

Thermodynamics for preparation of micron-sized, monodispersed, monomer-“adsorbed” polymer particles having “snowman” shape by utilizing the dynamic swelling method and the seeded polymerization

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Abstract: In a previous article, micron-sized, monodispersed, anomalous highly styrene-“adsorbed” particles having “snowman” shape were prepared by the dynamic swelling method (DSM) with tightly cross-linked polystyrene (PS)/poly(divinylbenzene) (PDVB) (PS/PDVB = 1/10, w/w) composite particles. In this article, the thermodynamic background of DSM for the preparation of such monomer-adsorbed particles was discussed.

Key words: Dynamic swelling method; particle; monomer adsorption; thermodynamics; snowman shape; seeded polymerization.

Introduction. Recently, micron-sized, monodispersed polymer particles have been applied in the biomedical field, microelectronics, etc. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized, monodispersed polymer particles.¹⁻⁴⁾ Corner⁵⁾ and Almog *et al.*⁶⁾ suggested that dispersion polymerization is a useful technique for the production of such particles. We have been producing micron-sized, monodispersed polymer particles having functional groups such as chloromethyl⁷⁾ and vinyl groups^{8,9)} by seeded dispersion copolymerization with corresponding functional monomers in the presence of about 2 μm -sized, monodispersed polystyrene (PS) particles as seed.

Moreover, for the production of monodispersed particles having the diameter above 5 μm , we suggested a novel swelling method to make polymer seed particles absorb a large amount of monomer prior to the seeded polymerization.¹⁰⁻¹⁷⁾ It was named “dynamic swelling method (DSM)”.

Recently, highly monomer-“adsorbed” polymer particles were successfully prepared by DSM with tightly cross-linked seed particles which do not dissolve in the adsorbed monomer.¹⁸⁾ In the monomer adsorbed particle, a part of the cross-linked particle was imbedded in the spherical monomer phase and the remains protruded as peak at the droplet surface. That is, they had

not spherical, but “snowman” shape.

In this article, the thermodynamic stability of the highly monomer-adsorbed polymer particles having the snowman shape prepared by the DSM will be discussed.

Materials. Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) was washed with 1N NaOH and deionized water to remove polymerization inhibitor before use. The supplied DVB included ethyl vinylbenzene, vinyltoluene and the purity was 55%. Deionized water was distilled with a Pyrex distillator. Reagent grade of 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were purified by recrystallization. Poly(vinyl alcohol) (PVA) as a stabilizer was supplied by Nippon Synthetic Chemical (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%). Reagent grade of ethanol was used as received.

Cross-linked PS/PDVB composite particles as seed. Monodispersed PS seed particles were produced by dispersion polymerization under the conditions listed in Table IA and observed with a JEOL JEM-200CX transmission electron microscope (TEM). The number-average diameter (D_n) and the coefficient of variation (C_v) were, respectively, 1.77 μm and 3.9%.

Swelling of the PS particles with DVB was carried out using DSM under the conditions listed in Table IB according to the previous article¹⁴⁾ as follows. The PS

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Table I. Productions of micron-sized, monodispersed PS seed particles by dispersion polymerization^{a)} and PS/PDVB composite seed particles by seeded polymerization^{b)}

Ingredients	A	B
PS particles ^{c)} (g)	—	0.12
Styrene (g)	40.0	
DVB (g)	—	1.2
AIBN (g)	0.67	
BPO (g)	—	0.024
PAA (g)	4.80	
PVA (g)	—	0.06
Ethanol (g)	274.0	28.0
Water (g)	80.0	12.0 + 160 ^{d)}

^{a)} 70 °C; 24 h; N₂; in flask with stirring rate, 60 rpm. ^{b)} 70 °C; 24 h; N₂; in sealed tube with shaking rate, 120 cycles/min (2-cm strokes). ^{c)} D_n , 1.77 μm ; C_v , 3.9%. ^{d)} Water (42.4 g) was added using a microfeeder at the rate of 10.6 ml/h for 4 h and residual water was added collectively. Abbreviations: PS, polystyrene; DVB, divinylbenzene; AIBN, 2,2'-azobisisobutyronitrile; BPO, benzoyl peroxide; PAA, poly(acrylic acid); PVA, poly(vinyl alcohol).

