# Preparation of Functional Polymer Microspheres by Suspension Copolymerization of Diallyl Phthalate with Carboxylic Monomers

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## Synopsis

A study was made of the suspension copolymerization of diallyl phthalate (DAP) and acrylic and methacrylic acid (AAc and MAc, respectively), which were charged after delay to the suspension of partially prepolymerized DAP) and the structure of resulting gel particles. In the copolymerization of DAP with AAc, the conversion of AAc leveled off despite an appreciable amount of AAc remaining in the aqueous phase, whereas in DAP–MAc copolymerization most MAc was polymerized in the particles. The particle structure depended significantly on the mode of comonomer charge. Earlier charge of the comonomer to the reaction system resulted in the formation of particles having comonomer unit-rich surface layer. This was interpreted in terms of phase separation through loosely crosslinked structure in the particles and supported by an adsorption test using a dye and the observation of surface structure of the particles. The timing of comonomer charge changed the amount of comonomer units in the surface layer from 0.06 to 0.60 mmole/g particle.

## INTRODUCTION

Many kinds of crosslinked polymer microspheres with the diameter from 0.1 to 1 mm have been put to practical use, mainly as ion exchangers, chelating agents, specific adsorbents, etc. Some specially tailored microspheres have been used as catalysts for some reactions in which relatively high-molecular-weight organic compounds participate.[1]

Such microspheres are generally prepared from suspension polymerization in the presence of crosslinking reagent. The structure of gel particles depends on the preparation methods which are classified into three categories in terms of the addition of solvent in the monomer phase. Polymerization without solvent is the simplest one. The resulting particles have micropores whose size is mainly dependent on the amount of crosslinking reagent. Using a solvent for both monomer and polymer leads to the formation of loosely crosslinked gel particles referred to as expanded network beads.[2] A monomer-soluble but polymer-insoluble solvent is used to prepare macrorecticular (MR) gel particles which are aggregates of microgels having macropores of diameter in the order of 10–100 nm.[3] The macropores facilitate the rapid adsorption and desorption of reacting species on and from the functional groups in the particles. High porosity is also advantageous to the relaxation of strain inside the particles caused by swelling and mechanical force. If polymer microspheres have their dense functional groups in the surface layer bound to crosslinked core, they will retain an efficient reactivity without relying on the macropore structure.

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Recently a method of fixing some functional groups to crosslinked polymer surface was proposed in which prepolymer gel plates were immersed in the aqueous solution of functional monomers and copolymerized with them.[4,5] Prepolymerization of a crosslinkable monomer followed by addition and co-polymerization of a hydrophilic monomer can be applied, in the suspension system, to prepare polymer microspheres having functional groups densely in the surface layer. In this study copolymer particles of diallyl phthalate with acrylic and methacrylic acid were prepared in this method and characterized.

## EXPERIMENTAL

### Materials

Diallyl phthalate (DAP, Wako Pure Chemical Co.), methacrylic acid (MAc, Tokyo Kasei Co.), and acrylic acid (AAc, Tokyo Kasei Co.) were distilled at 115°C/0.4 torr, 51°C/6 torr, and 43°C/14 torr, respectively. Benzoyl peroxide (BPO, Wako Pure Chemical Co.) was dissolved in chloroform and the solution was poured into an excess amount of methanol after filtration. The crystaline powder was dried *in vacuo*. Poly(vinyl alcohol) (PVA, Wako Pure Chemical Co., No. 163-03045, $\overline{P_n}$ = 500) was used without further purification. The degree of saponification was 91.6% which was determined by a conventional method.

### Polymerization

Polymerizations were carried out in a 500 mL round-bottom flask fitted with stirrer, thermometer, nitrogen gas inlet, and serum rubber for sampling at 80°C. In the flask 200 g of aqueous solution of PVA was bubbled with nitrogen and 10 g of DAP dissolving 0.4 g of BPO was added with a syringe. After a duration of 1, 2.5, or 4 h for prepolymerization of DAP, AAc or MAc was charged to copolymerize. Copolymerization in the system containing the comonomer from the beginning was also carried out. Polymerization systems were corded with three terms as $a$-($b$)-$c$ where $a$ is the kind of comonomer, $b$ is the duration (h) of DAP prepolymerization, and $c$ is the amount (g) of comonomer, e.g., AAc-(1)-5 and MAc-(4)-3. AAc-(0)-5 is the system in which 5 g of AAc was charged from the beginning of polymerization.

