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SHORT COMMUNICATIONS

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New method of producing mono-sized polymer gel particles using microchannel emulsification and UV irradiation

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Abstract It has been established that the combination of microchannel (MC) emulsification and UV-induced gelation is quite effective in producing mono-sized gel particles from acryloyl-type monomer/polymer solutions. MC emulsification allows one to produce the monomer solution droplets with less than ca. 5% relative standard deviation. On the other hand, using UV-induced gelation technique, pre-gel droplets containing a photoinitiator gelate by irradiation of UV light for a few minutes without requiring heating and/or intermediate adding of reaction accelerator. Conveniently, the particle size is adjusted from a few μm to ca. 100-μm by changing the slit size of the MC plate. Furthermore, gel particles may contain a variety of materials, such as metals, pigments, dyes, oils, bubbles, or others, suggesting various potential industrial applications.

Keywords UV-induced gelation · MC emulsification · Persulfate · N-isopropyl acrylamide · Gel particles

Introduction

In recent decades, various kinds of polymer gel particles have been produced and investigated for industrial purposes [1–13]. The important features of polymer gel particles are the high solvent-absorbing property and quick response to the surrounding conditions, so they have been applied to many products such as drug delivery systems, moisturizers, water-absorbing bases, small sensors, etc. However, some problems of polymer gel particle synthesis still remain to be solved. (1) One is particle size control. Most chemically cross-linked polymer gel particles have been produced by suspension or emulsion polymerization method. Although the particle size may be adjusted by changing the amount of surfactants or stirring speed, the adjustable size has been generally limited to be from tens of nm to some hundreds nm (emulsion polymerization) and from tens of μm to some hundreds μm (suspension polymerization) depending on physical endurance to stirring conditions. (2) The second problem is size distribution. It is very difficult to produce gel particles with a narrow size distribution using suspension/emulsion polymerization methods, particularly at the submicron level. (3) The last problem is the gelation method. Two major gelation methods are known, heat-induced [14–18] and low-temperature redox gelations [14, 19–22]. However, if the polymers and/or monomers are very sensitive to temperature, the heat-induced gelation method is not applicable, because heat-sensitive gel particles lack homogeneity, physical strength, and ability of containing solutions. In the case of redox gelation, on the other hand, an initiator and/or an accelerator must be added to the monomer solution droplets to start the gelation reaction after making the droplets, leading to enlarged droplet size distribution. In order to solve these problems, we propose a method of producing size-adjustable and mono-sized pre-gel solution droplets and making the droplets gelate without heating and intermediate adding.

The aim of this article is to report a novel method of producing mono-sized gel particles with a given diameter by combining microchannel (MC) emulsification [23, 24] and UV-induced gelation techniques [25, 26]. To our knowledge, this is the first report on making mono-sized µm-order gel particles without heating and intermediate adding. MC emulsification can produce mono-sized aqueous pre-gel droplets containing monomers (and/or polymers) in an organic solvent. The droplet size was controlled in the range of 3–100-µm within 5% of the relative standard deviation (RSD). Here, the RSD was defined by

$$\mathrm{RSD} = \frac{\sigma}{d_{\mathrm{ave}}}, \qquad (1)$$

where σ and d_{ave} are the standard deviation of particle diameter and the averaged particle diameter, respectively. Indeed, micron-order droplets produced by means of constant stirring have large size-distribution with more than 20% of RSD. On the other hand, the UV induced gelation method allowed the pre-gel solutions to undergo gelation by UV irradiation, using persulfate as UV photoinitiator in the pre-gel droplets. The gel particles obtained by this combination can contain various materials (metal particles, oil, pigments, etc), suggesting various potential industrial applications.

Experimental

Materials *N*-isopropyl acrylamide (NIPAm), ammonium persulfate (APS; UV-induced initiator), iso-octane (continuous phase solvent), and the non-ionic surfactant Span 80 were purchased from Wako. The NIPAm monomers were purified by re-crystallizing before use.