particles were dispersed to the homogeneous solution of ethanol, water, DVB, BPO, and PVA in a 300 ml glass cylindrical reactor. Then, 42.4 g of water was added to the mixture with a microfeeder at a rate of 10.6 ml/h for 4 h and the residual water of 117.6 g was added collectively under stirring with a magnetic stirrer. Seeded polymerization for the dispersion was carried out in a sealed glass tube which was horizontally shaken at 120 cycles/min (2-cm strokes) at 70 °C for 24 h. The produced particles were washed repeatedly by serum replacement with ethanol/water (6/4, w/w) mixture to remove any traces of by-produced PDVB particles, and PVA. The solid content of the redispersed particles was adjusted at 10 g/l.

Monomer adsorption onto the cross-linked PS/PDVB composite particles utilizing DSM. On the basis of the results in the previous article,¹⁸⁾ a large amount of styrene was adsorbed by the cross-linked PS/PDVB composite particles under the conditions listed in Table II as follows. Ethanol, water, styrene, and PVA were charged into a 50 ml glass cylindrical reactor (inside diameter: 31 mm). With this homogeneous solution, 2.0 g of the PS/PDVB composite seed emulsion (solid content 10 g/l) was mixed. Water (5.76 g) was added to the mixture with a microfeeder at a rate of 2.88 ml/h for 2 h at room temperature under stirring with a magnetic stirrer at 130 rpm.

Table II. Preparations of styrene-“adsorbed” PS/PDVB composite particles utilizing the dynamic swelling method

Ingredients	No. 1	No. 2
PS/PDVB particles ^{a)} (mg)	20	20
Styrene (mg)	400	400
V-65 (mg)	—	8
PVA (mg)	73	73
Ethanol (g)	6.0	6.0
Water (g)	4.0 + 10 ^{b)}	4.0 + 10 ^{b)} + 30 ^{c)}

^{a)} D_n , 3.81 μm ; C_v , 2.6%. ^{b)} Water (10 g) was added using a microfeeder at the rate of 2.88 ml/h for 3.5 h at room temperature. ^{c)} Water (30 g) was added collectively at room temperature. Abbreviations: PS, polystyrene; PDVB, polydivinylbenzene; V-65, 2,2'-azobis(2,4-dimethyl valeronitrile); PVA, poly(vinyl alcohol).

Observation of the cross-linked seed particles and styrene-“adsorbed” particles by optical microscope and their diameter measurements. The dispersions of the seed particles and monomer-adsorbed particles were dropped onto slide glass, and observed with a Nikon MICROPHOTO FXA optical microscope. D_n , the weight-average diameter (D_w) of the seed particles, and the number-average diameter (D_m) of spherical monomer phase in the monomer-adsorbed particle, and C_v were determined by measuring the diameters of 50–150 droplets and particles on optical micrographs taken at room temperature with the Personal Image Analysis System (PIAS Co., Ltd., LA-525, Japan).

Results and discussion. Fig. 1 shows optical micrographs of cross-linked PS/PDVB (1/10, w/w) composite particles produced by seeded polymerization and a series of the styrene-adsorbed particles prepared by the DSM under the conditions of No. 1 listed in Table II. In Fig. 1(a), the produced composite particles had a spherical shape and high monodispersity; D_n , 3.88 μm ; D_w/D_n , 1.004; C_v , 3.7%. In Fig. 1(b), styrene adsorbed onto each particle appeared like a small head of “snowman”. As shown in Figs. 1(c–f), the volume of the head increased with the water addition, and resulted in exchanging the volume balance between the head and body of each snowman particle. In Figs. 1(e, f), the “head” consists of the cross-linked particle and the “body” consists of the adsorbed styrene. Throughout the water addition, the monodispersity was maintained. The volumes of the adsorbed styrene in the snowman particles agreed well with the presumed volumes calculated from a solubility curve of styrene in the ethanol/water mixtures assuming all separated styrenes were adsorbed by the seed particles.

