Preparation of Small-Sized Carboxylated Latexes by Emulsion Polymerization Using Alkali-Soluble Random Copolymer

DOUG-YOUN LEE, JUNG-HYUN KIM

Department of Chemical Engineering, Yonsei University, 134 Shinchon-Dong, Sudaemoon-Ku, Seoul 120-749, Korea

ABSTRACT: Alkali-soluble random copolymer (ASR), poly(styrene/α-methylstyrene/acrylic acid) [M_n: 4,300; acid number: 190], was used as a polymeric emulsifier in the emulsion polymerization of styrene and methyl methacrylate, respectively. ASR containing a large number of carboxyl groups could form aggregates like micelles, and the solubilization ability of the aggregates was dependent on the neutralization degree of ASR. The polystyrene latexes prepared using ASR showed the small particle size (ca. 40 nm) and monodispersed particle size distribution. On the other hand, the particle size distribution of poly(methyl methacrylate) latexes became broader as the neutralization of ASR increased. This could be explained by the effects of water solubility of the monomer and the neutralization degree of ASR on particle formation. Thin layer chromatography/flame ionization detector analysis confirmed that the grafting reaction of polystyrene to ASR occurred during emulsion polymerization. The ζ potentials of final latexes showed high values due to ASR that was adsorbed and grafted on the surface of the latex particle. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 543–550, 1998

Key words: alkali-soluble random copolymer; polymeric emulsifier; aggregate; particle size distribution; ζ potential

INTRODUCTION

The carboxylated latexes have been found to result in the improvement of several significant properties, such as colloidal stability, mechanical and freeze-thaw stability, rheology, adhesion, etc.[1] There are many reports containing examples of the emulsion copolymerization of carboxylic comonomer.[1–4] However, these methods are greatly influenced by the introduction method of carboxylic monomer and have a limitation of the amount of carboxyl groups on the particle surface.

In this study, alkali-soluble random copolymer (ASR) containing a large number of carboxyl groups was used as a polymeric emulsifier in the emulsion polymerization to produce highly carboxylated latex particle. For conventional emulsion copolymerization of carboxylic comonomer, only a portion of the carboxyl groups are on the outside of the particle, and the remainder of the carboxyl groups exist inside the particle or in the continuous phase.[1] On the other hand, in emulsion polymerization using ASR, ASRs are concentrated on the surface of the final latex polymer. The latex was stabilized by ASR, which results in formation of a very stable particle without any surfactant.[5]

However, few publications can be found concerned with ASRs as a polymeric emulsifier in emulsion polymerization. It is well known that the amphiphilic polymers that consist of both hydrophobic and hydrophilic groups can stabilize polymer particles and can form aggregates, like micelles, as the result of the intermolecular and/

or intramolecular hydrophobic interactions.[6-9] The properties of ASRs are expected to be similar to those of other polymeric surfactants, but the behavior and contribution in emulsion polymerization would be different from those of conventional polymeric surfactants.

The present study was undertaken to investigate the contributions of ASR [poly(styrene/α-methylstyrene/acrylic acid)] in the emulsion polymerization of styrene and methyl methacrylate, respectively, with a water-soluble initiator, potassium persulfate. The aqueous solution behaviors of ASR, such as aggregate formation, and the effects of the concentration and neutralization degree (used here to denote OH/COOH ratio × 100) of ASR on the latex particle size and distribution were investigated.

The thin layer chromatography/flame ionization detector (TLC/FID) method was used for the direct qualitative analysis of the grafting reaction of ASR. The ζ potentials of latexes were measured to study surface characteristics of resulting latexes.

EXPERIMENTAL

Materials

ASR, poly(styrene/α-methylstyrene/acrylic acid) [M_n: 4,300; M_w: 8,600; acid number: 190], obtained from Morton, Inc. (Chicago, IL), was used as received. Styrene and methyl methacrylate (MMA) monomers were obtained from Junsei Chemical (Tokyo, Japan) and were distilled under the reduced pressure of nitrogen. Pyrene was purchased from Fluka (Ronkonkoma, NY). Potassium persulfate, sodium hydroxide, sodium chloride, ammonium hydroxide, tetrahydrofuran (THF), and toluene were all analytical-grade materials and were used without further purification. Distilled and deionized water was used throughout.

