**Colloid & Polymer Science** Colloid Polym Sci 272:422–426 (1994)

# Production of submicron-size monodisperse polymer particles having aldehyde groups by the seeded aldol condensation polymerization of glutaraldehyde (II)*)

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*Abstract*: Submicron-size monodisperse polystyrene/polyglutaraldehyde (PS/PGLA) composite particles having aldehyde groups at the surfaces were produced by the seeded aldol condensation polymerization of glutaraldehyde at various temperatures of 0 ~ 40 °C. Since a part of aldehyde groups was consumed by the Cannizzaro reaction (hemiacetal formation) as a intermolecular reaction of PGLA, the amount of aldehyde groups on PS/PGLA composite particles was varied by the competition between the aldol condensation reaction and the Cannizzaro reaction at the various temperatures.

*Key words*: Polymer emulsion – seeded polymerization – glutaraldehyde – aldol condensation polymerization – aldehyde group

## Introduction

Polymer particles having aldehyde groups are useful as a carrier of proteins which are used in bioreactors, biosensors, and bioseparators [1–3]. We recently developed a convenient technique for producing such particles, in which the seeded aldol condensation polymerization of glutaraldehyde (GLA) was carried out in the presence of submicron-size monodisperse polystyrene (PS) particles produced by emulsifier-free emulsion polymerization [4]. This novel technique has an advantage that the particle size and its monodispersity can be preliminarily controlled.

In this article, the effect of the polymerization temperature on the surface concentration of aldehyde groups will be examined for the purpose of controlling it.

## Experimental

### *Materials*

Styrene was distilled under reduced pressure in a nitrogen atmosphere. GLA (25% aqueous soln.) was of analytical grade and used as received. Potassium persulfate (KPS) of reagent grade was purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Other chemicals were of analytical grade.

### *Preparation of seed particle*

PS seed particles were produced by emulsifier-free emulsion polymerization with potassium persulfate initiator at 70 °C for 48 h according to the previous article [4]. The number-average particle diameter was 0.47 $\mu$m and its coefficient of

*) Part CXXXIX of the series "Studies on Suspension and Emulsion"

Table 1. Production of PS/PGLA composite particles by the seeded aldol condensation polymerization[a]) in the presence of PS particles

| Ingredient | | |
|---|---|---|
| PS seed emulsion[b]) | (ml) | 100 |
| GLA[c]) | (g) | 20 |

[a]) 0 ~ 40 °C, 6 h, pH 11.0 (with NaOH).
[b]) Solid, 100 g/l.
[c]) 25% aqueous solution.

variation was 3.6%. The produced PS particles were washed twice with water.

*Seeded aldol condensation polymerization*

PS/polyglutaraldehyde (PGLA) composite particles were produced by the seeded aldol condensation polymerization of GLA in the presence of the PS seed particles at various temperatures at pH 11.0 as listed in Table 1. The pH was maintained with 1 N NaOH solution using a pH stat. The conversion of GLA was measured by gas chromatography according to the previous article [4]. After the polymerization, the produced PS/PGLA composite particles were washed several times with water using centrifuge to remove the PGLA in aqueous phase and residual GLA.

*Determination of aldehyde groups*

The amount of aldehyde groups on the washed particle surfaces was determined according to the previous article [4] using the 2.5 pH method proposed by Smith et al. [5].

**Results and discussion**

Figure 1 shows the time-conversion curves at the polymerization temperatures of 0°, 15°, and 30 °C. The polymerization proceeded smoothly and was almost completed within 6 h at 30 °C.

Figure 2 shows the relationship between the polymerization temperature and the conversion after 6 h in the seeded aldol condensation polymerization of GLA. The conversion increased markedly with the rise of the polymerization temperature.

