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Pores and diffusion characteristics of porous gels

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Abstract

A simple porous gel synthesis method is proposed in this paper. We found that the sequential modification of conventional radical polymerization gives rise to pore formation in acrylamide gels and investigated the parameters that are responsible for controlling the number and the size of pores. Pore formation is dominated by the amount of polymerization initiator (ammonium persulfate), accelerator (*N*, *N*, *N′*, *N′*-tetramethylethylenediamine) and polymerization temperature. The initiator works as a pore nucleus. The accelerator helps the pore growth. However, temperature control is the easiest and the most effective way to create a number of large pores. Especially if the pregel solution is heated to or above 80°C, the pore formation is effectively promoted resulting in an increase in the number of pores and their size. Increase in the volume fraction of macro pores was found to result in the increase in the diffusion coefficients of the solution flowing through gels.

Keywords: Initiator; Accelerator; Temperature

1. Introduction

The property of a gel is characterized by its extraordinarily large volume change by a small environmental condition change, where the swollen gel volume sometimes reaches 100 times its collapsed volume [1,2]. Numerous types of environmental stimuli can induce this volume change, which is utilized in many applications of gels, such as drug delivery devices, actuators, etc. [1–16]. Among such gel applications, realization of gel actuator is by far difficult. One of the difficulties lies in the slow response of gels. This is because the gel volume change is dominated by a diffusion process [17]. This problem can be overcome partly by reducing the size of a gel specimen, since reduction in the gel size results in shortening of diffusion distance. Instead of gel specimen size reduction, a gel body with porous microstructure is expected to give rise to faster volume change, since the effective diffusion distance can be controlled by the average distance between the neighboring pores. Some attempts of pore creation have been made by other researchers [18–20]. Kabra et al. synthesized porous PVME gels by applying γ-rays to the pregel solution and extensively investigated the volume change property [18]. Wu et al. synthesized macroporous polyNIPPAm gels using HPC (hydroxypropylcellulose) as a pore formation agent [19]. They mixed the pregel solution with HPC and the HPC was removed from the gel body after the polymerization. Neither method is simple. The γ-ray radiation method needs a γ-ray facility, the HPC method implies a difficulty in removing the HPC from the polymerized gel. Chen et al. synthesized superporous hydrogels [20]. The gelation is induced in the presence of CO_2 gas bubbles generated by the decomposition of $NaHCO_3$ due to the addition of acid. Although this method appears to be simple and applicable to many different types of gels, our porous gel synthesis method is much simpler.

In this paper, a simple method of pore creation in polyacrylamide gels is proposed. We discuss in this paper the most effective processing parameters, which control the size and volume fraction of pores. The remaining part of the study is to elucidate the relationship between the diffusion coefficient of the solution flowing through gels and the pore volume fraction, and explain the importance and usefulness of the porous gel synthesis method proposed in this present paper.

2. Specimen preparation

A simple porous gel synthesis method is explained. A mixture of acrylamide (monomer), *N*, *N*-methylenebisacrylamide (crosslinker), *N*, *N*, *N′N′*-tetramethylethylenediamine (accelerator) and de-ionized water (solvent), is heated for 30 min. Then ammonium persulfate (polymerization

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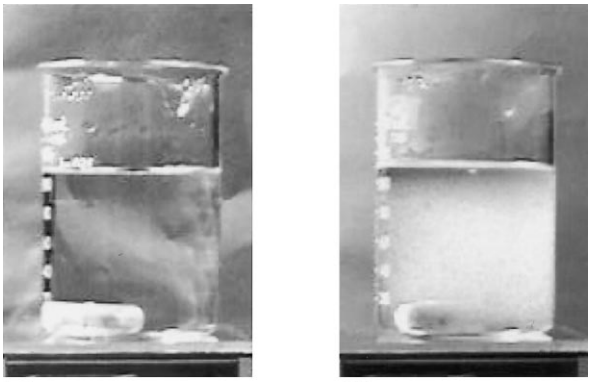