Emulsion Polymerization Using ASR

Batch polymerizations were conducted in a double-wall, round-bottom reactor equipped with a temperature controller, nitrogen inlet, and stirrer. In the reactor, ASR and NaOH were dissolved in distilled deionized water, and monomer was added. NaCl was added in the low NaOH concentration systems to adjust the ionic strength. The reactor was left for about 30 min for the contents

Table I Basic Recipe of Emulsion Polymerization Using ASR as a Polymeric Emulsifier

Components	Amount[a]
Distilled and deionized (DDI) water	350
ASR[b]	5, 10, 25, 35
NaOH	Variable[c]
NaCl	Variable[d]
Monomer	
Styrene or MMA	100
Initiator	
Potassium persulfate	0.5

[a] Wt % based on monomer.
[b] ASR: M_n = 4300, M_w = 8600, acid no. = 190.
[c] NaOH was added in all systems to change the degree of neutralization of ASR.
[d] NaCl was added in low NaOH concentration systems to adjust the ionic strength.

to attain the reaction temperature of 70°C. During this time, the contents of the reactor were stirred and flushed with nitrogen. The initiator was dissolved in the remaining water and added to the reactor. The addition of the initiator marked the start of the reaction. Polymerization was conducted under nitrogen atmosphere until the reaction was substantially completed. The basic recipe of emulsion polymerization in the presence of ASR is given in Table I.

Surface Tension

ASR was dissolved in distilled deionized water to prepare a 10% solution, which was then serially diluted. The surface tension of these solutions was measured by using a surface tensiometer (Surface Tensiomat 21; Fisher Scientific, Pittsburgh, PA).

Pyrene Solubility

A very hydrophobic probe, pyrene, was added to the ASR solution that consists of distilled deionized water, ASR, and NaOH. This solution was stirred for 24 h. Then, the solution was filtered and centrifuged. The pyrene absorbance of the solution was measured using UV spectrophotometer (Shimadzu, Columbia, MD) at 360 nm. Because the ASR solutions itself have UV absorption, the pyrene absorbance values were calibrated by the ASR solution.

Particle Size and Size Distribution

The average particle size and particle size distribution of the latex particles were determined using capillary hydrodynamic fractionation (CHDF 1100, Matec Applied Science, Warwick, RI) and transmission electron microscopy (TEM; Hitachi-600). The polydispersity index was given as D_w/D_n, where D_w is the weight average diameter of latex particles and D_n is the number average diameter.

Thin Layer Chromatographic Separation Technique

TLC was used to separate the polystyrene (PS) latexes into three components (i.e., the ungrafted ASR, ungrafted PS, and the ASR-grafted PS). Polymer solutions were prepared by dissolving the sample in THF at a concentration of 1 g L^{-1} and applying them to the TLC plate with a microsyringe. The detailed description of the TLC procedure has been reviewed elsewhere.[10,11]

The TLC/FID method was used for direct qualitative analysis. The separations were performed on thin quartz rods 0.9 mm in diameter and 150 mm long, and coated with silica gel 75-μm thick (Iatron Chromarod-SII). After development, the quartz rods were dried by vaporizing the developer solvent. At the end of the run, the rods were placed in an apparatus equipped with a FID (Iatroscan MK-5 TLC/FID analyzer) for analysis.

ζ Potential

The ζ potential of latex was measured by a ζ potential analyzer (Dynamic Laser Light Scattering, ZetaPlus, Brookhaven Instruments Co., Holtsville, NY). Its pH was adjusted by adding 0.1N HCl or NaOH solutions.