MC emulsification The MC plate and MC module were custom made by E.P.T. Co ltd (Hitachi, Japan). Each concentration of components used in the MC emulsification was 700 mM of NIPAm and 50 mM of APS in water as a disperse phase, and 5 wt% of Span 80 in iso-octane as a continuous phase. Note that it may be as well to add cross-linker (e.g., N,N'-methylenebisacrylamide) in order to increase the gel's physical strength. The details of the emulsification process are described in the following section. In this study, the operating pressure of MC emulsification corresponded to ca. 1–2 kPa and the maximum droplet productivity was ca. 10 ml/h. Now, a scale-up of the MC emulsification device is under development by Nakajima et al. [27, 28] and the droplet productivity will increase until more than a few hundred ml/h.

UV irradiation UV irradiation of the gathered pre-gel droplets in the vessel was performed using a 500-W Deep-UV lamp (USHIO Inc.,Tokyo, Japan) with an illuminance spectrum of $\lambda \leq 300$ nm. The UV-irradiation time was only a few minutes under N_2 bubbling.

Swelling Measurement Gel particles were immersed in a thermostatted chamber filled with distilled water. The temperature change was controlled with a liquid bath circulator (NESLAB RTE-211D) within an error of $\pm 0.1°$C. The measurement was carried out with an inverted microscope coupled with a CCD (charge capacity device) camera. The fed image was sent to a personal computer for accurate measurement of the particle diameter. Each diameter of 200 gel particles was measured. S_v at each temperature was determined by averaging the diameters of 200 gel particles.

Results and discussion

Here, the production process of mono-sized gel particles is illustrated for *N*-isopropyl acrylamide (NIPAm) gel particles. NIPAm gel is well known as a temperature-sensitive gel, which shows a volume-phase transition from a swollen state to a shrinking one with increasing temperature beyond ca. 34°C [29]. Figure 1 presents simplified diagrams of (a) the MC emulsification apparatus, (b) an MC plate, (c) enlargement of MC, and (d) a monitoring video system. In Fig. 1a, from the disperse phase reservoir, an aqueous solution containing 700 mM of NIPAm monomer and 50 mM of ammonium persulfate (APS, which acts as UV-photoinitiator) is injected by the gravitational pull into a gap between the MC plate and the glass plate on the bottom of the MC module. The MC plate, as shown in Fig. 1b, is made of silicon and has many slits on all sides. The enlargement of MC slits is shown in Fig. 1c. Aqueous pre-gel droplets are produced by passing the pre-gel solution through the slits and entering into the continuous phase, i.e. iso-octane solvent containing 5 wt% of non-ionic surfactant, Span 80. It should be noted that the MC plate and the glass plate were surface-modified hydrophobically beforehand with 1,1,1,3,3,3-hexamethyldisilazane for use in the water-in-oil system. As an improvement of the original module reported by Nakajima et al. [23, 24] the MC module used was made of hydrophobic teflon to avoid self-sticking of the obtained gel on the inside wall of the MC module. The emulsification process at the MC plate was monitored through the glass plate using a

