IBN Partition between St Monomer/Polymer and Water and Its Application in Miniemulsion Polymerization Initiated by AIBN

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DOI 10.1002/aic.12806

Isobutyronitrile has been selected as a stable substitute for the 2-cyano-2-propyl radical originating from 2,2′-azobis(isobutyronitrile) to study the behavior of this radical in miniemulsion polymerization. The partition of isobutyronitrile between styrene monomers/polymers and water has been investigated by carrying out equilibrium experiments under different conditions. Prediction based on a published kinetic model using the newly measured partition coefficient has also been compared with published experimental data and prediction based on the partition coefficient of 2,2′-azobis(isobutyronitrile). The partition coefficients for isobutyronitrile were found to be 10.98 for the styrene/water system and 4.34 for the polystyrene/water system, respectively. The partition coefficient was found to be unaffected by selected conditions. The model prediction based on the partition coefficient of isobutyronitrile agreed well with the published experimental data, thus, indicating that the partition coefficient of the primary radical should be used in theoretical calculations rather than that of the initiator. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 3135–3143, 2012

Keywords: isobutyronitrile, partition, styrene, miniemulsion polymerization, 2,2′-azobis(isobutyronitrile)

Introduction

Different emulsion polymerizations (including microemulsion, macroemulsion, and miniemulsion) are not distinguished by the particle size, but the synthesis mechanisms. Antonietti and Landfester[1] had summarized the difference between these emulsion polymerizations. Scheme 1 illustrates the different emulsion polymerization process vividly. In emulsion polymerizations, water-soluble initiators are often employed. Under these circumstances, primary radicals originating from the initiator propagate in the aqueous phase to reach to a critical length (becoming surface-active oligomeric radicals) before being absorbed by micelles or droplets.[2] In micro- and macroemulsion polymerization, oligomeric radicals usually enter into micelles leading to micelle nucleation. In miniemulsion polymerizations, however, oligomeric radicals prefer to enter into monomer droplets and monomer swelling particles, leading to so-called droplet nucleation.[1]

In the past few decades, oil-soluble initiators have also been widely employed in emulsion polymerization, especially in miniemulsion polymerization.[3–8] Compared to water-soluble initiators, their location shifts from the aqueous phase to the organic phase. Indeed, oil-soluble initiators have their own functions in emulsion polymerization that are not seen with water-soluble initiators. An initiator that is highly insoluble in water could be used to suppress Ostwald ripening of the monomer droplets in miniemulsion polymerization.[4,5] Such initiators are advantageous in producing stable organic-inorganic hybrid latex particles in miniemulsion polymerization stabilized by an anionic surfactant.[6,7] Silanol-functionalized latex has also been synthesized by miniemulsion polymerization using an oil-soluble initiator.[8] Such initiators can also be applied when nonionic latex products are desired.

Most researchers assume that the mechanism of emulsion polymerization initiated by water-soluble initiators is no longer applicable here, and much effort has been made to clarify the mechanism of emulsion polymerization initiated by oil-soluble initiators. Indeed, there is still an ongoing debate in the literature about the predominant source of effective radicals in emulsion polymerization using oil-soluble initiators. In the certain kinds or stages of emulsion polymerization (e.g., interval II, III in macroemulsion polymerization, seeded macroemulsion polymerization, and miniemulsion polymerization), the particle number is constant, and the kinetics of the polymerization is related only to the concentration of monomer in the particle, the size of the particle, and the average number of radicals per particle. However, the most important parameter is the last one. Primary radicals derived from decomposition of the oil-soluble initiator in the latex particle will undergo desorption, propagation, and mutual termination, while the small fraction of initiator dissolved in the aqueous phase will act as a water-soluble initiator. Some research groups have suggested that the free radicals responsible for particle nucleation originate from the small fraction of oil-soluble initiator dissolved in the

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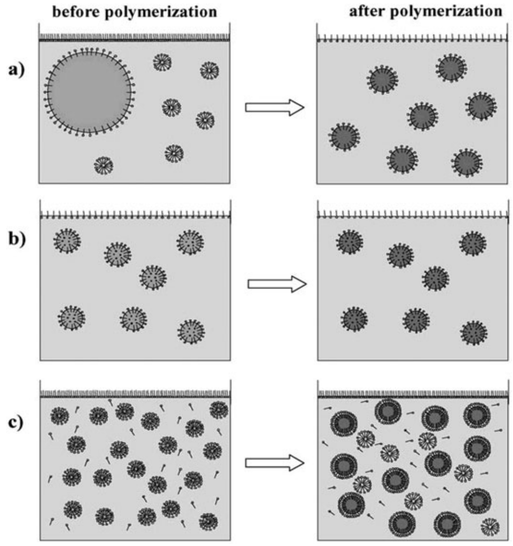

Scheme 1. Comparison of different emulsion polymerizations (a) macroemulsion polymerization, (b) miniemulsion polymerization, and (c) microemulsion polymerization.[1]

aqueous continuous phase, while primary radicals produced within the latex particle will mainly suffer rapid mutual termination.[9–11] On the other hand, other groups have proposed that one of the two newly generated primary radicals will desorb out of the particle before bimolecular termination can occur. Hence, the remaining radicals will propagate with the monomer in the particle.[3,12,13] The results of other authors support the desorption theory, but their findings simultaneously confirm that the desorbed radicals and radicals derived from the oil-soluble initiator dissolved in the aqueous phase also play important roles in the initiating process.[14]

