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ORIGINAL CONTRIBUTION

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Production of polydivinylbiphenyl particles by precipitation polymerization in supercritical carbon dioxide

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Abstract Polydivinylbiphenyl particles were produced by precipitation polymerization of divinylbiphenyl without any stabilizer in supercritical carbon dioxide as polymerization medium at ca. 30 MPa for 24 h at 65 °C at different initiator concentrations (0.5–58.1 mmol l^{-1}). The conversions in all polymerization systems were relatively high. An increase in initiator concentration led to increases in the degree of coagulation and in the amount of low-molecular-weight byproducts and to a decrease in the amount of vinyl groups in the particle.

Keywords Supercritical carbon dioxide · Precipitation polymerization · Crosslink · Divinylbiphenyl · Particle

Introduction

Up to the present, some polymer industries (for example, the paint industry) have used large amounts of volatile organic compounds as a medium to prepare polymer molecules. However, because of environmental problems, the use of environmentally favorable media is desirable. Water is one of the environmentally sound media. There are a number of reports on radical polymerizations in aqueous and alcohol/water media: emulsion, dispersion, and suspension polymerizations.

Recently, in addition to water, there is increasing interest in supercritical carbon dioxide (scCO_2). The use of scCO_2 as medium for polymerizations has several potential advantages: low cost, low toxicity, eases of medium removal and recycling. Also, scCO_2 exhibits marked variations of solubility power, viscosity, and polarity with relatively small changes in temperature and pressure without altering the composition of the medium. Works describing the dispersion polymerization of vinyl monomers such as styrene (S) and methyl methacrylate (MMA) in scCO_2 have been published in the past years [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11].

DeSimone and coworkers have pioneered the production of polystyrene (PS) particles by dispersion polymerizations of S in scCO_2 with 2,2'-azobis(isobutyronitrile) (AIBN) in the presence of PS-*b*-poly (1,1-dihydroperfluorooctyl acrylate) (PFOA) [1], PFOA [2], and poly(dimethylsiloxane) (PDMS)-based macromonomer [3] as colloidal stabilizers. Moreover, they reported that poly(methyl methacrylate) (PMMA) particles were produced by dispersion polymerizations of MMA in scCO_2 with AIBN in the presence of PFOA [4, 5, 6, 7, 8] and PDMS-based macromonomer [3] as colloidal stabilizers. Beckman and Lepilleur, Johnston and coworkers, and Cooper and coworkers also produced PMMA particles in scCO_2 using poly(methyl methacrylate-*co*-hydroxyethyl methacrylate)-*g*-poly (perfluoropropylene oxide) [9], PDMS-*b*-poly(methacrylic acid) [10], and PMMA-*b*-poly(fluoroalkyl methacrylate) [11], respectively. Such stabilizers, however, are generally expensive and difficult to synthesize. In a recent article, we reported the production of PMMA particles by dispersion polymerization of MMA in $scCO_2$ using commercially supplied PDMS-based azoinitiator as inistab (initiator + stabilizer) [12]. Some fluorinated polymers and PDMS-based polymers have been identified as being soluble in CO_2 or CO_2-philic and used as colloidal stabilizers. Moreover, in dispersion polymerization, some stabilizers remain adsorbed or grafted on particle surfaces and those may operate as impurities in some applications.

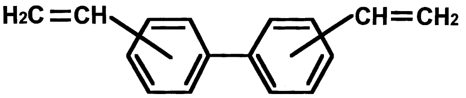
Precipitation polymerization is one of the methods for preparation of stabilizer-free particles with a clean surface [13, 14, 15, 16, 17, 18]. This method requires only monomer, radical initiator, and solvent. Stöver and coworkers produced highly crosslinked, monodisperse polydivinylbenzene (PDVB) particles by precipitation polymerization of divinylbenzene (DVB) in acetonitrile [13, 14, 15]. Recently, Cooper and coworkers reported that PDVB particles were also produced by precipitation polymerization of DVB in $scCO_2$ with AIBN [16, 17]. There have been strong demands for crosslinked polymer particles with superior heat resistance, solvent resistance, and clean surface to serve as carriers for chromatography, immobilizers of biomolecules, and various spacers.