RESULTS AND DISCUSSION

Aggregate Formation of ASR in Aqueous Solution

Amphiphilic polymers, having both hydrophobic and hydrophilic groups, can form aggregates in aqueous solution. To find out whether the random copolymer (ASR) forms aggregates in aqueous solution, the solubility of a very hydrophobic probe (pyrene) and surface tension of ASR solution were studied.

It is well known that the solubility of aliphatic and aromatic hydrocarbons in water can be enhanced in the presence of surfactants or hydro-
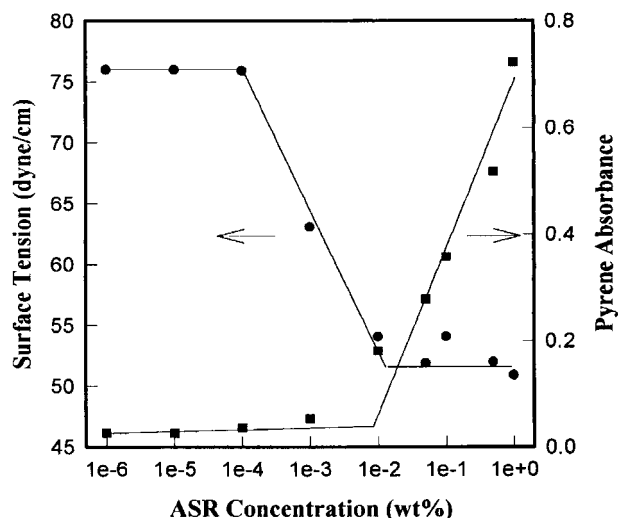

Figure 1 Pyrene absorbance and surface tension of ASR solution as a function of ASR concentration (wt % based on total concentration).

phobically associating polymers.[8] Pyrene is an aromatic hydrocarbon exhibiting a very low solubility in pure water ([Py]$_{s,\text{water}} \approx 7 \times 10^{-7}$ M) and is largely used as a probe for the study of micelles and other hydrophobic aggregates in water.[8] Figure 1 shows the pyrene absorbance at 360 nm and the surface tension of the ASR solution as a function of ASR concentration. The increase in pyrene absorbance with ASR concentration indicated the formation of polymer aggregates like micelles in aqueous solution. The increase in solubility of pyrene could be attributed to an increase in the number of aggregates. This trend is similar to that observed for conventional surfactants.

Also, a gradual decrease and leveling off of surface tension as a function of ASR concentration indicated that the water contained surface active component (ASR), and ASR formed aggregates instead of transferring to the air–water interface when the surface tension became constant. From this evidence, it was concluded that ASR formed aggregates in aqueous solution and could provide polymerization locus.

Effects of Neutralization Degree of ASR on Aggregate

The size and solubilization ability of aggregates are sensitive to internal (hydrophobic structure, etc.) and external (pH, electrolyte content, etc.) factors.[12,13] To study the effects of the neutralization degree of ASR on the solubilization ability of
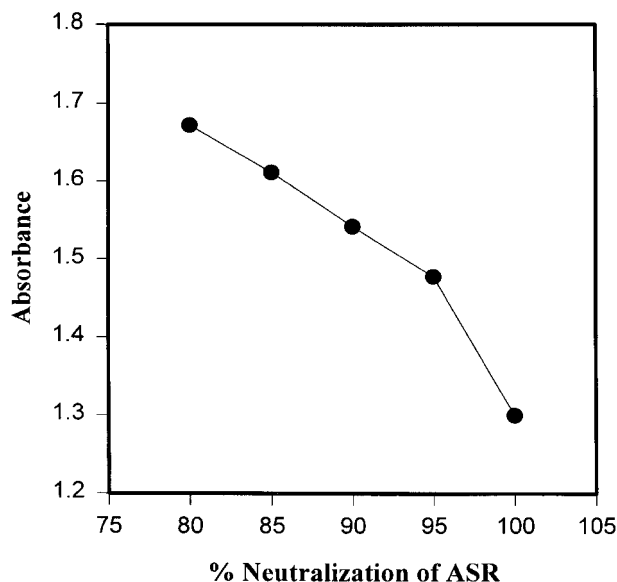
Figure 2 Absorbance of pyrene at 360 nm *versus* degree of neutralization of ASR; [ASR] = 10 wt % based on water.