Most polymerizations were continued for 24 h and the resulting suspensions were filtrated to separate the particles from the aqueous phase. As the filtrates from DAP–MAc suspensions contain fine particles, the filtrates were centrifuged to get the transparent aqueous phase. The change in the amount of comonomer in the aqueous phase during the polymerization was examined by conductometric titration of the supernatant in the sample drawn from the reaction system at each time interval. The conversion was calculated from the weight of the solid remaining after rinsing the particles with methanol followed by drying. The composition of polymer particles was determined from elemental analysis, that is, from the hydrogen/carbon ratio in the polymer.

### Characterization of Polymer Particles

More than 200 particles were sized on the light micrographs. The number average diameter, $D_n$, and surface average diameter, $D_s$ (= $\sum D_i{}^3 N_i/\sum D_i{}^2 N_i$ where $N_i$ is the number of the particles with diameter $D_i$), were calculated as

was the dispersity of particle size, $D_s/D_n$. The surface of freeze-dried particles was observed by a scanning electron microscope JEOL JFSM-30.

To determine the total amount of carboxyl groups bound to the particles ($C_p$) and the amount of carboxyl groups in the surface layer ($C_s$), some conductometric titrations (Table I) were carried out by use of a Toa CM-2 conductometer and a Metrohm Herisau Multi-Dosimat E 415 titrator. According to Table I, for example, the direct titration of particles is abbreviated as $A$–$p$ and the back titration of suspension is as $B$–$s$. The titrations $A$ and $B$ were carried out to determine the distribution of carboxylic monomer units in the suspension whereas the titration $C$ was done to determine $C_s$.

The copolymer suspension contains both carboxylic monomer units bound to the particles and those free in the aqueous phase. As the former have less ionic conductivity than the latter, owing to less mobility, it was expected that the titration of the suspension would result in a conductometric titration curve having an intersection and the amount of both units could be determined from the titration ranges before and after the intersection, as demonstrated by Hen[6] in the titration of polymer latexes. (An example of the titration curve is shown in Fig. 1, where the abbreviations $s$–$p$ and $s$–$w$ are, respectively, the titration ranges for carboxyl groups bound to the particles and in the aqueous phase.)
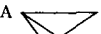
## RESULTS AND DISCUSSION

### Suspension Polymerization of DAP

The polymer particle size resulting from suspension polymerization depends on many factors, including the shape of the reactor and the agitator, the agitation rate ($G$), the volume fraction of monomer ($V$), the amount of suspension stabilizer ($C_{PVA}$), the reaction temperature, etc. There are some semiempirical equations[7,8] expressing the mean particle size as functions of $G$, $V$, the shape of agitator, etc. Narkis modified these equations to fit them to his results on suspension polymerization of unsaturated polyester beads.[9] The reported value of $n$ in $D \propto G^n$ ranges from $-1.2$ to $-2.0$. In the suspension polymerization of DAP at 80°C, $V$ 0.0427, and $C_{PVA}$ $10^{-3}$ g/g water, the $n$ was about $-1.6$ (from the data in Table II), which is close to Hopff's ($-1.5$).[7]

The effect of $C_{PVA}$ on $D$ was complex in DAP suspensions and a maximum $D$ was given at $C_{PVA}$ $1.5 \times 10^{-3}$ g/g water. This result might imply that the $C_{PVA}$ range employed by us would cover both ranges by Narkis ($D$ increased with $C_{PVA}$)[9] and by Hopff ($D$ decreased with $C_{PVA}$).[7] The particle size dispersed with

TABLE I
Titration Methods

| Titration method | Abbreviation | Sample | Abbreviation |
|---|---|---|---|
| Direct titration with NaOH | A | Suspension | $s$ |
| Back titration with HCl after immersing the sample in NaOH for 24 h | B | Particle[a] | $p$ |
| Back titration with HCl immediately after NaOH addition[b] | C | Supernatant[a] | $w$ |

[a] Separated each other from the suspension.

[b] NaOH was added in a slight excess compared with the amount of carboxyl groups expected to be near the particle surface and the titration was finished within 5 min after NaOH addition.
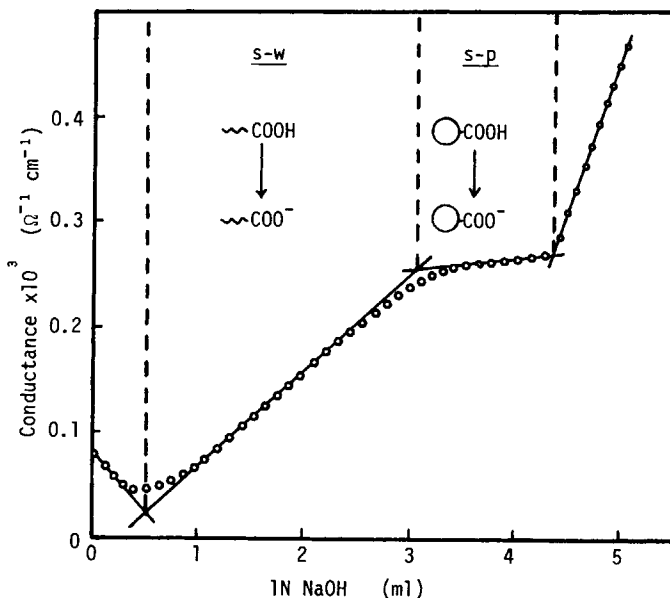
Figure 1. Representative curve obtained by the direct titration of DAP–AAc copolymer suspension: ⌇COOH, carboxyl group in the aqueous phase; O–COOH, carboxyl group bound to a particle. Sample, AAc-(4)-3 suspension 6.2g.

