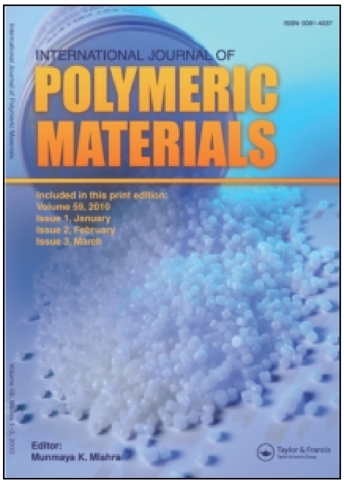

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A Comparison of Emulsion and Microemulsion Copolymerization of Styrene and Acrylonitrile

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The synthesis of styrene-acrylonitrile (SAN) copolymers by emulsion or microemulsion polymerization using either a water-soluble (potassium persulfate or KPS) or a water-insoluble (AIBN) initiator is presented here. The surfactant used was dodecyltrimethylammonium bromide (DTAB) or sodium dodecylbenzenesulfonate (SDBS). Polymerization in DTAB microemulsions initiated with AIBN are faster and have higher conversions than those initiated with KPS, but the opposite effect is observed for emulsion polymerization. In both emulsion and microemulsion polymerizations, high molecular weights (2–4 × 10^6 Dalton) SAN copolymers are produced with composition richer in styrene (S/AN = 81/19 w/w) than the initial feed composition (75/25 w/w). Latex produced by microemulsion polymerization contain particles two- to three-fold smaller than those prepared by emulsion polymerization.

INTRODUCTION

Styrene-acrylonitrile copolymers (SAN) are thermoplastics of commercial importance because their flexural impact, tensile strength and chemical resistance are significantly better than those of polystyrene and other similar polymers.[1,2] SAN copolymers also have good gloss, transparency and high deflection temperature. The physical properties of SAN copolymers are enhanced by increasing molecular weight and acrylonitrile content up to about 35 mol%, although there is a loss of processability and a slight decrease in transparency.[2] Because of their improved

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properties, SAN copolymers are used in the appliance industry, in electronic parts, in the construction industry and in medical applications.[1,2]

SAN copolymers are produced by mass, suspension or emulsion polymerization processes.[3,4] In particular, emulsion polymerization allows the synthesis of high molecular weight SAN copolymers with fast reaction rates and easy control of reaction. However, to our knowledge, the synthesis of SAN copolymers in microemulsion media has not been reported before.

Microemulsion polymerization is a new process that allows the synthesis of high molecular weight polymers with fast reaction rates in the form of latex containing particles ten-fold smaller than those produced by emulsion polymerization.[5,6] Here a comparison between emulsion and microemulsion copolymerization of styrene and acrylonitrile using a water-soluble (potassium persulfate) or a water-insoluble (AIBN) initiator is reported.

EXPERIMENTAL SECTION

Dodecyltrimethylammonium bromide (DTAB) was 99% pure from Tokyo Kasei. It was further purified by recrystallization from a 50:50 acetone-ethanol mixture. Sodium dodecylbenzenesulfonate (SDBS) was from Tokyo Kasei. Reagent grade styrene and acrylonitrile (Scientific Polymer Products) were passed through DTR-7 and DHR-4 columns (SPP), respectively, to remove inhibitor. Potassium persulfate (KPS) and hydroquinone were reagent grade from Aldrich. AIBN (2,2'-azobisisobutyronitrile) from Dupont was purified by recrystallization from methanol. Doubly distilled water was used.

The single-phase microemulsion regions at 25 and 60°C were determined visually by titrating aqueous micellar solutions of DTAB with mixtures of styrene and acrylonitrile (S/AN) in a weight ratio of 75/25. Phase boundaries were checked by preparing samples with compositions slightly below and above the titration-determined phase boundaries in sealed glass ampules. The phase diagram at 60°C was determined with monomers containing inhibitor (20 ppm) to avoid thermal polymerization. Microemulsion conductivities were measured with an Orion 101 conductimeter and YSI immersion cell (cell constant equal to 0.91 cm^{-1}).