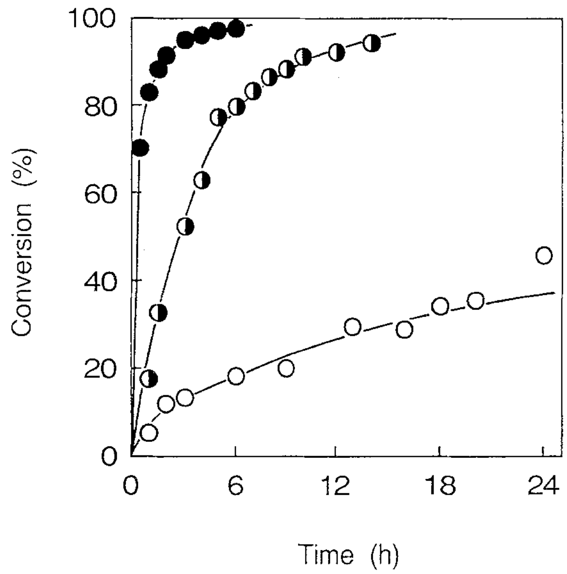



Fig. 1. Time-conversion curves of the seeded aldol condensation polymerizations of GLA in the presence of PS particles at various temperatures: polymn. conditions: PS, 10 g; GLA (25% aq. soln.), 20 ml; water, 90 ml. Polymn. Temp. (°C): ○, 0; ◑, 15; ●, 30

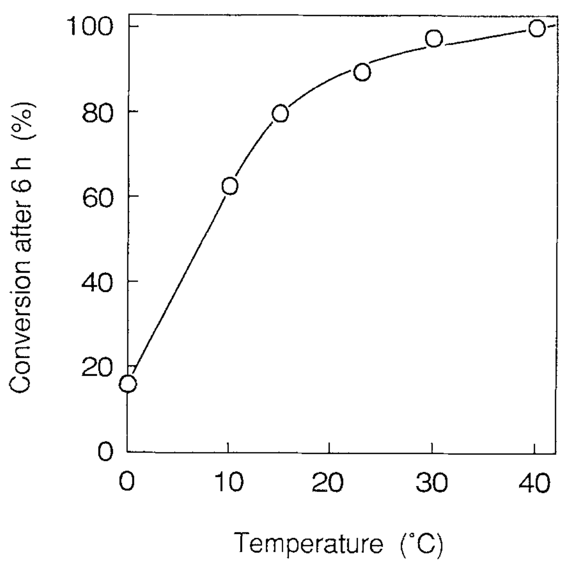



Fig. 2. Relationship between the polymerization temperature and the conversion after 6 h in the seeded aldol condensation polymerization of GLA in the presence of PS particles: PS, 10 g; GLA (25% aq. soln.), 20 ml; water, 90 ml; pH 11 (with NaOH)

Figure 3 shows the relationship between the polymerization temperature and the amount of aldehyde groups on the PS/PGLA composite particles washed with a large quantity of water. The amount of aldehyde groups indicates a maximum value at 23 °C. That is, with the rise in the polymerization temperature above 23 °C, the amount of aldehyde groups on the washed PS/PGLA composite particles decreased, though the amount of PGLA produced in the system increased as shown in Fig. 2. The reason may be

$$-CH_2-\overset{\overset{\displaystyle CHO}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2 \longrightarrow -CH_2-\overset{\overset{\displaystyle CHO}{|}}{C}=CH-CH_2- \qquad (1)$$

$$2\text{-}CH=\overset{\overset{\displaystyle CHO}{|}}{C}-(CH_2)_2- + NaOH \longrightarrow -CH=\overset{\overset{\displaystyle CO_2Na}{|}}{C}-(CH_2)_2- + -CH=\overset{\overset{\displaystyle CH_2OH}{|}}{C}-(CH_2)_2- \qquad (2)$$

considered as follows.