2,2′-Azobis(isobutyronitrile) (AIBN) has been frequently used as an initiator for the polymerization of vinyl monomers. Meanwhile, it is one of the most extensively studied azoalkanes because, in contrast to peroxide initiators, it decomposes into a nitrogen molecule and a pair of 2-cyano-2-propyl radicals without other byproduct radicals.[15–17] It usually serves as a typical oil-soluble initiator, and can be used in many circumstances. Many literature reports focusing on emulsion polymerization using oil-soluble initiators often cite AIBN as the chosen typical initiator.[10,12–14,18,19] Also, mathematical models always employ parameters pertaining to AIBN, especially employing the partition coefficient of AIBN between the organic and aqueous phases, which is the main difference from other oil-soluble initiators. From the viewpoint of suppressing Ostwald ripening, for example, the solubility of the initiators is important. Where as the radical desorption is mentioned in literature modeling the process of miniemulsion polymerization, it is more suitable to pay more attention to the primary radicals originated from the initiator, but not the initiator itself

$$\mathrm{AIBN} \xrightarrow{\Delta} \mathrm{N_2} + 2(\mathrm{CH_3})_2\overset{*}{\mathrm{C}}\mathrm{CN}$$

In this study, we present results from experiments performed to measure the partition coefficients of isobutyronitrile (IBN) between styrene (St) and water, and between polystyrene (PSt) and water. IBN was selected because its chemical structure most closely resembles that of the 2-cyano-2-propyl radical, differing only in the additional hydrogen atom. Experiments were also performed to determine the influences of temperature, pH, oil/water ratio, hexadecane, and surfactant on the partition between St and water, and of the particle size, nature of the surfactant, and monomer content on the partitioning between PSt particles and water. To the best of our knowledge, the partition coefficients of IBN between styrene monomers/polymers and water and the influences of the aforementioned factors on IBN partitioning have not hitherto been reported in the literature. Furthermore, measuring the partition of IBN will be of great help for understanding the partition behavior of the 2-cyano-2-propyl radical. However, the partition behavior of the 2-cyano-2-propyl radical directly affects the radical desorption in emulsion polymerization, further the average number of radicals per particle and the polymerization kinetics. The newly measured partition coefficient was subsequently applied in a mathematical model to calculate the kinetics of miniemulsion polymerization initiated by AIBN, and the results were compared with experimental data.

Experimental Section

Materials

Distilled water was used in all experiments. St (99.5%) was first washed with two portions of 10% aqueous NaOH solution to remove quinone inhibitor, then further washed with distilled water until the washings became neutral, dried over Na_2SO_4 for 1 h, and then over $CaCl_2$ for a further 24 h. Crude St was distilled under reduced pressure. Typically, some copper powder was added to a three-necked flask equipped with a capillary tube and a Vigreux distillation column. The pressure was maintained at 5.33 kPa by a pump attached to the outlet of the condenser. The middle part of distillate was collected and kept in a refrigerator before use. AIBN was recrystallized twice from ethanol. IBN (98.9%), potassium persulfate (KPS), sodium dodecyl sulfate (SDS), hexadecyl trimethylammonium bromide (CTAB), hexadecane (HD), hydroquinone (HQ), tetrahydrofuran (THF), hydrochloric acid, NaOH, Na_2SO_4, and $CaCl_2$ were used as received.

IBN partitioning experiments

All partition experiments were carried out in a 50 cm^3 jacketed glass vessel equipped with a thermometer. St/IBN/water partition experiments were carried out by charging the partitioning vessel with water, IBN, St, and other substances as necessary. The contents were stirred with a magnetic agitator and heated to the desired temperature by means of a water bath. The pH of the aqueous phase was adjusted by adding a few drops of hydrochloric acid or aqueous NaOH solution. Partition was allowed to maintain for at least 30 min to ensure the attainment of phase equilibrium.

Before samples were withdrawn from the partition vessel, the agitation was stopped and the mixture was allowed to stand isothermally for at least 45 min to permit complete separation of the small oil droplets suspended in the aqueous phase. The oil layer and the aqueous solution of the lower layer were withdrawn with syringes, transferred to respective volumetric flasks, and weighed. Then, a known quantity of THF was added as an internal standard for gas chromatography (GC, Agilent 6890 equipped with INNOWAX capillary column), which also served as a solvent preventing phase separation when the samples were cooled. Samples were then

Table 1. Summary of the Partition Experiment Recipe for Each System

Equilibriums	Water (g)	IBN (g)	Miniemulsion (g)	St (g)	Temperature (°C)	HD (g)	pH	HQ (g)
1	42.5	0.0335~0.1214	---	7.5	70	---	7	---
2	42.5	0.0607	---	7.5	50~80	---	7	---
3	42.5	0.0607	---	7.5	70	0~0.45	7	---
4	34~46	0.0607	---	16~4	70	---	7	---
5	42.5	0.0607	---	7.5	70	---	1.5~10	---
6	---	0.0335~0.1214	run a[a], 40	---	70	---	---	0.02
7	---	0.0335~0.0911	run b[a], 40	---	70	---	---	0.02
8	---	0.0335~0.1214	run c[a], 40	---	70	---	---	0.02
9	---	0.0911	samples of run b[a] at different time intervals, 40	---	70	---	---	0.02

[a] run a, b, c refer to miniemulsion stated in Table 2

subjected to GC analysis by the internal standard method utilizing a relative mass correction factor for peak areas.

PSt/water/IBN partition experiments were carried out under the same operating conditions. Miniemulsion (prepared as in the following description) and IBN were introduced into the partitioning vessel, and a small amount of HQ was added to prevent postpolymerization of the miniemulsion. After the mixture had reached equilibrium, samples were withdrawn and centrifuged at room temperature. The aqueous phase was carefully transferred by means of a syringe to a volumetric flask and weighed, and then a known quantity of THF was added. The ‘‘solid phase’’ was collected up and treated as described earlier. A small amount of ‘‘solid phase’’ solution in THF was used for GC analysis; the remainder was dried in a vacuum oven at 110°C to determine the solid content therein, which was then used to determine the actual particle content in the ‘‘solid phase’’. The compositions for the partition experiments on St/IBN/water and PSt/water/IBN are listed in Table 1. In Table 1, each equilibrium represents a group of experiments, and ‘‘~’’ means the variation of independent factors of that group.

