

Novel Synthesis of Gel Capsule by Esterification of Poly(acrylic acid) Gel

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ABSTRACT: To synthesize a novel gel capsule containing a hydrophobic shell and hydrophilic core portions, we investigated the esterification of poly(acrylic acid) gel-1,8-diazabicyclo[5,4,0]undec-7-ene salt (DAA) with alkyl bromides. The esterification of DAA with benzyl bromide proceeded almost quantitatively in *N*-methyl-2-pyrrolidone (NMP) from the surface, although small amounts of carboxylic acids were produced as side products. The reaction gave a new gel capsule consisting of a hydrophilic unreacted core and hydrophobic esterified shell, and finally afforded poly(benzyl acrylate) gel. Reactions of DAA with alkyl bromides were carried out under various conditions, and analyzed kinetically. The observed reaction rate markedly affected the molecular size of the alkyl halides and solvents rather than reactivity of their combinations. This suggests that the overall reaction depends markedly on diffusion rate of alkyl bromides and solvents through the reacted shell layer. The thickness of the shell layer was easily controlled by reaction conditions. The swelling of the gel capsule and release of Rose-Bengal from the gel capsule were studied. The results suggested that the structure of the shell layer controls properties such as the swelling rate, burst time, and releasing rate of chemicals.

KEY WORDS Gel Capsule / Esterification / Poly(acrylic acid) / 1,8-Diazabicyclo[5,4,0]undec-7-ene / Chemical Release /

Neutralized poly(acrylic acid) gels are famous as superabsorbent gels.¹ The gels are able to soak up to one thousand times their own weight of pure water. Applications such as disposal diapers have been developed based on this swelling. Also, they store many water-soluble chemicals. However, water-swollen gels are easily broken, although the surface coating and surface crosslinking with glycerin² or ethylene glycol diglycidyl ether³ are performed to improve swelling rate. Therefore, they are not used widely for storage and release of chemicals. The synthesis of 100 μm order size of core-shell type particles; hydrophilic neutralized poly(acrylic acid) gels covered with hydrophobic poly(alkyl acrylate) shell layer has been reported by two-stage reverse suspension polymerization.⁴ This hydrophobic shell layer would not only reinforce the gel, but also control the chemical release and occlusion. However, the boundary between core and shell does not have enough strength to cope with strong swelling pressure of the neutralized poly(acrylic acid) core, and the gel breaks easily when swollen in water.

Recently, we investigated a new reinforced core-shell type gel "gel capsule" composed of a continuous network between a hydrophilic core and hydrophobic shell parts. The gel capsule would be more durable for swelling or deswelling than the normal core-shell type gel consisting of two distinct networks of core and shell. The gel capsule can be synthesized according to two synthetic routes. One is the selective thermal acid-catalyzed deesterification of internal poly(*t*-butyl methacrylate) gel.⁵ The other is selective esterification of external poly(carboxylic acid) gels. The esterification of linear poly(carboxylic acid) has been investigated by many methods.^{6,7} In these methods, the reaction of poly(carboxylic acid) with an alkyl halide is suitable for chemical modification using 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as an acid acceptor, because quantitative esterification is achieved by this method in a short time under mild conditions.^{7c,f}

Previous communication⁸ reports that heterogeneous esterification of DBU salt (DAA) of poly(acrylic acid) gel with alkyl bromide proceeds in an aprotic polar solvent from the surface into the interior to give the corresponding poly(alkyl acrylate) gel through the gel capsule. Reactions of DAA with alkyl chlorides also afford gel capsules,⁹ and can be simulated using the homogenous model.¹⁰ However, the reaction mode of DAA with alkyl bromide is very different from that with alkyl chloride,⁹ and the detailed reaction mechanism has not been determined.

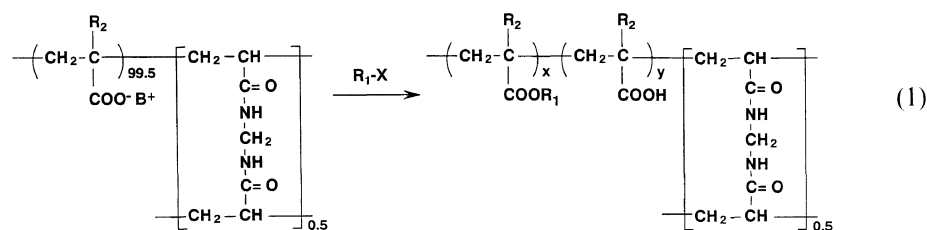
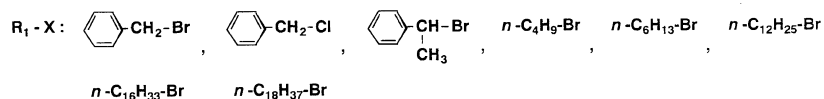
This paper reports the esterification of DBU, triethylamine (TEA), and sodium salts of poly[(meth)acrylic acid] gel with alkyl bromides in a solvent to determine the reaction mechanism (Scheme 1). Esterification from the outer gives a gel capsule consisting of a hydrophilic unreacted core and a hydrophobic esterified shell (Scheme 2). We discuss the swelling of the obtained gel capsule and release of chemicals from the gel.