Copolymerization of styrene and acrylonitrile was carried out at 60°C in a 100-ml glass reaction vessel. The reaction vessel was loaded with DTAB/water/styrene-acrylonitrile mixture and heated to 60°C before adding a concentrated KPS aqueous solution. In the case of AIBN, a solution of DTAB in water was loaded in the reactor and heated to 60°C before adding the monomer mixture containing AIBN at the required concentration. The sample becomes turbid when the monomers are added but it clears again in seconds when the composition is within the one-phase microemulsion region, otherwise the emulsion that forms is milky white. The system was continuously stirred and sparged with nitrogen. Samples were withdrawn during the reaction and quenched with a cold hydroquinone aqueous solution (0.05 mM). Polymer was isolated by evaporating the water and the non-reacted monomers in a vacuum oven. Then the residue was washed with water to partially remove the surfactant and dried. Copolymer composition was determined by infrared spectroscopy (Nicolet 5ZDA FTIR spectrophotometer) using the ratio of the intensity of the $C{\equiv}N$ stretching band for acrylonitrile at 2240 cm^{-1} to that of the skeletal stretching mode of the phenyl group of styrene at 1610 cm^{-1}.[7]

Quasielastic light scattering (QLS) measurements were made with a Malvern 4700C light scattering apparatus. The magnitude of the scattering vector, $\mathbf{q} = (4\pi n/\lambda_0) \sin(\theta/2)$, was varied by changing the scattering angle, θ, from 30° to 120°. Here n is the index of refraction and λ_0 ($=488$ nm) is the wavelength of the light in vacuum. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $\langle\Gamma\rangle$ ($=2q^2D$), where D is the diffusion coefficient, and the variance, ν ($=[\langle\Gamma\rangle^2 - \langle\Gamma^2\rangle]/\langle\Gamma\rangle$), which is a measure of the width of the distribution of the decay rates. The measured diffusion coefficients were represented in terms of apparent radii by using Stokes law and assuming the solvent has the viscosity of water. Latex was diluted up to 1000 times before QLS measurements to minimize particle-particle interactions. Average molecular weights were determined with a Shimadzu LC-4A liquid chromatograph and a refractive index detector using TSKH-gel Toyo Soda columns with molecular weight ranges from 10^4 to 10^7. Columns were calibrated with polystyrene molecular weight standards from Polyscience, Inc. Molecular weights of SAN copolymers were corrected by the universal calibration method[8] using the Mark-Houwink constants reported elsewhere.[9]

Transmission electron microscopy (TEM) characterization of the latex was carried out in a JEOL-100CX microscope. The smallest (50 μm) condenser aperture was used to diminish the radiation dose to the specimens. The samples were stained with an osmium tetroxide solution (1%) prior to TEM observation and imaged in bright field mode at 80 keV under axial illumination conditions. Three to five samples were analyzed in each case to rule out possible contrast artifacts in the microscope and to assure good representability. The microemulsion samples were deposited onto standard 100 mesh copper grids, previously covered with an amorphous carbon film.

RESULTS

One phase microemulsions of styrene-acrylonitrile (S/AN = 75/25 w/w), DTAB and water were found at 25 and 60°C near the water-rich corner (Figure 1). The one phase region at 60°C is slightly larger than the one at 25°C. One-phase microemulsions are optically transparent and of low viscosity for DTAB concentrations up to 20 wt%. At higher DTAB concentrations, microemulsions are transparent and non-birefringent when observed through cross-polarizers, but highly viscous. Hence upper phase boundaries (indicated by dotted lines) were not determined exactly.

Microemulsion conductivities are high (>5 mS/cm) and increase with surfactant content and temperature but they decrease as the concentration of monomers is increased. The composition selected for microemulsion polymerization (75 wt% water, 15% wt% DTAB, 7.5% wt% styrene and 2.5 wt% acrylonitrile) is indicated by the solid dot in the phase diagram (Figure 1).