Miniemulsion preparation

First, the costabilizer was dissolved in the monomer to form the oil phase. This oil phase was then added to an aqueous solution containing the surfactant, and the mixture was pre-emulsified by vigorous magnetic agitation for 30 min in an ice bath, then homogenized to form nanodroplets through sonication for 10–20 min using a pulsed sequence (10 s sonication followed by 5 s break) with a 560 W duty cycle under magnetic agitation in an ice bath. The miniemulsion was then introduced into the jacketed reactor and purged with nitrogen. The temperature was raised to 70°C, and an aqueous solution of KPS was fed into the reactor to start the polymerization. During the polymerization process, samples were withdrawn at specific time intervals, as appropriate. For polymerizations initiated by AIBN, the initiator was predissolved in the oil phase before the pre-emulsification and homogenization steps required to generate the miniemulsion. Typical compositions and experimental conditions for the miniemulsion polymerization are given in Table 2. The particle size was measured by dynamic light scattering (DLS, Zetasizer 3000HSA, Malvern) at 25°C at a fixed scattering angle of 90°. The conversion of different samples are determined gravimetrically.

Results and Discussion

Definition of partition coefficient

Partition coefficient is frequently used in emulsion polymerization and for accurately assessing the monomer concentration in the aqueous phase and monomer-swollen particles.[20] Because the concentration of water-insoluble monomers in the aqueous phase is quite low, Henry's law may be used to describe the phase equilibrium between the monomer-swollen particles and the aqueous phase, which should yield a straight line passing through the origin, the slope of which may be taken as the partition coefficient. Hence, IBN partition coefficients for the St/IBN/water and PSt/IBN/water systems may be defined as

$$m_{org,IBN} = \frac{[IBN]_{org}}{[IBN]_{aq}} \tag{1}$$

where $[IBN]$ represents the concentration of IBN in mol/dm^3 the subscript *org* denotes the organic phase (*St* represents styrene, and *p* represents PSt particles), and *aq* represents the aqueous phase. For a simple measurement, the partition coefficient may be directly obtained by dividing the concentration of IBN in the organic phase by the concentration in the aqueous phase. For a more rigorous measurement, different amounts of IBN were added to generate pairs of concentrations, and a straight line through the origin was fitted, its slope being the required partition coefficient.

Theoretical prediction

Relationship between IBN partition coefficient and Henry's law constants in the St/IBN/water system. The whole partition system is a heterogeneous closed system. Each phase may be considered as a homogeneous closed system. Therefore, the phase equilibrium criterion is

$$\hat{f}_i^{(1)} = \hat{f}_i^{(2)} = \ldots = \hat{f}_i^{(M)} \ (i = 1, 2, \ldots, \mathrm{N}) \tag{2}$$

where $\hat{f}$ is the component fugacity, subscript i is the component symbol, and superscript (M) is the phase mark. In our system, i = 3 and $(M) = 2$.

Table 2. Recipes for Miniemulsion Polymerization

Runs	Water (g)	SDS (g)	CTAB (g)	St (g)	HD (g)	KPS (g)	AIBN (g)	pH	Particle size (nm)	Final conversion (%)
a	170	0.15	---	30	0.9	0.2	---	unbuffered	131.2	97.47
b	340	0.12	---	60	1.8	0.4	---	unbuffered	182.8	94.78
c	170	---	0.0758	30	0.9	---	0.2428	unbuffered	171.2	94.12

The IBN concentration used in all experiments was quite low (lower than 0.25 wt % with respect to the total reagent). Hence, Henry's law could be simplified as

$$\hat{f}_{IBN}^{(M)} = H_{IBN,Solvent} \cdot x_{IBN,M} \tag{3}$$

where $H_{IBN,\mathrm{Solvent}}$ is the Henry's law constant of IBN in solvent, $x_{IBN,M}$ is the mole fraction of *IBN* in phase *M*.

Inserting Eq. 3 into Eq. 2 leads to

$$\frac{H_{IBN,water}}{H_{IBN,St}} = \frac{x_{IBN,St}}{x_{IBN,water}} \tag{4}$$

If a small amount of IBN does not affect the density of St and water, and $x_{IBN,M}$ is quite small, the concentration of *IBN* in the St and aqueous phase will be

$$[IBN]_{St} = \frac{x_{IBN,St} \cdot \rho_{St}}{Mw_{St}} \text{ and } [IBN]_{water} = \frac{x_{IBN,water} \cdot \rho_{St}}{Mw_{water}} \tag{5}$$

where Mw is the molecular weight, and ρ is the density.

From the definition of partition coefficient in Eq. 1, we get to

$$\frac{H_{IBN,water}}{H_{IBN,St}} = \frac{x_{IBN,St}}{x_{IBN,water}} = m_{St,IBN} \frac{Mw_{St} \cdot \rho_{water}}{\rho_{St} \cdot Mw_{water}} \tag{6}$$

Equation 6 is the final expression relating the Henry's law constants and the partition coefficient. If the Henry's law constants of IBN in water and St are known, the partition coefficient may be calculated according to Eq. 6. Conversely, if the partition coefficient of IBN between St and water and one of the Henry's law constants are known, the other Henry's law constant may be predicted.