Fig. 1. Pore formation and gelation process of polyacrylamide gel where a white bar on the bottom of the beaker is a stir bar. (a) Pregel solution in a beaker and gel color is transparent. (b) Pore formation in the gel with its color becoming opaque with time due to the pore formation.

initiator) is added. Pore formation as well as the gelation is invoked simultaneously. This method is different from the conventional gel synthesis method in the sense that the initiator is added to the pregel solution after heating [2]. Fig. 1 are photos of the pore formation and the gelation process of acrylamide gel, where the white bar on the bottom of the beaker is a stir bar. This gel consists of 11.56 g of monomer, 0.154 g of crosslinker, 0.75 g of accelerator, 100 g of solvent and 0.08 g of initiator, and the heating temperature was 75°C. Although the pregel solution is transparent, Fig. 1(a), the polymerized gel becomes opaque, Fig. 1(b). As long as the acrylamide gel is prepared by following the conventional processing procedure, the whole ingredients of the gel are dissolved in solvent before heating up, no pore formation is observed and the gel is transparent just like the pregel solution shown in Fig. 1(a).

Table 1
The synthesis conditions (for the synthesis of all the gels shown in this table, the amount of monomer (acrylamide), crosslinker (*N*, *N′*-methylenebisacrylamide) and solvent (de-ionized water) used are 11.56, 0.154 and 100 g, respectively)

	Gel I^{i}	**Gel II**^{i}	**Gel III**^{i}	**Gel IV**^{i}
Initiator[a](g)	0.08	0.16	0.24	0.60
Accelerator[b](g)	0.03	0.03	0.03	0.03
Temperature[c](°C)	70	70	70	70
	Gel I^{ad}	**Gel II**^{a}	**Gel III**^{a}	**Gel IV**^{a}
Initiator[a](g)	0.08	0.08	0.08	0.08
Accelerator[b](g)	0.03	0.06	0.09	0.30
Temperature[c](°C)	70	70	70	70
	Gel I^{T}	**Gel II**^{T}	**Gel III**^{T}	**Gel IV**^{T}
Initiator[a] (g)	0.16	0.16	0.16	0.16
Accelerator[b] (g)	0.06	0.06	0.06	0.06
Temperature[c] (°C)	50	60	70	80

[a] Ammonium perfulfate is used as a polymerisaton initiator.
[b] *N*, *N*, *N′*, *N′*-tetramethylethylenediamene is used as an accelerator.
[c] Polymerization temperature.
[d] **Gel I**^{a} is identical to **Gel I**^{i}.

The opaqueness of the gel shown in Fig. 1(b) is due to the pore formation in the gel body.

2.1. Controllability of the pore size and the number

Porous polyacrylamide gels were prepared by the method described above under different synthesis conditions. Acrylamide, *N*, *N′*-methylenebisacrylamide, ammonium persulfate and *N*, *N*, *N′*, *N′*-tetramethylethylenediamine were used as monomer, crosslinker, polymerization initiator and accelerator, respectively. All chemicals were purchased from Aldrich (Milwaukee, WI) and used without further purification.

2.1.1. Initiator

By varying the amount of the initiator, four different gels were prepared, **Gel I**^{i}, **Gel II**^{i}, **Gel III**^{i} and **Gel IV**^{i}. The monomer (11.56 g), the crosslinker (0.154 g) and the accelerator (0.03 g) were dissolved in de-ionized water (100 g). This pregel solution was heated up to 70°C for 30 min, then the initiator was added. **Gel I**^{i}, **Gel II**^{i}, **Gel III**^{i} and **Gel IV**^{i} were prepared by using initiator amounts of 0.08, 0.16, 0.24 and 0.60 g, respectively.

2.1.2. Accelerator

By varying the amount of the accelerator, four different gels were prepared, **Gel I**^{a}, **Gel II**^{a}, **Gel III**^{a} and **Gel IV**^{a}. The pregel solution consisted of the monomer (11.56 g), the crosslinker (0.154 g), the accelerator and de-ionized water (100 g), where **Gel I**^{a}, **Gel II**^{a}, **Gel III**^{a} and **Gel IV**^{a} were prepared by using accelerator amounts of 0.03, 0.06, 0.09 and 0.30 g, respectively. The amount of the initiator used was 0.08 g for all gels. **Gel I**^{a} is identical to **Gel I**^{i}.