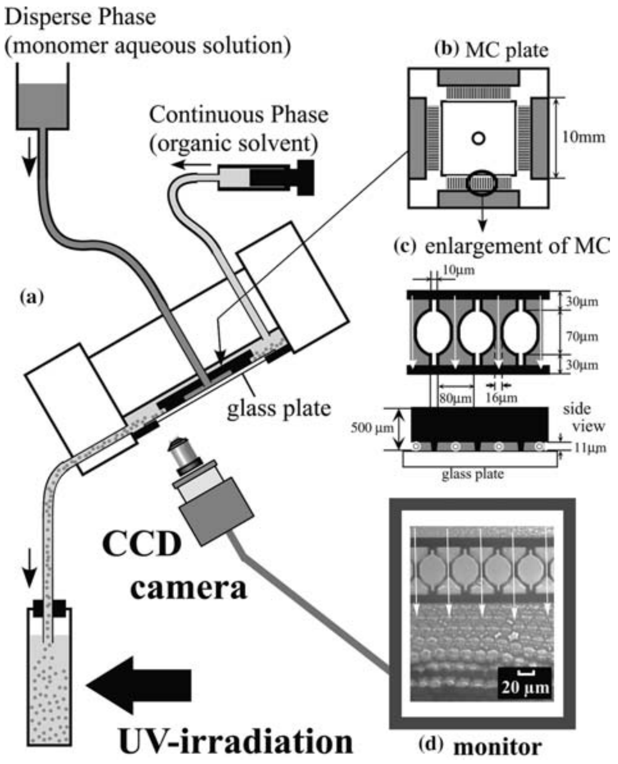

Fig. 1 **a** Experimental apparatus of MC emulsification and UV irradiation, **b** the surface view of silicon MC plate, **c** enlarged view of MC, and **d** the monitoring video system

microscope video system, as shown in Fig. 1d. In the monitor display, the white arrows indicate the flow path of the pre-gel solutions passing through the slits. Many pre-gel droplets are produced below the slits in the display. The solution droplets obtained are automatically flowed and collected in the quartz vessel as shown in Fig. 1a. Here, the organic solvent was not flown, and the solution droplets obtained fell into the vessel by their own weight (The details of MC emulsification are described elsewhere [23, 24].) Then, the gathered pre-gel droplets undergo the gelation directly in the continuous phase by UV irradiation for a few minutes, as described in the following.

As already reported in a previous paper,Ikkai et al. [25, 26] developed a novel UV-induced gelation method, using ammonium persulfate (APS) as the UV-photoinitiator. APS has been employed so far as a reaction initiator for the heat-induced and low-temperature redox polymerizations where the active radicals are generated by APS dissociation. The UV-induced gelation method, the fact that APS acted as a UV-photoinitiator, was the important finding. This method has an edge over the other gelation methods because of the following points: (1) No cross-linker is necessary, that is, the polymer gel obtained consists of a single kind of monomer. (2) No temperature control is required. (3) No additives, such as a reaction accelerator or pH-adjustment agent, are required. (4) The initiator is colorless and water soluble. Indeed, APS has a strong absorbance in the range 190 nm $\leq \lambda \leq$ 220 nm, probably leading to the generation of active radicals. As a result, the UV-induced gelation method enabled the aqueous acryloyl-type monomer solution to undergo gelation without heating and/or requiring intermediate operation, so it was suitable to let the pre-gel droplets gelate in an organic solvent. Figure 2 shows typical structures of gelable and ungelable monomers/polymers for the UV-irradiation method. Acryloyl-type monomers (A) and polymers (B) were the most effective using this method. The acryloyl-type monomer/polymer solutions gelated from within a few minutes to tens of minutes. Combining a vinyl group ($CH_2{=}CH$–) and carbonyl group ($C{=}O$) is known to form a conjugated structure, which increases the monomer reactivity towards active radicals. This is why acryloyl-type monomers/polymers readily undergo the UV-induced gelation. However, simple vinyl-type $CH_2{=}CH\text{-}R$ monomer (C), methacryloyl monomer having a methyl group on theα-carbon (D), and acryloyl monomer with a quaternary ammonium (E) did not undergo the UV-induced gelation, probably because of unconjugated structure, structural hindrance effect, and the strong electrostatic repulsion between side chains, respectively. Monomers/polymers of category (A) or (B) include, for example, NIPAm, acrylamide, acrylic acid, *N*,*N*'-dimethyl acrylamide, poly(acrylic acid), poly (acrylamide), etc, which are commonly used in industrial fields.