decreasing particle size and with increasing agitation rate. All the polymerizations mentioned hereafter were carried out under a fixed condition with respect to agitation (at 500 rpm, using a semicircular Teflon-made agitator of 6 cm diam) and $C_{PVA}$ ($5 \times 10^{-3}$ g/g water).

## Comparison of the Titration Methods

Prior to analyzing the suspension copolymerization of DAP with AAc or MAc and characterizing the resulting copolymer particles, the meaning of the values obtained by the different titration methods shown in Table I should be discussed and the most suitable titration methods to determine $C_p$ and $C_s$ must be chosen.

Two samples, AAc-(4)-3 and AAc-(4)-5, were titrated by all the methods in Table I and some other samples were titrated by a few methods. The results are shown in Table III.

TABLE II
Dependence of Poly–DAP Particle Size on Polymerization Conditions[a]

| DAP (g) | PVA (g) | Agitation rate (rpm) | $D_n$ ($\mu m$) | $D_s/D_n$ |
|---|---|---|---|---|
| 10 | 0.2 | 300 | 151 | 1.23 |
|  |  | 400 | 116 | 1.13 |
|  |  | 500 | 74 | 1.37 |
| 20 | 0.2 | 300 | 162 | 1.52 |
|  | 0.3 |  | 190 | 1.16 |
|  | 1.0 |  | 101 | 1.75 |

[a] Water 200 g, BPO–DAP 0.04 (w/w), and temperature 80°C.

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TABLE III

Amount of carboxylic Monomer Units Detected by Different Titration Methods (Percentage to the Amount of Carboxylic Monomer Charged)

</div>

| Sample | Titration Method[a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | | | | B | | | | C |
| | A-p | A-w | A-s-p[b] | A-s-w[b] | B-p | B-w | B-s-p | B-s-w | |
| AAC-(0)-5 | | | | | 46.1 | 53.0 | | | 4.68 |
| (4)-3 | 1.7 | 8.9 | 14.4 | 32.2 | 10.8 | 61.1 | 12.5 | 59.1 | 0.65 |
| (4)-5 | 2.0 | 6.3 | 6.1 | 30.3 | 31.8 | 51.9 | 38.9 | 60.2 | 1.37 |
| MAc-(0)-5 | | | | | 94.7 | 12.9 | | | 15.70 |
| (4)-5 | | | | | 64.0 | 16.4 | | | 0.52 |

[a] See Table I.
[b] See Figure 1.

## Direct Titration (A)

The amount of carboxylic monomer units detected by direct titrations were extremely small as shown in the columns of A of Table III. For example, the sum of the values in $A–p$ and in $A–w$ for AAC-(4)-3 was only about 10% of the amount of AAc charged. Such trend in the direct titration of undissociated polymeric carboxylic acid with NaOH was pointed out by Kim[10] and attributed to the tight conformation of the undissociated polymer chain. It was found, although the data are not shown here, that an increase in the ionic strength of the medium increased the amount of detected carboxyl groups to some extent.

The result obtained by direct titration of the suspension, $A–s$, is shown in Figure 1, in which two kinds of carboxyl groups—those bound to the particles and those in the aqueous phase—are easily distinguishable. But, as predicted from the effect of ionic strength mentioned above, both carboxyl groups influence each other and the amount detected for each did not correspond to their real amounts. This indicates that the Hen method is inapplicable to the determination of the distribution of ionic comonomer units in the suspension. Recently a similar result was reported by Egusa and Makuuchi[11] on the direct titration of carboxylated polymer latexes. It was concluded that $C_p$ could not be obtained from any direct titrations.