ASR aggregates, the UV absorbance of the pyrene solubilized in ASR solution was measured at different NaOH concentrations. The effects of NaOH are complicated by the fact that, as the concentration of NaOH increases, not only the neutralization degree of ASR but also electrolyte contents in aqueous solution change. NaCl was added in a low NaOH concentration system to adjust the ionic strength to be equivalent to that of the 100% neutralization system.

Figure 2 shows the solubility for pyrene expressed as the absorbance at 360 nm as a function of the neutralization degree of ASR. The absorbance of pyrene decreased with increasing the neutralization degree of ASR. This means that the solubilization ability of ASR aggregate is affected by the neutralization degree of ASR under the same concentration of ASR.

In general, the amount of hydrophobic material that can be solubilized in the aggregates increases with the hydrophobicity of emulsifier, parallel to an increase in aggregate size.[12,13] The dissociation of carboxyl group depends on the degree of neutralization.[14] By increasing the neutralization degree of carboxyl groups, the hydrophobicity of ASR decreases. The decrease of the solubilization ability is attributed to the decreased hydrophobicity of ASR aggregates.

As described previously, the properties of ASR aggregates, such as their ability to solubilize and release hydrophobic species, depends on the neutralization degree of ASR.

Latex Particle Size and Particle Size Distribution

It is suggested that both the solubility of the monomer in water and its polarity affect the mechanism of particle formation.[15–17] For the conventional emulsion polymerization of styrene, examined by Harkins,[15] the most important sites of particle generation are monomer-swollen emulsifier micelle; with the increase of monomer solubility in water, the locus of particle nucleation may move to the aqueous phase.[16,17] The particle formation in emulsion polymerization using ASR would be affected by the properties of ASR aggregates that depends on the neutralization degree of ASR, as well as the water solubility of the monomer.

The particle size and polydispersity of latexes prepared in the presence of ASR are listed in Table II. The PS and poly(MMA) (PMMA) latexes showed the very small particle size (ca. 40 nm), compared with that observed for conventional emulsion polymers. Figure 3 showed that the PS latex particle size decreased with increasing the concentration of ASR. This result was similar to that obtained in the emulsion polymerization using conventional surfactants.

The polydispersity of both PS and PMMA particles is plotted as a function of the degree of neutralization of ASR in Figure 4. The PS latexes showed relatively monodispersed particle size distribution. On the other hand, the particle size distribution of PMMA latexes became broader as the neutralization degree of ASR increased. This could be explained by the effects of the water solubility of monomer and the neutralization degree of ASR on particle formation.

Figures 5 and 6 show the particle size distributions of PS and PMMA latexes prepared at different degrees of neutralization of ASR, respectively. In the case of water-insoluble monomer, such as styrene, the micellar nucleation is the predominant mechanism in the polymerization process.[15] With increasing the neutralization degree of ASR, the number of aggregates increases as the size decreases. Accordingly, the particle size of PS latexes was found to decrease slightly as the neutralization degree of ASR increased.

However, the polydispersity of PMMA latexes was found to increase with increasing the neutralization degree of ASR, and bimodal particle size distribution was obtained at 100% neutralization.

Table II   Particle Size Analyses of Latex Particles Prepared Using ASR

Monomer	ASR[a]	% Neutralization of ASR	D_n (nm)	D_w (nm)	PDI (D_w/D_n)
Styrene	5	100	45.7	56.3	1.23
Styrene	10	100	42.8	50.5	1.18
Styrene	25	100	38.6	44.0	1.14
Styrene	35	80	37.4	42.5	1.14
Styrene	35	90	36.2	40.3	1.11
Styrene	35	100	34.2	37.8	1.11
MMA	35	80	40.6	50.0	1.23
MMA	35	90	40.4	50.9	1.26
MMA	35	100	40.1	59.9	1.49

PDI, polydispersity index; D_n, number average diameter; D_w, weight average diameter.

