(18) Dzhabiyev, T. S.; D'Yachkovskii, F. S.; Shilov, A. Ye. *Vysokomol. Soyedin, Ser. A* **1971**, *13*, 2474.
(19) Aldissi, M. J.; Schue, F.; Giral, L.; Rolland, M. *Polymer* **1982**, *23*, 246.
(20) Schen, M. A.; Karasz, F. E.; Chien, J. C. W. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2787.
(21) Gibson, H. W.; Weagley, R. J.; Prest, W. M., Jr.; Mosher, R.; Kaplan, S. *J. Phys. Colloq.* **1983**, *44*, 123.
(22) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1943.
(23) Bates, F. S.; Baker, G. L. *Macromolecules* **1983**, *16*, 704.
(24) Baker, G. L.; Bates, F. S. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 15.
(25) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.
(26) Bradley, D. C.; Mehrota, R. C.; Swanick, J. D.; Wardlaw, W. V. *J. Chem. Soc.* **1953**, 2025.
(27) Hoffmann, E. *Ann. Chem.* **1960**, *629*, 104.
(28) Baker, G. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *24*(2), 225.
(29) Mole, T.; Jeffrey, E. A. *Organoaluminum Compounds*; Elsevier: New York, 1972; Chapter 15.
(30) Baker, G. L.; Shelburne, J. A., III; Bates, F. S. *J. Am. Chem. Soc.* **1986**, *108*, 7377.
(31) Weinberger, B. R.; Ehrenfreund, E.; Pron, A.; Heeger, A. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1980**, *72*, 4749.
(32) Horton, M. E.; Bradley, D. D. C.; Friend, R. H.; Chai, C. K.; Bott, D. D. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 51.
(33) Thomann, H.; Baker, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 1569.

Photoinitiated Polymerization of Styrene in Microemulsions

Ping-Lin Kuo and Nicholas J. Turro*

Chemistry Department, Columbia University, New York, New York 10027

Chi-Ming Tseng, Mohamed S. El-Aasser,* and John W. Vanderhoff

Departments of Chemical Engineering and Chemistry and Emulsion Polymers Institute, Lehigh University, Bethlehem, Pennsylvania 18015. Received July 7, 1986

ABSTRACT: Photoinitiated polymerization of styrene in oil/water microemulsions has been successfully performed by using dibenzyl ketone (DBK) as initiator. The system remains transparent during the whole polymerization process. The molecular weights of polymers produced are in the order of 10^5, and the polydispersity indexes (PDI) are in the range 1.6–2.2. The particle sizes of the latexes produced are in the range 30–60 nm, with polydispersity indexes 1.05–1.08. The degree of polymerization (D_p) and the rate of polymerization (R_p) were studied as a function of initiator concentration ([DBK]) and light intensity (L). It is found that $D_p \propto [\mathrm{DBK}]^{-0.4}L^{-0.2}$; $R_p \propto [\mathrm{DBK}]^{0.2}L^{0.2}$. The mechanism of polymerization in microemulsions is discussed on the basis of polymerization rate and particle size.

Introduction

Emulsion polymerization has been a widely used industrial process for water-insoluble and sparsely soluble monomers.[1] Conventional emulsion polymerization is sometimes referred to as "macroemulsion" polymerization[2] because of the large size of monomer droplets (hundreds of microns) in the system compared to those in a "microemulsion" system (tens of nanometers). Between these two extremes, there is another type of emulsion that has been termed as "miniemulsion".[2,3]

Polymerizations in microemulsion systems have gained some attention in the past few years. Atik and Thomas[4] reported microemulsion polymerization of styrene with azobis(isobutyronitrile) (AINB) as an initiator and γ-irradiation as an initiating source. Jayakrishnan and Shah[5] studied polymerizations of styrene and methyl methacrylate microemulsions using oil-soluble initiators AIBN and benzoyl peroxide. Tang[6] reported the microemulsion polymerization of styrene using both water-soluble ($K_2S_2O_8$) and oil-soluble (AIBN) initiators. All of these are oil/water (o/w) systems. Candau[7] carried out w/o microemulsion polymerization of acrylamide using AIBN and $K_2S_2O_8$.