EXPERIMENTAL

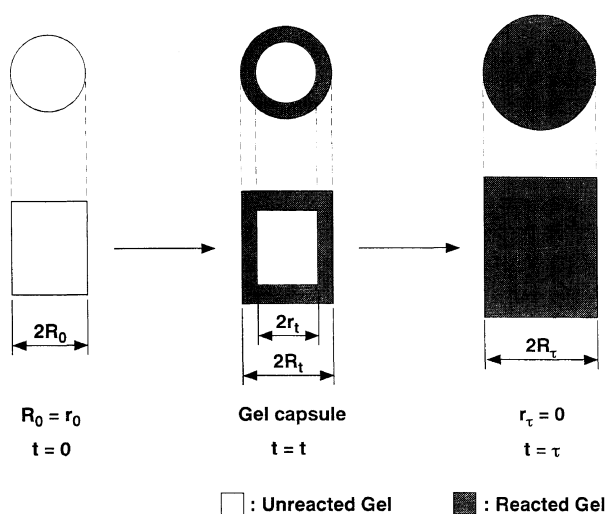
Materials

Monomers and solvents were distilled prior to use. Commercial alkyl halides were used as purchased. *N,N'*-methylenebisacrylamide, sodium chloride, DBU, TEA, tetrabutylammonium bromide (TBAB), and tetraethylammonium bromide (TEAB) were used without further purification. Cylindrical DAA (length and diameter: 3, 5, and 7 mm) was prepared as reported previously.^{8,9} The neutralization of DAA was 98 % calculated by the back-titration using 0.1*N* aqueous HCl solution-0.05*N* aqueous NaOH solution. Poly(methacrylic acid) gel-DBU salt (DMA), poly(acrylic acid) gel-sodium salt (NAA), and poly(acrylic acid) gel-TEA salt (TAA) were prepared by the neutralization of the corresponding poly(carboxylic acid) gels with bases in the same way.

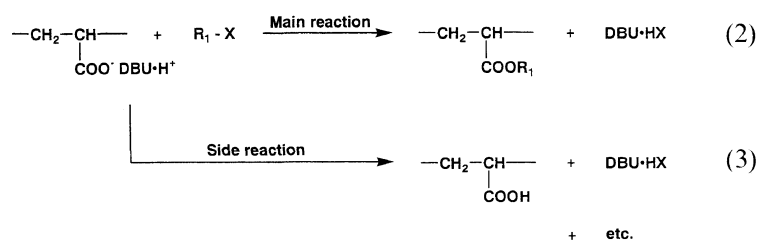
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DAA ($\text{B}^+ = \text{DBU} \cdot \text{H}^+$, $\text{R}_2 = \text{H}$), TAA ($\text{B}^+ = \text{TEA} \cdot \text{H}^+$, $\text{R}_2 = \text{H}$),DMA ($\text{B}^+ = \text{DBU} \cdot \text{H}^+$, $\text{R}_2 = \text{CH}_3$), NAA ($\text{B}^+ = \text{Na}^+$, $\text{R}_2 = \text{H}$)

Scheme 1. Esterification of poly(acrylic acid) salts with alkyl halides.



Scheme 2. Changes in shape of gel in reaction.



Scheme 3. Reaction mechanism of DBU salt of carboxylic acid with alkyl halide.

Apparatus

The reaction was recorded by a SONY model DCR-VX 1000 digital video camera. IR spectra were obtained on a JASCO model IR-700 spectrophotometer. UV spectra were measured on a Shimadzu model UV 2100S spectrophotometer.

Esterification of DAA and Measurement

A typical esterification was as follows. Benzyl bromide solution in *N*-methyl-2-pyrrolidone (NMP) (1.0 mol L^{-1} , 50 mL) was charged into a 50 mL cylindrical cell in a water bath at 80°C . To the solution was added a sample of DAA (0.301 g). The gel began swelling and divided into a swollen shell and unswollen core. The reaction was recorded by a digital video camera. The radii of the shell and core, R_t and r_t , after t min were measured by

microcomputer imaging. After the disappearance of the core, the esterified gel was washed with acetone by a Soxhlet extractor and dried *in vacuo* at 110°C until constant weight. The weight of the esterified gel was 0.209 g. The gel was dipped in TEA solution in tetrahydrofuran (THF) (10 mmol L^{-1} , 25 mL) at room temperature for 24 h. Free carboxylic acid in the gel was determined by neutralization titration of the filtrate with 0.01 N aqueous HCl solution. Esterification calculated from the back-titration and from the change of weight before and after the reaction was 91% and 92%, respectively.