[a] Wt % based on monomer.

TEM photographs of PMMA latexes are presented in Figure 7.

The solubilization ability of the ASR aggregate would be the factor determining the particle nucleation mechanism and the breadth of the particle size distribution in batch polymerization. At low neutralization of ASR, the hydrophobicity of the ASR chain is higher, which resulted in an increase in the size and solubilization ability of ASR aggregates. With the increase of neutralization degree of ASR, however, the locus of the PMMA particle nucleation might move to the aqueous phase because of the decreased solubilization ability of ASR aggregates and the higher water solubility of the MMA monomer. The nucleation could be in between the homogeneous mech-anism enhanced by higher water solubility of MMA and the micellar mechanism inside ASR aggregates.

The conclusion drawn from these results was that the particle formation of MMA was more strongly affected by the neutralization degree of ASR than that of styrene.

Grafting Reaction of ASR

TLC was used to identify the grafted ASR in the PS latex. The PS latex prepared with 35 wt % of ASR at 100% neutralization was used. Distilled and deionized (DDI) water–ammonium hydroxide mixture was a suitable developer solvent for ungrafted ASR and toluene, in which ASR
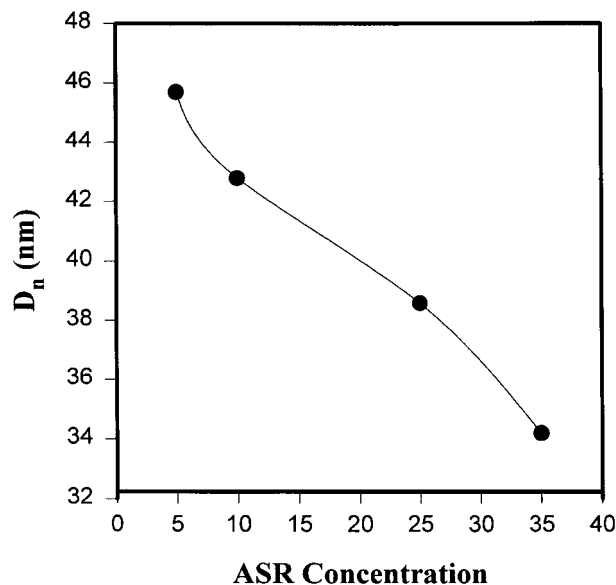

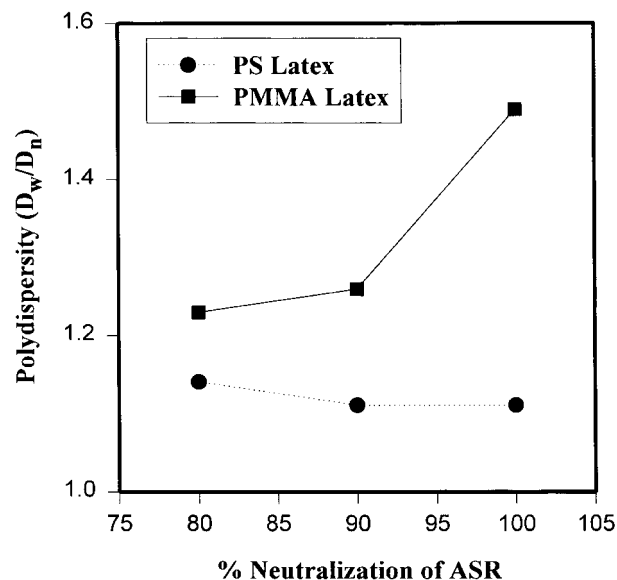**Figure 3**   PS latex particle size as a function of ASR concentration (wt % based on monomer).