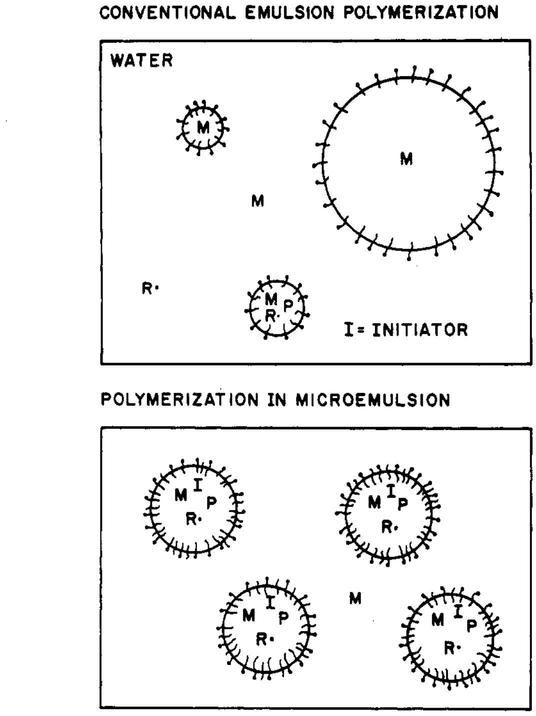
In a conventional emulsion polymerization, the reaction system can be represented by the simplified scheme shown in Figure 1a. During polymerization, monomer is located in the following four locations: (1) monomer droplets, (2) inactive micelles containing monomer, (3) active micelles that become monomer-swollen polymer particles where polymerization occurs, and (4) solute monomer in aqueous phase. The o/w microemulsion reported in this paper can be presented by the simplified scheme shown in Figure 1b. Three characteristics of o/w microemulsion polymerization are different from those of conventional emulsion polymerization: (1) No monomer droplets and no inactive micelles exist. (2) All of the initiator exists in the microemulsion droplets; thus polymerization occurs only in the monomer reservoir encapsulated in the particle. (3) The system is optically transparent.

Because of the transparency of microemulsion systems, light provides an interesting method to initiate polymerization not only because the polymerization rate can be made to be fast but also because the polymerization rate and the molecular weight of the polymer can be easily varied by controlling the light intensity and the time of irradiation. Photoinduced polymerization in conventional emulsion polymerization with dibenzyl ketone (DBK) as an initiator has been reported.[8] In the present work, the effects of the light intensity and initiator concentration on polymerization were studied in terms of molecular weight of polymer, polymerization rate, and percent conversion.

Experimental Section

Materials. Styrene (Aldrich) was washed with 10% sodium hydroxide 3 times and dried over anhydrous sodium sulfate after repeated washing with water. Further purification was carried out by distillation at 35 °C under aspirator pressure, and the purified sample was stored at 0 °C under nitrogen. Sodium dodecyl sulfate (SDS, Bio-Rad Laboratories) was recrystallized once from water and then once from ethanol. Pentanol (Aldrich) was purified by drying over potassium carbonate and by distilling at 45–46 °C under aspirator pressure. Dibenzyl ketone (DBK, Aldrich) was purified by three crystallizations from ether. Water was triple-distilled from $KMnO_4$/NaOH and purged with argon.

0024-9297/87/2220-1216$01.50/0 © 1987 American Chemical Society


CONVENTIONAL EMULSION POLYMERIZATION

POLYMERIZATION IN MICROEMULSION

Figure 1. Simplified representation of (a) conventional emulsion polymerization and (b) microemulsion polymerization.

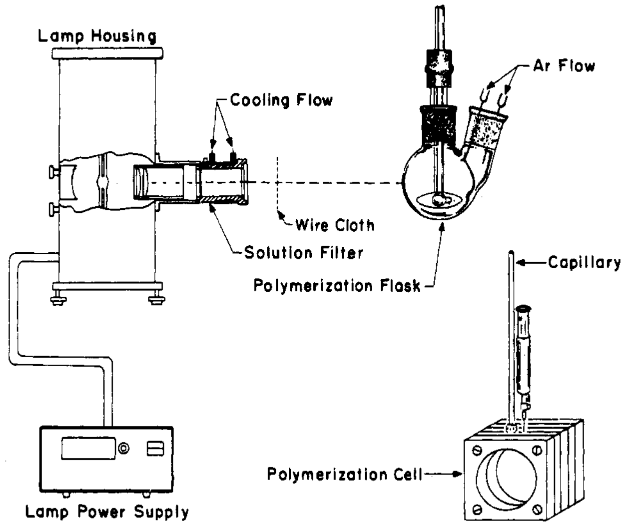


Figure 2. Apparatus for photoinitiated polymerization.

Methods. Preparation and Polymerization in Microemulsions. A typical o/w microemulsion recipe used in this study consisted of SDS, 0.67 g; toluene, 0.5 mL; styrene, 0.5 mL; pentanol, 0.8 mL, water, 10 mL; DBK, 0.05–2 mM based on water. Photoinitiator (DBK) was dissolved in SDS aqueous solution by ultrasonic treatment followed by mechanical stirring in a 25-mL Pyrex glass flask equipped with a air-tight stirring shaft. After 30 min, styrene, toluene, and pentanol were added to the system and stirred at a rate of ca. 500 rpm for 20 min. The whole procedure was carried out under argon atmosphere. The apparatus for polymerization is shown in Figure 2. The UV source used was a 1000-W high-pressure mercury lamp (Oriel Co.) operated at 22 V × 26 A. A liquid filter with potassium chromate solution was attached to the lamp to reduce heat transmission and allow transmission of only UV light with wavelength 313 ± 10 nm. The flask was positioned at a distance of 4 cm from the UV source. The UV intensity was measured to 3.6 W/cm^2 at this distance. To vary the light intensity, layers of 40-mesh stainless steel wire screen were placed in front of the UV source. The transmission of light by the mesh screen was calibrated with a UV/vis spectrophotometer (Perkin-Elmer 559A) at wavelength 313 nm.