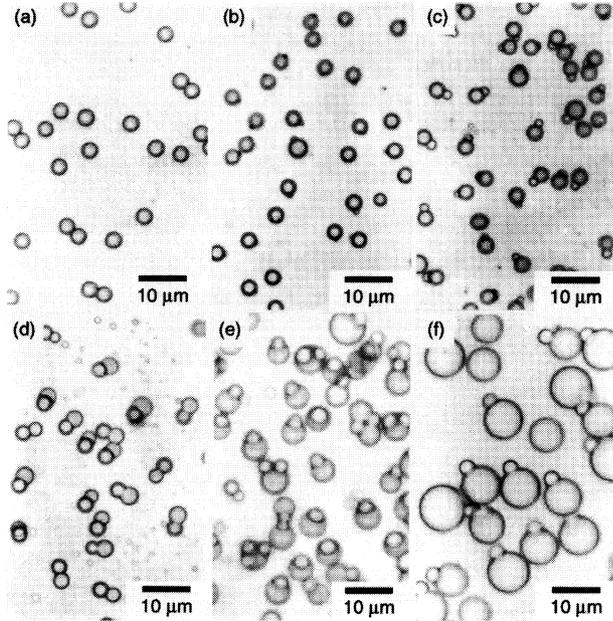


Fig. 1. Optical micrographs of PS/PDVB (1/10, w/w) composite seed particles (a) prepared by seeded polymerization and styrene-“adsorbed” PS/PDVB cross-linked particles (b–f) as a function of the amounts of water post-added at the rate of 2.88 ml/h: amount of water post-added (ml): (b) 1.7; (c) 1.9; (d) 2.2; (e) 2.9; (f) 5.8.

Interfacial free energy of “snowman”-shape morphology. In general, the total interfacial free energy (G) is equal to the sum of the products of the respective interfacial areas and tensions,^{19), 20)}

$$G = \sum \gamma_{ij} A_{ij} \quad [1]$$

where γ_{ij} is the interfacial tension between i and j -th phases, and A_{ij} is the corresponding interfacial area.

Fig. 2 shows schematic models for the two kinds of monomer-adsorbed particles (snowman; core-shell) and separated state in which polymer particle and monomer droplet exist individually. The snowman particle with angles, θ_m and θ_p which define the structure of the snowman shape was shown according to another literatures.²¹⁾⁻²³⁾ The core-shell monomer-adsorbed particle consists of a polymer core and a monomer shell. The interfacial free energy changes, $\Delta G_{SNOW-CORE}$ and $\Delta G_{SNOW-SEPA}$, respectively, from the core-shell and separated states to the snowman state can be expressed as follows:

$$\Delta G_{SNOW-CORE} = G_{SNOW} - G_{CORE} \quad [2]$$

$$\Delta G_{SNOW-SEPA} = G_{SNOW} - G_{SEPA} \quad [3]$$

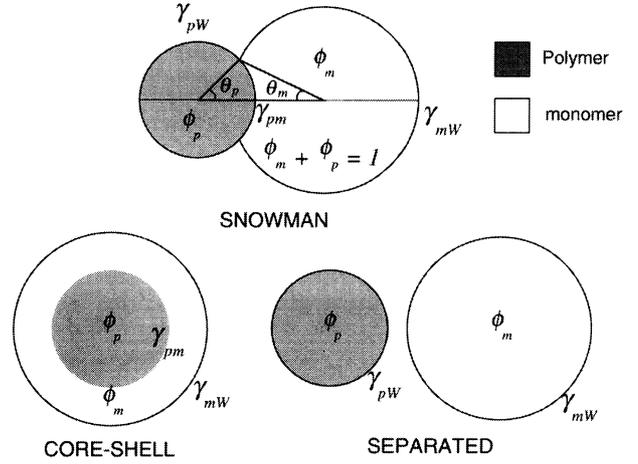


Fig. 2. Three morphological structures of the monomer-“adsorbed” particles dispersed in water. The angles, θ_m and θ_p , shown in snowman define the structure of the “snowman” shape.