Figure 4   Polydispersity of latex particle *versus* degree of neutralization of ASR.
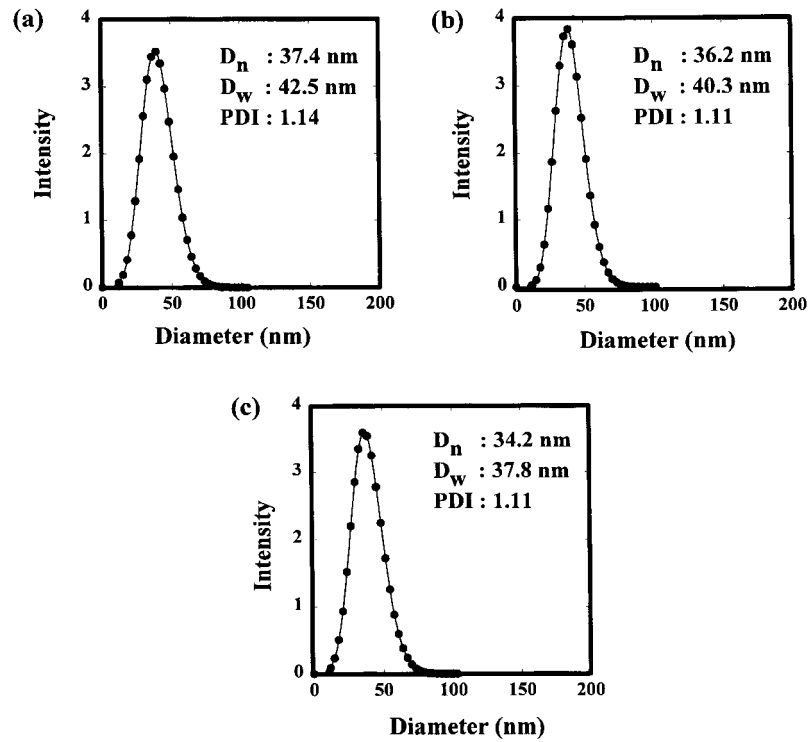
Figure 5 Particle size distributions of PS latexes prepared at different degrees of neutralization of ASR. % neutralization: (a) 80%, (b) 90%, and (c) 100%.
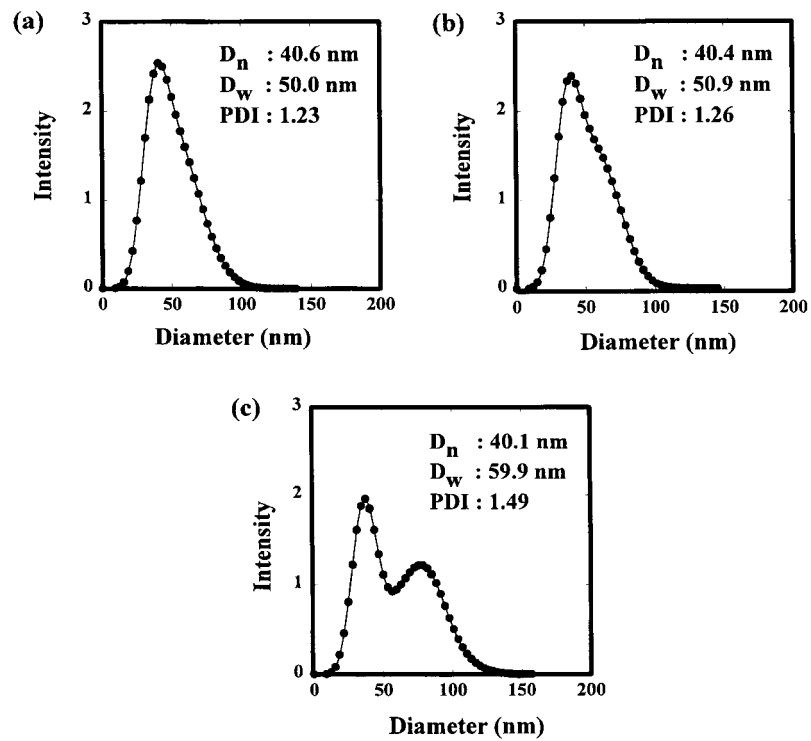