Simple Model Predicting the Partition Coefficient between PSt and Water. Morten,[21] Vanzo[22] and Gardon et al.[23] have studied latex particles saturated by monomer, which had limited solubility in the aqueous phase, and a model was deduced to predict the monomer concentration in monomer-swollen particles and the aqueous phase, the so-called Vanzo equation (Eq. 7)

$$\ln\left(1 - v_p\right) + v_p\left(1 - \frac{1}{\overline{M}_n}\right) + \chi v_p^2 + \frac{2\overline{V}_m \cdot \gamma v_p^{1/3}}{r_0 \cdot RT} = \ln\left(\frac{[M]_{aq}}{[M]_{aq,sat}}\right) \tag{7}$$

where v_p is the volume fraction of polymer in the particle, $\overline{M}_n$ the number-average degree of polymerization, R is the gas constant, T is the temperature, χ is the Flory-Huggins interaction parameter, $\overline{V}_m$ is the partial molar volume of the monomer, γ is the particle-water interfacial tension, r_0 is the unswollen radius of the particle, $[M]_{aq}$ the concentration of monomer in the aqueous phase, and $[M]_{as,sat}$ the saturation concentration of monomer in the aqueous phase.

In order to study the partition of primary radicals in the latex particles, more simplification may be obtained. In experiments to determine the partition of primary radicals, $\overline{M}_n$ is always large and its multiplicative inverse is substantially smaller than 1. Therefore, the second term on the lefthand side could be simplified as v_p. This simplification has been testified as being reliable by Maxwell et al.[24] The primary radical concentration is always quite low in swollen particles. For example, for one radical in a 100 nm particle, the concentration is 3.17×10^{-6} mol/dm^3, which means that the polymer fraction always equals approximately 100%. Hence, we could insert $v_p = 1$ in the last three items on the lefthand side. However, $v_p = 1$ could not be inserted into the first term on the lefthand side, because $\ln(1-v_p)$ will become a large negative value when v_p is close to 1. At the same time, if correlative parameters are inserted into the last item on the lefthand side, its value will be considerably smaller than the second and third terms. Therefore, the last term on the lefthand side will be ignored as well. As a result, Eq. 7 may be simplified as

$$\ln\left(1 - v_p\right) + 1 + \chi = \ln\left(\frac{[M]_{aq}}{[M]_{aq,sat}}\right) \tag{8}$$

which may be rewritten as

$$m_{p,M} = \frac{[M]_p}{[M]_{aq}} = \frac{\rho_M}{[M]_{aq,sat} \cdot \exp(1 + \chi)} \tag{9}$$

where ρ_M is the density of the monomer. Equation 9 is the most simplified model for determination of the partition coefficient of a monomer between latex particles and water when the concentration of monomer in the latex particles is low. From Eq. 9, we can predict that the partition coefficient will only depend on the saturated solubility of the model substance and its interaction with the polymer.

St/IBN/water system

Understanding the partition of IBN between St and water directly clarifies the partition behavior of 2-cyano-2-propyl radicals and the mechanism in the early stage of emulsion polymerization, such as the origin of the radicals responsible for nucleation. It is for this reason that the partition experiments were performed.

Partition Coefficient. The partition of IBN between St and water at 70°C at various concentrations is shown in Figure 1. It is apparent that the partition of IBN is linear over the range of concentrations studied, which is in accordance with the theoretical analysis by Henry's law. The slope of the straight line is 10.98. It is much lower than the reported partition coefficient of AIBN between St and water ($m_{St,AIBN} = 115$).[9] When the oil content was 15%, the AIBN molecules in the aqueous phase only constituted 4.7% of the total amount, while the IBN molecules in the aqueous phase constituted 34%. This means that in emulsion polymerization the AIBN molecules may stay in the particles, but the primary radicals derived from the decomposition of AIBN prefer to desorb from the particles and reside in the aqueous phase. Actually, the solubility of IBN in water (3.48 wt %) is quite high compared to that of AIBN (0.04 wt %).[4,25] This is expected since AIBN contains more hydrophobic groups compared to IBN, which should reduce its solubility in water. Also, the polar group (-CN) and its isostructural form will render IBN (and, hence, the 2-cyano-2-propyl radicals) more water-soluble such that they preferentially reside in the aqueous phase rather than the oil phase.

Temperature. The appropriate temperature range for emulsion polymerization is 50–80°C, as this gives a moderate AIBN decomposition rate so as to provide radicals continuously and a rapid propagation rate for the monomer. In this temperature range, it seems that the partition coefficient

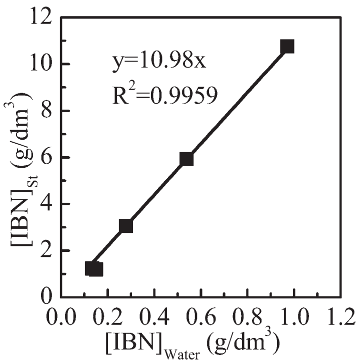

Figure 1. Partition of IBN between St and water at 70°C.

is independent of the temperature, as shown in Figure 2. In idealized models, the solubility of an organic solvent in water will increase with increasing temperature, as is the case with St.[26] Nevertheless, temperature really has no effect on the solubility of IBN in water over a wide range.[25] At the same time, IBN and St are mutually soluble, which implies that the solubility of IBN in St will not change with temperature. These phenomena may reasonably explain why the partition coefficient is not affected by the temperature. Another reasonable interpretation arises from Eq. 6. The partition coefficient is related to the ratio of the Henry's law constants of IBN in water and the St. The Henry's law constant is related to temperature and pressure. In our experiments, the pressure is constant (atmospheric pressure), and the Henry's law constant is only dependent on temperature. The Henry's law constant always increases with temperature. Therefore, the Henry's law constants of IBN in both phases may increase, and the quotient of the two will probably remain constant, and, hence, also the partition coefficient. On the basis of Eq. 6, the partition coefficient and the two Henry's law constants could be calculated reciprocally. Henry's law constant for IBN in water at 25°C is $H_{IBN,\mathrm{water}} = 303$ kPa.[27] If we assume that the partition coefficient is still 10.98 at 25°C, the corresponding value for IBN in St is $H_{IBN,St} = 4.10$ kPa.