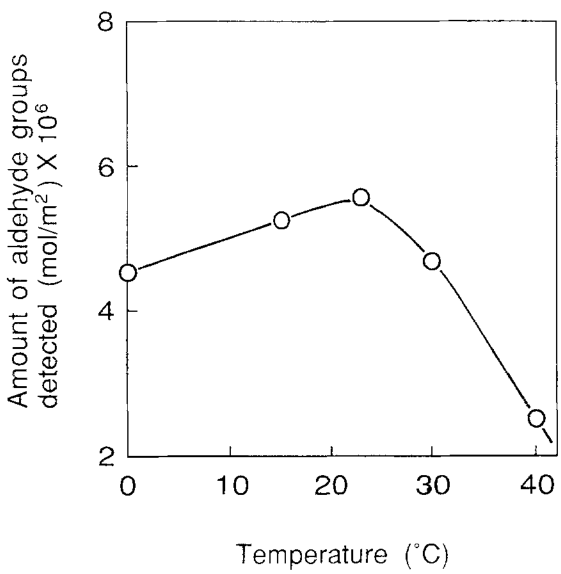



Fig. 3. Relationship between the polymerization temperature and the amount of aldehyde groups on the PS/PGLA composite particles produced by the seeded aldol condensation polymerization of GLA in the presence of PS particles for 6 h

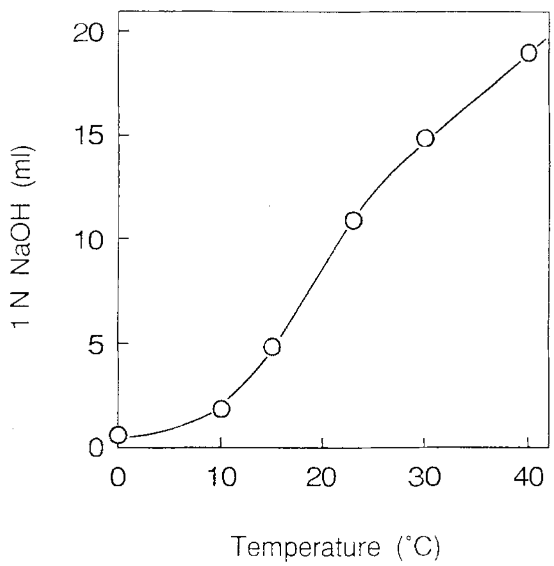



Fig. 4. Relationship between the polymerization temperature and the amount of NaOH consumed throughout the seeded aldol condensation polymerization of GLA in the presence of PS particles: PS, 10 g; GLA (25% aq. soln.), 20 ml; water, 90 ml; pH 11 (with NaOH)

For PGLA which has one aldehyde group per one GLA unit the dehydration reaction may occur under strong alkaline condition as shown in Eq. (1). Subsequently, as shown in Eq. (2), Cannizzaro reaction enables the aldehyde groups in PGLA to convert a hydroxyl group and a carboxyl group, where NaOH should be consumed stoichiometrically.

Figure 4 shows the relationship between the polymerization temperature and the amount of NaOH solution consumed to keep the pH value at 11.0 throughout the aldol condensation polymerization. The amount of consumed NaOH solution increased with the rise of the polymerization temperature. Since NaOH is consumed only by the Cannizzaro reaction, the result indicates that the Cannizzaro reaction proceeded actively at high polymerization temperatures, resulting in the decrease of aldehyde groups in PGLA.

Figure 5, which was obtained from the combination of Figs. 2 and 4, shows the relationship between the polymerization temperature and the percentage of aldehyde groups consumed by the Cannizzaro reaction based on total aldehyde groups in PGLA. Most of aldehyde groups in PGLA were consumed at the high polymerization