2.1.3. Temperature

By varying the heating temperature, four different gels were prepared, **Gel I**^{T}, **Gel II**^{T}, **Gel III**^{T} and **Gel IV**^{T}. The pregel solution consisted of the monomer (11.56 g), the crosslinker (0.154 g), the accelerator (0.06 g) and the de-ionized water (100 g). The amount of the initiator used was 0.16 g. **Gel I**^{T}, **Gel II**^{T}, **Gel III**^{T} and **Gel IV**^{T} were prepared by heating up the pregel solution for 30 min at 50, 60, 70 and 80°C, respectively.

All the synthesis conditions are summarized in Table 1.

2.2. Effect of pore volume fraction on solution diffusion through gel

By varying the gelation temperature, gel specimens with different volume fraction of pores were prepared. To study solvent diffusion through the gels, starch particles and saturated iodine were used in addition to the ingredients of the gel. They were purchased from Aldrich (Milwaukee, WI).

Monomer (11.56 g), crosslinker (0.154 g), accelerator (0.09 g) and starch particles (0.56 g) were dissolved in de-ionized water (100 g). This pregel solution was heated

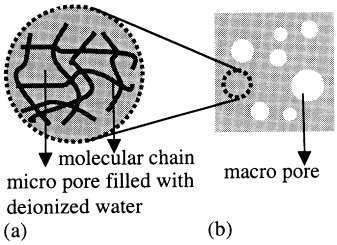

Fig. 2. Definition of pore: (a) acrylamide gel with micro pores; and (b) acrylamide gel with micro and macro pores.

up at each gelation temperature for 30 min followed by the addition of initiator (0.24 g). The pregel solution was poured into a mold in order to make a 4.97 mm thick gel sheet.

3. Measurement

3.1. Pore size and the number

A slice of gel was prepared as a specimen. Using an optical microscope, the number and the size of pores were investigated. This observation must be performed within a short time soon after the completion of the gelation process, since the pore visibility tends to deteriorate gradually with time, and pores fill up with the solution remaining in the gel or flatten, as time goes by.

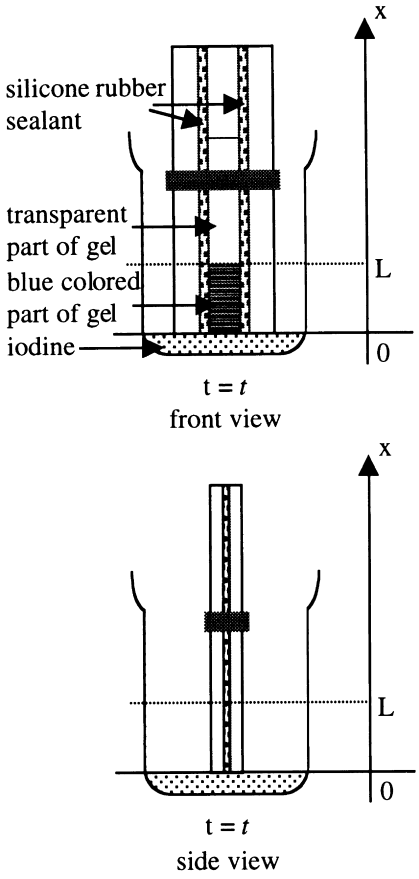

Fig. 3. Experimental setup for observation of the diffusion process. The specimen is dipped in saturated iodine solution. The length of blue color region of gel by the iodostarch reaction is L where time $t = t$.