Hexadecane (HD). HD is an efficient co-stabilizer in miniemulsion polymerization. In a typical composition, 3–5 wt % HD is used to prevent Ostwald ripening. In our experiments, the HD content was varied over this typical range. The results of experiments performed to clarify the effects of added HD on the partition of IBN between St and water at 70°C are summarized in Table 3. It can be seen from Table 3 that the data obtained from experiments performed with added HD are almost the same as those obtained earlier without HD. This implies that the addition of HD will not affect the partition of IBN between *St* and water.

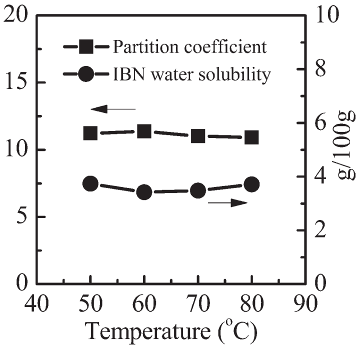

Figure 2. IBN partition coefficient between St and water and solubility at different temperature.

Table 3. Measured Partition Coefficient for IBN with Different Content of HD in Oil

HD content (wt%)	Partition coefficient
0.00	10.98
3.50	10.25
5.67	10.15

Oil Content. In emulsion polymerization, different solid contents are applied under different circumstances. Hence, the influence of solid content that is, oil content is considered. The monomer concentration and primary radical concentration in each phase are all so-called intensive properties. An intensive property is the one that is not related to the extensive property, which is quantity of the reactant in this system. For this reason, the oil content will not influence the IBN concentrations in the organic and aqueous phases, and hence will not affect the partition coefficient. The results of experiments supporting this interpretation are presented in Table 4.

pH. Sometimes, in order to obtain a more stable emulsion polymerization process or other functional structures besides latex particles, it is necessary to adjust the pH of the aqueous phase. Hence, we also performed experiments to determine whether the pH of the aqueous phase influences the partition of IBN between St and water. Data collected at various pH values of the aqueous phase are listed in Table 5. In these experiments, both acidic and alkaline conditions were examined. It can be seen from Table 5 that pH has no effect on the partition of IBN, even under strongly acidic conditions. As pH represents the H^+ or OH^- concentration in an aqueous solution, high and low pH values also mean greater ionic strength. IBN is not dissociated in an organic solvent, and no ion can be released from the IBN molecule. Consequently, the H^+ or OH^- concentrations will not affect the solubility of IBN.

PSt/IBN/water system

To clarify the partition behavior of 2-cyano-2-propyl radicals in the whole emulsion polymerization process, we also conducted experiments to measure the partition coefficient of IBN between PSt and water.

Partition coefficient. Experimental data on the partition of IBN between PSt and water are presented in Figure 3. The concentrations of IBN in the aqueous solution and the PSt particles show a linear relationship. The slope of the straight line passing through the origin is 4.34, which means that the partition coefficient is 4.34, smaller than that in the St/IBN/water system. The variation in the partition coefficient from St to PSt indicates that the driving force of radical desorption increases continuously as the polymerization progresses. IBN is not a solvent for PSt, which is one

Table 4. Measure Partition Coefficient of IBN with Different Oil Content

Oil content (wt%)	Partition coefficient
7.58	10.42
14.92	11.01
24.87	10.87
32.45	10.20

Table 5. The Influence of pH on the Partitioning

pH	Partition coefficient
10.00	10.30
7.00	10.89
4.00	10.53
1.50	10.90

Table 6. Parameter Values used in Calculating Flory-Huggins Interaction Parameter

Parameter	Value	Ref.
V_S(cm^3/mol)	89.70	29
λ_S(kJ/mol)$^{1/2}$	18.62	estimated from ref 29 and 28
λ_P(kJ/mol)$^{1/2}$	18.60	28
τ_S(J/cm^3) $^{1/2}$	11.02	estimated from ref 29 and 28
Ψ(J/cm^3)	68.62	estimated from ref 28

possible reason why the partition coefficient for the PSt/IBN/water system is smaller than that for the St/IBN/water system. As stated in the theoretical prediction section, the partition coefficient in the PSt/IBN/water system is only affected by the saturation concentration of IBN in water and the Flory-Huggins interaction parameter between PSt and IBN. The saturated concentration of IBN in water is 3.54 wt %.[25] The only unknown parameter is the Flory-Huggins interaction parameter. Unfortunately, its value is difficult to determine and depends on the volume fraction of polymer. However, the concentration of IBN in the system is quite low and will not change too much, and the Flory-Huggins interaction parameter may remain constant, allowing its prediction according to reference[28] for a polar solvent and a nonpolar polymer

$$\chi = \frac{V_s}{RT}\left[(\lambda_S - \lambda_P)^2 + \frac{T^*}{T}\left(\tau_S^2 - 2\Psi\right)\right] + 0.34 \qquad (10)$$

Here, V_S is the molar volume of the solvent, λ_S is the nonpolar solubility parameter of the solvent, λ_P is the nonpolar solubility parameter of PSt, τ_S is the polar solubility of the solvent, Ψ is a parameter determined experimentally that relates to $\lambda_P \tau_S$, and T^* is the actual temperature.

The parameter values used in the prediction are listed in Table 6. The Flory-Huggins interaction parameter between PSt and IBN estimated from Eq. 10 is 0.61. This value is larger than 0.5, and PSt is not soluble in IBN. The results are consistent with the Flory-Huggins criterion for complete solvent–polymer miscibility, that is, if the solvent–polymer system is miscible, the Flory-Huggins interaction should be less than 0.5. The partition coefficient was then calculated from the most simplified equation $m_{PSt,IB}N = 4.35$. This predicted value is in good agreement with that determined experimentally.

Particle Size.