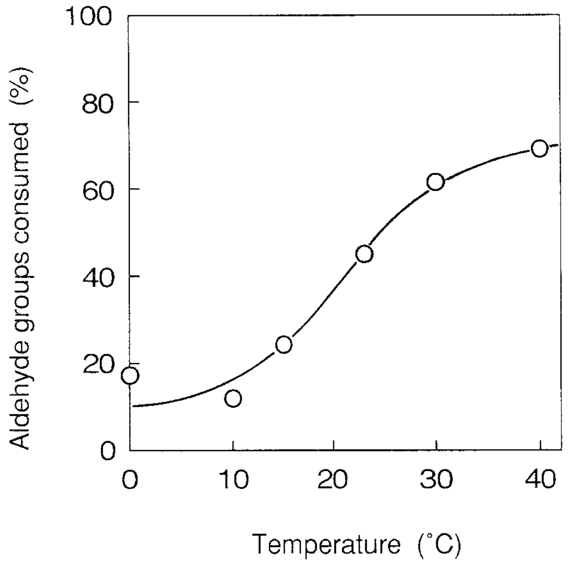



Fig. 5. Relationship between the polymerization temperature and the percentage of aldehyde groups consumed by the Cannizzaro reaction based on total aldehyde groups in PGLA formed by the seeded aldol condensation polymerization of GLA in the presence of PS particles for 6 h

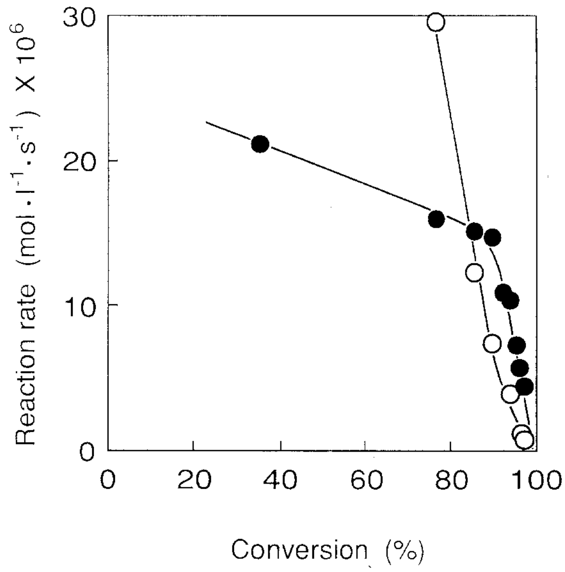



Fig. 6. Relationships between the conversion of GLA and reaction rates of the seeded aldol condensation polymerization of GLA (○), and of the Cannizzaro reaction of PGLA (●) at 30 °C

temperatures. This seems to be the reason why the amount of aldehyde groups developed on the PS/PGLA composite particles decreases with the rise of the polymerization temperature above 23 °C.

Figures 6 and 7 show the variations of the rates of the polymerization ($R_p$) and the Cannizzaro reaction ($R_c$) as a function of the conversion, respectively, at 30° and 0 °C. The $R_p$ values were calculated from slopes of time-conversion curves shown in Fig. 1, although the data above about 50% at 0 °C were not shown therein. Both the rates at 30 °C were much larger than those at 0 °C. At 30 °C, the $R_p$ was larger than the $R_c$ below the conversion of 85%, and the $R_c$ passed over the $R_p$ above its level. At 0 °C, the $R_c$ passed over the $R_p$ at the conversion of 80%. These results suggest that the amounts of aldehyde groups in PGLA produced at 30° and 0 °C increased with the conversion below the conversion of about 80%.

Figure 8 shows the relationships between the conversion and the amount of aldehyde groups on the PS/PGLA composite particles produced by the seeded aldol condensation polymerizations at 0° and 30 °C. At both the polymerization temperatures, the surface aldehyde concentrations had