## Back Titration (B)

Back titration B seems to give more reliable results (see columns B in Table III). In the back titration of AAc-(0)-5 and MAc-(0)-5, the sum of the values in $B–p$ and in $B–w$ almost coincided with the amount of comonomer charged. In these cases, therefore, the values in $B–p$ and in $B–w$ can be referred to as $C_p$ and $C_w$ (the amount of comonomer units remaining in the aqueous phase), respectively. Strictly speaking, the carboxylic compounds in the aqueous phase consist of not only comonomers but also phthalic acid, because hydrolysis of DAP to phthalic acid during polymerization is confirmed from the UV absorption at 282 nm. The intensity of the UV absorption of the aqueous phase after 24-h copolymerization indicated that the fractions of phthalic acid were 1.4% of DAP charged in the DAP–MAc system and 2.5% in the DAP–AAc system. Therefore, the difference between the value in $B–w$ and the amount of hydrolyzed DAP might have to be referred to as the exact $C_w$, but here $C_w$s obtained neglected the amount of hydrolyzed DAP because it was too small compared to the value in $B–w$.

When the values by the back titration of the suspension ($B$–$s$) were compared with those by the back titrations of the particles ($B$–$p$) and of the supernatant ($B$–$w$) for AAc-(4)-3 and AAc-(4)-5, it was found that the values in $B$–$s$–$p$ and $B$–$s$–$w$ were close to those in $B$–$p$ and $B$–$w$, respectively. This means that the Hen method is applicable to the back titration of the suspension. Thus there is a remarkable difference between direct titration and back titration.

In some cases the sum of the values in $B$–$p$ and in $B$–$w$ were less than 100%. The tendency became more appreciable in the copolymerization system where the carboxylic monomer was added later. This phenomenon may be attributed to either or both of two cases shown below: (1) the carboxyl groups localized deeply inside the particle core cannot be neutralized in spite of immersion of the sample in NaOH for 24 h, or (2) NaOH permeates to the core and neutralizes the carboxyl groups there, but the resulting COO⁻ Na⁺ is not turned back by the back titration because the carboxyl groups in the surface layer that have been protonated by the titration interfere more permeation of HCl into the core. The back titration curve shown in Figure 2 may imply that the range $MN$ corresponds to the amount of carboxyl groups remaining unprotonated in the core after the titration. If this is the case, the range $LN$ can be referred to as $C_p$. Actually the sum of the amount of carboxyl groups calculated from $LN$ and the $C_w$ obtained from $B$–$w$ became close to the amount of carboxylic monomer charged.

The conclusions in this section are (1) the back titration of the particles does not always induce $C_p$, and (2) the most probable $C_p$ can be obtained by sub-
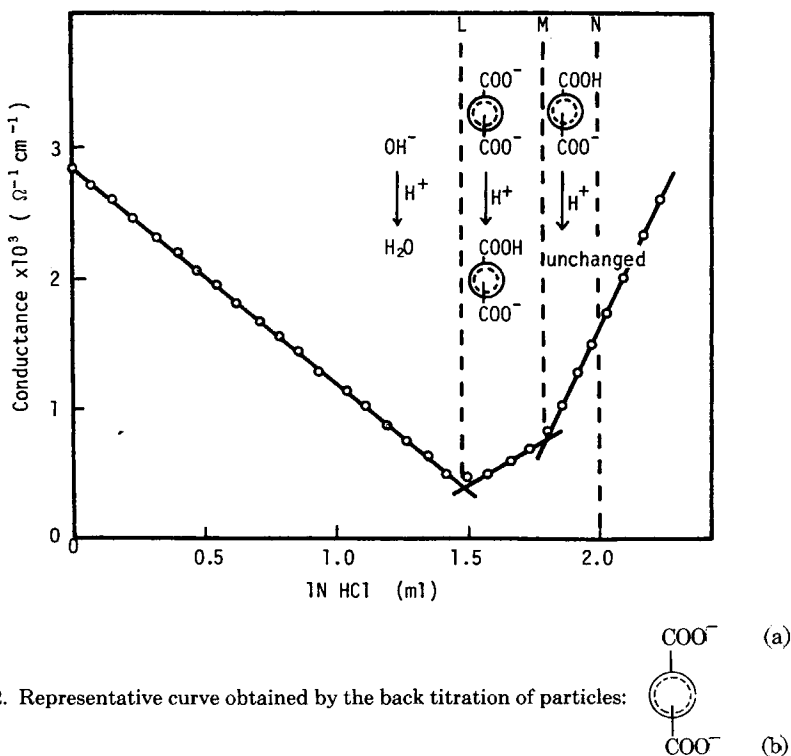


Figure 2. Representative curve obtained by the back titration of particles:

where (a) is the carboxylic ion near the particle surface, and (b) is the carboxylic ion in the core. AAc-(4)-5 particles (1.83 g) were immersed in 2.0 mL 1$N$ NaOH for 24 h and then back titrated.

stracting $C_w$ (obtained from the values in $B-w$ or $B-s-w$) from the amount of comonomer charged.

