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Kinetics of Polymerization of Acrylamide in Aerosol OT W/O Microemulsions

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Time dependence of the conversion of acrylamide (AAm) initiated with potassium peroxodisulfate (KPS) was examined at various [AAm] and [KPS] in W/O microemulsions of 1,4-bis(2-ethylhexyl) sodium sulfobutanedioate in cyclohexane media at 45 °C. The rate of polymerization (R_p) calculated from the conversion-time profiles yielded the following equation: $R_p \propto [\text{AAm}]^{1.0}[\text{KPS}]^{0.5}$. From these values of reaction orders for AAm and KPS, it was found that the polymerization of acrylamide in W/O microemulsions can be regarded as normal radical polymerization and biradical termination between polymer radicals.

Since the polymerization of methyl acrylate in sodium dodecyl sulfate/water/pentanol systems was studied by Stoffer et al.,[1,2] much attention have been paid for the preparation of monodisperse and fine polymer particles having high molecular weight. Recent years, Candau et al. have been systematically studying the kinetics and mechanisms of polymerization of AAm initiated with azobisisobutyronitrile and KPS in W/O microemulsions of 1,4-bis(2-ethylhexyl) sodium sulfobutanedioate (AOT) as anionic surfactant at 45 °C.[3,4] They have showed that the kinetics for the polymerization of acrylamide in AOT microemulsion differs from that for normal free radical polymerization, but in their system there is an enhancement of the polymerization rate by $NaHSO_3$ contained as an impurity in AOT.[3] Since the kinetics in this microemulsion system is an important factor to realize the mechanism of the polymerization and the action of the surfactant molecules, therefore, it may be necessary to determine whether the correct values of reaction orders for monomer and initiator concentrations are reported by Candau et al. or not.[3] In this paper, carefully purified AOT was utilized for the kinetic study of polymerization of AAm initiated with KPS in the surfactant W/O microemulsions at 45 °C. Temperature dependence of polymerization was further investigated.

Experimental

1,4-bis(2-ethylhexyl) sodium sulfobutanedioate of specially prepared reagent grade (>98.8%, Nacalai Tesque Inc.) was purified according to a previous method,[5] i.e., AOT was employed three time by a distribution method in which a solvent system of water and benzene to remove electrolytes and catalyst. The benzene phase had been evaporated and dried under vacuum, and then the resulting AOT was treated with activated carbon twice in methanol. The purified AOT was dissolved in dry methanol and filtered with a membrane filter, and then evaporated and dried at 70 °C under vacuum. Acrylamide of specially prepared reagent grade (Nacalai Tesque Inc.) was sublimated at 50 °C under vacuum. Potassium peroxodisulfate was recrystallized twice from water and dried under vacuum. Water was doubly distilled.

Acrylamide in W/O microemulsions of AOT/water/cyclohexane system, bubbled thoroughly with nitrogen, was polymerized by injecting an aqueous KPS solution. The conversion of acrylamide was determined by the absorbance of 240 nm band of acrylamide in UV spectra of the W/O microemulsion solution, which was recorded on a Shimadzu UV-200S spectrophotometer. The molecular weight of polymer was measured by a GCP apparatus (Nihon Seimitu Kagaku Co., Ltd.), equipped with Shodex KB-802.5 and KB-806 columns.

Results and Discussion

In the study on solubilization of 0.08 mol kg^{-1} AAm in 0.10 mol kg^{-1} AOT cyclohexane solution, W/O microemulsions, involving bulk-like water in the interior of reversed micelles, were found to form in the range of 15 to 35 as $R_w = [H_2O]/[\text{AOT}]$ at 45 °C.[6,7] The presence of bulk-like water in AOT W/O microemulsions was verified from the near infrared spectra measurements.[6,7] In the W/O microemulsions, no polymerization of acrylamide occurred at any R_w in the absence of KPS at 45 °C.