Experiments were performed to determine the partition coefficient of IBN with different particle sizes. Two latex samples were synthesized utilizing SDS as a surfactant (runs *a* and *b*), while another was synthesized utilizing CTAB as a surfactant (run c). The effect of particle size is shown in Figure 4. The particle size was increased from 131.2 nm to 182.8 nm, but the partition coefficient did not change with the particle diameter. This was to be expected based on Eq. 9. The influence of the diameter is included in the last term on the lefthand side of Eq. 7, and this term is a minor one compared with the first three terms. Hence, the partition coefficient could be used in all kinds of emulsion polymerizations without considering the particle size or the particle growth during the polymerization. It also provides evidence of the reliability of our simple model (Eq. 9).

Surfactant. That the partition coefficient will not be affected by the particle size has previously confirmed. From Figure 4, we could also deduce another conclusion, that is, that the surfactant has no influence on the partition coefficient. This phenomenon is similar to the influence of pH on the partition coefficient between St and water. Latex particles with SDS or CTAB as surfactants have negative or positive charges on their surfaces, respectively. However, IBN is a stable molecule that will not dissociate into ions, and will not have an influence on the electronic charge. Although the surfactant will somewhat change the composition of the latex particle (if we consider the polymer particle and surfactant layer as a whole latex particle), the amount of surfactant used in a miniemulsion system is extremely small. Actually, such a small fraction of surfactant will not change the partition coefficient at all, regardless of the property changes that it induces.

Conversion. Last, and perhaps most importantly, the influence of the polymerization conversion has a significant effect on the partition coefficient. Latex particles with different conversions imply that they are composed of different amounts of St and PSt. The partition coefficient of IBN between St and water is 10.98, while the corresponding coefficient between PSt and water is 4.34. Hence, we can predict that the partition coefficient of IBN between particles with

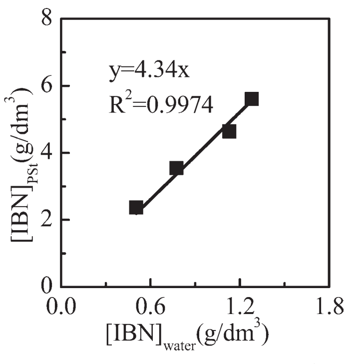

Figure 3. Partition of IBN between PSt particle and water.

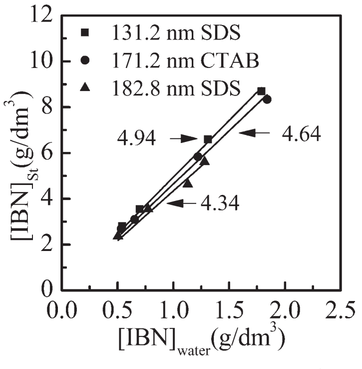

Figure 4. Partition of IBN between PSt particle and water differing by particle size and surfactant.

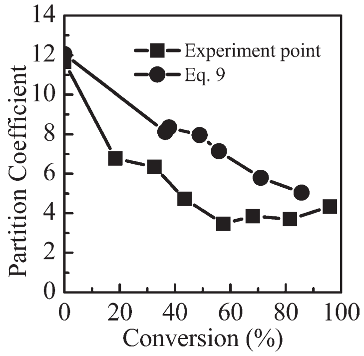

Figure 5. Comparison of theoretical predictions and the experiment measurements of IBN partition for latex particle with different conversion of particles.

different conversions and water will be larger than 4.34, but smaller than 10.98 and will decrease with increasing conversion. The partition coefficients of IBN at different degrees of polymerization conversion are displayed in Figure 5. From Figure 5, it can be seen that the partition coefficient of IBN decreases continuously from about 11 to about 4, which was determined by performing partition experiments with samples from the same reactor but taken after different time intervals.

Noël et al.[30] extended the Vanzo equation to predict the partial swelling of latex particles with two monomers with limited solubility in water through Eq. 11

$$\frac{v_{pi}}{v_{pj}} = \frac{[M_i]_{aq}}{[M_j]_{aq}} \cdot \frac{[M_i]_{aq,sat}}{[M_j]_{aq,sat}} \tag{11}$$

where i and j represent the different monomers.

This equation indicates that if the partition coefficient of one monomer and the saturated concentrations of both monomers are known, the partition coefficient of the other one may be predicted. Under our experimental conditions, one of the monomers is St, the partition behavior of which can be readily gleaned from the literature.[2,24] Hence, the partition of IBN at different degrees of polymerization conversion is also plotted in Figure 5. The first and last prediction points are in good agreement with the experiment. However, obvious deviation is observed in the middle conversion range. This deviation could be related to the simplification within the deducing of Eq. 11. Fortunately, the deviation of the partition coefficient between experiment and prediction will not significantly affect the primary radical desorption (which will be shown in the next section), so that Eq.11 may be used because of its simple expression and readily accessible parameters.

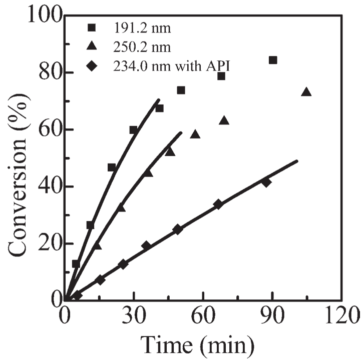

Figure 6. Assessment of the partition coefficient by first principle mathematical model and Luo and Schork's experimental data.[14] ■ (191.2 nm), ▲ (250.2 nm), ◆ (234.0 nm with API) are from Luo and Schork's experiment[14]; Solid lines are from Autran's model[18] with newly measured partition coefficient of this work.