Chemical Release from the Gel Capsule

The gel capsule was dipped into a solution (0.1 mmol L^{-1}) of Rose-Bengal in methanol-acetone mixture (1 : 1)

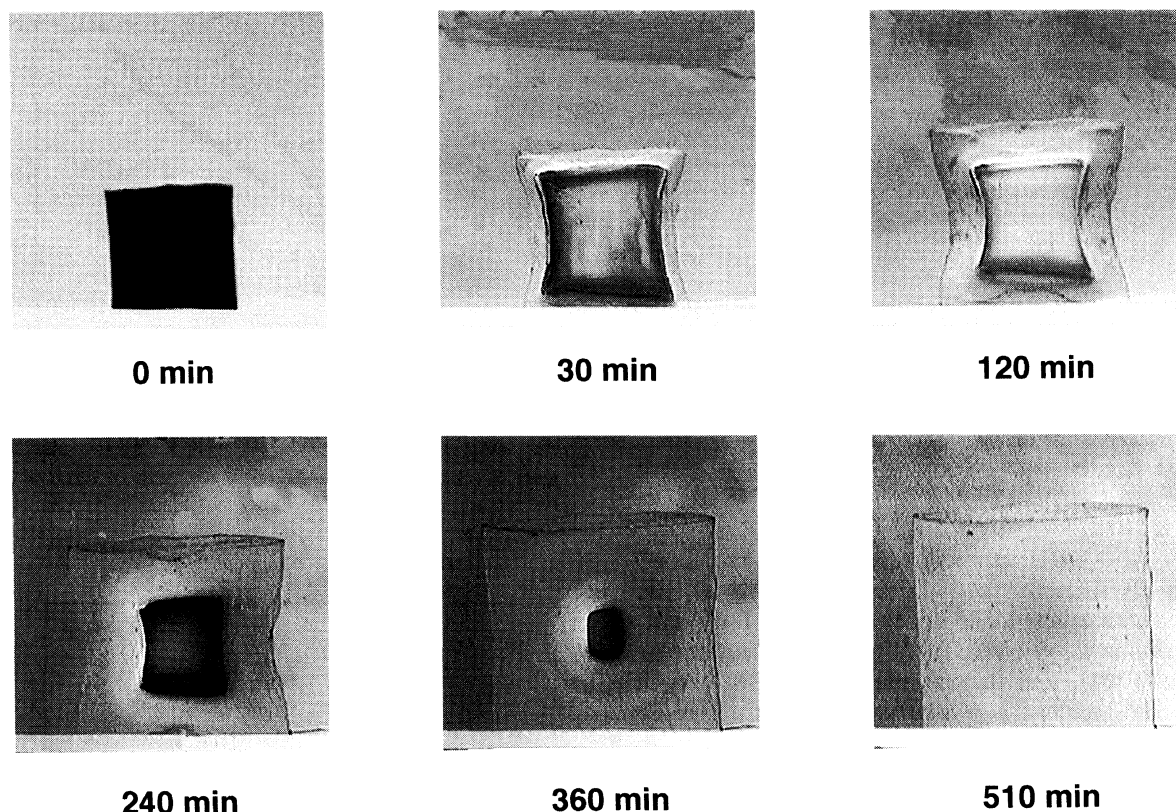


Figure 1. Typical photographs in reaction of DAA with benzyl bromide in NMP at 80°C.

and allowed to swell for 1 day at 30°C. After drying, the shell layer was selectively washed with acetone by a Soxhlet extractor and dried again. The sample was placed in 300 mL water or aqueous 1 wt% NaCl solution at 50°C. A_t , absorbance of the solution at 548 nm after t min, was measured by a UV spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of Gel Capsule by Esterification of Poly(acrylic acid) Gel

Salts of poly(acrylic acid) gel with DAA, NAA, and TAA were prepared by the copolymerization of acrylic acid with 0.5 mol% of *N,N'*-methylenebisacrylamide in Teflon tubes. Neutralization of the resulting gel was conducted with excess bases such as DBU, sodium hydroxide, and TEA in methanol. DMA was prepared from reaction of poly(methacrylic acid) gel with DBU. DAA did not swell in usual solvents except water, alcohols, and dimethyl sulfoxide (DMSO). When cylindrical DAA (length the same as diameter; 7 mm) was placed in NMP containing excess benzyl bromide at 80°C, swelling occurred, and DAA was divided into a swollen shell and unswollen core (Figure 1). The shell expanded with decreasing radius (r_i) of the core. The cylindrical shape of core was similar to the original until high conversion. The radius (R_i) of shell increased gradually for a long time after the core disappeared. The resulting shell layer did not swell in water or methanol, although the hydrophilic core swelled well in these solvents. The IR spectrum of the shell part is shown in Figure 2. The spectrum showed strong absorption of ester at 1733 cm^{-1} (C=O of ester, stretching), and wide absorption at $2500\text{--}3500\text{ cm}^{-1}$ and discernible shoulder