### Rapid Back Titration (C)

In addition to $C_p$, the amount of carboxylic monomer units on the particle surface is needed to characterize the particles. But the particle surface cannot be well defined because there is no distinct boundary between the surface and interior of the particles.

In the study on the preparation of polymer plates having functional groups in their surface layer, it was reported that MAc diffused into 60% prepolymerized DAP gel plate up to the depth of 120 $\mu$m and copolymerized there.[4] The depth was determined by staining the cross-section of the plate with methylene blue. The thickness cited above is comparable with the size of our particles. In the same article, the surface density of carboxyl groups on the plate was determined by flame photometry by which the amount of $Na^+$ released from the on-surface COONa groups was measured after the plate was immersed in HCl in a short time. By reference to this method, the amount of carboxyl groups determined by a rapid back titration (C) was defined as $C_s$. Some results are shown in Table III and the details will be discussed later. It would be noteworthy that the values were in the same order with those for gel plates mentioned above.

### Suspension Copolymerization

Suspension homopolymerization of DAP proceeds slowly at 80°C as shown in Figures 3 and 4. When AAc or MAc was added to the suspension of partially polymerized DAP, the conversion curves jumped up immediately. The trend of jumping was especially remarkable in DAP–MAc copolymerization. It was found, from analysis of the cumulative copolymer composition, that not only does
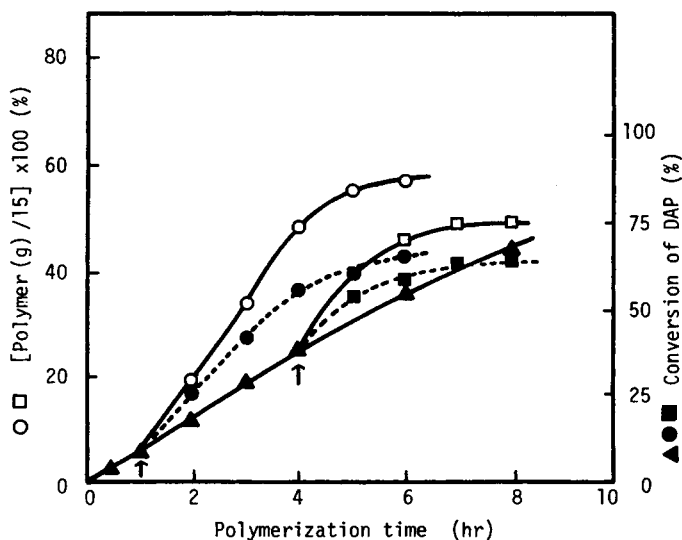


Fig. 3. Time–conversion curves of DAP (10 g)–AAc (5 g) copolymerization: (O, □) total conversion in copolymerization where comonomer was charged at the point marked as ↑; (▲, ●, ■) conversion of DAP.

Fig. 4. Time–conversion curves of DAP (10 g)–MAc (5 g) copolymerization: (○, □) total conversion in copolymerization where comonomer was charged at the point marked as ↑; (▲, ●, ■) conversion of DAP.
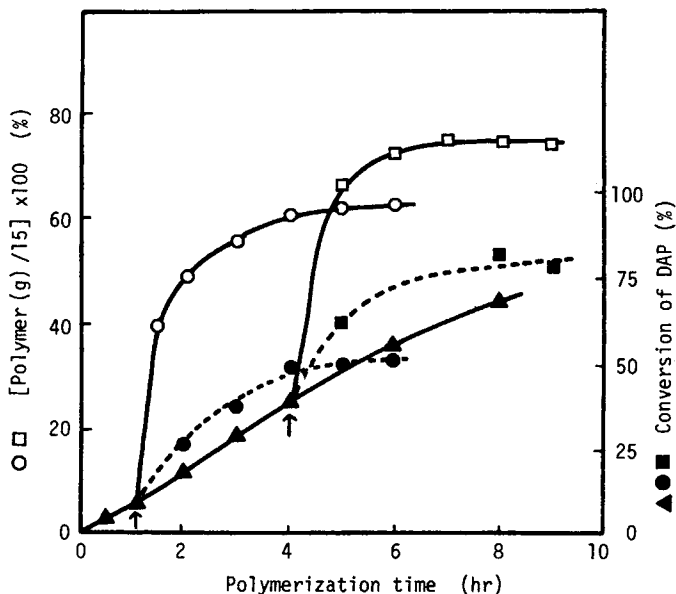
the conversion of AAc or MAc increase rapidly after comonomer addition and levels off soon afterward but also that of DAP (shown by dotted lines in Figs. 3 and 4). The values of $C_w$ measured by the titration $B-w$ are also shown in Figure 5 as a function of copolymerization time. The monomer ratio in the particles
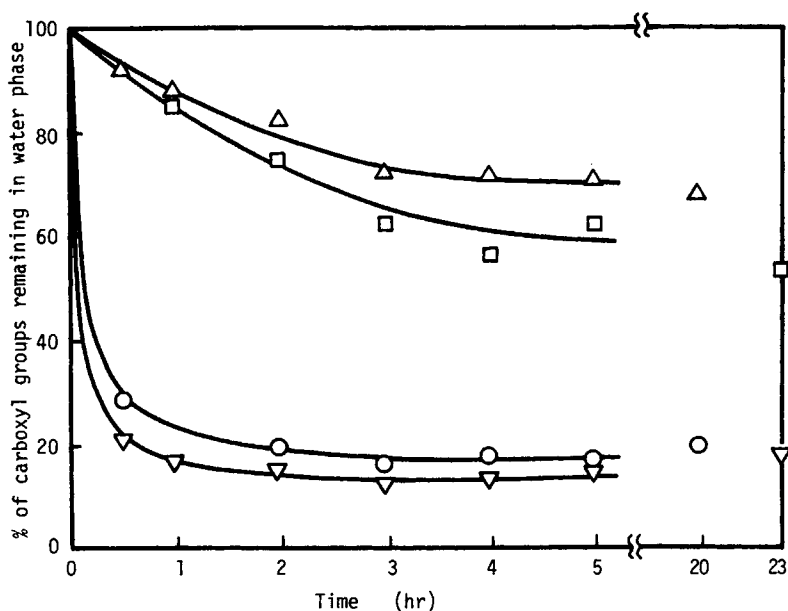