where G_{SNOW} and G_{CORE} are, respectively, the interfacial energies of the snowman and core-shell particles, and G_{SEPA} is sum of those of polymer particle and monomer droplet. They are expressed according to another literature,²⁶⁾

$$G_{SNOW} = \left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \phi_p^2 \left(\gamma_{pW}(1 + \cos \theta_p) + \gamma_{mW}(1 + \cos \theta_m) \frac{\sin^2 \theta_p}{\sin^2 \theta_m} + \gamma_{pm}(1 - \cos \theta_p) \right)$$

$$G_{CORE} = 2 \left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \phi_p^2 \left(\gamma_{pm} \phi_p^{\frac{2}{3}} + \gamma_{mW} \right)$$

$$G_{SEPA} = 2 \left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \phi_p^2 \left(\gamma_{pW} \phi_p^{\frac{2}{3}} + \gamma_{mW} \phi_m^{\frac{2}{3}} \right).$$

ϕ is a fractional volume value in the monomer-adsorbed particle and subscripts, m , p and W denote monomer, polymer and water, respectively.

Since it is difficult to measure the respective interfacial tensions, γ_{pW} and γ_{pm} in these equations, eqs. [2] and [3] are, respectively, transformed as following eqs. [4] and [5],

$$\Delta G_{SNOW-CORE} = \left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \phi_p^2 \gamma_{mW} \left((1 + \cos \theta_p) \left(\frac{\gamma_{pW} - \gamma_{pm}}{\gamma_{mW}} \right) + (1 + \cos \theta_m) \frac{\sin^2 \theta_p}{\sin^2 \theta_m} - 2 \left(\frac{1}{\phi_p} \right)^{\frac{2}{3}} \right). \quad [4]$$

$$\Delta G_{SNOW-SEPA} = \left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \phi_p^2 \gamma_{mW} \left((1 - \cos \theta_p) \left(\frac{\gamma_{pW} - \gamma_{pm}}{\gamma_{mW}} \right) + (1 + \cos \theta_m) \frac{\sin^2 \theta_p}{\sin^2 \theta_m} - 2 \left(\frac{1 - \phi_p}{\phi_p} \right)^{\frac{2}{3}} \right). \quad [5]$$

The expression of the term including γ_{mW} , γ_{pW} and γ_{pm} in

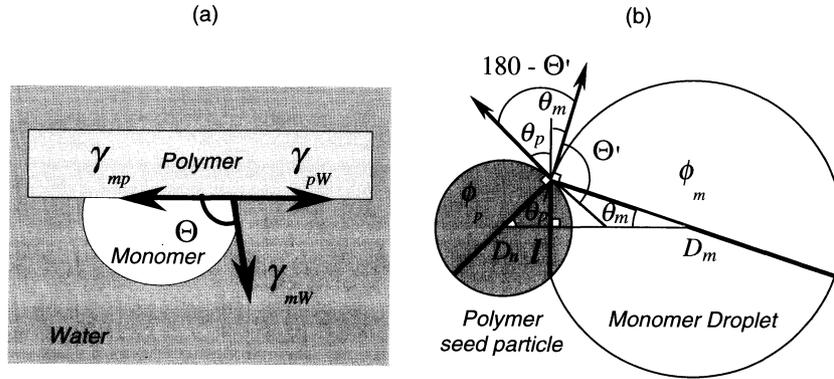


Fig. 3. Relationship between the contact angle and the angles, θ_m and θ_p which define the structure of the "snowman" shape of monomer-"adsorbed" polymer particles