Characterization of Polymers. The microemulsion after polymerization was poured into ethanol and the precipitated polymer was separated and further purified by reprecipitation from toluene/ethanol. Polymers were analyzed on a Du Pont Model 8800 size exclusion chromatograph with two SE 4000 columns using THF as eluent solvent. The molecular weight averages and distributions were calculated by computer from the height and retention time of the chromatograms.

Particle Size Determination. The droplet sizes of unpolymerized microemulsions and the particle sizes of polymerized latexes were determined with a Philips 300 transmission electron microscope. The unpolymerized microemulsions were fixed with osmium tetraoxide (OsO_4) before examination. The polymerized latexes were examined with or without phosphotungstic acid (PTA) staining. For OsO_4 fixation, one drop (0.4 mL) of 2% OsO_4 aqueous solution was added to 0.8 mL of the unpolymerized microemulsion. The microemulsion turned dark gradually. Five minutes after adding OsO_4, one drop of the microemulsion was then diluted in 2 mL of deionized distilled water. One drop of the diluted dispersion was then put on a 200-mesh stainless steel grid that had been coated with a thin layer of Formvar and carbon. The grid was allowed to dry in air before examination. The method of negative staining with PTA has been widely used for examining acrylic latexes to improve contrast and resolution of the image.[9] The method has also been applied by Scholsky and Fitch[10] in examining small polystyrene latex particles. In this study, one drop of polymerized latex was added to 2 mL of 0.3% PTA aqueous solution. One drop of the diluted latex was then put on a grid and allowed to dry in air.

Kinetics Studies. The kinetics studies were carried out with a cell built at Lehigh University (LU cell), which has been used in a previous study.[11] The cell consisted of three machined Teflon blocks that hold two circular quartz plates (6.3-cm diameter) at a fixed distance (0.091 cm) apart. Two aluminum blocks were placed next to the side Teflon blocks in order that sufficient pressure could be applied to prevent leakage. The whole apparatus was held together with four sets of screws and nuts. A 0.048-cm-i.d. and 40-cm-long capillary was attached to the center Teflon block for monitoring fluid volume shrinkage from polymerization. The completed cell had a fluid volume of 2.45 mL.

Microemulsions for kinetics studies were prepared in a way similar to that described above. After the microemulsion was degassed for 5 minutes, it was injected with a syringe into the cell through a valve attached to the center Teflon block. The fluid was continuously forced out of the capillary until air bubbles were no longer observed. The loaded cell was then placed at a distance of 25 cm from the UV source, with a quartz window facing the UV lamp and the capillary sticking out sidewards. A total of 5–10 min was allowed for the cell to reach thermal equilibrium. An aluminum foil in front of the UV source for blocking the UV light was then lifted off and the cell was illuminated. The UV intensity at the cell window was measured to be 0.9 W/m^2. Fluid level in the capillary was recorded every 5 min for 1 h to follow monomer-to-polymer conversion.

Results

The o/w microemulsion prepared by the above-mentioned recipe was nearly as optically transparent as water (the transmissions at 700 nm for the microemulsion system and for water in a 1-cm cubic cell were 81% and 90%, respectively) and remained stable for more than 3 mo. During the whole polymerization process, the system remained stable and transparent. For example, 62% transmission at 700 nm was measured for a sample polymerized in the LU cell for 30 min.

The existence of toluene in the oil phase played a significant role in maintaining the transparency of the microemulsion during the process of polymerization. Without toluene, the microemulsion became cloudy after the irradiation of ca. 5 min, and the conversion after the polymerization of 2 h was below 10%.

Molecular Weight and Particle Size Investigation. The effect of initiator (DBK) concentration, light intensity, and reaction time on M_n, M_w, and the polydispersity index

Table I
Dependence of M_w, M_n, and M_w/M_n on [DBK], Light Intensity, and Reaction Time

[DBK], mM	reactn time, min	light intensity, % trans	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n
0.05	30	100	533	238	2.24
0.5	30	100	256	132	2.06
2.0	30	100	110	60	1.83
0.5	30	16	367	176	2.09
2.0	10	100	104	49	2.14
2.0	120	100	158	61	2.57
2.0	30	16	139	65	2.13

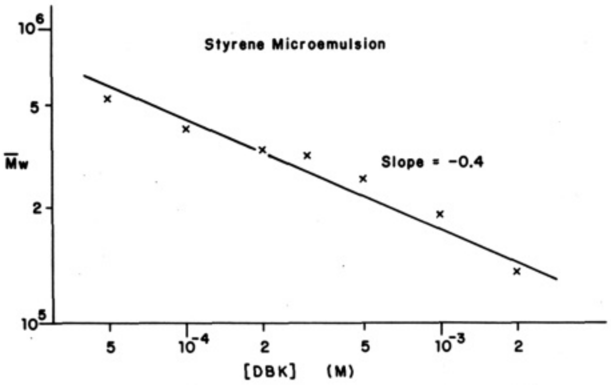


Figure 3. Change of M_w as a function of photoinitiator concentration.