3.2. Effect of pore volume fraction dependence on solution diffusion through gel

The objective was to measure the diffusion coefficient of iodine solution flowing through a porous gel as a function of pore volume fraction. First, it is necessary to define what pores are. Even if no pore formation reaction is induced in an acrylamide gel body, initially it may consist of voids. Namely, water swollen acrylamide gel consists of small volume molecular chains and large volume voids filled with the de-ionized water (Fig. 2(a)). Thus the gaps among molecular chains are considered to be all voids, and hereafter such a type of void is called a “micro pore”. On the contrary, the pores created by the pore formation reaction described earlier are different types of voids. Their sizes are larger compared with micro pores as shown in Fig. 2(b). Hereafter these type of voids created by the present process are called “macro pore”. The method to calculate the volume fractions of micro and macro pore, which are designated as Vf_{micro} and Vf_{macro}, respectively, is explained, where the total pore volume fraction is given by $Vf_{total} = Vf_{micro} + Vf_{macro}$. The total gel weight is the same as total weight of gel ingredients, 112.604 g, and its volume can be measured experimentally, 108 cm^3, as long as there exist no macro pores. Therefore, the density of gel without macro pores, ρ, is 112.604 g/108 cm^3 = 1.0426 g cm^{-3}. If there are no macro pores in the gel specimen, its volume, V_{gel}°, should be 3 cm × 1 cm × 4.97 cm = 1.491 cm^3.

However, if there exist macro pores in the gel specimen, its volume excluding the macro pores, V_{gel}, should be given by Eq. (1).

$$V_{gel} = \frac{W_{gel}}{\rho} = \frac{W_{gel}}{1.0426} \tag{1}$$

Therefore, Vf_{macro} is given by Eq. (2):

$$Vf_{macro} = \frac{(V_{gel}^{\circ} - V_{gel})}{V_{gel}^{\circ}} = \frac{\left(1.491 - \dfrac{W_{gel}}{1.0426}\right)}{1.491} \tag{2}$$

Since all the micro pores are filled with de-ionized water, the volume ratio of the micro pores to the gel specimen except for the macro pores should be the same as the volume ratio of the total de-ionized water used (100 cm^3) to the total gel volume prepared (108 cm^3), which is 0.9259. Therefore, Vf_{micro} is given by Eq. (3):

$$Vf_{micro} = 0.9259(1 - Vf_{macro}) \tag{3}$$

The method of measuring diffusion coefficients is roughly explained here. Immediately after the synthesis, the porous

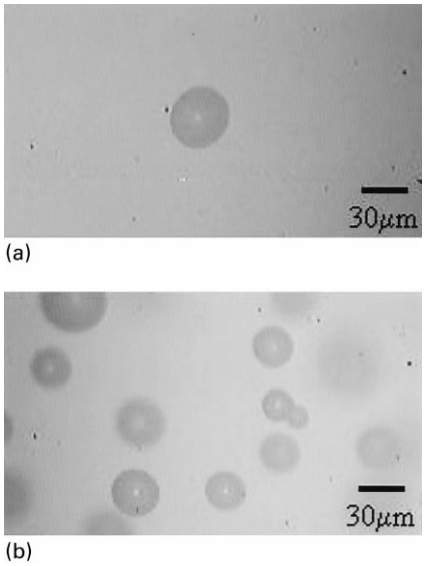

Fig. 4. Photographs of typical macro pores created in **Gel I**^{i} and **Gel III**^{i}: (a) macro pore in **Gel I**^{i}; and (b) macro pores in **Gel III**^{i}. The macro pores exist sparsely in **Gel I**^{i} than in **Gel III**^{i}.

gel sheet was cut into a 3 cm-length × 1 cm-width strip. Its weight, W_{gel}, was measured, and it was sandwiched between the acrylic plates with silicone rubber sealant, and the edge of the gel was dipped in iodine solution where this moment was defined as $t = 0$ (t: time), Fig. 3. Owing to the iodostarch reaction, the gel strip changed its color from transparent to blue. The displacement of the boundary between the blue colored and transparent regions of the gel, L, as depicted in Fig. 3 was measured as a function of time, at 20°C. If the macro pore volume fraction was quite large, the gel volume decreased immediately after the synthesis due to gas release from these pores. Therefore, in such a case, the gel was immersed in de-ionized water until it was fully swollen in order to open those flattened pores completely again.