In this article, stabilizer-free polydivinylbiphenyl (PDVBP) particles with clean surface, having superior heat resistance and high refractive index in comparison with PDVB [19], will be produced by precipitation polymerization of divinylbiphenyl (DVBP) in $scCO_2$ with AIBN.

Experimental

Materials

DVBP, whose formula is given below, was supplied by Nippon Steel Chemical Co., and the purity was 51.7% [19]. DVBP was washed with 1 N NaOH aqueous solution and deionized water to remove polymerization inhibitors before use (Structure 1).



Reagent grade AIBN was purified by recrystallization. Industrial grade CO_2, with a purity of 99.5% or more, was used as received.

Precipitation polymerization in $scCO_2$

Polymerization was carried out in a 10-ml stainless steel reactor under the conditions listed in Table 1.

The reactor was charged with DVBP, AIBN, and three 3/16-inch-sized stainless steel balls to mix in the reactor and purged with N_2. Then the reactor was pressurized with CO_2 to 10 MPa at 25 °C using a high pressure pump (Nihon Seimitu Kagaku, NP-D-321 J) and shaking vigorously. The polymerization was started by heating the mixtures to 65 °C, at which the pressure in the reactor reached ca. 30 MPa, with shaking at 60 cycles min^{-1}. After 24 h, the reactor was cooled in an ice water bath and the CO_2 was vented slowly. The produced particles were observed with a Hitachi S-2500 scanning electron microscope (SEM). The particle size distributions were examined with a disc centrifuge photosedimentometer particle sizer (Union Giken, PA-101).

Angle of repose

The fluidity of PDVBP powder was estimated by measuring the angle of repose as follows. Obtained PDVBP powder was gently charged into a glass funnel that had a circular opening of about 3 mm, with its opening blocked by a finger. By removing the finger, the powder was allowed to flow directly onto a flat stainless steel disk (10 mm diameter) to form a powder heap. The circular opening was set 30 mm higher just above the flat stainless steel disk. A still photograph was then taken for the determination of the angle of repose, defined as the angle of the free surface to the horizontal plane.

BET measurement

Specific surface area of PDVBP particles was determined from the amount of nitrogen gas adsorbed at the temperature of liquid nitrogen using a Gemini-Micromeritics 2360 (Shimadzu). The PDVBP particles were dried under vacuum overnight and in a nitrogen atmosphere at 80 °C for 4 h just prior to BET measurement.

Mass spectroscopy

The mass spectra were obtained with a Hitachi M-1200H quadrupole mass spectrometer. Atmospheric pressure chemical ioniza-

Table 1 Recipes for the production of PDVBP particles by precipitaion polymerizations of DVBP in supercritical CO_2[a] (10-ml stainless steel reactor)

Ingredients		AIBN concentration (mmol l^{-1})							
		0.5[c]	1.0[c]	2.0[d]	4.9[d]	9.7[d]	19.4[e]	38.7[e]	58.1[e]
DVBP[b]	(g)	2	2	2	2	2	2	2	2
AIBN	(mg)	0.8	1.6	3.2	8.0	15.9	31.8	63.5	95.4

[a] ca. 30 MPa; 65 °C; 60 cycles/min; 24 h

[b] Purity 53% (by catalog); 1.0 mol l^{-1} (20 w/v%)

[c] R_i ($2kd\,f$[I]), 10^{12}~10^{13} ml^{-1} s^{-1}; kd, 7.7×10^{-6} s^{-1}; f, 0.9

[d] R_i ($2kd\,f$[I]), 10^{13}~10^{14} ml^{-1} s^{-1}; kd, 7.7×10^{-6} s^{-1}; f, 0.9

[e] R_i ($2kd\,f$[I]), 10^{14}~10^{15} ml^{-1} s^{-1}; kd, 7.7×10^{-6} s^{-1}; f, 0.9

tion (APCI) in the positive ion mode was used to obtain the mass spectra in the mass range of 70–2000 m/z. Methanol was used as a solvent. The operation temperatures of the nebulizer and desolvator were 180 °C and 400 °C, respectively. The PDVBP powders (0.5 g) were centrifugally washed with methanol (25 g), and supernatant solutions containing low-molecular-weight byproducts were used as samples for mass spectroscopy.