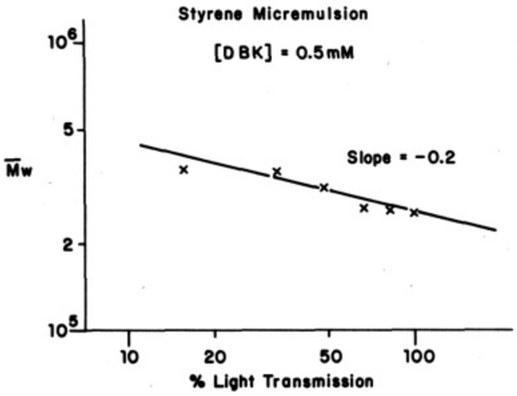


Figure 4. Change of M_w as a function of light intensity.

(PDI, M_w/M_n) for polymerization carried out in the Pyrex glass flask reactor are summarized in Table I.

For seven latexes polymerized with 100% light intensity (3.6 W/m^2) and over 30 min, M_n decreased from 2.4×10^5 to 0.6×10^5 and M_w from 5.3×10^5 to 1.1×10^5 as DBK concentration increased from 0.05 mM to 2 mM (based on water). The PDI of these polymers were in the range 1.6–2.2. If the M_w of the polymer was plotted against [DBK] on log–log scale, a straight line with a slope of –0.4 was obtained (Figure 3).

For six latexes polymerized with 0.5 mM DBK and for 30 min of irradiation, M_w increased from 2.6×10^5 to 3.7 10^5 as light intensity decreased from 100% to 16%. The relationship is shown in Figure 4. A straight line with a slope of –0.2 was obtained via a log–log plot. These results can be summarized in the following relation, where D_p is the degree of polymerization and L is the light intensity:

$$D_p \propto [\mathrm{DBK}]^{-0.4} L^{-0.2}$$

As the reaction time increased from 10 to 120 min, both M_w and M_n of the polymer increased ca. 50% and 30%, respectively.

Figure 5a shows a TEM micrograph of an unpolymerized microemulsion fixed with OsO_4. Most of the identifiable droplets are in the size range 10–30 nm. Figure 5b shows a micrograph of a latex polymerized from the microemulsion in a Pyrex glass flask reactor. The polymerization was carried out with 2.0 mM DBK photoinitiator, 100% light intensity, and a reaction time of 30 min. A micrograph of the same latex with PTA staining is given on Figure 6c. A much better contrast and resolution were obtained with the latter method.

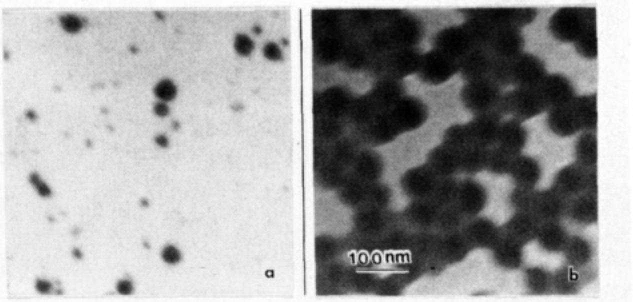


Figure 5. TEM micrographs of (a) unpolymerized microemulsion fixed with OsO_4, (b) latex polymerized from microemulsion with 2.0 mM DBK, 100% light intensity and 30-min reaction time.

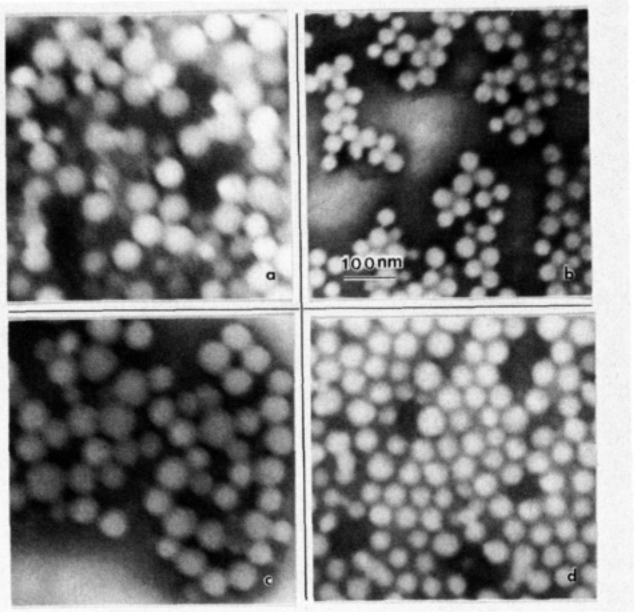


Figure 6. TEM micrographs of PTA-stained latexes polymerized with (a) 0.5 mM DBK, 100% light intensity, 30 min; (b) 0.5 mM DBK, 16% light intensity, 30 min; (c) 2.0 mM DBK, 100% light intensity, 30 min; (d) 2.0 mM DBK, 100% light intensity, 120 min.