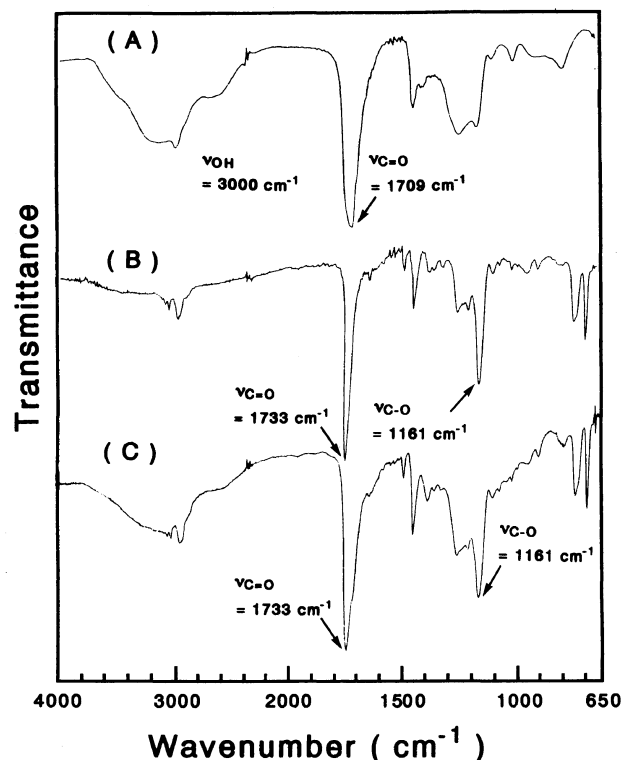


Figure 2. IR spectra. (A) soluble poly(acrylic acid); (B) soluble poly(benzyl acrylate); (C) poly(benzyl acrylate) gel.

near 1710 cm^{-1} based on free carboxylic acid. This seems to agree with that of poly(benzyl acrylate) containing small amounts of acrylic acid unit. The reaction of DAA with an alkyl halide can be explained by Scheme 3. When excess alkyl halide and DBU were used, esterification of

Table I. Reactions of poly(acrylic acid) salt with alkyl bromides in NMP at 80°C

Poly(acrylic acid)	<i>R</i>	Conv. ^a	Conv. ^b
		%	%
DAA	Benzyl bromide	91	92
DAA	1-Phenylethy bromide	83	81
DAA	<i>n</i> -Butyl bromide	94	96
DAA	<i>n</i> -Hexyl bromide	90	92
DAA	<i>n</i> -Dodecyl bromide	89	90
DAA	<i>n</i> -Hexadecyl bromide	93	89
DAA	<i>n</i> -Octadecyl bromide	92	90
NAA	Benzyl bromide + TEAB ^c	75	—
NAA	Benzyl bromide + TBAB ^c	72	—
TAA	Benzyl bromide	85	82

^a Obtained by neutralization analysis. ^b Obtained by weight change. ^c 4 mmol of tetraalkylammonium bromide was used as PTC.

carboxylic acid-DBU salt with alkyl halide proceeded quantitatively since the resulting by-product carboxylic acid reacts with excess DBU to reproduce the DBU salt. This reaction was carried out in the presence of equimolar amount of DBU, and thus a small amount of acrylic acid unit remained in the gel as a by-product. Carboxylic acid in the reacted gel was determined by back-titration using TEA solution-aqueous HCl solution (Table I). Esterification of gels obtained from the complete reaction was calculated from change of weight before and after reaction. Esterification of gels calculated by both methods was almost the same, and the reaction gave gels with more than 90 mol% esterification, except for the reaction with secondary 1-phenylethyl bromide. Esterification is thus very high in the swollen parts, and the shell is the corresponding poly(alkyl acrylate) gel with small amounts of carboxylic acids. The reaction proceeded gradually from the surface of DAA to the interior to give an amphiphilic core-shell. The reaction mode was different from that of DAA with alkyl chloride reported previously.⁹

The reaction has three rates; intrinsic esterification rate of DBU salt of carboxylic acid with alkyl bromide, diffusion rate of alkyl bromide through a swollen part, and diffusion rate of alkyl bromide through an unswollen part. The diffusion rate through the swollen part is much faster than that through an unswollen part in the system. Reactions of carboxylic acids-DBU salts with alkyl bromides are very fast in aprotic polar solvents.⁷ Reactions of DBU salts of benzoic acid and linear poly(methacrylic acid) with alkyl bromide proceeded quantitatively at 30°C within 10 min and 1 h.^{11,7c,f} Only the part with high esterification swells in the solvent. The rate of intrinsic esterification of DAA with alkyl bromide and diffusion rate through a swollen part are thus much faster than the diffusion rate through an unswollen part, and the reaction zone is restricted to the boundary between the swollen part and the unswollen part as shown in Scheme 2. This is similar to the unreacted-core model well-known for burning of cokes and roasting of ores,¹² and is different from that of DAA with less reactive alkyl chloride affected strongly by the diffusion through an unswollen part⁹ and simulated by the homogenous model.¹⁰ The unreacted-core model has the following two rate-controlling steps.