Fig. 5. Amount of carboxyl groups in the aqueous phase as a function of copolymerization time counted from comonomer charge:  AAc (□, △):  DAP prepolymerization time of 1h and 4h, respectively.  MAc (▽, ○):  DAP prepolymerization time of 1h and 4h, respectively.

TABLE IV
Kinetic Analysis of Suspension Copolymerization of DAP with Comonomer Added After Delay

| System | Amount of Comonomer Diffusable into Particles Just After Charged (g)[a] | $d[DAP]/d[comonomer]$[b] | |
|---|---|---|---|
| | | Calculated[a] | Experimental |
| AAc-(1)-5 | 0.103 | 1.41 | 1.36 |
| (4)-5 | 0.063 | 1.35 | 0.60 |
| MAc-(1)-5 | 0.36 | 0.20 | 0.18 |
| (4)-5 | 0.26 | 0.19 | 0.10 |

[a] Calculated using the following constants: partition coefficient of carboxylic monomer between DAP and water, 0.47 for AAc and 1.99 for MAc.[5] Monomer reactivity ratio $r_1 = 0.0443$ and $r_2 = 19.1$ for DAP–AAc, and $r_1 = 0.0209$ and $r_2 = 44.1$ for DAP–MAc.
[b] Composition of copolymer formed instantaneously after comonomer charge.

at each instant was calculated from $C_w$, the partition coefficient, and the conversions of monomers. In the calculation the partition coefficients measured by Ohtsuka, Kaneko, and Takami[4] at 90°C were used. (Judging from their data measured at varied temperatures, the difference in the temperature by 10°C seems to have little effect on the partition coefficient.[5]) By substituting the monomer ratio and monomer reactivity ratio (see in Table IV) into the Mayo–Lewis equation, the composition of instantaneously formed polymer was obtained and the results are shown in Table IV. According to the table, the copolymerization seems to start in the manner obeying the Mayo–Lewis equation when AAc and MAc were charged to less prepolymerized DAP suspension. On the other hand, when the comonomers are charged after an extensive prepolymerization of DAP, the succeeding copolymerization is not ideal from its start. In the intermediate stage of copolymerization, regardless of the timing of comonomer charge, the comonomers polymerize more preferentially than expected.

Figures 3 and 5 indicate that the leveling off of AAc polymerization is attributed to no further diffusion of AAc from the aqueous phase to the particles despite a significant amount of AAc remaining in the aqueous phase. It is likely that the formation of an AAc unit-rich domain near the particle surface depresses further supply of AAc to the particles. According to Table V, not only does the absolute value of $C_p$ increase with increasing comonomer charge but also the ratio of $C_p$ to the amount of comonomer charged. This might mean that the ability for the surface layer to depress the diffusion of AAc is not so strong.