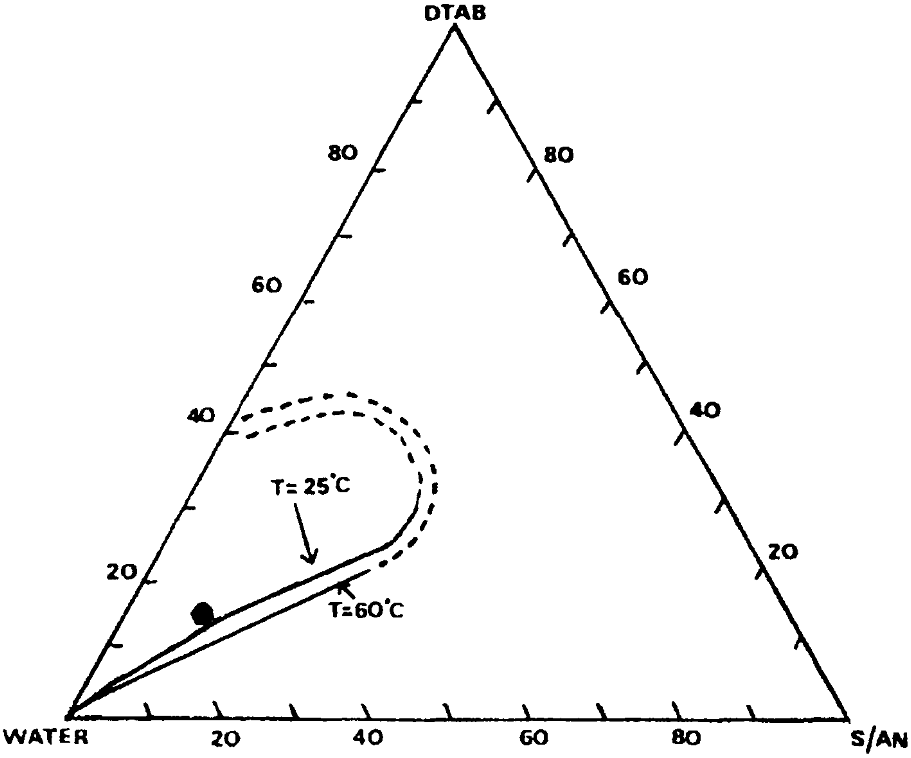

FIGURE 1 Extent of the one-phase region in a partial phase diagram of DTAB/water/styrene-acrylonitrile (S/AN) at 25 and 60°C. S/AN weight ratio was 75/25. Microemulsion composition used in polymerization (75 wt% water, 15 wt% DTAB/10 wt% monomers) is indicated as a solid dot in phase diagram.

Conversion versus reaction time as a function of AIBN concentration is shown in Figure 2. Polymerization rates are fast and increase with AIBN concentration. Final conversions are higher than 90% and increase with initiator concentration. The induction period shrinks with increasing initiator concentration.

Slower reaction rates and smaller final conversions are obtained with KPS (Figure 3). Polymerization rates and final conversions also increase with initiator concentration. The induction period decreases as initiator concentration increases. Similar results have been reported for the polymerization of styrene in o/w microemulsions made with DTAB.[9,10]

The transparent microemulsions become increasingly turbid as polymerization proceeds because of particle growth and an increase in the refractive index difference between the aqueous medium and the dispersed particles. QLS measurements as a function of reaction time for the microemulsion polymerization using KPS demonstrate particle growth in the earlier stages of the reaction but then particle size remains constant (Table I) in agreement with visual observations. No phase separation nor precipitation (coagulation) is visually detectable. Latex are stable and quite monodisperse as inferred from the small variances of the correlation function decays (≤0.1). With both initiators, polymerizations carried out with