Bromine titration

The amount of vinyl groups in PDVBP particles was measured by bromine titration method using an Aqua counter AQ-1 (Hiranuma Sangyo.). The residual monomers within the particles were removed by centrifugal washing with methanol prior to the measurement. After bromines (A moles) were generated by electrolysis in 70 ml of potassium bromide aqueous solution in a glass reactor, PDVBP particles (having X moles of vinyl groups) dispersed in methanol were injected with a syringe into the reactor. The vinyl groups were allowed to react with the bromine for a fixed reaction time. When the reaction time was up, sodium thiosulfate (B moles) aqueous solution, which quickly reacts completely with the residual bromines, was injected into the reactor. Afterwards, the unreacted sodium thiosulfate was titrated with bromine regenerated by electrolysis (C moles). The amount of vinyl groups (X moles) in the particles was calculated from the following equation.

$$X = A + C - B$$

Results and discussion

Precipitation polymerizations of DVBP were carried out with AIBN initiator in $scCO_2$ at ca. 30 MPa for 24 h at 65 °C in the 10-ml stainless steel reactor under the conditions listed in Table 1. The AIBN concentrations were determined on the basis of the idea described below. Initiation rate of radical polymerization, R_i is given by $R_i = f\rho_i$, where f is the initiator efficiency and ρ_i is the generation rate of radicals. The ρ_i is expressed as $\rho_i = 2k_d[I]$, where k_d is the rate coefficient for initiator decomposition, and [I] is the initiator concentration. In general, homogeneous radical polymerizations were carried out in the R_i range of 10^{13}–10^{14} ml^{-1} s^{-1} [20, 21, 22]. DeSimone and coworkers reported that k_d and f values of AIBN in $scCO_2$ were, respectively, ca. 2.5 times lower and ca. 1.5 times higher than those in benzene at the same temperature and at atmospheric pressure because of low dielectric constant and low viscosity of $scCO_2$ [23]. On the other hand, precipitation polymerizations in $scCO_2$ were often carried out in the relatively high R_i range of 10^{14}–10^{15} ml^{-1} s^{-1} [16, 17, 18], which was calculated in consideration of k_d and f values of AIBN in $scCO_2$. In this article, in order to clarify the effects of R_i on the precipitation polymerization of DVBP in $scCO_2$, the AIBN concentration was changed in the wide R_i range of 10^{12}–10^{15} ml^{-1} s^{-1}. The k_d and f values used in the calculation were 7.7×10^{-6} s^{-1} and 0.9, respectively. These values calculated for pure $scCO_2$ may be somewhat different from that for the mixture of $scCO_2$ and DVBP in the polymerization system.