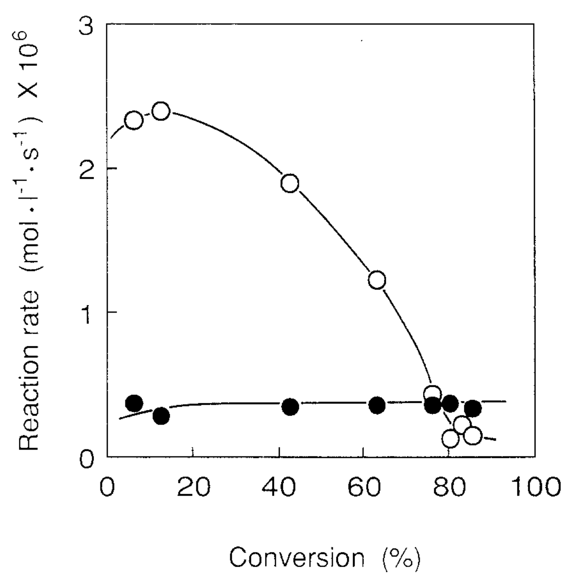



Fig. 7. Relationships between the conversion of GLA and reaction rates of the seeded aldol condensation polymerization of GLA (○), and of the Cannizzaro reaction of PGLA (●) at 0 °C

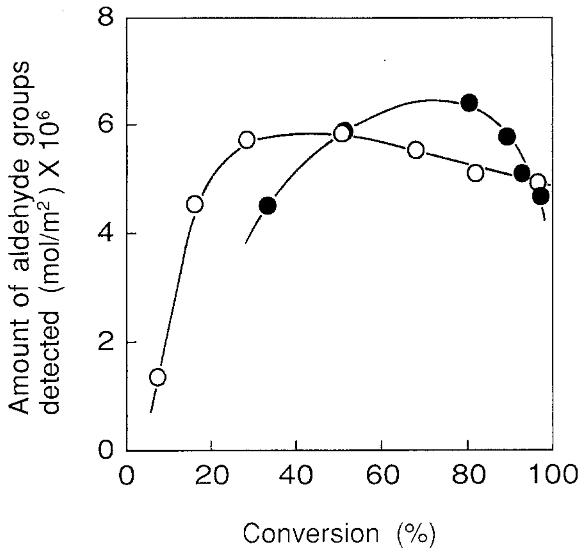
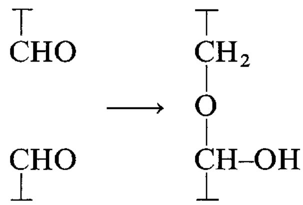



Fig. 8. Relationship between the conversion and the amount of aldehyde groups on the PS/PGLA composite particles produced by the seeded aldol condensation polymerization of GLA in the presence of PS particles: PS, 10 g; GLA (25% aq. soln.), 20 ml; water, 90 ml. Polymn. temp. (°C): ○, 0; ●, 30

maxima at certain conversions, at which the $R_c$ passed over the $R_p$. This may suggest that the Cannizzaro reaction and/or hemi-acetal formation with cross-linking in the PGLA at the surfaces of PS seed particles occurred effectively than in the aqueous solution because the aldehyde concentration at the particle surfaces was higher than that in the solution.

In order to get information about the Cannizzaro reaction at the particle surfaces, the amount of carboxyl groups in the dispersion of the washed PS/PGLA particles (solid, 9.6%) (30 ml) was estimated by a potentiometric titration with 1 N NaOH solution. However, carboxyl groups were hardly responsible for titration. This suggests that the Cannizzaro reaction at the PS/PGLA composite particles hardly proceeds because of the restriction of a mobility of PGLA molecule due to the cross-linked structure,




(3)

although almost all PGLA containing carboxyl groups introduced by the Cannizzaro reaction are desorbed out of the polymer surface because of high hydrophilicity. Therefore, the hemiacetal formation seems to proceed preferentially on the PS seed particles, resulting in the PGLA network thereon.

From the above results, it is concluded that the surface concentration of aldehyde groups at the PS/PGLA composite particles can be controlled by changing the polymerization temperature and the time, although the related factors were complicated.

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Received April 6, 1993; accepted September 7, 1993

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