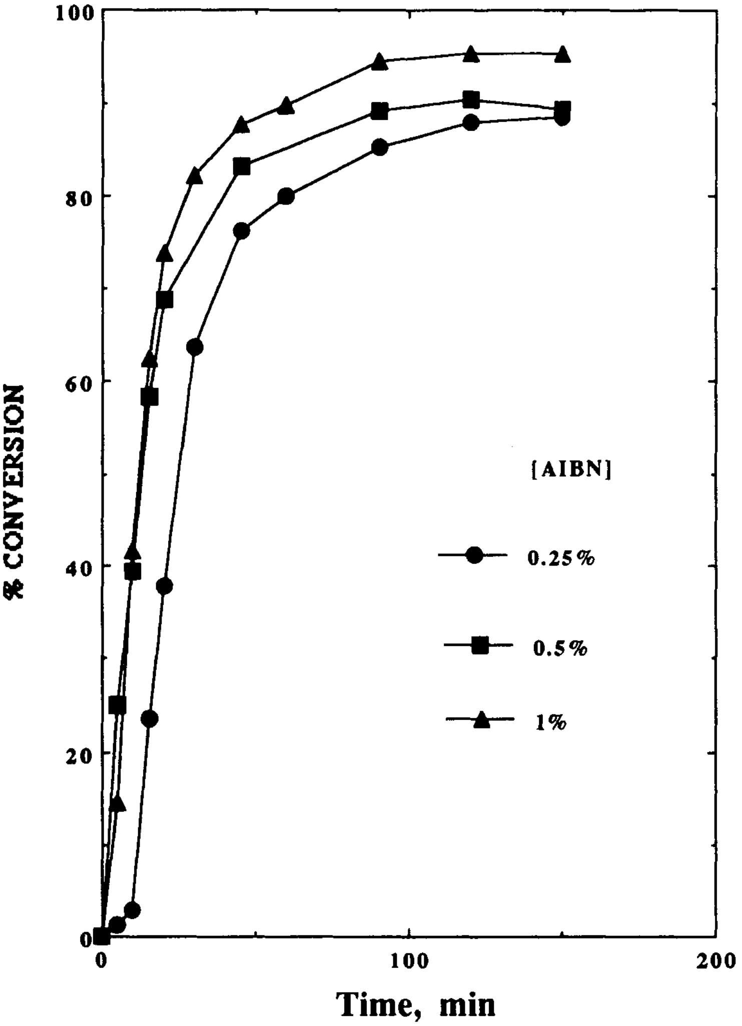

FIGURE 2 Conversion as a function of time for the microemulsion polymerization at 60°C of styrene and acrylonitrile using various concentrations of AIBN as initiator.

higher initiator concentrations produce latex containing smaller particles and consequently they appear less turbid to the naked eye.

Final copolymer compositions, particle size and molecular weights of copolymers produced with KPS or AIBN are reported in Table II. Styrene content in copolymers (80 wt%) is higher than that in monomer feed (75 wt%). Copolymer composition remains fairly constant throughout the reaction (Table III). Molecular weights are high and they do not depend on initiator concentration. AIBN yields SAN copolymers with higher molecular weights than those obtained with KPS. Particle size, on the other hand, decreases as the concentration of AIBN or KPS increases (Table II).

Figure 4 depicts a TEM micrograph.of the SAN latex prepared by microemulsion polymerization using 1% AIBN. The micrograph shows particles with a relatively

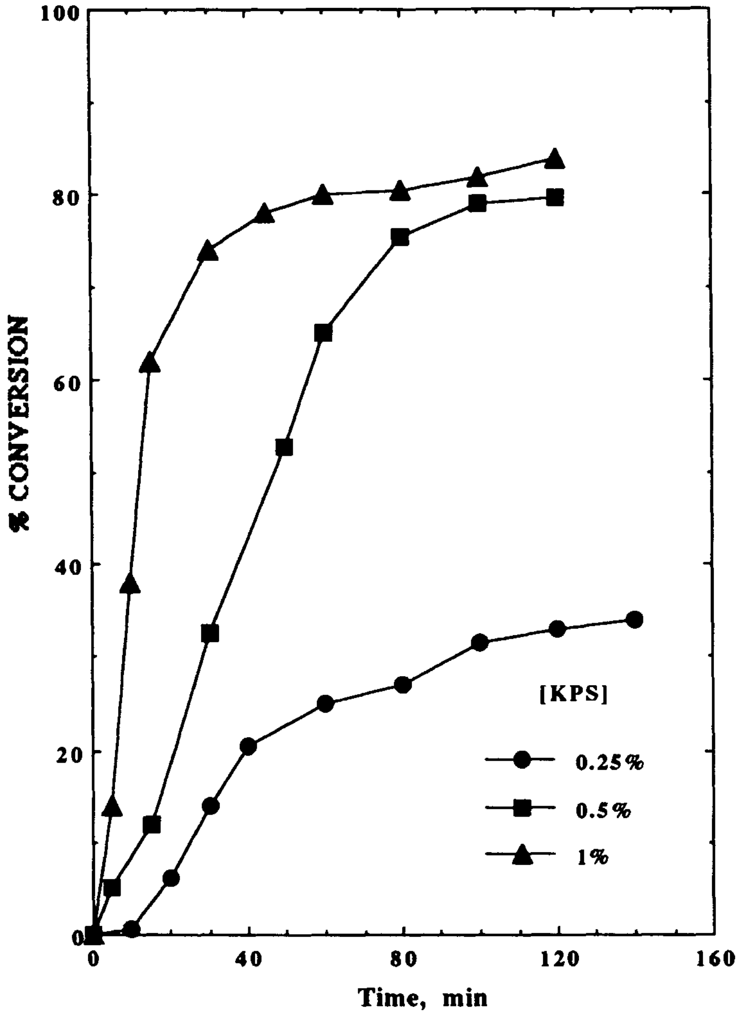

FIGURE 3 Conversion as a function of time for the microemulsion polymerization at 60°C of styrene and acrylonitrile using various concentrations of KPS as initiator.