Figure 6 compares latexes prepared from the same microemulsion but polymerized under different conditions: (a) with 0.5 mM DBK, 100% light intensity, and polymerized for 30 min; (b) 0.5 mM DBK, 16% light intensity, and 30 min; (c) 2.0 mM DBK, 100% light intensity, and 30 min; (d) 2.0 mM DBK, 100% light intensity, and 120 min. The following number-average particle diameters were determined from the micrographs: (a) 53, (b) 35, (c) 56, and (d) 47 nm. The latex polymerized for 120 min (d) had a smaller apparent average than the latex polymerized for 30 min (c). This could be attributed to the fact that the former had a higher conversion; thus the particles had a less tendency of "flattening" on drying. The polydispersity indexes of these latexes were in the range 1.05–1.08, comparable to those obtained in a miniemulsion polymerization using an oil-soluble initiator (number-average diameter 130–160 nm, PDI = 1.07–1.09).

Kinetic Studies. The kinetics of photopolymerization was investigated by the capillary height method.[11] The influences of initiator concentration and light intensity on

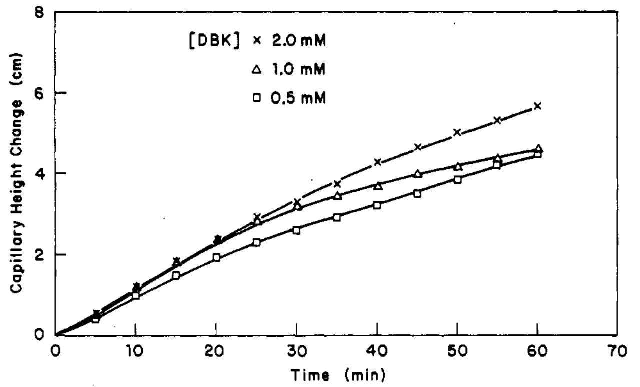


Figure 7. Change of capillary height with time for polymerization with different photoinitiator concentrations.

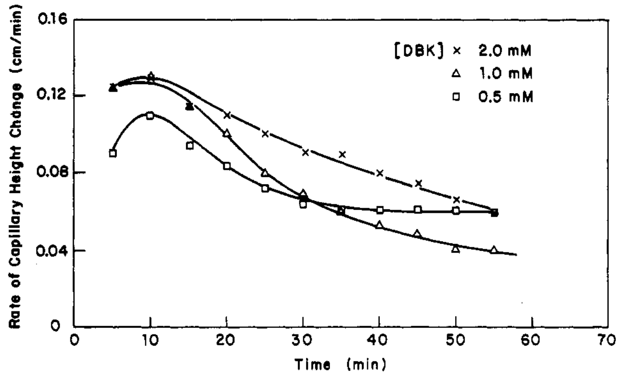


Figure 8. Rate of capillary height change as a function of time for polymerizations with different photoinitiators.

the rate of polymerization were determined. Figure 7 shows capillary height change as a function of time for polymerizations with three different concentrations of photoinitiator DBK: 0.5, 1.0 and 2.0 mM. A 8.2-cm capillary height change is equivalent to 100% monomer-to-polymer conversion (based on theortical calculations). The curves indicate that 50–70% conversion was achieved in 1 under these polymerization conditions. The rate of capillary height change, which was proportional to the polymerization rate, was obtained by taking the slope from the curves and plotted against time (Figure 8). In general, the polymerization rate increased with increasing DBK concentration for the first 30 min. For all runs, the polymerization rate increased with time and reached a maximum in about 10 min and decreased thereafter. The average polymerization rate over the first 30 min was plotted against DBK concentration on a log–log scale (Figure 8). A straight line with a slope of 0.2 was obtained, indicating that the polymerization rate was proportional to the 0.2 power of photoinitiator concentration.

Two more experiments with 0.5 mM DBK were conducted with different light intensities. The intensity was adjusted by placing layers of stainless steel wire cloth in front of the UV source as described above. Thus 62% and 16% light transmissions were obtained, respectively. The capillary height change and the rate of height change were plotted vs. time in a similar way in Figures 10 and 11. Again, the rate of capillary height change reached a maximum in about 10 min for each run. Also the rate increased with increasing light transmission. The average rate of capillary height change for the first 30 min was plotted against light transmission on a log–log scale (Figure 9). A straight line with a slope of 0.2 was obtained. These results can be summarized in the following relation, where R_p is the polymerization rate:

$$R_p \propto [\mathrm{DBK}]^{0.2} L^{0.2}$$

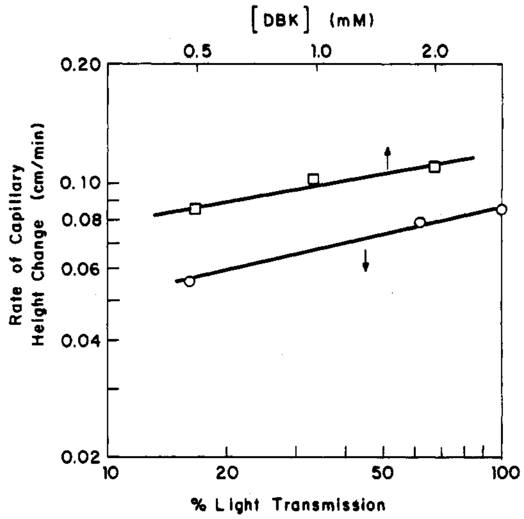


Figure 9. Dependency of rate of capillary height change on photoinitiator concentration and light intensity.