Figure 1 shows the relationship between the AIBN concentration and the conversion of DVBP in the precipitation polymerizations in $scCO_2$ at different polymerization times of 3, 8, and 24 h. The conversion was determined by the gravimetrical method described below. The purity of DVBP was 51.7% and other components in monomer mixture were ethylvinylbiphenyl (23.6%), methylvinylbiphenyl (6.2%), vinylbiphenyl (5.8%), diethylbiphenyl (4.7%), and solvents (8.0%) (Nippon Steel Chemical Co., personal communication).The total weight percentage of reactive components in the monomer mixture was 87.3%. After the polymerizations, the products were centrifugally washed with methanol for the removal of the residual monomers and solvents. The conversion of DVBP was defined as weight percentage of the products after centrifugal washing to total reactive components in monomer mixture. The conversions increased with an increase in the AIBN concentration at 3 h and 8 h. The conversions at 24 h were relatively high (81%–96%) in all polymerization systems, even at the low AIBN concentrations of 0.5 and 1.0 mmol l^{-1}, and free-flowing white PDVBP powder was obtained. This is a remarkable point in this polymerization system as compared with the case of DVB. The conversion of DVB in the precipitation polymerization in $scCO_2$ at AIBN concentration of 24.4 mmol l^{-1} under similar conditions (at 31 MPa for 24 h at 65 °C) was 71% and that of 97.4 mmol l^{-1} managed to reach 89%. Cooper et al. showed that rather high AIBN concentrations seemed necessary to achieve good monomer conversions. The higher conversion of DVBP, even at the low AIBN concentrations in comparison with DVB, might be accounted for by the fact that the rate of crosslinking reaction of the second vinyl groups of PDVBP is faster than that of PDVB [19].

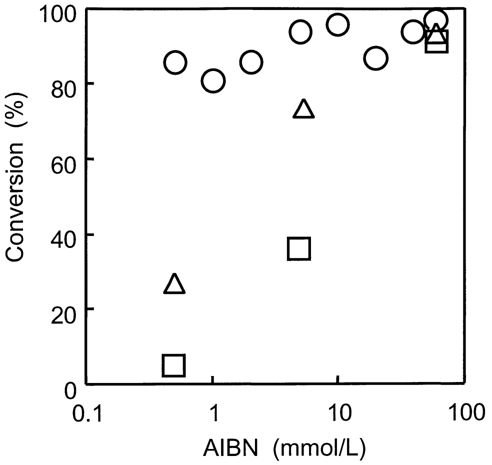


Fig. 1 Relationship between the AIBN concentration and the conversion of DVBP in the precipitation polymerizations in $scCO_2$ at the different polymerization times 3 h (*squares*), 8 h (*triangles*), and 24 h (*circles*)

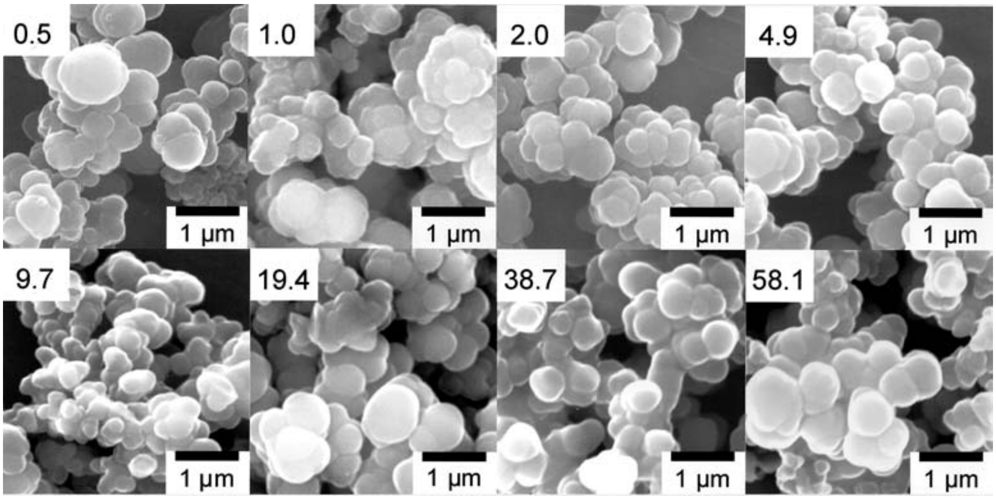


Fig. 2 SEM photographs of PDVBP particles produced by the precipitation polymerizations of DVBP in $scCO_2$ for 24 h at different AIBN concentrations (mmol l^{-1})