Figures 1 and 2 show the time dependence of conversion of AAm obtained at various [AAm] and [KPS], respectively, in 0.1 mol kg^{-1} AOT cyclohexane solution of $R_w = 20$. Here, the total mass of the dispersed phase, $M_{AOT} + M_{AAm} + M_{H_2O} + M_{KPS}$, was adopted as [AAm], according to Candau et al.[3] As can be seen in Figs. 1 and 2, the conversion in any system rapidly increased

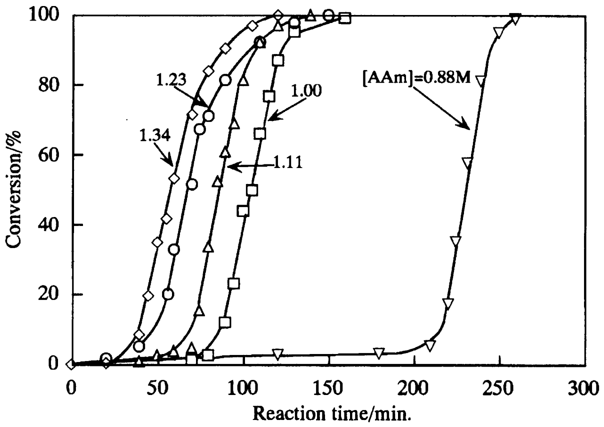

Fig. 1. Conversion–time curves of acrylamide at various [AAm] in AOT/cyclohexane system. [AAm] = 1.00 M is identical with 0.08 mol kg^{-1} AAm AOT/cyclohexane solution. 1 M = 1 mol dm^{-3}.

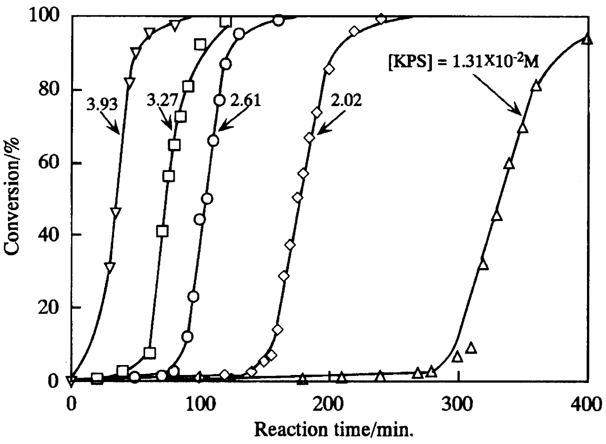

Fig. 2. Conversion-time curves of acrylamide at various [KPS] in AOT/cyclohexane system.

from a certain time and then reached almost 100%. Then the maximum rates of polymerization (R_p) were calculated from the slopes of the liner portion in each conversion curve. Figure 3 shows the linear relation of $\log R_p$ with $\log[\mathrm{AAm}]$ or $\log[\mathrm{KPS}]$. This relation can be expressed as the following equation.

$$R_p \propto [\mathrm{AAm}]^{1.0}[\mathrm{KPS}]^{0.5}. \tag{1}$$

These reaction orders for AAm and KPS indicate normal free radical polymerization and biradical termination between polymer radicals. In addition, the kinetics of AAm polymerization in W/O microemulsions in this study correspond to those in water[8] or dispersion polymerizations[9] with water-soluble initiators. This agreement is due to the fact that the polymerization field is in the bulk-like water of W/O microemulsions.[6,7]

To estimate the overall activation energy of polymerization of acrylamide, conversion–time curves at various temperature from 45 to 55 °C in 0.1 mol kg^{-1} AOT cyclohexane solution of $R_w = 20$ and [AAm] = 1.00 M system were also measured. Conversion curves similar to those in Figs. 1 and 2 were obtained at each temperature, thus the values of R_p were calculated from the slopes of the linear portions. Figure 4 shows plots of $\log R_p$ against reciprocal of temperature, and the slope of the plots provided an activation energy of 66 kJ mol^{-1}. This value was almost equal to the value obtained by polymerization of acrylamide in water.[10] This agreement is also due to the polymerization in bulk-like water of W/O microemulsions.