TABLE I

Particle size as a function of time for the copolymerization of styrene and acrylonitrile (S/AN = 75/25) using 1 wt% (with respect to monomers) AIBN

Time (min)	10	20	45	90	100
D_p (nm)	36	43	43	43.6	41.8

narrow diameter distribution, ranging from 216 A up to 450 A, in agreement with QLS results. A careful look to the particles shows that they exhibit some interesting structure which, however, can not be further explored due to the low signal-to-noise ratio in the image, to the lack of complete stability of the sample under the electron beam and also to the contrast interference of the underlying carbon film.

TABLE II

Molecular weight (M_w), particle size and copolymer compositon at the end of reaction for the copolymerization of styrene and acrylonitrile (S/AN = 75/25). Initiator type and concentration are indicated in Table

Initiator concentration	SAN composition (wt% styrene)	$M_w \times 10^{-6}$ (daltons)	D_p (nm)
0.25% AIBN	81.4	1.66	49.0
0.50% AIBN	80.5	1.65	49.0
1.0% AIBN	81.3	1.47	41.8
0.2% KPS	80.8	1.62	93.8
0.50% KPS	81.5	1.40	62.2
1.0% KPS	81.3	1.40	40.6
5.0% KPS	80.5	—	23.4

TABLE III

Copolymer composition at two different reaction times in microemulsion polymerization. KPS concentration is with respect to monomer concentration

% KPS	SAN composition at 10 min (% styrene)	SAN composition at 150 min (% styrene)
1.0	82.0	81.3
0.50	81.8	81.5
0.25	83.0	80.8

To compare with the microemulsion process, emulsion polymerization of styrene/acrylonitrile at the same ratio used for microemulsion polymerization, i.e., S/AN = 75/25, was carried out using DTAB or SDBS. Emulsion composition was 87.42 wt% water, 0.93 wt% DTAB (or SDBS) and 11.65 wt% monomer mixture. Conversion versus time as a function of initiator (AIBN or KPS) and surfactant type is shown in Figure 5. Polymerization reaction rates are faster and induction times smaller with KPS with both emulsifiers. Also polymerization rates are faster and conversions are higher when SDBS is used as emulsifier. Final copolymer compositions are similar to those obtained in microemulsion polymerization, but molecular weights (Table IV) and particle size ($D_P > 100$ nm) are larger than those obtained by microemulsion polymerization.

DISCUSSION

The unpolymerized one-phase microemulsions are optically transparent and show low viscosity for DTAB concentrations smaller than 20 wt%. The one phase regions at 25 and 60°C are larger than those observed in DTAB microemulsions containing only styrene.[10] This is probably the result of the high solubility of acrylonitrile in water and in styrene, so it can partition among the disperse and continuous media and at the interface, where it behaves as a cosurfactant. As temperature increases, the one-phase microemulsion region increases slightly due to the increase on solubility of both monomers. Stoffer and Bone reported that water-soluble initiators