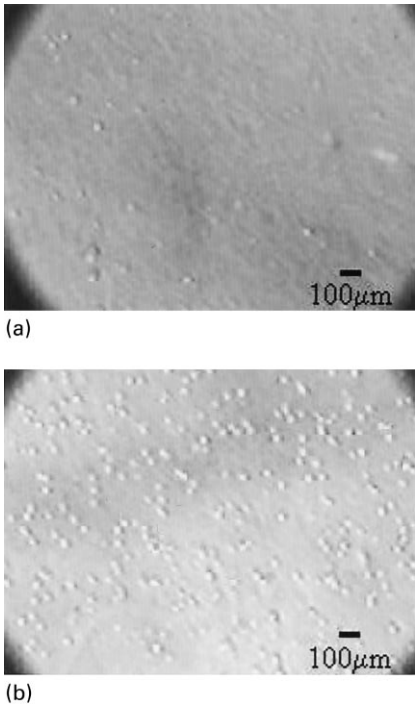

Fig. 5. The textures of **Gel I**^{i} and **Gel III**^{i}: (a) entire image of **Gel I**^{i}; and (b) entire image of **Gel III**^{i}. The macro pores exist sparsely in **Gel I**^{i} than in **Gel III**^{i}.

4. Results and discussion

4.1. Controllability of the pore size and the number

4.1.1. Initiator

The pregel solution was first heated up in a beaker. Once the initiator was added to the pregel solution, the polymerization, the creation of macro pores and their growth can be observed even with naked eyes. The gel itself becomes opaque with time due to the growth of macro pores. In all the four gels, mainly spherical pores are created. In Fig. 4, the photographs of pores created in **Gel I**^{i} and **Gel III**^{i} are shown as examples. It was difficult to obtain the size (diameter) distribution of macro pores, since the diameter of some macro pores was too small to be measured from the optical microscope image, and we could not obtain a clear image of **Gel IV**^{i} due to the creation of too many macro pores in a small region. However, in **Gel I**^{i}, **Gel II**^{i} and **Gel III**^{i}, the pores of 20–30 μm diameter were observed mainly. Although it was difficult to count the number of macro pores in the gels, it was found from the optical microscope image that the number of macro pores increased in the order of **Gel I**^{i}, **Gel II**^{i}, **Gel III**^{i}, **Gel IV**^{i}. Especially, **Gel III**^{i} and **Gel IV**^{i} exhibited much more macro pores than **Gel I**^{i} and **Gel II**^{i}. The number of macro pores is not proportional to the actual amount of initiator used. Fig. 5 are the photographs of **Gel I**^{i} and **Gel III**^{i} textures. Although both of them have almost same size of spherical macro pores, the macro pore density is much sparse in **Gel I**^{i} than in **Gel III**^{i}, which is obvious from Fig. 4 as well as Fig. 5. This might be due to the gelation speed effect. The gelation speed of **Gel I**^{i} and **Gel II**^{i} may not be fast enough to trap the bubbles created in them due to the small amount of initiator used, while the amount of initiator used for **Gel III**^{i} and **Gel IV**^{i} is large enough to invoke fast gelation for trapping gas bubbles in them. In fact, it was observed that larger amount of initiator accelerated the gelation speed. The initiator does not appear to influence the macro pore growth so significantly, but the number of macro pores certainly becomes larger with higher amount of initiator. Since the creation of small gas bubbles, which soon grow into macro pores, is observed as soon as the initiator is added to the pregel solution, the initiator must have worked as a macro pore nucleus. This is supported also by the experimental result that the number of macro pores increases with the amount of initiator.