Assessment of the newly measured partition coefficient

Recently, a first principle model was developed by Autran et al.[18] It successfully described miniemulsion polymerization with AIBN as the initiator in the presence and absence of an aqueous phase inhibitor (API) as proposed by Luo and Schork.[14] However, some differences in parameter selection can be identified in the two articles.[14,18] First, the propagation rate coefficient (k_p) selected by Luo and Schork[14] in their experiments was 4198 dm^3/mol·s, and they stated the polymerization should be a 0-1 system and that the k_p value they chose is closest to the real k_p value for their discussion, while k_p listed in Autran's model was 22,500 dm^3/mol·s. Although Autran et al.[18] did not state why they chose the k_p value, their group had also paid more attention to the propagation-rate constant.[31] So, each of them has their own reasons. However, with Autran's k_p value, their model could only predict the average number of radicals per particle, but not the relationship between conversion and time. Second, the propagation rate coefficient of adding a monomer to a primary radical (k_{pI}) is the same as k_p, which is not mentioned in Luo and Schork's article, and that $k_{pI} = k_p$ may lead to underestimation of the activity of the primary radical. Hence, the model was recalculated by replacing some previous parameters by newly set parameters, including the partition coefficient of the primary radical. The parameters used in the recalculation of Autran's model were the same as Autran's parameters, except that $k_p = 4198$ dm^3/mol·s, $k_{pI} = 8k_p$, $k_{pl} = 4k_p$, and $m_I = m_{IBN,St} = 10.98$. The recalculated results are listed in Table 7 and Figure 6.

From Table 7 and Figure 6, it can be seen that the average number of radicals per particle and the kinetics are consistent

Table 7. Summary of the Results of the Experiment from Luo and Schork[14] of the Model Prediction from Autran et al.[18] and this Work

	Experiment parameters from ref. [14]					
Conversion (%)	$N_p \times 10^{-16}$ (particles)	d_p (nm)	API	$\bar{n}_{\mathrm{exp.,Luo}}$	$\bar{n}_{\mathrm{model,Autran}}$	$\bar{n}_{\mathrm{model,thiswork}}$
13	2.26	191.2	No	0.235	0.235	0.240
20	1.00	250.2	No	0.334	0.316	0.333
17	3.23	169.5	Yes	0.017	0.050	0.039
19	1.23	234.0	Yes	0.103	0.115	0.100

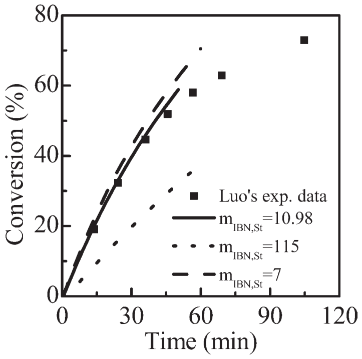

Figure 7. Comparing of Luo and Schork's experimental data (250.2 nm)[14] and Autran's model[18] with different partition coefficient.

with the experiments by Luo and Schork.[14] This provides evidence that the model is reliable and that the newly measured partition coefficient may be used in describing miniemulsion polymerization. Meanwhile, the influence of the partition coefficient on the kinetics is shown in Figure 7. It is obvious that if the partition coefficient of AIBN is selected in this model,[18] there will be great deviation between the theoretical prediction and Luo and Schork's experiment.[14] A tiny change in the partition coefficient will not significantly affect the model results in Figure 7, and Eq. 11 maybe used for an approximation when no direct experiment data are accessible.

Conclusion

IBN has been employed as a substitute for the 2-cyano-2-propyl radical in exploring the partition behavior between the organic phase and the aqueous phase and clarifying the kinetics of miniemulsion polymerization. Partition coefficients of IBN between styrene monomers/polymers and water under different conditions have been successfully measured through respective partition experiments. The newly measured partition coefficient has been employed in a first principle model, which predicted the kinetics of miniemulsion polymerization quite well.

The partition coefficient of IBN between St and water is 10.98, which is considerably smaller than that of AIBN between St and water. Besides, the partition coefficient is not affected by temperature, the HD content in the organic phase, the oil/water ratio, or the pH of the aqueous phase. The partition coefficient could be analyzed in terms of Henry's law, and the Henry's law constant for IBN in St was calculated to be 4.10 kPa at 25°C. The variation in the aforemnetioned partition experiments covers many aspects in emulsion polymerization. Thus, it can be concluded that the partition coefficient may be widely used in emulsion polymerization of St.

The partition coefficient of IBN between PSt and water was measured as 4.34, even lower than that between St and water. Some impact factors were also considered, including the particle size, the nature of the surfactant, and the swelling degree of the latex. As predicted, the particle size and the nature of the surfactant were found not to influence the partition. This result makes it convenient for us to directly apply the partition coefficient to emulsion polymerizations under different conditions. The partition coefficient between swelling PSt and water decreases with decreasing swelling degree, from about 11 to about 4. This trend provides evidence that the driving force of primary radical desorption changes continuously throughout the whole polymerization process.

The newly measured partition coefficient has been tested by comparing the model prediction with the experimental results of different authors. The model fits the experimental data well when using the partition coefficient of IBN. Thus, the partition coefficient of the primary radical (or its substitute) should be used in mathematical models, not the partition coefficient of the initiator.

Acknowledgments

The authors thank the financial supports from the National Natural Science Foundation of China (No. 21176210), the New Century Excellent Talent Project of Education Ministry (NCET-05-0512), Outstanding Youth Foundation of Zhejiang Province (R4110199), and Innovation Research Team of Zhejiang Province (2009R50016).