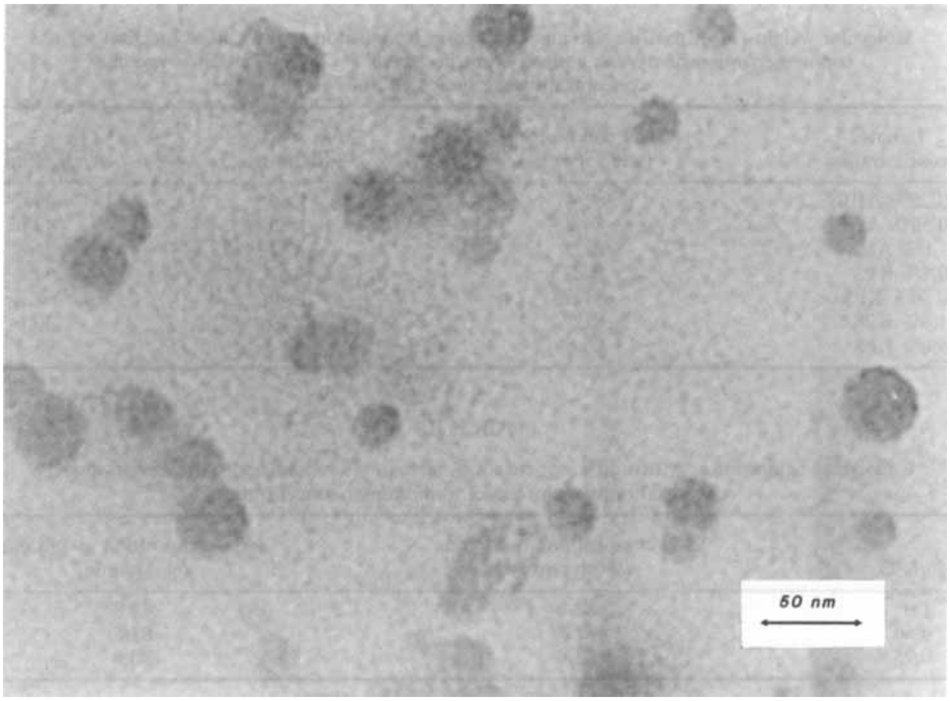

FIGURE 4 Micrographs of latex particles from the microemulsion copolymerization of styrene and acrylonitrile using 1 wt% AIBN.

can change the phase diagrams.[11,12] However, the phase boundaries reported here do not change upon addition of KPS or AIBN, probably because of the small concentrations used here.

The high conductance (>5 mS/cm) and the high water-content imply that SAN microemulsions are water-continuous (o/w). QLS and SANS measurements made on DTAB microemulsions of similar compositions but containing only styrene indicated the presence of DTAB micelles swollen with styrene dispersed in a DTAB-saturated aqueous phase.[13] It is unlikely that the addition of the relatively small amounts of acrylonitrile changes the structure of the microemulsions reported here.

Higher conversions and faster reaction rates are obtained with AIBN than those detected with KPS (cf. Figures 2 and 3). Similar results were reported elsewhere for the polymerization of styrene[14] and of methylmethacrylate[15] in DTAB microemulsions. The molecular weights of the SAN copolymers obtained by microemulsion polymerization are high ($M_w > 10^6$) and they are practically independent of the initiator concentration. However, particle size depends on type and concentration of initiator, being slightly larger with KPS. Similar results were reported by Gan *et al.* for the polymerization of styrene in four-component microemulsions.[16]

That final conversions are higher with AIBN (oil-soluble initiator) than with KPS (water-soluble initiator) can be explained by considering the loci of initiation and chain-transfer reactions to surfactant counterions. In the microemulsions studied here, acrylonitrile partitions among the microemulsion droplets, the interface