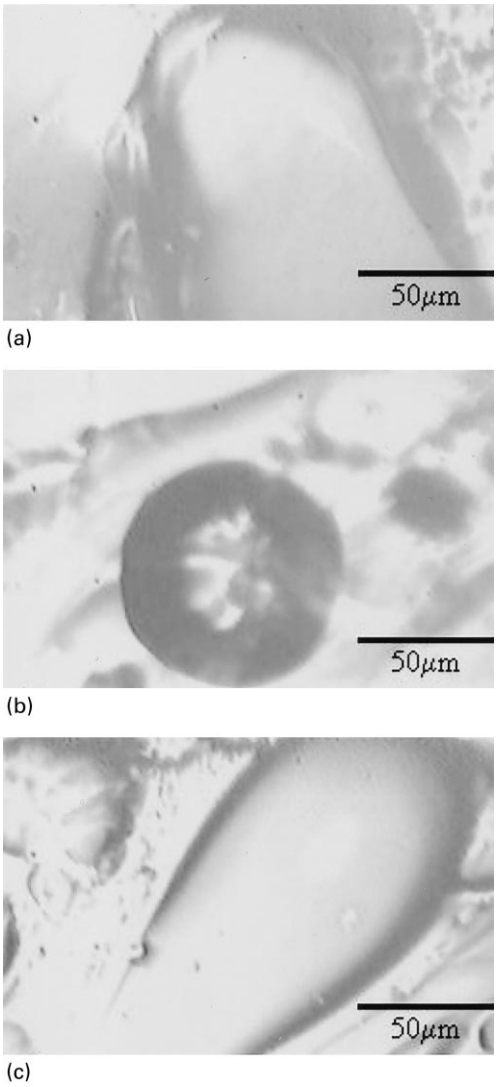

Fig. 6. Photographs of typical macro pores created in **Gel V**[a] (a) and (c) are the typical unshaped macro pores, while (b) is spherical in shape. Pores in (a) and (c) stick out from the photo frame due to their huge size.

4.1.2. Accelerator

Once the gas bubbles were created in the pregel solution by the addition of initiator, they grew gradually and the gel became more opaque with time. Owing to the same reason described above, it is not possible to obtain the size distribution of macro pores, but **Gel I**[a], **Gel II**[a] and **Gel III**[a] appear to contain mainly macro pores of 20–30 μm diameter, and **Gel IV**[a] appears to contain mainly pores of 50–60 μm diameter. This evidence suggests that the macro pore diameter increases with the amount of accelerator, but it is not clear enough. In order to confirm this conclusion, another gel, **Gel V**[a], was prepared using a larger amount of accelerator (0.90 g). Fig. 6 shows the photographs of typical macro pores created in **Gel V**[a], indicating larger macro pore sizes than those of the macro pores created in **Gel IV**[a]. This evidence strongly supports the conclusion that the accelerator directly influences the macro pore growth. It is noted in Fig. 6(a) and (c) that there exist unshaped (non-spherical) macro pores. This implies the continuation of macro pore growth even after the completion of gelation. Due to the completion of gelation, macro pores could not grow into pure spherical shapes, instead they grow in the direction along which the gel body strength is the weakest, namely the less polymerized region. The creation of unshaped macro pores is also attributed to the coalescence of macro pores with one another. Though the use of higher amounts of initiator resulted in the creation of an extraordinarily larger number of macro pores as described earlier, the use of the higher amount of accelerator does not seem to have the same effect. Even **Gel IV**[a] does not have the obviously larger number of macro pores as compared with **Gel I**[a], **Gel II**[a] and **Gel III**[a]. The macro pores created in these four gels exist sparsely just like in **Gel I**[i] as shown in Fig. 5(a). Thus the accelerator was found to play the role of a macro pore growth agent.

4.1.3. Temperature

We could not obtain the size distribution of the macro pores, and we could not obtain a clear image of **Gel IV**[T] due to the creation of too many macro pores in a small region. However, it was clear that the macro pore size increased with the temperature. Especially, the appearance of **Gel IV**[T] texture exhibited so many macro pores compared to **Gel III**[i] shown in Fig. 5(b). **Gel I**[T] contains mainly macro pores less 10 μm in diameter. **Gel II**[T] and **Gel III**[T] appear to have mainly macro pores of 20–30 μm diameter. But **Gel IV**[T]