TABLE V
Dependence of Distribution of AAc Units in Copolymer Suspension on Reaction Conditions[a]

| AAc (g) | Duration of DAP prepolymeriza- tion (h) | $\dfrac{C_p}{\text{AAc charged}}$ (%) | $\dfrac{C_s}{\text{AAc charged}}$ (%) | Apparent Surface Density of AAc Units (unit/A$^2$) |
|---|---|---|---|---|
| 1 | 4 | 7.0 | 0.59 | 0.3 |
| 3 | 4 | 39.9 | 0.65 | 0.5 |
| 5 | 0 | 47.0 | 4.68 | 22.6 |
| | 1 | 47.0 | 3.75 | 15.1 |
| | 2.5 | 50.0 | 1.73 | 9.0 |
| | 4 | 44.0 | 1.37 | 5.6 |
| 7 | 4 | 56.8 | 2.16 | 12.8 |

[a] DAP–BPO–H$_2$O = 10/0.4/200 (in g) at 80°C.

A less hydrophilic comonomer, MAc, can permeate to the particles more easily than AAc as shown in Figure 5. The diffusion rate of comonomers depends partially on the density of crosslinking. AAc and MAc can diffuse faster into the particle when they are added to the less prepolymerized, that is, less cross-linked, particle.

The time–conversion curves of DAP in the copolymerization systems intersect the conversion curve of DAP homopolymerization several hours after addition of comonomers. The time for DAP polymerization to level off apparently coincides with the time for comonomers to be consumed in the particles. Therefore, the leveling off seems to result from trapping of radicals in poly-AAc or poly-MAc rich domain or from a decrease in the diffusion rate of DAP owing to precipitation of poly-AAc or poly-MAc rich chains in the partially crosslinked DAP polymer–monomer system.

The particle diameter ranged from 70 to 80 $\mu$m and the dispersity, $D_s/D_n$, ranged from 1.3 to 1.4 regardless of the reaction conditions in DAP–AAc co-polymerization. In DAP–MAc copolymerization the particle diameter was about 10% larger than that of DAP–AAc copolymerization.

## Comonomer Unit Distribution and Surface Structure

The values of $C_s$ and the apparent surface density of carboxylic monomer units calculated from $C_s$ are shown in Tables V and VI. According to them, a larger amount of comonomer units were localized in the surface layer when they were added earlier to the polymerization system. This result is explained as follows: The comonomers AAc and MAc, which are soluble in DAP, diffuse into the partially prepolymerized DAP phase and then polymerize at a higher rate compared with DAP. Hydrophilic monomer unit-rich polymer chains formed in this manner lose the compatibility with DAP phase. If crosslinking is less developed, the hydrophilic polymer chain can phase-separate from the DAP phase and diffuse into the particle surface. Therefore, earlier addition of co-monomer to the DAP particles results in the formation of the polymer particles having more conomoner units in the surface layer.

The comonomer unit distribution relates to the distribution of crosslinking, that is, comonomer unit-rich shell corresponds to loosely crosslinked shell. Such shell structure is expected to permit some cationic molecules of relatively high molecular weight to diffuse into it. A cationic dye, methylene blue, was adsorbed

TABLE VI
Dependence of Distribution of MAc Units in Copolymer Suspension on Reaction Conditions[a]

| MAc (g) | Duration of DAP prepolymerization (h) | $\dfrac{C_s}{\text{MAc charged}}$ (%) | Apparent Surface Density of MAc (unit/A$^2$) |
|---|---|---|---|
| 1 | 4 | 0.3 | 0.5 |
| 3 | 4 | 0.9 | 2.9 |
| 5 | 0 | 15.7 | 70 |
| | 1 | 9.4 | 33 |
| | 2.5 | 1.0 | 3.0 |
| | 4 | 0.5 | 1.7 |
| 7 | 4 | 2.6 | 18 |

[a] DAP–BPO–H$_2$O = 10/0.4/200 (in g) at 80°C.

TABLE VII
Relation between Adsorption of Dye and On-Surface Carboxylic Monomer Units

| Sample | $C_p$ | $C_s$ | Methylene blue adsorbed (mmole dye/g particle) |
|---|---|---|---|
| | (mmole monomer/g particle) | | |
| AAc-(0)-5 | 2.61 | 0.262 | 0.92 |
| (4)-5 | 2.09 | 0.007 | 0.092 |
| MAc-(0)-5 | 3.67 | 0.606 | 2.24 |
| (4)-5 | 3.56 | 0.019 | 0.013 |

onto the various particles prepared. The dependence of the amount of the adsorbed dye on the particle structure is shown in Table VII and it supported the above-mentioned speculation. Namely, the particles having a larger $C_s$ adsorbed much more dye molecules although a quantitative analysis could not be done because the definition of surface layer was obscure.