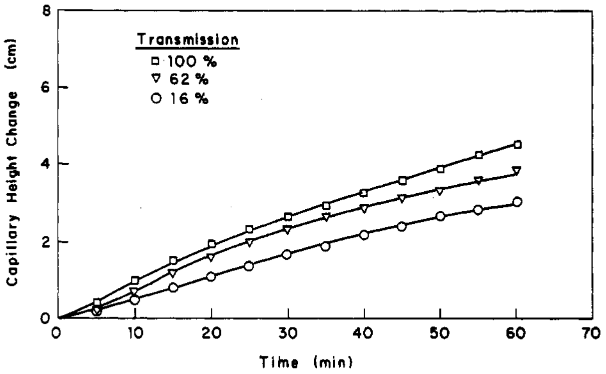


Figure 10. Change of capillary height with time for polymerization with different light intensities.

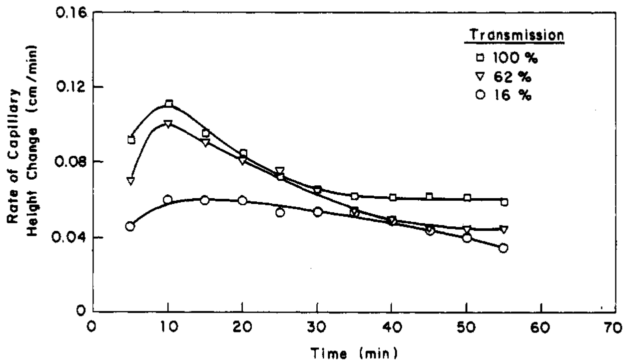


Figure 11. Rate of capillary height change as a function of time for polymerizations with different light intensities.

For a comparison, conversion–time curves for polymerizations carried out in the Pyrex glass flask reactor with 2.0 mM or 0.5 mM DBK and 10% or 33% light intensity are shown in (Figure 12). The conversions were calculated from the amounts of polymer precipitated from the samples taken out of flask during the polymerization. A similar trend can be found from these reactions to the results observed in the dilatometry study in the LU cell: a higher DBK concentration and a higher light intensity gave a higher initial polymerization rate (initial slope on the curves) and reached a higher conversion for the first 60 min; however, the relationship did not hold after 60 min.

Discussion

The mechanism involving radical pair chemistry of DBK in aqueous micellar system in summarized in Figure 13. For the o/w microemulsion system, this scheme also can

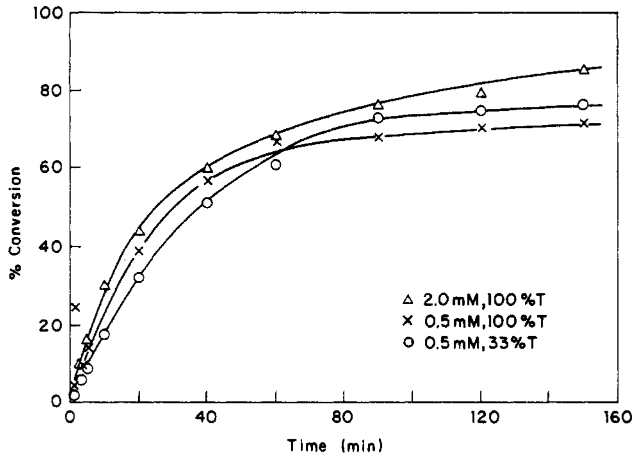


Figure 12. Conversion–time curves for polymerizations carried out in Pyrex glass flask with different DBK concentrations and light intensities.

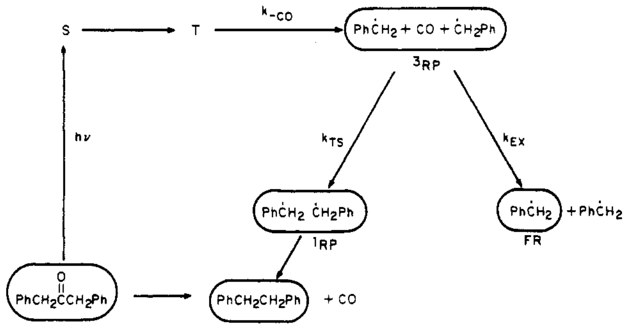


Figure 13. Postulated mechanism involving radical pair chemistry of DBK in microemulsion. ^{3}RP and ^{1}RP are triplet and singlet radical pairs, respectively. FR corresponds to free radicals. $k_{-\mathrm{CO}}$, k_{EX}, and k_{TS} are rate constants for decarbonylation, radical exit, and triplet–singlet intersystem crossing, respectively.

be used to interpret the behavior of the photochemistry of DBK. The triplet radical pair (^{3}RP in Figure 13) produced by decarbonylation either undergoes combination reaction or escapes from the microemulsion particulates to the bulk aqueous phase. It is assumed that only the radicals existing in the particles initiate or terminate polymerization.