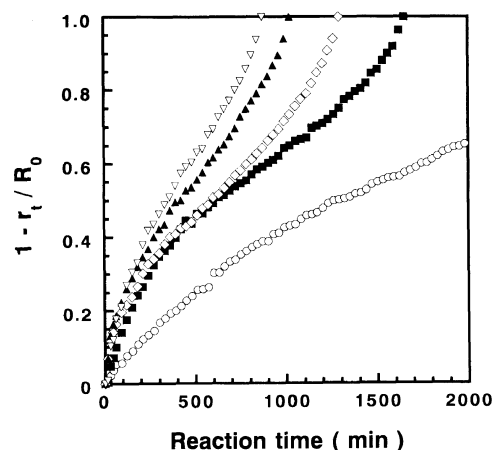


Figure 3. Effects of temperature on reactions of DAA with benzyl bromide in NMP at [▽] 80°C; [▲] 70°C; [◇] 60°C; [■] 50°C; [○] 30°C.

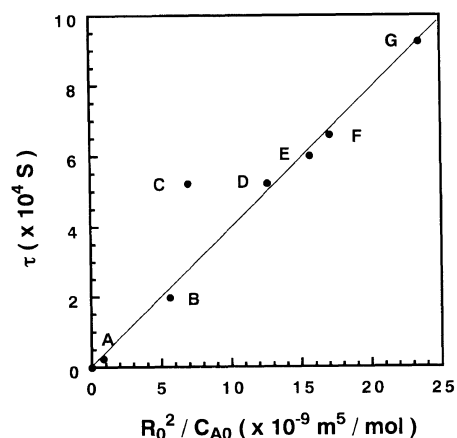


Figure 4. Relations between R_0^2/C_{A0} and τ in NMP at 80°C.

Step 1. When the esterification rate is much slower than the diffusion rate through the swollen part, the rate-controlling step is the intrinsic esterification. Reaction time (t) is proportional to decreasing of the radius of the core part as shown in eq 4, where the time for complete reaction of the gel is τ .

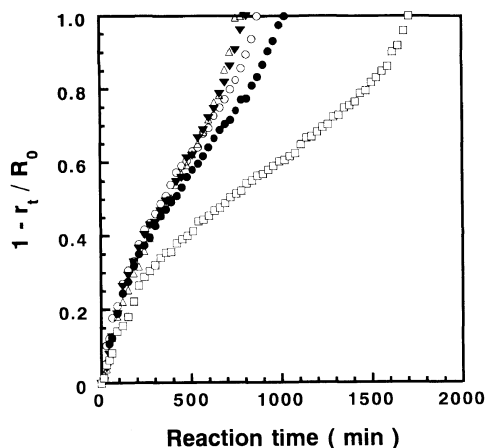
$$t/\tau = 1 - r_t/R_0 \quad (4)$$

Step 2. When the esterification rate is much faster than the diffusion rate through the swollen part, the resistance to diffusion through a swollen part controls the reaction. The observed $1 - r_t/R_0$ is larger than t/τ at the initial reaction, because diffusion resistance of the shell layer increases with thickness.

Esterification of DAA was carried out under various conditions. The rate of disappearance of the core part increased with reaction temperature (Figure 3). The observed $1 - r_t/R_0$ was larger than t/τ at the initial reaction. If a gel is considered an infinite cylinder and intrinsic reaction is the rate-controlling step of the unreacted-core model, τ exhibits eq 5, where C_{A0} is the initial concentration of alkyl halide.^{12b} However, τ did not agree with eq 5, but was proportional to R_0^2/C_{A0} except for C (Figure 4). A, B, C, D, E, F, and G in this figure show the conditions of the experiment (Table II). C shows that the concentration of benzyl bromide as

Table II. Reactions of DAA with alkyl bromides in NMP at 80°C

Sample	A	B	C	D	E	F	G
R_0/mm	0.90	2.37	3.54	3.56	3.56	3.58	3.58
$C_{A0}/\text{mol L}^{-1}$	1.00	1.00	2.00	1.00	0.75	0.66	0.50
$\tau \times 10^4/\text{S}$	0.25	1.98	5.22	5.22	6.00	17.09	23.46