Pictures of the particle surface by a light microscope and a scanning electron microscope are shown in Figures 6 and 7. The light micrographs of MAc-(0)-5 and MAc-(1)-5 particles appear far differently than others. The particles are opaque because of diffused reflection from the rough surface. The detailed surface structure were observed by SEM, which indicates that earlier addition of MAc to a DAP polymerization system results in the formation of the particles having rough surfaces. The rough surfaces are attributed to hydrophilic monomer unit-rich polymers localized on the surfaces. Similar rough surfaces were also observed on the micrographs of DAP–MAc copolymer gel plates.[4] In the case of DAP–AAc copolymer particles, the surface was much smoother than that of DAP–MAc particles even if AAc was added at an early stage of polymerization. The scanning electron micrographs in Figure 7 show that some small humpy particles formed on each large DAP–AAc particle regardless of the polymerization condition.
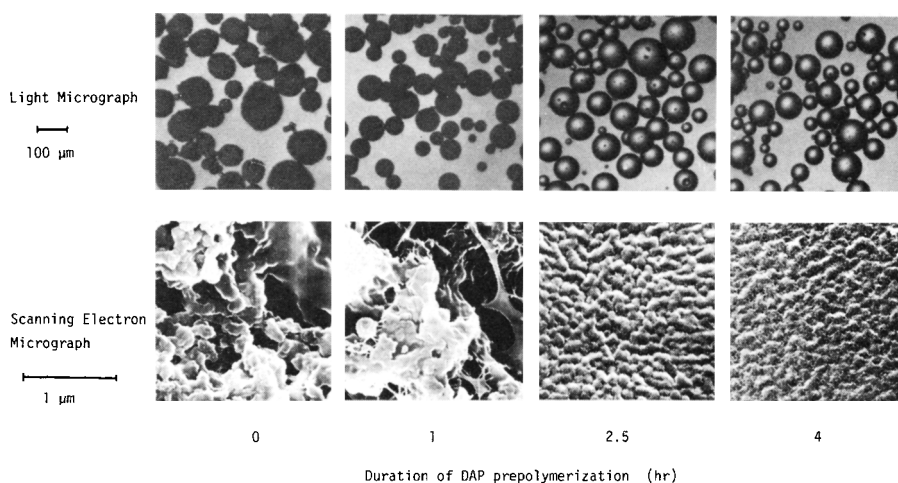


Fig. 6. Micrographs of DAP–MAc copolymer particles and their surface: polymerization condition, DAP–MAc–water = 10/5/200 (in g) at 80°C.
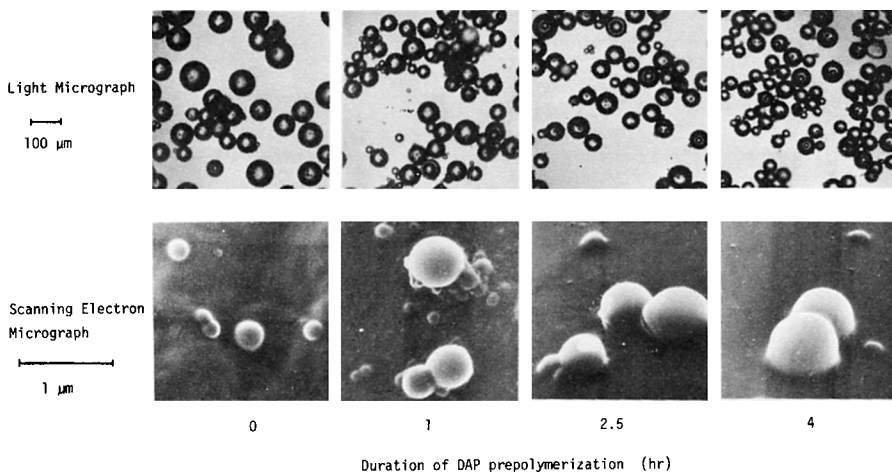
Fig. 7. Micrographs of DAP–AAc copolymer particles and their surface:  polymerization condition, DAP–AAc–water = 10/5/200 (in g) at 80°C.

## CONCLUSIONS

Diallyl phthalate (DAP) was suspension copolymerized with acrylic acid (AAc) and methacrylic acid (MAc) to prepare functional gel particles.  AAc was not copolymerized to high conversion because only a limited amount of AAc could diffuse into the particles.  Kinetic analysis suggested that the copolymerization did not proceed in an ideal manner.

The apparent surface density of carboxyl groups on the gel particles ranged from 0.3 to 70 units/$A^2$ or from 0.003 to 0.6 meq/g particle, and the distribution of comonomer units in the particles depended mainly on the mode of monomer charge.  When the comonomer was charged at an earlier stage of polymerization, the resulting particles had the surface layer composed of comonomer-rich polymer.  Such particles had rough surface structures and they adsorbed much larger amounts of cationic dye molecules than the particles in which comonomer units were distributed broadly.

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