Finally, we show the size distribution of the gel particles obtained by the combination of the MC emulsification and UV-induced gelation. Figure 3 shows the optical micrographs and the size distribu-

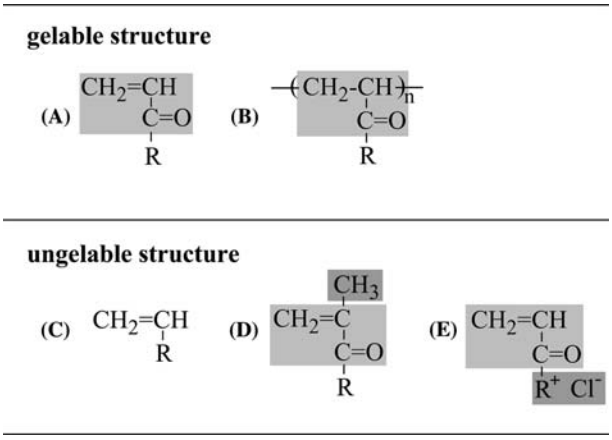

Fig. 2 Classification of monomers and polymers for UV-induced gelation

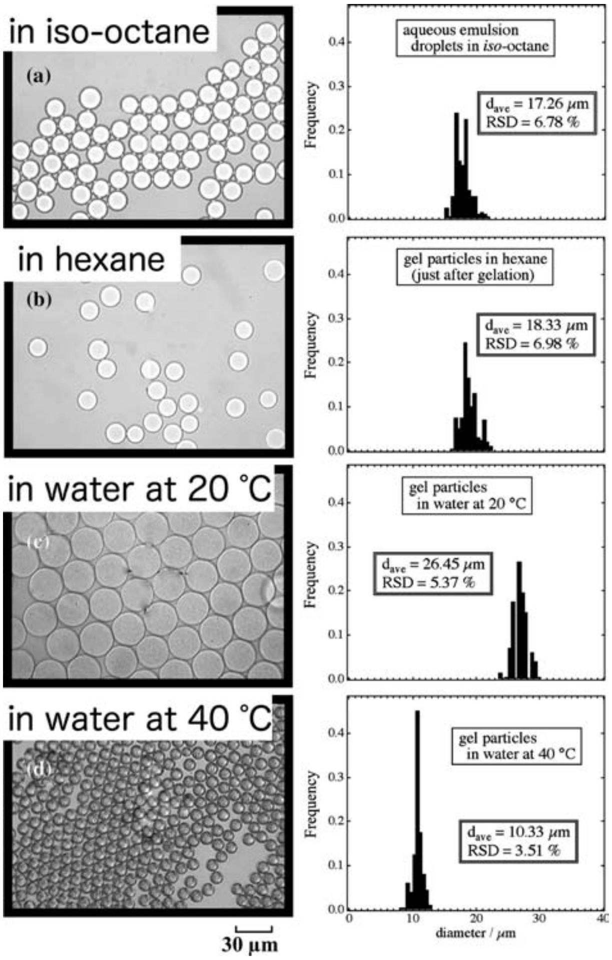

Fig. 3 Pictures and size distribution of gel particles at each step: **a** NIPAm emulsion droplets after MC emulsification, **b** gel particles in washing process just after gelation, **c** gel particles in water at 20°C, and **d** gel particles in water at 40°C

tions at each step of the gel making process. Figure 3a corresponds to the NIPAm monomer solution droplets just after the MC emulsification. Here, the average droplet size was 16-μm, with a narrow distribution. After the gelation by UV-irradiation, the gel particles collected as shown in Fig. 1a were washed several times with plenty of hexane and finally dried. Fig 3b is the picture of the washing process of the gel particles. The gel particles still have the same size distribution as the droplets, meaning that the gelation process hardly affected the size. After drying, the gel particles were sunk in water at 20°C (Fig. 3c). Then, the gel particles absorbed water and swelled to d_{ave} = 26.45-μm. As made by temperature-sensitive NIPAm polymers, these particles shrunk beyond the critical temperature (over ca. 34°C) as shown in Fig. 3d, which is an intrinsic property of chemically crosslinked NIPAm gels. It is vitally important that the shrinking process occurred while keeping the narrow size distribution with less than ca. 5% of RSD. It should be noted that the swelling/shrinking behavior occurred reversibly when the temperature changed.