Literature Cited

1. Antonietti M, Landfester K. Polyreactions in miniemulsions. *Prog Polym Sci.* 2002;27:689–757.
2. Maxwell IA, Morrison BR, Napper DH, Gilbert RG. Entry of free radicals into latex particles in emulsion polymerization. *Macromolecules.* 1991;24:1629–1640.
3. Blythe PJ, Klein A, Phillips JA, Sudol ED, El-Aasser MS. Miniemulsion polymerization of styrene using the oil-soluble initiator AMBN. *J Polym Sci A Polym Chem.* 1999;37:4449–4457.
4. Alduncin JA, Forcada J, Asua JM. Miniemulsion polymerization using oil-soluble initiators. *Macromolecules.* 1994;27:2256–2261.
5. Reimers JL, Schork FJ. Lauroyl peroxide as a cosurfactant in miniemulsion polymerization. *Ind Eng Chem Res.* 1997;36:1085–1087.
6. Cao ZH, Shan GR. Miniemulsion copolymerization of gamma-methacryloxypropyltrimethoxysilane and styrene initiated by oil-soluble and water-soluble initiators. *Acta Polym Sin.* 2008;941–946.
7. Cao ZH, Shan GR, Fevotte G, Sheibat-Othman N, Bourgeat-Lami E. Miniemulsion copolymerization of styrene and gamma-methacryloxypropyltrimethoxysilane: Kinetics and mechanism. *Macromolecules.* 2008;41:5166–5173.
8. Zhang SW, Zhou SX, Weng YM, Wu LM. Synthesis of silanol-functionalized latex nanoparticles through miniemulsion copolymerization of styrene and gamma-methacryloxypropyltrimethoxysilane. *Langmuir.* 2006;22:4674–4679.
9. Nomura M, Ikoma J, Fujita K. Kinetics and mechanisms of particle formation and growth in the emulsion polymerization initiated by the oil-soluble initiator, 2,2′-azobisisobutyronitrile. *Acs Symp Ser.* 1992;492:55–71.
10. Nomura M, Ikoma J, Fujita K. Kinetics and mechanisms of emulsion polymerization initiated by oil-soluble initiators. IV. Kinetic modeling of unseeded emulsion polymerization of styrene initiated by 2,2′-azobisisobutyronitrile. *J Polym Sci A Polym Chem.* 1993;31:2103–2113.
11. Mørk PC, Makame Y. Compartmentalized polymerization with oil-soluble initiators. Kinetic effect of single radical formation. *J Polym Sci A Polym Chem.* 1997;35:2347–2354.
12. Asua JM, Rodriguez VS, Sudol ED, El-Aasser MS. The free-radical distribution in emulsion polymerization using oil-soluble initiators. *J Polym Sci A Polym Chem.* 1989;27:3569–3587.
13. Alduncin JA, Forcada J, Barandiaran MJ, Asua JM. On the main locus of radical formation in emulsion polymerization initiated by oil-soluble initiators. *J Polym Sci A Polym Chem.* 1991;29:1265–1270.
14. Luo YW, Schork FJ. Emulsion and miniemulsion polymerizations with an oil-soluble initiator in the presence and absence of an aqueous-phase radical scavenger. *J Polym Sci A Polym Chem.* 2002;40:3200–3211.
15. Pryor WA, Bickley HT, Morkved EH. Homolysis of some radical initiators. Viscosity dependence and cage return. *J Organic Chem.* 1972;37:1999–2005.
16. Rubio LHG, Ro N, Patel RD. Ultraviolet analysis of benzoyl peroxide initiated styrene polymerizations and copolymerizations. 1. *Macromolecules.* 1984;17:1998–2005.
17. Overberger CG, O'shaughnessy MT, Shalit H. The preparation of some aliphatic azo nitriles and their decomposition in solution. *J Am Chem Soc.* 1949;71:2661–2666.

18. Autran C, de la Cal JC, Asua JM. (Mini)emulsion polymerization kinetics using oil-soluble initiators. *Macromolecules.* 2007;40:6233–6238.
19. Nomura M, Yamada A, Fujita S, Sugimoto A, Ikoma J, Fujita K. Kinetics and mechanism of emulsion polymerization initiated by oil-soluble initiators. II. Kinetic-behavior of styrene emulsion polymerization initiated by 2,2′-azoisobutyronitrile. *J Polym Sci A Polym Chem.* 1991;29:987–994.
20. Ni KF, Sheibat-Othman N, Shan GR, Fevotte G, Bourgeat-Lami E. Kinetics and modeling of hybrid core-shell nanoparticles synthesized by seeded emulsion (co)polymerization of styrene and gamma-methacryloyloxypropyltrimethoxysilane. *Macromolecules.* 2005;38:9100–9109.
21. Morton M, Kaizerman S, Altier MW. Swelling of latex particles. *J Coll Sci.* 1954;9:300–312.
22. Vanzo E, Marchessault RH, Stannett V. The solubility and swelling of latex particles. *J Coll Sci.* 1965;20:62–71.
23. Gardon JL. Emulsion polymerization. VI. Concentration of monomers in latex particles. *J Polym Sci A1 Polym Chem.* 1968;6:2859–2879.
24. Maxwell IA, Kurja J, Van Doremaele GHJ, German AL, Morrison BR. Partial swelling of latex-particles with monomers. *Makromol Chem.* 1992;193:2049–2063.
25. Stephenson RM. Mutual solubility of water and nitriles. *J Chem Eng Data.* 1994;39:225–227.
26. Ma JW, Cunningham MF, McAuley KB, Keoshkerian B, Georges MK. Nitroxide partitioning between styrene and water. *J Polym Sci A Polym Chem.* 2001;39:1081–1089.
27. Meylan WM, Howard PH. Bond contribution method for estimating Henry's law constants. *Environ Toxicol Chem.* 1991;10:1283–1293.
28. Blanks RF, Prausnitz JM. Thermodynamics of polymer solubility in polar and nonpolar systems. *Ind End Chem Fundam.* 1964;3:1–8.
29. Lide DR.*CRC Handbook of Chemistry and Physics*. 85th ed. Chemical Rubber Co.;2003.
30. Noël LFJ, Maxwell IA, German AL. Partial swelling of latex particles by two monomers. *Macromolecules.* 1993;26:2911–2918.
31. Asua JM. Emulsion polymerization: From fundamental mechanisms to process developments. *J Polym Sci A Polym Chem.* 2004;42:1025–1041.

Manuscript received May 30, 2011, and revision received Aug. 12, 2011.