Figure 2 shows SEM photographs of PDVBP particles produced by the precipitation polymerizations of DVBP in $scCO_2$ at the different AIBN concentrations. In all AIBN concentration systems, the produced PDVBP particles partially coagulated and there was little difference in the particle size in all the systems. As far as we are aware, there has been no study on the relationship between the initiator concentration and the degree of coagulation, though the degree of coagulation will play an important role when the applications of the particles produced are taken into consideration. The degree of coagulation could not be estimated directly from SEM photographs because it was difficult to separate individual PDVBP particles from the aggregate. To examine the effect of AIBN concentration on the degree of coagulation, for convenience, the angle of repose was measured as it shows a general index to fluidity of powder [24, 25, 26]. It is known that the angle of repose increases with a decrease in the fluidity of powder, which seems to be caused by the increase of the degree of coagulation.

Figure 3 shows the relationship between the AIBN concentration and the angle of repose of the PDVBP powders. The angle of repose decreased (the fluidity of PDVBP powder increased) with a decrease in the AIBN concentration. This result indicates that the degree of coagulation decreased with the decrease in the AIBN concentration.

Figure 4 shows the relationship between the AIBN concentration and the specific surface area of the PDVBP particles. The specific surface area increased with the decrease in the AIBN concentration. Consid-

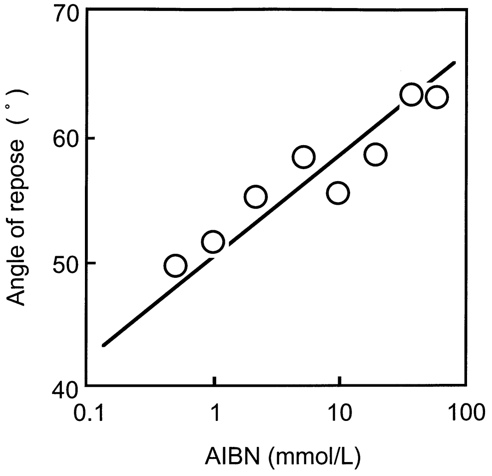


Fig. 3 Relationship between the AIBN concentration and the angle of repose of PDVBP particles produced by the precipitation polymerizations of DVBP in $scCO_2$ for 24 h

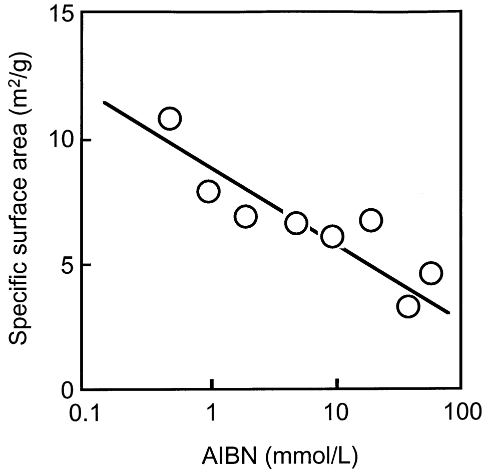


Fig. 4 Relationship between the AIBN concentration and the specific surface area of PDVBP particles produced by the precipitation polymerizations of DVBP in $scCO_2$ for 24 h

ering that the particle sizes observed in the SEM photographs were not so different in all the systems, this result indicates that the degree of coagulation decreased with the decrease in the AIBN concentration. This tendency agreed with that of the angle of repose.

Figure 5 shows the particle size distributions of PDVBP particles produced at AIBN concentrations of 0.5 and 58.1 mmol l^{-1}, measured with disc centrifuge photosedimentometer particle sizer. In the low AIBN concentration system, the particle size distribution was relatively sharp and the particle size was mostly less than 2 μm, which shows relatively good agreement with the results of the SEM observation. On the other hand, in the high AIBN concentration system, the particles size and the particle size distribution were larger and broader (1–8 μm and over) in comparison with the results of the SEM observation. In these ways, the high AIBN concentration, which seemed to be generally used in the reported experiments [16, 17, 18], caused a high degree of particle coagulation in the precipitation polymerization of DVBP.