To sum up, the combination of MC emulsification and UV-induced gelation is quite effective in producing mono-sized gel particles from acryloyl-type monomer/polymer solutions. MC emulsification allows one to produce the monomer solution droplets with less than ca. 5% relative standard deviation. On the other hand, using UV-induced gelation technique, pre-gel droplets gelate without requiring heating and/or intermediate adding. Conveniently, the particle size is adjusted from a few μm to ca. 100 μm by changing the slit size of the MC module. Furthermore, gel particles may contain a variety of materials, such as metals, pigments, dyes, oils, bubbles, etc.

References

1. Fernandez-Nieves A, de las Nieves FJ, Fernandez-Barbero A (2004) J Chem Phys 120:374
2. Frank M, Burchard W (1991) Makromol Chem, Rapid Commun 12:645
3. Horiguchi S, Miyamoto K, Tokita M, Komai T (1998) Colloid Polym Sci 276:362
4. Ito S, Ogawa K, Suzuki H, Wang B, Yoshida R, Kokufuta E (1999) Langmuir 15:4289
5. Kamijo Y, Fujimoto K, Kawaguchi H, Yuguchi Y, Urakawa H, Kajiwara K (1996) Polym J 28:309
6. Kawaguchi H, Fujimoto K, Saito M, Kawasaki T, Urakami Y (1993) Polymer Int 30:225
7. Kawaguchi H, Fujimoto K, Nakazawa Y, Sakagawa M, Ariyoshi Y, Shidara M, Okazaki H, Ebisawa Y (1996) Colloid Surf A: Physicochemi Eng Aspec 109:147
8. Kihara N, Kanno C, Fukutomi T (1997) J Polym Sci A: Polym Chem 35:1443
9. Pelton R (2000) Adv Colloid Interfac Sci 85:1
10. Takata S, Shibayama M, Sasabe R, Kawaguchi H (2003) Polymer 44:495
11. Wu C, Zhou S, Au-Yeng SCF, Jiang S (1996) Die Angewandte Makromolekulare Chemie 240:123
12. Zhou S, Chu B (1998) J Phys Chem B 102:1364
13. Plunkett KN, Kraft ML, Yu Q, Moore JS (2003) Macromolecules 36:3960
14. Matyjaszewski K, Davis TP (2002) Wiley& Sons, New York
15. Takata S, Norisuye T, Shibayama M (1999) Macromolecules 32:3289
16. Ikkai F, Masui N, Karino T, Naito S, Kurita K, Shibayama M (2003) Langmuir 19:2568

17. Wu XS, Hoffman AS, Yager P (1992) J Polym Sci, A: Polym Chem 30:2121
18. Nisato G, Munch JP, Candau SJ (1999) Langmuir 15:4236
19. Norisuye T, Shibayama M, Nomura S (1998) Polymer 39:2769
20. Fang L, Brown W, Konak C (1990) Polymer 31:1960
21. Geissler E, Hecht AM, Horkay F, Zrinyi M (1998) Macromolecules 21:2594
22. Moussaid A, Schosseler F, Munch JP, Candau SJ (1993) J Phys II 3:573
23. Sugiura S, Nakajima M, Iwamoto S, Seki M (2001) Langmuir 17:5562
24. Iwamoto S, Nakagawa K, Sugiura S, Nakajima M (2002) AAPS PharmSciTech 3:25
25. Ikkai F (2004). L'Oreal, Japan Patent Disclos; 2004–099789
26. Ikkai F, Adachi E (2004) Macromol Rapid Commun 25:1514
27. Kobayashi I, Nakajima M, Chun K, Kikuchi Y, Fujita H (2002) AIChE J 48:1639
28. Kobayashi I, Nakajima M, Mukataka S (2004) ICEF9 p 610
29. Hirokawa Y, Tanaka T (1984) J Chem Phys 81:6379