Figure 6 Particle size distributions of PMMA latexes prepared at different degrees of neutralization of ASR. % neutralization: (a) 80%, (b) 90%, and (c) 100%.
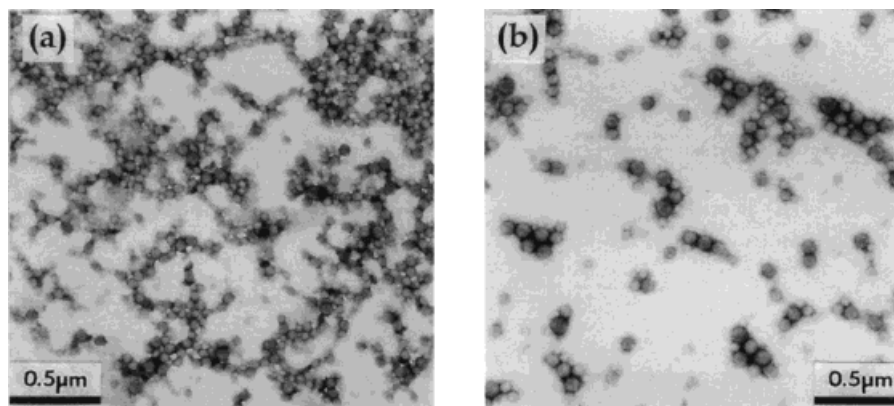
Figure 7 TEM photographs of PMMA latex prepared with 35 wt % of ASR. Degree of neutralization of ASR: (a) 80% and (b) 100%.

was insoluble, was a developer solvent for un-grafted PS.

The TLC separation was made in a two-stage development: the initial developer, water–ammonium hydroxide mixture, was chosen so that the ungrafted ASR migrated up to the solvent front, whereas the ungrafted PS and ASR-grafted PS remained immobile on the starting level. In practice, the solvent front was set at 15 cm above the starting level. This development was repeated more than three times.

After the initial development had been completed, the plate was subjected to secondary development with toluene as the developer. With this procedure, only the ungrafted PS migrated up to a solvent front set at 7 cm. The sample was separated into three components. Figure 8 shows the TLC/FID chromatographic scanning curve of the PS latex prepared with 35 wt % of ASR. The TLC/FID analysis confirmed that the PS latex contained ASR-grafted portion, which indicated that the grafting of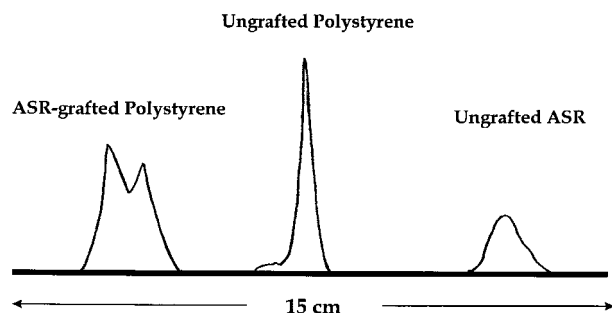 PS to ASR occurred during emul-sion polymerization. This grafting in the PS latex probably resulted from chain transfer of monomer to ASR.