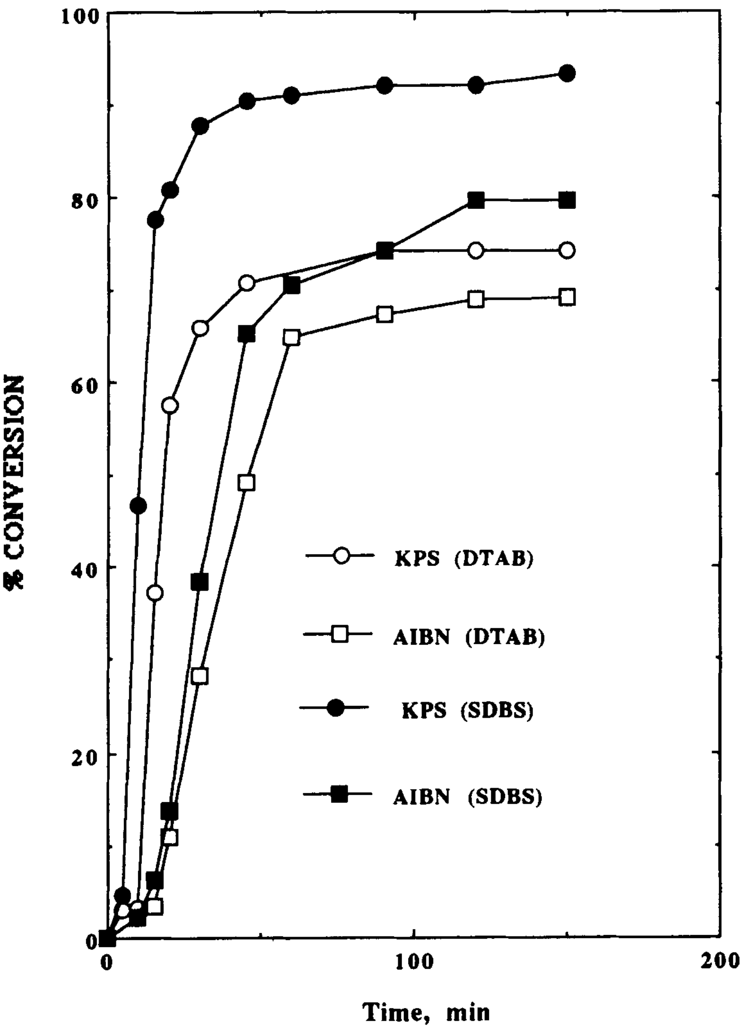

FIGURE 5 Emulsion polymerization of styrene and acrylonitrile using DTAB (or SDBS) as emulsifier and 1 wt% KPS (or AIBN) as initiator. Emulsion composition was 0.93 wt% surfactant, 87.42 wt% water and 11.65 wt% monomer mixture (S/AN = 75/25).

TABLE IV

SAN composition and molecular weight (M_w) at the end of the reaction of emulsion polymerization of styrene and acrylonitrile using 1 wt% DTAB or SDBS as emulsifier

Surfactant	Initiator (1%)	SAN composition (% styrene)	$M_w \times 10^{-6}$
DTAB	KPS	78.5	3.70
DTAB	AIBN	83.1	3.98
SDBS	KPS	80.2	3.30
SDBS	AIBN	83.2	3.80

and the aqueous region whereas styrene is mainly located inside the microemulsion droplets (swollen micelles). The number of droplets is larger than the number of free radicals, and if the efficiency of free radical capture is low, as it appears to be the case for miniemulsion and microemulsion polymerization,[17,18] only a fraction of the droplets is initiated during the reaction. In the case of the water soluble initiator, the free radicals, which form in the aqueous phase, can react there with dissolved styrene or acrylonitrile to form small oligomers, before they diffuse to the microemulsion droplets to continue the reaction. However, because of the electrostatic attraction between SO_4^--free radicals and the positively charged surface of the DTAB microemulsion droplets, the sulfate free radicals can be trapped at the droplet surfaces, reducing their efficiency to initiate the reaction with a concomitant slowing down of the overall rate of reaction. This effect, called "the electrostatic cage effect,"[19] is particularly important in microemulsion polymerization because of the enormous amount of surface area of the charged microemulsion droplets.[14,15]

Also, bromide ions are effective scavengers of persulfate free radicals.[20] The sulfate free-radical generated from the decomposition of persulfate can react with bromide ions of DTAB to produce free radicals which do not react with styrene. In fact, the rate constant for the reaction of sulfate free radicals with bromide ions ($k = 3.5 \times 10^9$ l/mol/s) is larger than that with styrene molecules ($k = 2 \times 10^9$ l/mol/s).[20]

However, when SO_4^--free radicals react with styrene molecules in the aqueous phase to produce very hydrophobic oligomeric radicals,[21] they can easily enter into the droplets to continue the reaction there. On the other hand, when SO_4^--free radicals react with acrylonitrile, whose aqueous concentration is much larger than that of styrene, there is a larger possibility that this monomeric radical will react with styrene molecules than with acrylonitrile molecules, even in the aqueous phase, because of the reactivity between a radical terminated in acrylonitrile with acrylonitrile monomer is much lower than with styrene molecules ($r_2 = 0.04$).[22] Both events are favored when there are noninitiated microemulsion droplets which can maintain the equilibrium concentration of styrene in the aqueous phase by diffusion. When all the unreacted droplets that supply styrene are consumed, styrene concentration in the aqueous phase should diminish rapidly as reaction proceeds, and so free radicals must react mainly with acrylonitrile in the aqueous phase, which being a base, can also be trapped by the positively charged droplets causing a slowing down of the reaction rate. Our results indicate that styrene is depleted from the aqueous phase (i.e., all styrene is inside initiated droplets) at fairly low conversions (below 30%). This is inferred since after about 30% conversion, particle size remains almost constant and reaction rate goes through a maximum and then decreases steadily. This indicates that very few reaction sites are created after that conversion, because practically all the water-insoluble monomer must be present in the particles that have been already initiated (irrespectively of being active or not). At this stage new particles can be generated mainly by homogeneous nucleation of acrylonitrile in the aqueous medium. However, there is a low probability of SAN copolymer formation because acrylonitrile oligomers are quite hydrophilic so they rather remain in the aqueous phase than enter in the styrene-rich droplets;

also, as acrylonitrile oligomers grow they become increasingly insoluble in styrene. So probably low molecular weight polyacrylonitrile forms as well.