In the case of the higher DBK concentration, the generated ^{3}RP concentration is higher. As a result, more polymer chains are initiated and the probability for radicals to terminate the propograting polymer becomes higher. Consequently, polymer with lower molecular weight is produced. In our microemulsion systems, the degree of polymerization (D_p) is found to be proportional to the –0.4 power of initiator concentration. The absolute value of the exponent is lower than that of the conventional emulsion polymerization initiated by water-soluble initiators (–0.6). Since ^{3}RP also forms diphenylethane as the cage combination product, [^{3}RP] should be proportional to [DBK] with a power less than 1; i.e., for $[^3\mathrm{RP}] \propto [\mathrm{DBK}]^x$, ≤ 1. For a water-soluble initiator in conventional polymerization, however, all of initiators contribute to producing radicals for polymerization. This may be the reason that the exponent value for [DBK] in polymerization microemulsions is smaller than that for water-soluble initiator in conventional emulsions.

The optical density of the microemulsion containing 2 mM DBK is not too high in the range 300–330 nm (OD ca. 0.3). No intermolecular energy self-absorption occurs and all of the absorbed light energy can be reasonably assumed to excite DBK molecules in our experiments ([DBK] ca. 2 mM). Therefore, increasing light intensity increases the rate of the formation of ^{3}RP, which, in turn, generates a higher ^{3}RP concentration in the microemulsion for a given DBK concentration (Figure 13). For reasons similar to those mentioned above, the degree of polymerization decreases with the increase in light intensity with the relation $D_p \propto L^{-0.2}$.

In a conventional emulsion polymerization using a water-soluble initiator, the principal locus for generation of initiator is believed to be in the aqueous phase. Radicals generated in the aqueous phase enter monomer-swollen emulsifier micelles and rapidly polymerize the monomer,[12,13] or radicals react with solute monomer molecules to form oligomeric radicals which then precipitate to form primary latex particles.[14,15] The monomer emulsion droplets are not considered to be significant loci for initiation but serve as reservoirs that feed monomer to polymerizing particles by diffusion through the aqueous phase. Emulsion polymerization of styrene is known to follow the Smith–Ewart case II kinetics[16] and the polymerization rate is proportional to the number of particles generated, which in turn is proportional to the 0.4 power of initiator concentration.

In a miniemulsion system, the principal locus for initiation of polymerization in miniemulsion is believed to be in the monomer droplets instead of the aqueous phase.[3] The polymerization rate in a styrene miniemulsion was found[17] to be proportional to the particle number, which in turn was proportional to the 0.4 power of the initiator concentration when a water-soluble initiator, potassium persulfate, was used and was proportional to the 0.2 power of the initiator concentration when an oil-soluble initiator, 2,2′-azobis(2-methylbutyronitrile), was used. In either case, the number-average particle size of the final latex was found to be larger than the size of the initial monomer droplets and to decrease with increasing initiator concentration. The growth in particle size was attributed to the diffusion of monomer through the aqueous phase, i.e., only a fraction of the miniemulsion droplets were initiated and converted to particles while the rest of the droplets served as reservoirs and fed monomer to polymerizing particles. A higher concentration of initiator (or higher temperature of a given initiator concentration) initiated more particles and resulted in a higher polymerization rate and a smaller final particle size.

In the microemulsion polymerization of styrene, the initial average droplet size is even smaller than that in a miniemulsion. The principle locus for initiation of polymerization is likely to be in monomer droplets. In this study, an oil-soluble photoinitiator DBK was used. Coincidently the polymerization rate was found to be proportional to the 0.2 power of the initiator concentration as well as the light intensity. The same dependency of polymerization rate on oil-soluble initiator concentration as in the miniemulsion polymerization suggests that there is a similarity in initiation mechanism between these two types of polymerization.

Figure 6 shows that all of the latexes have average diameters larger than the diameter of the original microemulsion droplets. Since these latexes were polymerized to different conversions, it is difficult to derive a straightforward relationship between the particle size and the initiator concentration. Nevertheless, the particle size seems to increase with increasing initiator concentration and with increasing light intensity. A possible mechanism for the particle growth in microemulsion polymerization is a combination of coagulation and monomer diffusion. As soon as polymers were formed in droplets, the microemulsion became less stable. The droplet-converted particles gradually coagulated to larger sizes so that interparticle electrostatic repulsion could better stabilize them. A higher initiation rate, from either higher initiator concentration or higher light intensity, converted more droplets into particles, and thus gave a higher initial polymerization rate and also a faster coagulation rate of the primary particles. The decrease in particle number due to coagulation accounts for the rapid decay of polymerization rate after it reached the maximum in a short time. The decrease in monomer concentration and slight decrease in the transparency of the system also contribute to the decrease in polymerization rate with time. (The final transmission of the system decreases to ca. 80% of original one.)