ζ Potential of Final Latexes

In emulsion polymerization using ASR, ASRs containing a large number of carboxyl groups are adsorbed and grafted on the surface of the final latex polymer, which results in very small-sized carboxylated latexes. Figure 9 schematically represents the highly carboxylated latex particle adsorbed and grafted with ASR.
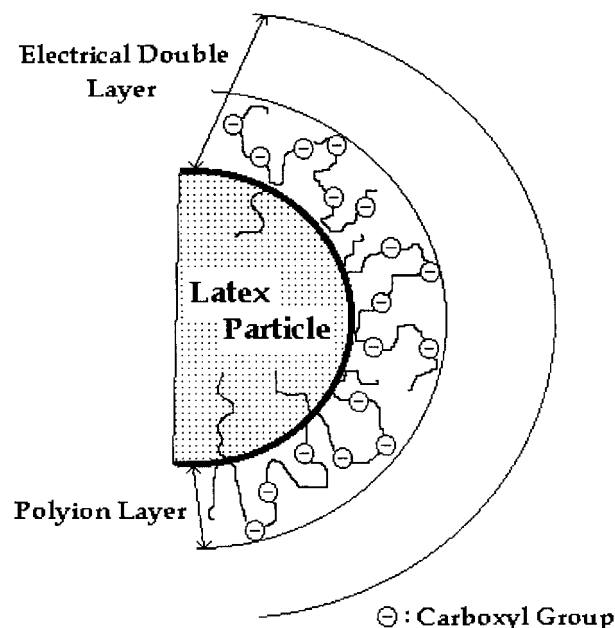

Figure 8 TLC/FID chromatographic scanning curve of PS latex prepared with 35 wt % of ASR at 100% neutralization.

Figure 9 Schematic representation of highly carboxylated latex particle adsorbed and grafted with ASR.
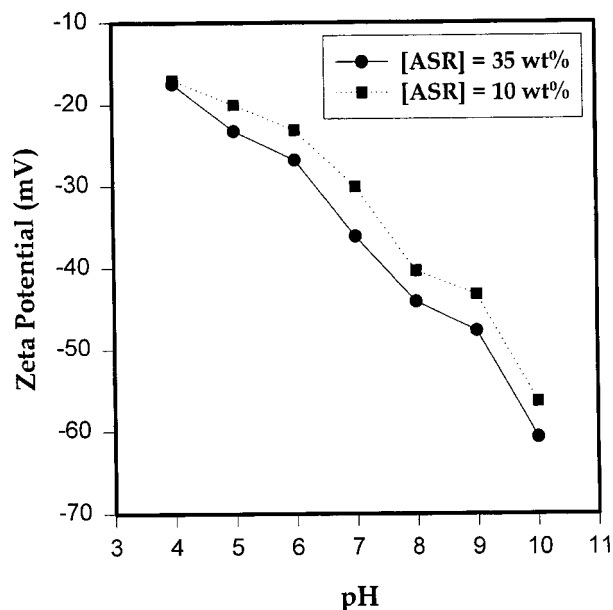
Figure 10 ζ potential of PS latex particle prepared at different concentration of ASR.

The ζ potentials of latexes were measured to study surface characteristics of resulting latexes. Figure 10 shows the ζ potentials of PS particles prepared at 100% neutralization of ASR as a function of pH. The ζ potentials of final latexes showed high values due to ASRs, which were concentrated on the surface of the latex particle.

As ASR concentration increased, the ζ potential was higher. With increased pH, the dissociated fraction also increased, and it resulted in an increase of ζ potential. At pH 4, the carboxylated latexes showed ζ potential value of ca. −20 mV. These potentials would be due to sulfate groups that originated from initiators.

CONCLUSIONS

The ASR containing a large number of carboxyl groups formed aggregates like micelles. The solubilization ability of the aggregates was sensitive to neutralization degree of ASR. The PS and PMMA latexes prepared using ASR showed the very small particle size (ca. 40 nm), compared with that observed for conventional emulsion polymers. The polydispersity of the latex particle

was influenced by both the water solubility of the monomer and the neutralization degree of ASR. It was found that the particle formation of MMA was more strongly affected by the neutralization degree of ASR than that of styrene. TLC/FID analysis confirmed that the PS latex contained an ASR-grafted portion. This result indicated that the grafting of PS to ASR occurred during emulsion polymerization. ASRs were adsorbed and grafted on the surface of the final latex particle, which resulted in small-sized carboxylated latexes. The ζ potentials of final latexes showed high values due to ASRs, which were concentrated on the surface of the latex particle.

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