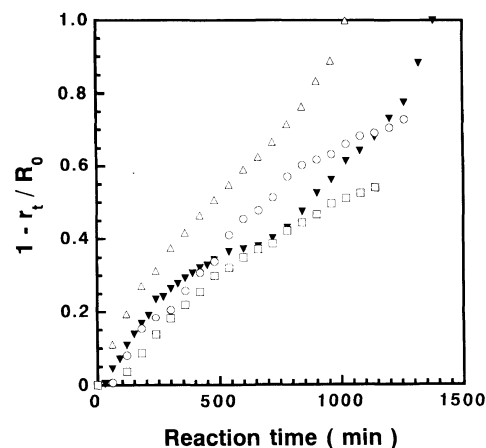
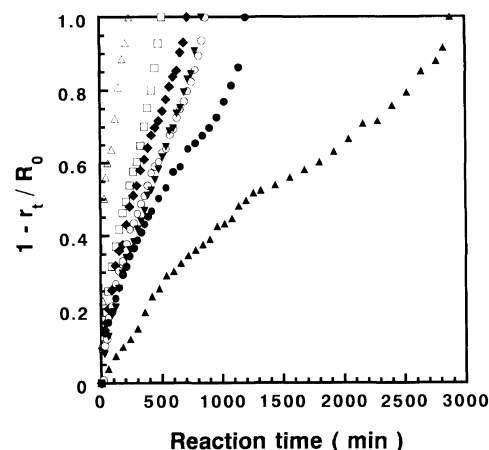

Figure 5. Reactions of DAA with various alkyl halides in NMP at 80°C. [Δ] *n*-butyl bromide; [∇] *n*-hexyl bromide; [\circ] benzyl bromide; [\bullet] benzyl chloride; [\square] 1-phenylethyl bromide.

more than 20 vol% and so high that the solution was not regarded as NMP. Intrinsic esterification is thus not the rate-controlling step. This relation (eq 6) holds when the diffusion through the shell layer is the rate-controlling step of the unreacted-core model for unchanging shell size.^{12b} This cannot mean directly that the diffusion through the swollen part is the rate-controlling step because an external diameter of shell layer increased during the reaction and the diffusion constant was not uniform in the swelled layer. However, the reaction is strongly affected by mass transfer through the swollen part. Under these conditions, the observed reaction rate is associated with molecular size of the used alkyl bromide or solvent.

$$\tau \propto \frac{R_0}{C_{A0}} \quad (5)$$

$$\tau \propto \frac{R_0^2}{C_{A0}} \quad (6)$$

The reaction was carried out with various alkyl halides such as benzyl bromide, *n*-butyl bromide, *n*-hexyl bromide, and 1-phenylethyl bromide in NMP (Figure 5). The reaction of DAA with benzyl bromide was completed a little more slowly than that with *n*-butyl bromide and *n*-hexyl bromide, although benzyl bromide showed a higher reactivity than the other alkyl bromides in the corresponding homogeneous esterification. Bulky 1-phenylethyl bromide showed much lower reactivity than benzyl bromide. The esterification of DAA was studied with various *n*-alkyl bromides containing long alkyl chains such as *n*-decyl bromide, *n*-hexadecyl bromide, and *n*-octadecyl bromide, which would show almost the same reactivity in the intrinsic esterification (Figure 6). The exact τ was not detected in the reaction of DAA


Figure 6. Reactions of DAA with *n*-alkyl bromides. [Δ] *n*-hexyl bromide; [∇] *n*-dodecyl bromide; [\circ] *n*-hexadecyl bromide; [\square] *n*-octadecyl bromide. ^a $C_{A0} = 0.5 \text{ mol L}^{-1}$.

Figure 7. Reactions of DAA with benzyl bromide in various solvents at 80°C. [Δ] acetonitrile; [\square] DMF; [\blacklozenge] DMAc; [\circ] NMP; [\bullet] DMSO; [\blacktriangledown] nitrobenzene; [\blacktriangle] 1,4-dioxane. ^a The reaction was carried out at 70°C.

with *n*-hexadecyl bromide and *n*-octadecyl bromide because the gels with high esterification floated on the solvent. From the figure, τ can be estimated to increase with alkyl chain length of alkyl bromide. The reaction may thus depend on the steric hindrance of alkyl bromides. Reaction with benzyl bromide was carried out at 80°C in various solvents (Figure 7). The reaction was very fast when performed in acetonitrile at 70°C. The rate increased nearly with decreasing molecular size of solvent in following order; Acetonitrile > *N,N*-dimethylformamide (DMF) > *N,N*-dimethylacetamide (DMAc) > NMP. Therefore, the reaction of DAA with alkyl bromides is strongly affected by the molecular size of alkyl bromides and solvents rather than intrinsic reactivity of their combinations. This means that the reaction depends markedly on the diffusion of the alkyl bromide solution in the swollen part.