Figure 6 shows SEM photographs of the PDVBP particles produced at the high AIBN concentration (58.1 mmol l^{-1}) before (a) and after (b) centrifugal washing with methanol. After washing, the boundary among the particles became clearer, which seems to be due to the removal of sticky low-molecular-weight byproduct on PDVBP particles, and the decrease in weight of PDVBP particles (0.6 wt%) was observed. Such sticky low-molecular-weight byproducts may be PDVBP oligomers and thermal decomposition products of AIBN, such as tetramethylsuccinodinitrile and isobutyronitrile that are generated, respectively, from the recombination and the disproportionation of primary radicals. Methacrylonitrile, which is also generated from the disproportionation of the primary radicals, should copolymerize with DVBP to be incorporated in PDVBP particles [27] under the consideration that both methacrylonitrile and DVBP are conjugated monomer. At the high AIBN concentration (58.1 mmol l^{-1}), a number of primary radicals are generated and collision frequency between the radicals is high, which should result in the generation of the byproducts. At the low AIBN concentration (0.5 mmol l^{-1}), the boundary among the particles was comparatively clear even before washing (data were omitted), and the decrease in weight of PDVBP particles after washing was negligible.

Figure 7 shows total ion charge (TIC) chromatogram of the low-molecular-weight byproducts generated in the process of the precipitation polymerizations of DVBP in $scCO_2$ at the two AIBN concentrations of 0.5 and 58.1 mmol l^{-1}. The arrows show sample injection times. The TIC peak strength of the high AIBN system was stronger than that of the low AIBN system. This result indicates that the low-molecular-weight byproducts were prepared less in the low AIBN system than in the high AIBN system. Such a low-molecular-weight byproduct should cause the increase of coagulation of the particles and is not desirable because of a decline in product quality.

Figure 8 shows the relationship between the square root of brominate reaction time and the amount of vinyl groups detected for the PDVBP particles produced at the two AIBN concentrations. The total amount of detected vinyl groups in the particles was 6.1×10^{-4} mol g^{-1}

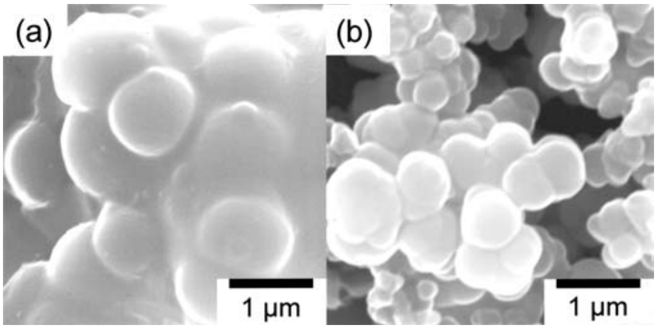
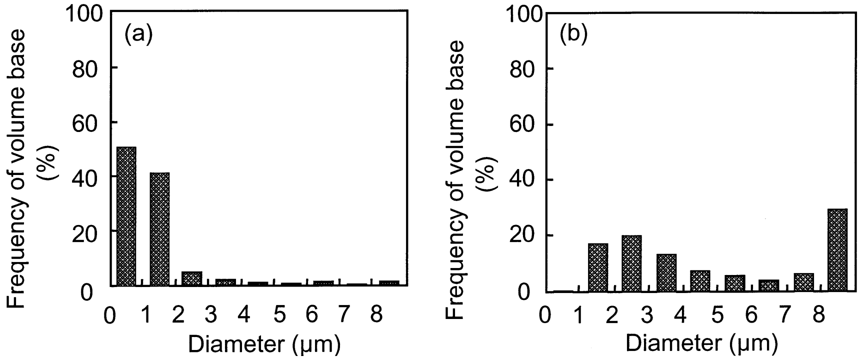


Fig. 6 SEM photographs of PDVBP particles produced by the precipitation polymerization of DVBP in $scCO_2$ for 24 h before (**a**) and after (**b**) centrifugal washing with methanol: AIBN concentration, 58.1 mmol l^{-1}