When AIBN is used, initiation can occur inside the microemulsion droplets and reaction can proceed to high conversions. Here the monomer from other noninitiated droplets also diffuses toward the activated particles. However, final molecular weights are high in spite that AIBN decomposes in radical pairs inside the droplets. Hence, AIBN-free radicals can desorb from the microemulsion droplets to the aqueous phase to initiate the reaction there, so the overall polymerization rate and the molecular weights are also affected by the entry of radicals from the aqueous phase.[23] The desorbed radicals can be terminated in the aqueous phase by reacting with other radicals or by entering again into the droplets to initiate (noninitiated droplets) or to terminate (initiated droplets) the reaction. Because the neutral AIBN-free radicals do not interact electrostatically with the microemulsion droplets and because they do not react with bromide ions, AIBN free radicals can generate more particles which will result in larger overall reaction rates (cf. Figures 2 and 3) and smaller particles in final latex (Table II). The high molecular weights produced with both initiators, however, indicates that the main termination mechanism is by chain transfer to monomer.

Slower reaction rates, compared to microemulsion polymerization, were obtained by emulsion polymerizations with DTAB and AIBN or KPS (cf. Figures 2 and 3 with 5). Emulsion polymerization rates are higher with KPS than with AIBN probably because (i) AIBN free radicals need to desorb from emulsified droplets into the aqueous phase whereas SO_4^- free radicals form in the aqueous phase; (ii) the efficiency of the monomer-swollen micelles on trapping and inhibiting SO_4^--free radicals in emulsion polymerization must be much smaller compared to that of microemulsion droplets, so SO_4^--free radicals can effectively initiate polymerization in the aqueous phase[19]; and (iii) the concentration of the free-radical-scavenger bromide ions is reduced 15-fold in the emulsion system (compared to the microemulsion) so transfer reactions between SO_4^-- and bromide should diminish appreciably. However, to show that the electrostatic cage effect and chain-transfer reactions with bromide ions are also important in emulsion polymerization, the copolymerization of styrene and acrylonitrile using an anionic emulsifier, sodium dodecylbenzenesulfonate (SDBS), was investigated. Faster polymerization rates and higher conversions were obtained with SDBS than with DTAB in support to our hypothesis. Also, with SDBS, KPS yields faster reaction rates and higher conversions than AIBN (Figure 5).

The high molecular weights obtained in emulsion polymerization also indicates that chain transfer to monomer is the main mechanism of termination. Molecular weights are higher in emulsion polymerization probably because the kinetics of microemulsion polymerization appears to be diffusion-controlled[24] and because monomer concentration in particles is smaller than that in emulsion polymerization. In fact, monomer from emulsified droplets is present at high conversions (ca. 60% for styrene) in emulsion polymerization, whereas uninitiated microemulsion droplets which are the source of monomer for reacting particles, disappear at early stages of reaction (15 to 30% conversion).[14-16,18]

In the case of the emulsion polymerization of two monomers with substantially different solubility in water, it is the less water-soluble monomer which becomes incorporated in the polymer to a greater extent than in bulk polymerization employing the same overall feed composition.[21] For styrene-acrylonitrile reaction, Fordyce and Chapin[25] concluded that if the aqueous phase were the principal locus of reaction, then it would be expected that the more water-soluble monomer would become preferentially incorporated in the copolymer during the course of the reaction, which it is not the case (Table IV). That final SAN copolymer compositions in emulsion and microemulsion polymerization are similar and richer in styrene demonstrates that propagation reaction is taking place inside the swollen-micelles and microemulsion droplets, respectively.

In summary, high molecular weight SAN copolymers were produced with fast reaction rates by emulsion and microemulsion polymerization using water-soluble or oil-soluble initiators. Copolymer compositions are similar in both processes and they are independent on type and concentration of initiator. Microemulsion polymerization yields latex with particles two- to three-fold smaller than those produced by emulsion polymerization.

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