Esterification with benzyl bromide was carried in NMP at 80°C using other salts of poly(acrylic acid) such as TAA and NAA (Figure 8). The reaction of TAA was slower than that of DAA. Similar results were observed in homogeneous esterification reactions such as the polycondensation of dicarboxylic acids with dihalides¹¹

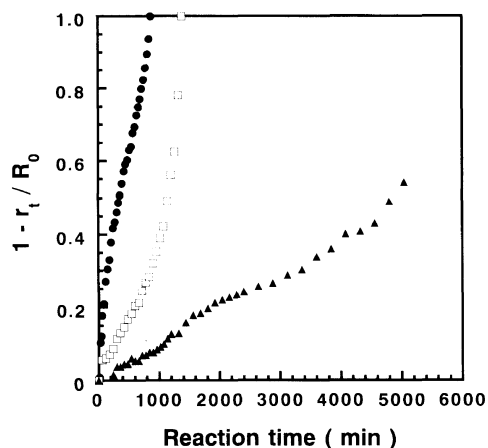


Figure 8. Esterification of TAA and NAA with benzyl bromide in NMP at 80°C. [●] DAA; [□] TAA; [▲] NAA.^a
^a 4 mmol of TBAB was used as a PTC.

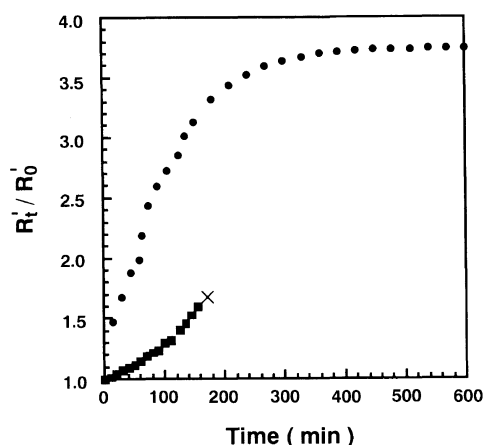


Figure 9. Swelling curves of gels in water at 50°C. [●] DAA; [■] gel capsule ($r_t/R_0=0.8$) prepared from reaction of DAA with hexyl bromide.

and esterification of benzoic acid with poly(*p*-chloromethylstyrene).¹³ The reactivity of the salt of carboxylic acid is attributed to the basicity of the base, because DBU ($pK_a=11.5$) is a stronger base than TEA ($pK_a=10.9$). DBU is bigger than TEA. This may influence the diffusion rate of a gel, and cause reactivity to change. The synthesis of gel capsules was tried by reaction of NAA with benzyl bromide in NMP at 80°C. The reaction hardly took place without any phase transfer catalyst (PTC) because NAA is very hydrophilic and does not swell in a solvent. The addition of TBAB or TEAB as a PTC caused the reaction to proceed. However, the reaction was much slower than that of DAA. When NAA stood in the solution of benzyl bromide for about 1 day, the swollen layer was broken and became like a sherbet. Therefore, it is difficult to synthesize gel capsules from the reaction of NAA. Esterification of gels obtained from TAA and NAA was lower than that of DAA as shown in Table I. It is thus concluded that DAA is suitable for the synthesis of gel capsules.

Properties of a Gel Capsule

The swelling of gel capsules ($r_t/R_0=0.8$) prepared from the reactions of DAA and DMA with hexyl bromide in NMP at 80°C for 1 h and 40 min, was carried out in

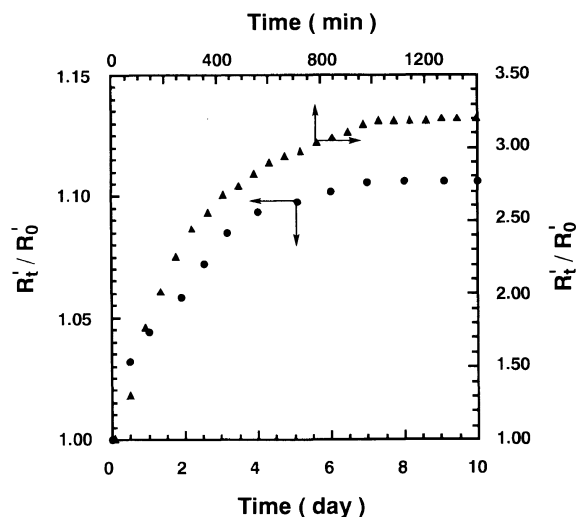


Figure 10. Swelling curves of gels in water at 50°C. [▲] DMA; [●] gel capsule ($r_t/R_0=0.8$) prepared from reaction of DMA with hexyl bromide.

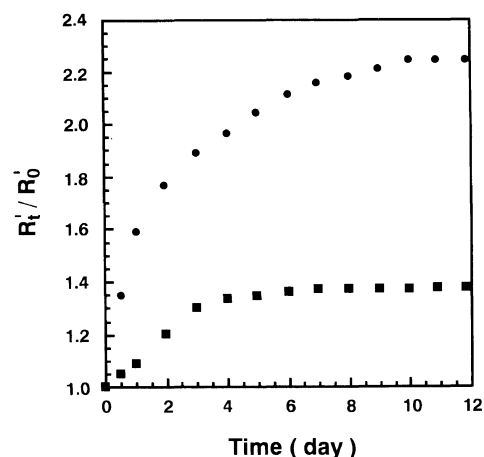


Figure 11. Swelling curves of gels in aqueous solution at 50°C. [●] gel capsule ($r_t/R_0=0.8$) in aqueous 1 wt% NaCl solution; [■] gel capsule ($r_t/R_0=0.8$) in aqueous 3 wt% NaCl solution.