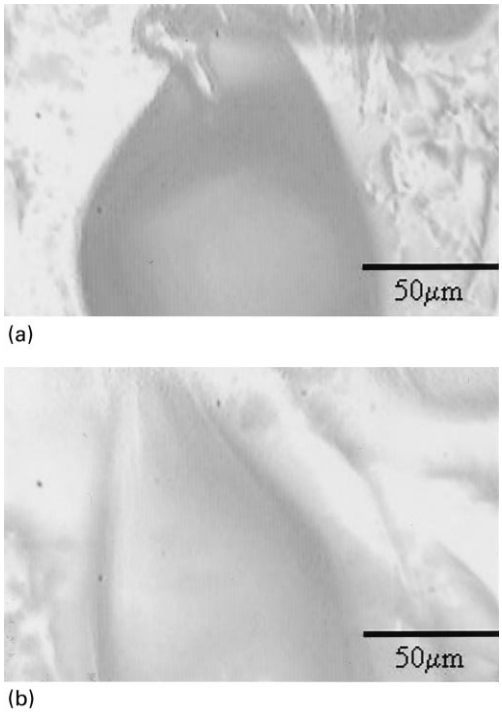

Fig. 7. Photographs of typical macro pores created in **Gel IV**[T] (a) and (b) are the typical macro pores created in gel. They stick out from the photo frame due to their huge size.

contains quite large macro pores of around 100 μm, Fig. 7. The macro pore size abruptly becomes larger around 80°C. This is due to the expansion of macro pores, often resulting in the rupture of gel body of **Gel IV**^{T}. We also observed many unshaped macro pores in **Gel IV**^{T}. This is attributed to the same reason associated with **Gel V**[a]. For the synthesis of **Gel IV**^{T}, the amount of initiator and accelerator used were only 0.16 and 0.06 g, respectively, but there exist many huge-sized macro pores. Among **Gel II**^{T}, **III**^{T} and **IV**^{T}, there is a trend that the number of macro pores per unit volume increases with temperature. However, only **Gel I**^{T} does not follow this trend. The number of macro pores in **Gel I**^{T} is larger than that in **Gel II**^{T} and **Gel III**^{T}. Since macro pores created in **Gel I**^{T} could not expand, they did not coalesce together. Thus the number of macro pores in **Gel I**^{T} became larger than that of the other gels. Fig. 8 is a photograph of macro pores created in **Gel I**^{T}. Many smaller macro pores exist in the narrow region. If the temperature increased, the macro pores would grow and merge together. For example, three macro pores circled in Fig. 8 are located in a narrow region where the circle diameter is only 30 μm, which is almost equivalent to the size of macro pores created in the other gels. Once they grow, the three macro pores would presumably coalesce to form only one unshaped macro pore, but they did not grow until coalescence.

Generally speaking, heating up the pregel solution, especially at and above 80°C to induce gel expansion, is a very effective way to create a number of macro pores, even though the amount of initiator and accelerator are small. Fig. 9 shows the gelation temperature dependence of the macro pore volume fraction created in a gel. It is clear from Fig. 9 that the volume fraction of macro pore reaches as high as 45% at 95°C and that little macro pore formation is expected below or at 50°C. Above 80°C, the dependence of the macro pore volume fraction on the heating temperature is critical. Here we have to pay attention to the macro pore volume fraction. Mold prevented the macro pores from growing into larger sizes. Especially at the higher temperature, the macro pore growth is significantly suppressed by the mold. Therefore if no molds are used, volume fraction of macro pores is expected to be far larger than that shown in Fig. 9.

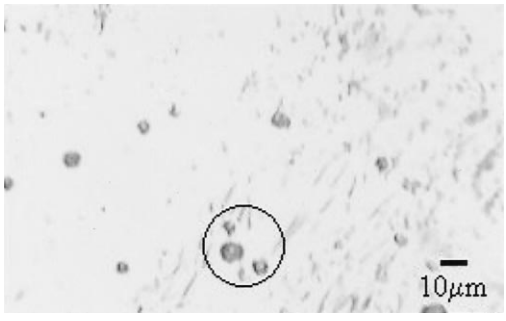

Fig. 8. Photograph of typical macro pores created in **Gel I**^{T}. The circle diameter is 30 μm. Each macro pore size is quite small compared with those in the other gels.