eqs. [4] and [5] is the same as those in the well-known Young-Dupré equation^{(24), (25)} as described below,

$$\frac{\gamma_{pW} - \gamma_{pm}}{\gamma_{mW}} = \cos \Theta \quad [6]$$

where Θ is the contact angle (see Fig. 3a). As shown in Fig. 3b, the angles, θ_m and θ_p relate to the contact angle Θ as follows:

$$\Theta' = 180 - (\theta_m + \theta_p). \quad [7]$$

In this treatment, it might be reasonable that Θ' value is equal to the Θ value. Consequently, the $\Delta G_{SNOW-CORE}$ and $\Delta G_{SNOW-SEPA}$, respectively, could be expressed by eqs. [8] and [9] as functions of θ_p , θ_m and θ_p ,

$$\begin{aligned} \Delta G_{SNOW-CORE} = & \left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \phi_p^{\frac{2}{3}} \gamma_{mW} \left(-(1 - \cos \theta_p) \cos(\theta_m + \theta_p) \right. \\ & \left. + (1 + \cos \theta_m) \frac{\sin^2 \theta_p}{\sin^2 \theta_m} - 2 \left(\frac{1}{\phi_p}\right)^{\frac{2}{3}} \right). \quad [8] \end{aligned}$$

$$\begin{aligned} \Delta G_{SNOW-SEPA} = & \left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \phi_p^{\frac{2}{3}} \gamma_{mW} \left(-(1 - \cos \theta_p) \cos(\theta_m + \theta_p) \right. \\ & \left. + (1 + \cos \theta_m) \frac{\sin^2 \theta_p}{\sin^2 \theta_m} - 2 \left(\frac{1 - \phi_p}{\phi_p}\right)^{\frac{2}{3}} \right). \quad [9] \end{aligned}$$

It is possible to understand that the snowman state is more thermodynamic stable than the core-shell and separated states if both ΔG values which are expressed by eqs. [8] and [9] are below zero.

Thermodynamic stability of the "snowman" particle. Fig. 4 shows variations of angles, θ_m , θ_p , and Θ' , as a function of ϕ_m values in the styrene-adsorbed particles. The ϕ_m values were determined from the measured D_n and D_m values. The angles of θ_m and θ_p in

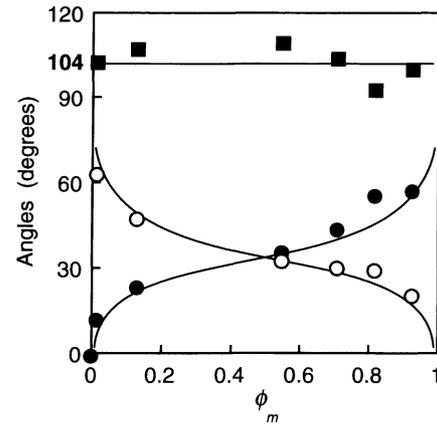


Fig. 4. Variations of the angles, θ_m (○), θ_p (●), and Θ' (■) as a function of ϕ_m value in the styrene-"adsorbed" polymer particles having "snowman" shape with monomer adsorption by the dynamic swelling method with tightly cross-linked PS/PDVB composite particles.

the monomer-adsorbed particle having snowman shape in the process of the DSM were determined using following equations with the D_n , D_m , and the lengths, l shown in Fig. 3,

$$\theta_p = \sin^{-1}\left(\frac{l}{D_n}\right), \quad \theta_m = \sin^{-1}\left(\frac{l}{D_m}\right). \quad [10]$$

The Θ' values were calculated using eq. [7] with θ_m and θ_p values. In Fig. 4, as the ϕ_m value increased, the θ_m (○) decreased and θ_p (●) increased. These indicate that the volume of imbedded part of the polymer particle in the styrene phase increased with the amount of adsorbed styrene. The Θ' values (■) were almost constant in the process of the DSM regardless of ϕ_m values. The average was 104 degrees. This indicates that the shape of the monomer-adsorbed particle is determined by the Θ' value.

