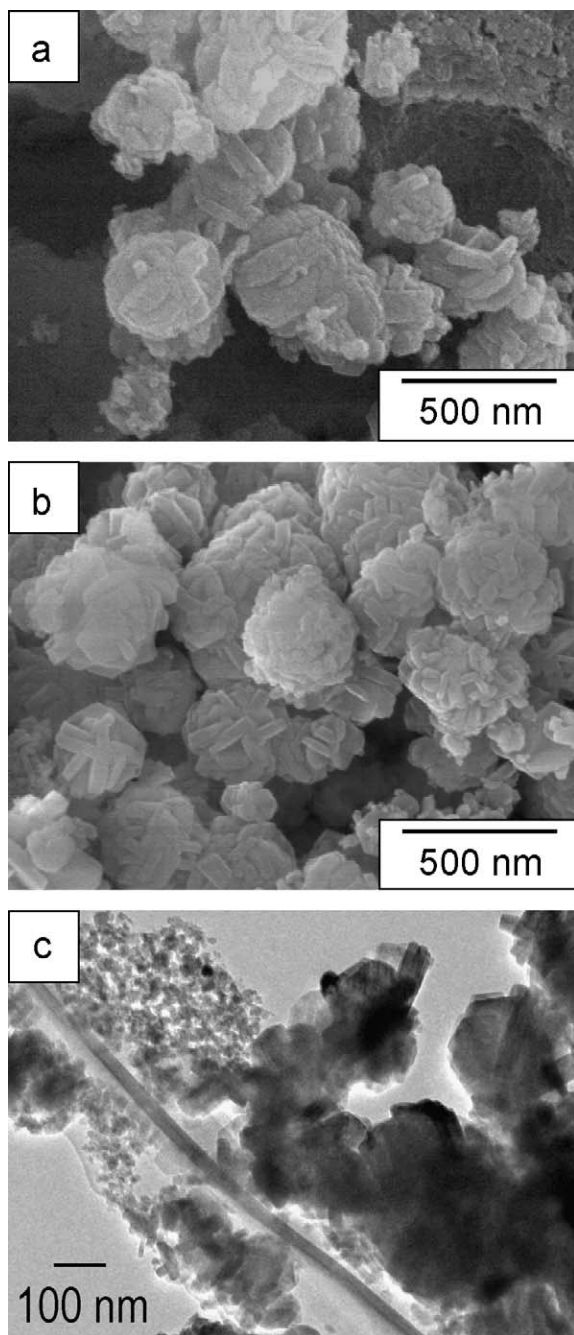


Fig. 5. (a, b) SEM and (c) TEM micrographs of products obtained from the PHA–MnA (2.0 mol%) composite gel obtained by (a) one-step heat treatment at 800 °C and (b, c) two-step heat treatment of 500/800 °C.

#### 4. Conclusion

Low-temperature formation of  $\alpha$ -alumina was attempted using composite gels prepared from PHA solution and various hydroxy acids. The PHA–hydroxy acid composite gels began to transform into  $\alpha$ -alumina at around 500 °C. Interaction between the functional groups of PHA and the hydroxy acids appears to play an important role in the course of gelation and the calcination processes for unique low-temperature  $\alpha$ -transformation. Both the type and amount of

hydroxy acid influenced the low-temperature  $\alpha$ -transformation. The MnA, CA, and LA hydroxy acids were effective additives for low-temperature  $\alpha$ -transformation. The  $\alpha$ -fraction of the product obtained from the PHA–MnA (2.0 mol%) composite gel at 800 °C reached to 28 mass%. Low-temperature  $\alpha$ -transformation was further promoted by employing a two-step heat-treatment method. The  $\alpha$ -fraction of the product obtained from two-step heat treatment (500/800 °C) of the PHA–MnA (2.0 mol%) composite gel was 58 mass%. Fine  $\alpha$ -alumina particles formed at the first-treatment temperatures probably act as seeds in the course of the second-step heat-treatment to promote further  $\alpha$ -transformation.

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