water at 50°C as shown in Figures 9 and 10. The swelling was evaluated by R'_t/R'_0 , where R'_0 and R'_t are external radii of the dried gel and the gel swelled in the solvent for t min, respectively. Although the core part swelled in water, the swelling of the gel capsules was slower than that of the unreacted DBU salts. This suggests that the shell layer prevents swelling of the core part. The swelling of gel capsules obtained from DMA and unreacted DMA reached the equilibrium swelling radius. However, the gel capsule obtained from DAA swelled faster than that obtained from DMA, and burst in a few hours. This means that the shell layer composed of poly(alkyl acrylate) is too soft to cope with strong swelling pressure of the neutralized poly(acrylic acid) core. The swelling of the gel capsule obtained from DAA was tried in aqueous 1 wt% and 3 wt% NaCl solutions at 50°C (Figure 11). The gel capsule was not broken under these conditions, and showed slower swelling than DAA. The rate of swelling decreased with increase of concentration of aqueous NaCl solution.

Release of Rose-Bengal from the gels was carried out in aqueous 1 wt% NaCl solution at 50°C using the gel

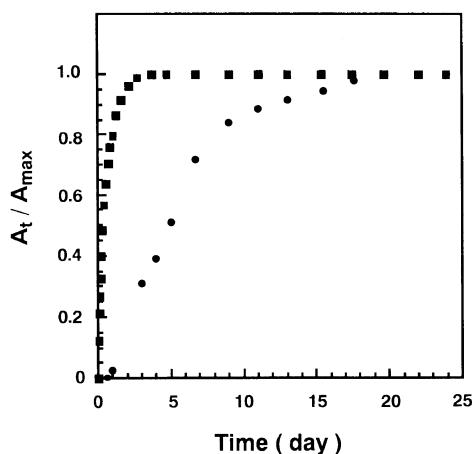


Figure 12. Change in absorbance of aqueous solution with a gel at 50°C: [■] DAA with Rose-Bengal; [●] gel capsule ($r_i/R_0=0.8$) containing Rose-Bengal in the core part.

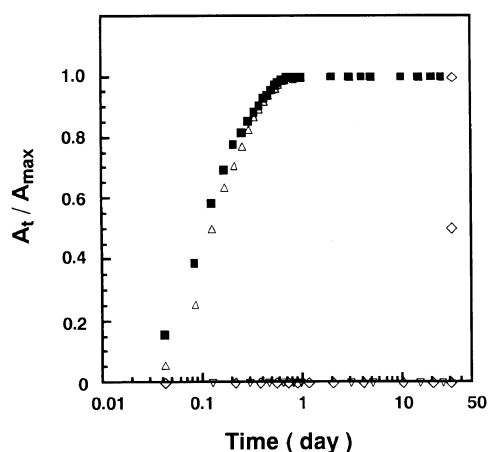


Figure 13. Change in absorbance of aqueous solution with a gel at 50°C: [■] DMA with Rose-Bengal; [△] gel capsule ($r_i/R_0=0.95$); [▽] gel capsule ($r_i/R_0=0.9$); [◇] gel capsule ($r_i/R_0=0.8$). All gel capsules contained Rose-Bengal in the core part.

capsule ($r_i/R_0=0.8$). Typical release of Rose-Bengal is shown in Figure 12. DAA containing Rose-Bengal was used as a normal drug carrier to compare with the gel capsule. The gel capsule showed characteristic chemical release, where the release of Rose-Bengal from DAA took place with swelling of the gels. The release from gel capsule did not occur for 1 day until Rose-Bengal in the core part passed through the shell layer. After the induction period, chemical release from gel capsule started. The release was slower than that of DAA, and the A_t/A_∞ increased linearly with time until high degree of release. Gel capsules obtained from DMA with various thicknesses of shell layer were dipped in water at 50°C (Figure 13). The burst time became longer with increase of thickness of shell layer. The gel capsule having the

thickest shell layer ($r_i/R_0=0.8$) was not broken when dipped in water for more than 100 days. The release of dye from the gel capsules was not observed until broken, where release from DMA was complete in 1 day. After the burst time, the release took place similarly to that from DMA. The shell layer thus inhibits the chemical release of Rose-Bengal. Since burst time can be controlled by the thickness of shell layer, the gel capsule should be applicable to drug carriers with a new function: chemical release starts after a definite (burst) time.

It is concluded that amphiphilic gel capsule is prepared by the esterification of poly(acrylic acid) gel-DBU salt with alkyl bromide. The resulting shell layer works as a permeability barrier to chemicals and water, and the structure of the shell layer controls the rate of chemical release and burst time. The gel capsule is thus suitable for chemical release.

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