Fig. 5 shows simulations of the changes of $\Delta G_{SNOW-CORE}$

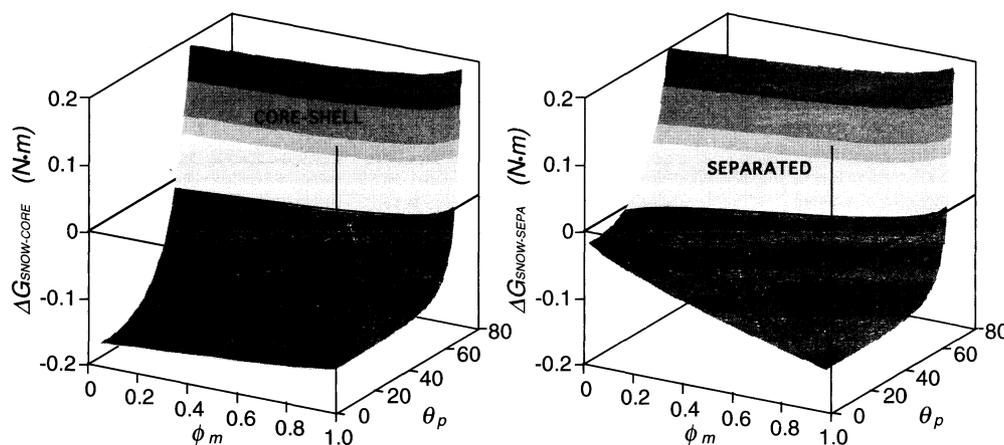


Fig. 5. Simulations of the changes of $\Delta G_{SNOW-CORE}$ and $\Delta G_{SNOW-SEPA}$ as functions of ϕ_m and θ_p values in the styrene-“adsorbed” particles, respectively, using eqs. [8] and [9] with a γ_{mW} value of 28 mN/m and a constant Θ values of 104 degrees. “Snowman” shape of adsorption proceeds in the regions below zero of $\Delta G_{SNOW-CORE}$ and $\Delta G_{SNOW-SEPA}$ values.

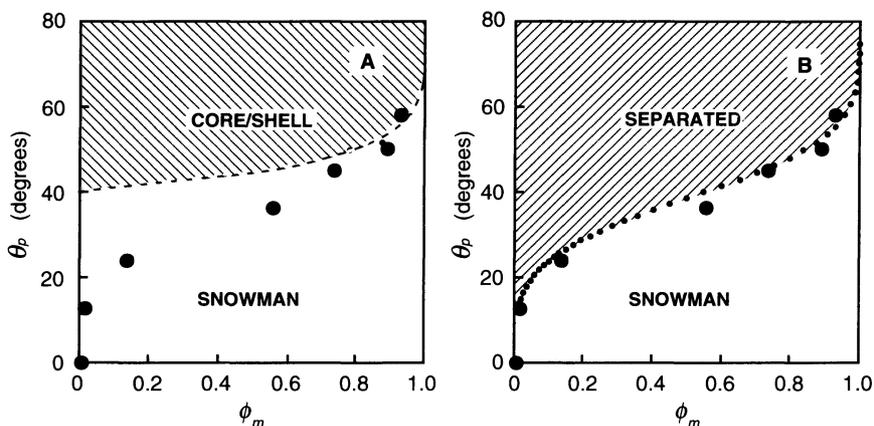


Fig. 6. Variation of θ_p as a function of ϕ_m value in the styrene-“adsorbed” particles prepared by DSM with tightly cross-linked PS/PDVB composite particles. Broken and dotted lines, respectively, shown in A and B indicate that θ_p values calculated as a function of value using eqs. [8] and [9] with a γ_{mW} value of 28 mN/m and a constant Θ values of 104 degrees at zero of $\Delta G_{SNOW-CORE}$ and $\Delta G_{SNOW-SEPA}$. “Snowman” shape of adsorption proceeds in the white regions below the broken and dotted lines.