Fig. 5 Particle-size distributions of PDVBP particles produced at different AIBN concentrations: (**a**) 0.5 mmol l^{-1}, (**b**) 58.1 mmol l^{-1}, measured with disc centrifuge photosedimentometer particle sizer



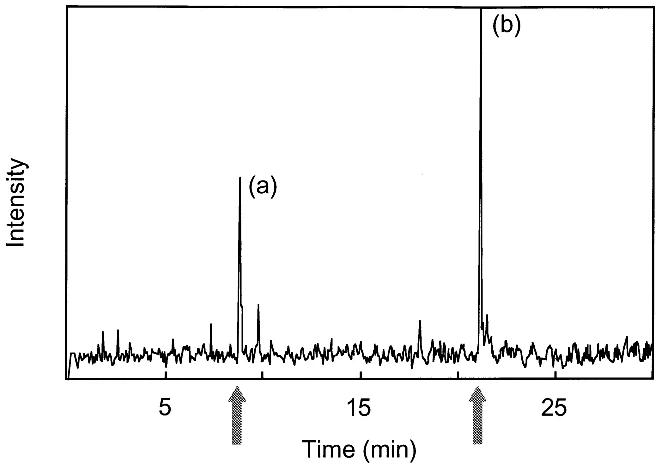


Fig. 7 Total ion charge chromatogram of low-molecular-weight byproducts generated in the process of the precipitation polymerizations of DVBP in $scCO_2$ for 24 h at different AIBN concentrations: (**a**) 0.5 mmol l^{-1}, (**b**) 58.1 mmol l^{-1}. The *arrows* show sample injection times

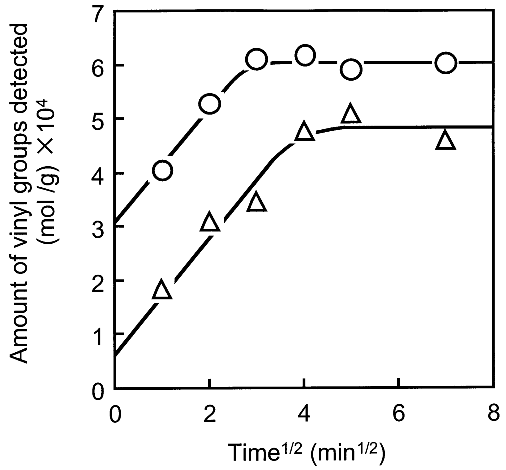


Fig. 8 Relationship between the square root of brominates reaction time and the amount of vinyl groups detected for two kinds of PDVBP particles produced by the precipitation polymerizations of DVBP in $scCO_2$ for 24 h at different AIBN concentrations: *circles* 0.5 mmol l^{-1}, *triangles* 58.1 mmol l^{-1}

in the low AIBN system, which was larger than that (4.9×10^{-4} mol g^{-1}) in the high AIBN system. The amount of vinyl groups detected at 0 min, which is determined by extrapolation, means the amount of vinyl groups at the particle surfaces [28]. The amounts of vinyl groups at the particle surfaces in the low and high AIBN systems were 3.1×10^{-4} and 0.6×10^{-4} mol g^{-1}, respectively. The occupied area of each vinyl group was 5.8 $\mathrm{Å}^2$ in the low AIBN system, which was calculated from the amount of vinyl groups at the particle surfaces and the specific surface area. This value was smaller than that (12.7 $\mathrm{Å}^2$) in the high AIBN system. These results suggest that a number of primary radicals generated in the high AIBN system decrease the second vinyl groups of PDVBP.

From the above results, it was concluded that stabilizer-free PDVBP particles with clean surface were successfully produced by the precipitation polymerization of DVBP in $scCO_2$ even at the low AIBN concentration. When the production and the applications of the crosslinked polymer particles are taken into consideration, it is advantageous that the particles with clean surface and low degree of coagulation are produced at the low AIBN concentration.

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