The results from the plot of conversion against reaction time (Figure 12) show that the percent conversion was lower with the lower initiator concentration and light intensity during the first 60 min of polymerization. This is consistent with the results from the dilatometry method. The trend did not hold after 60 min, probably due to the decrease in particle number and transparency of the system as discussed above. This study shows that there are some similarities between a microemulsion polymerization and a miniemulsion polymerization, such as the dependency of polymerization rate on initiator concentration and the polydispersity of particle size. But they are quite different in other aspects, such as the dependency of final particle diameter on initiator concentration. The comparisons of microemulsion polymerization and miniemulsion polymerization in terms of mechanism of particle growth and polymerization kinetics are subjects of future study.

Conclusion

The styrene microemulsions employed in this investigation remain transparent during the whole polymerization process. The polymerization is successfully performed under different initiator concentrations and light intensities. Unlike conventional emulsion polymerization, the polymerization in microemulsions only occurs in the monomer reservior encapsulated in the particle. The molecular weights of the produced polymers are in the order of 10^5, and their polydispersity indexes (M_w/M_n) are in the range 1.6–2.2. The particle sizes of the produced latexes are in the range of 30–60 nm, and the polydispersity indexes are in the range 1.05–1.08. The increasing DBK concentration and light intensity decrease the degree of polymerization as $D_p \propto [\mathrm{DBK}]^{-0.4}L^{-0.2}$. The polymerization rate determined by the capillary height change of dilatometer shows that increasing DBK concentration and increasing light intensity increase the polymerization rate as $R_p \propto [\mathrm{DBK}]^{0.2}L^{0.2}$. The measurement of percent conversion shows an identical trend for polymerization rate as determined by the dilatometer. The same dependency of polymerization rate on DBK concentration suggests that there is a similarity in initiation mechanism between the polymerization in microemulsion and in miniemulsion. A possible mechanism for particle growth in microemulsion polymerization is a combination of coagulation and monomer diffusion.

Acknowledgment. The authors at Columbia thank the Air Force Office of Scientific Research and the 3M Corp. for their generous support of this research.

Registry No. DBK, 102-04-5; PhCH=CH$_2$, 100-42-5; poly(styrene), 9003-53-6.

References and Notes

(1) Piirma, I., Ed. *Emulsion Polymerization*; Academic: New York, 1976.
(2) Shah, D. O., Ed. *Macro and Microemulsion: Theory and Practices*; American Chemical Society: Washington, DC, 1985; *ACS Symp. Ser.*, *272*.
(3) (a) Ugestad, J.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 503. (b) Azad, A. R. M.; Ugelstad, J.; Fitch, R. M.; Hansen, F. K. *Emulsion Polymerization*; American Chemical Society: Washington, DC, 1976; *ACS Symp. Ser. 24*, 1. (c) Chamberlain, V. J.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans 1* **1982**, *78*, 591. (d) El-Aasser, M. S.; Lack, C. D.; Choi, Y. T.; Min, T. I.; Vanderhoff, J. W.; Fowkes, F. J. *Colloid Surf.* **1984**, *12*, 79.
(4) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4279.
(5) Jayakrishnan, A.; Shah, D. O. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 31.
(6) (a) Tang, H.-I.; Johnson, P. L.; Gulari, E. *Polymer* **1984**, *25*, 1357. (b) Johnson, P. L.; Gulari, E. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3967.
(7) (a) Leong, Y. S.; Candau, F. *J. Phys. Chem.* **1982**, *86*, 2269. (b) Candau, F.; Leong, Y. S.; Pouyet, G.; Candous, S. *J. Colloid Interface Sci.* **1984**, *101* 167. (c) Candou, F.; Leong, Y. S.; Fitch, R. M. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 193.
(8) (a) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Tung, C.-H. *J. Am. Chem. Soc.* **1983**, *105*, 1572. (b) Turro, N. J.; Arora, K. S. *Macromolecules* **1986**, *19*, 42.
(9) Shaffer, O. L.; El-Aasser, M. S.; Vanderhoff, J. W. *Proc. Microsc. Soc. Am., 41st* 1983, 30.
(10) Scholsky, K. M.; Fitch, R. M. *J. Colloid Interface Sci.* **1985**, *104*, 592.
(11) Sudol, E. D.; El-Aasser, M. S.; Micale, F. J.; Vanderhoff, J. W. *Org. Coat. Plast. Chem.* **1980**, *42*, 162.
(12) Harkins, D. *J. Am. Chem. Soc.* **1947**, *69*, 1428.
(13) Harkins, D. *J. Polym. Sci.* **1950**, *5*, 217.
(14) Roe, C. P. *Ind. Eng. Chem.* **1968**, *60*, 20.
(15) Fitch, R. M. *Polymer Colloids*; Fitch, R. M., Ed.; Plenum: New York, 1971; p 73.
(16) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592.
(17) Choi, Y. T.; El-Aasser, M. S.; Sudol, E. D.; Vanderhoff, J. W. *J. Polym. Sci.* **1985**, *23*, 2973.