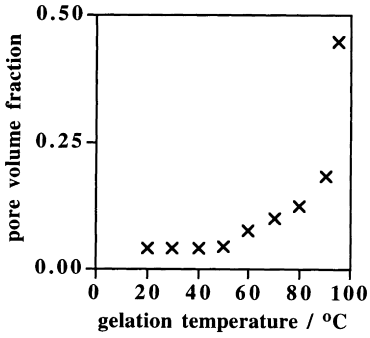

Fig. 9. Gelation temperature dependence of macro pore volume fraction created in gel.

4.2. Pore volume fraction dependence of solution diffusion through gel

The borderline displacement, L, reached by the diffused iodine tracer is plotted as a function of (time)$^{1/2}$, $t^{1/2}$, in Fig.10. All data exhibit approximately a linear relationship between L and $t^{1/2}$. This specific relationship between L and $t^{1/2}$ must be dominated by a certain rule. One-dimensional diffusion equation, $x = \sqrt{2Dt}$, holds the linear relationship between L and $t^{1/2}$. Iodine solution flow must be dominated by diffusion in this case. By the least square analysis on Fig. 10, the absolute value of the diffusion coefficient, D, is calculated, and the results are summarized in Table 2. Diffusion coefficient drastically increases with the increase of Vf_{macro} as described above, despite that Vf_{total} remains constant and Vf_{micro} decreases. This evidence suggests that the creation of macro pores is necessary to enhance the solution flow rate in gel. Otherwise, the solution is strongly trapped by gel network, even if a high volume faction of micro pore exists in the gel body.

5. Conclusion

In this research, ammonium persulfate is used as the pore formation agent as well as the polymerization initiator. We also used potassium persulfate (Aldrich, Milwaukee, WI)

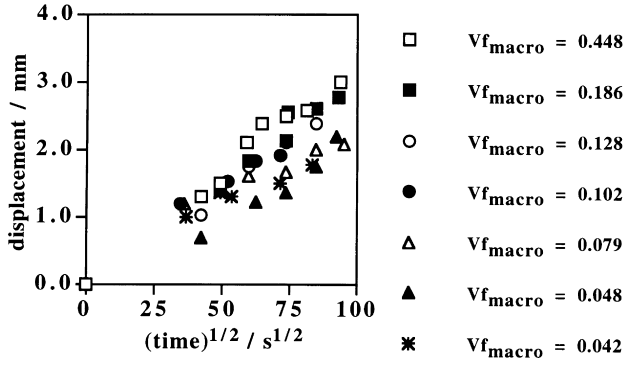

Fig. 10. Diffusion distance (displacement), L, vs square root of elapsed time, $t^{1/2}$.

Table 2
The volume fraction of the micro, macro and total pores and the diffusion coefficient

Vf_{micro} [a]	0.37	0.76	0.85	0.88	0.92	0.93	0.93
Vf_{macro} [b]	0.60	0.18	0.09	0.05	0.01	0.00	0.00
Vf_{total} [c]	0.97	0.94	0.94	0.93	0.93	0.93	0.93
D ($\times 10^{-6}$ cm^2 s^{-1})	5.45	4.81	4.21	3.92	2.21	2.42	2.21

[a] Micro pore volume fraction.
[b] Macro pore volume fraction.
[c] Total pore volume fraction.

instead of ammonium persulfate for the synthesis, which resulted in formation of porous gel, too. Therefore, potassium persulfate will work in the same way just like ammonium persulfate. It can probably be used for the control of the number of pores, too.

It was found from the present study that use of higher amounts of initiator results in higher macro pore density, and use of higher amounts of accelerator results in larger sized pores. But heating up the pregel solution at higher temperature is the most effective way to create a number of larger macro pores. Effectiveness of the macro pore formation by heating up the pregel solution was evaluated. The macro pore formation is accelerated especially at and above 80°C.

The solution diffusion is found to be enhanced by the creation of macro pores and the proposed macro pore formation method in present work is quite easy to create such a type of pores in gel body. This pore formation method creates reasonably large enough pores to enhance the solution flow rate, which is required to realize the fast volume change of gels.

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