and $\Delta G_{SNOW-SEPA}$ as functions of ϕ_m and θ_p values in the styrene-adsorbed particles, respectively, using eqs. [8] and [9] with the γ_{mW} value of 28 mN/m quoted from the literature²⁶⁾ and the Θ value of 104 degrees obtained in Fig. 4. As shown in Fig. 5, the $\Delta G_{SNOW-CORE}$ and $\Delta G_{SNOW-SEPA}$ values were negative and both $-\Delta G$ values increased with a decrease of θ_p value. These simulations indicate that the snowman state is the most thermodynamically stable in comparison with the core-shell and separated states at small θ_p value. The effect of θ_m on the shape of the monomer-adsorbed particle was not clear.

Fig. 6 shows variation of θ_p as a function of θ_m value in the styrene-adsorbed particles prepared by DSM. Broken and dotted lines, respectively, shown in A and B were simulation curves at zero of $\Delta G_{SNOW-CORE}$ and $\Delta G_{SNOW-SEPA}$ in Fig. 5. The simulation curves indicate

that the adsorption proceeds to give the snowman particle in the white regions below the broken and dotted lines. Almost all measured θ_p values (●) were located in the stable regions to form the snowman state. These results indicate that the preparation of the styrene-adsorbed particles having the snowman shape by DSM with tightly cross-linked PS/PDVB composite particles can be reasonably explained from thermodynamic treatment.

Fig. 7 shows relationships between PVA concentration and contact angle (Θ) value of a styrene drop on a PDVB film in PVA aqueous solutions at room temperature and $(\theta_m + \theta_p)$ value calculated from Θ value. The PDVB film was directly obtained by bulk polymerization of DVB (3 g) using BPO (0.06 g) as initiator at 70 °C for 24 h under a nitrogen atmosphere. The contact angle

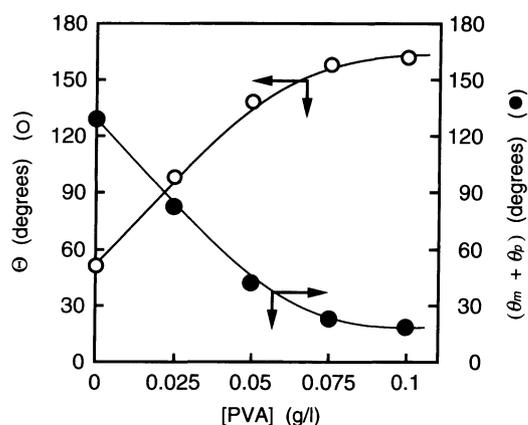


Fig. 7. A relationship between PVA concentration and Θ value of styrene drop on PDVB film in PVA aqueous solutions at room temperature and $(\theta_m + \theta_p)$ value calculated from each Θ value.

increased with PVA concentration, approaching to 180 degrees. This suggests that the styrene drop does not spread on the surface of PDVB film, which is occupied by the adsorbed PVA. The droplet surface might also adsorb by PVA molecules before it contacts with the PDVB film. Similar adsorptions of PVA molecules as stabilizer on the styrene phase and the cross-linked PS/PDVB composite particles should occur in the preparation of the styrene-adsorbed particle having the snowman shape using the DSM. This gives low wettability between them.

From these results, it is concluded that the "snowman"-shaped morphology of the styrene-adsorbed particle prepared using the DSM is thermodynamically stable and based on the low wettability between the composite particle and the adsorbed spherical styrene phase, because of existence of PVA molecules at the interfacial layer between them. Moreover, seeded polymerization for the dispersion of the monomer-adsorbed particles successfully gave the composite polymer particles having a similar "snowman" shape. This experimental detail of the seeded polymerization will be appeared elsewhere.

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