On the other hand, from the molecular weight of polyacrylamide ($M_w = 1.4 \times 10^6$) and the number of monomers per W/O microemulsion ($n = 680$), approximately 40 W/O microemulsions was found to con-

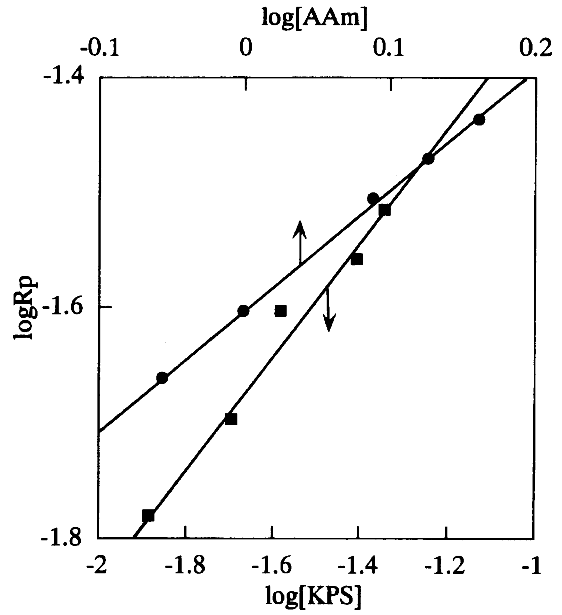

Fig. 3. Dependence of the polymerization rate on the initial concentrations of monomer (●) and initiator (■).

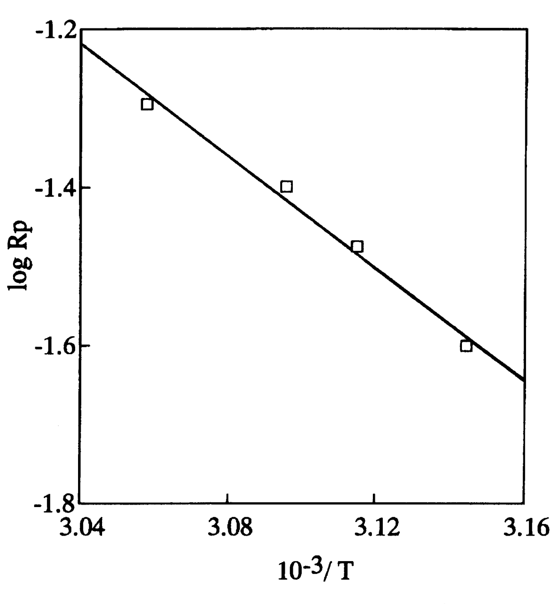

Fig. 4. Plot of $\log R_p$ against $1/T$.

tribute the formation of one polymer chain. The result means that acrylamide molecules are supplied to each polymer radical of each reaction site by collision between W/O microemulsions. Thus, it is expected that the kinetics depart from the resulting kinetics regarded as normal free radical polymerization with respect to [AAm] as mentioned above, since the polymerization may be hindered by a diffusion control of monomer due to AOT molecules surrounding the monomer. However, this effect might be invalidated due to much faster intermicellar exchange of monomer by the collisions between W/O microemulsions than the propagation of polymerization.[11—13]

The kinetics in this study differ from the result reported by Candau et al., that is, their R_p was proportional to $[\mathrm{AAm}]^{1.5}$ and $[\mathrm{KPS}]^{0}$.[3,4] They reported that the departure from first order kinetics of monomer concentration can be explained by the cage effect or complex theory and $[\mathrm{KPS}]^{0}$ is due to residual hydrogensulfite contained in AOT. Further, they also reported that R_p was proportional to $[\mathrm{AAm}]^{1.0}$ without initiator. Thus, we infer that R_p of polymerization in their system might be proportion to $[\mathrm{AAm}]^{1.0}$ if no impurity acting as initiator was contained, as in the results of this work or of polymerization in water.

As can be seen in Figs. 1 and 2, the appearance of the longer induction time observed in each system may be due to residual oxygen dissolving in W/O microemulsions. However, during these induction times, polyacrylamide having lower molecular weight ($M_\mathrm{w}=1\times10^5$) was obtained, indicating that one polymer chain is formed from monomer molecules included in one W/O microemulsion. Thus, this implies that a blocking effect of surfactant is another reason for the induction time, though it was not clear in this study.

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