Characterization of Water-Soluble Oligomer in Acrylic Acid-Styrene Emulsion Copolymerization

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SYNOPSIS

Low molecular weight species, formed during the emulsion copolymerization of styrene and acrylic acid, were isolated and characterized. Samples of the reaction mixture were taken at different times during seeded and unseeded batch reactions. Reactions were stopped via injection of the samples into hydroquinone solutions and cooling with dry ice. Low molecular weight copolymers were separated and FTIR spectroscopy, mass spectroscopy, and ^{13}C-NMR spectroscopy techniques were used to measure the oligomer composition, molecular weight, and copolymer sequence distribution, respectively.

The molecular size measurements should relate to the size of oligomeric radicals that grow in the water phase and enter polymer particles and the measurements should also relate to any water-soluble polymer that is formed by termination in the aqueous phase. The molecules, found for copolymers formed from 90/10 weight ratios of styrene and acrylic acid, were comprised of 6–9 monomer units with 2–3 being styrene. Those formed from 60/40 styrene/AA ratios contained 13–16 monomer units with 1–2 styrene. Differences were observed between seeded and unseeded systems, especially in the amount and nature of the water-soluble material formed early in the reaction. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Carboxylic acid monomers, such as acrylic acid (AA) and methacrylic acid (MAA), are widely used in emulsion polymerization to impart desirable properties to the latex and latex films.[1-4] The carboxylated latexes can have higher mechanical and freeze-thaw stability, improved adhesion to polar substrates, enhanced film tensile strength, higher tolerance to the addition of mineral fillers, and increased aging resistance.

The industrial importance of carboxylated latexes, and the unusual reaction phenomena associated with highly water-soluble comonomers, makes a study of the mechanisms and kinetics of emulsion copolymerization involving acid monomers of practical as well as of scientific interest. Emulsion copolymerization studies have been reported by a number of workers, including reports by van Do-

remaele et al.[5] in the Netherlands, Kokeler et al.[6] at Lehigh University, and Shoaf[7] and Lange[8] in this laboratory. These studies have focused on the overall kinetic scheme, in order to predict reaction rates, copolymer compositions, particle concentrations, and sizes. The conversion of monomer to polymer in these systems takes place primarily in the monomer swollen polymer particles. Reaction in the water phase, however, can exert a significant influence on the overall course of the reaction and on important properties of the latex produced.

The present work involves studies of styrene-acrylic acid emulsion copolymerization in seeded and unseeded systems. Experimental work has included measurements of monomer unit sequence distributions and the characteristics of the low molecular weight species reacting or formed in the aqueous phase. Measurements of copolymer composition, molecular weights, and triad sequence distributions are used to estimate the critical size and structural nature of the water-borne oligomeric radicals that enter latex particles in these emulsion copolymerization reactions.

Table I   Recipe and Reaction Conditions for Preparation of Styrene–Divinylbenzene Seeds[a]

Recipe:	
Styrene	98.28 g
55% Divinylbenzene[b]	1.82 g
Sodium Dodecyl Sulfate (SDS)	3.00 g
Potassium Persulfate	1.00 g
Deionized Water	200 g
Reaction Conditions:	
55°C for 3 h, 70°C for 3 h, 80°C for 3 h	

[a] 25 g of mixed bed ion exchange resin was added to 100 g seed latex to remove the emulsifier before the seeds were used.

[b] Other components are ethyl styrene and diethylbenzene.

EXPERIMENTAL

Materials

Styrene and acrylic acid (Aldrich) were used after distillation under reduced pressure. Divinylbenzene (Aldrich) was washed with sodium hydroxide solution. Sodium dodecyl sulfate (BDH England), potassium persulfate, potassium chloride, hydroquinone, hydrochloric acid, and dioxane (all from Fisher) were used as received. The water was deionized.

Emulsion Copolymerization

Monodispersed styrene-divinylbenzene (S-DVB) seeds were synthesized in a two liter, four-necked, round bottomed flask, equipped with a glass stirrer, thermometer, nitrogen inlet tube, and condenser. The recipe and reaction conditions are shown in Table I. The reaction conversion reached 99%. The diameters and polydispersity of the seeds, as measured by light scattering (Malvern Autosizer II c, England), were 75–79 nm and 1.08, respectively.

Emulsion copolymerization of styrene with acrylic acid was carried out in the same reactor. The recipes for unseeded and seeded emulsion copolymerization reactions are shown in Table II. The monomer was preemulsified for the unseeded emulsion copolymerization by adding 100 g of monomer mixture to the soap solution in the stirred reactor. This mixture was heated to 50°C and, subsequently, the initiator solution (1 g $K_2S_2O_8$ in 40 mL 0.1 mol/L HCl/KCl buffer solution) was injected into the reactor. Reaction samples were removed at different times, were mixed into a hydroquinone solution (0.1 g hydroquinone in 2 mL water), and then were chilled with dry ice. The monomer mixture in the seeded reaction was added to the agitated reactor over a period of about 1 h and was agitated for ad-

ditional 2 h. The initiator (1 g $K_2S_2O_8$ in 40 mL buffer solution) was then added to the reactor over a period of 30 min. The remaining part of the reaction cycle was the same as for the unseeded emulsion copolymerization reactions.

Separation of Water Soluble Oligomer

The latex samples were dried in a oven at 50–55°C. The dried samples were dissolved in dioxane [sample/dioxane = 1/10 (g/mL)]. The dioxane solution was dispersed in water [solution/water = 1/15 (mL/mL)] to obtain a copolymer precipitate and a water solution, which contained water soluble copolymer, emulsifier, and salt. The water phase was separated from the copolymer and was evaporated in a rotary evaporator under reduced pressure to obtain a dry sample.

Measurement of Oligomer Composition and its Molecular Weight

The composition of the oligomer was analyzed by FTIR. The samples, obtained as described above, were dissolved in reagent alcohol. Most of the salt and some emulsifier were removed as a precipitate. The alcohol solution was deposited on a KBr IR crystal window and was dried at 40–45°C. IR spectroscopy was recorded on a Nicolet 520 FTIR Spectrometer. The oligomer composition was calculated by the absorption of carbonyl and phenyl groups at 1731 and 701 cm^{-1}.

The molecular weight of oligomer was measured with a VG 70-SE Mass Spectrometer. The spectro-

Table II   Recipes for Unseeded and Seeded Emulsion Copolymerization of Styrene and Acrylic Acid at 50°C

Unseeded Copolymerization, SA-10 and SA-40:	
Styrene + Acrylic Acid	100 g
Acrylic Acid in Monomers (wt %)	10, 40
SDS	2.5 g
$K_2S_2O_8$	1.0 g
Deionized Water[a]	300 g
Seeded Copolymerization, SAS-10 and SAS-40:	
Solid Polymer of Styrene–Divinylbenzene Seed	50 g
Styrene + Acrylic Acid	50 g
Acrylic Acid in Monomers (wt %)	10, 40
SDS	0.3 g
$K_2S_2O_8$	1 g
Deionized Water[a]	300 g

[a] The water contains KCl (0.1 mol/L) and HCl (0.2 mol/L).

scopic recording conditions were: energy, 8 KV; mass range, 330–2000; resolution, 1000; ion model, positive; data system, 11–250 J; matrix, m NBA; EB geometry.

Sequence Distribution of Copolymers

The copolymer sequence distribution was measured by ^{13}C–NMR. The copolymer spectra of ^{13}C–NMR were obtained with a Varian XL-400 spectrometer, operating at 100 MHz. The measurement conditions were: sample concentration 0.1 (g/mL), spectral width 20,000 Hz, acquisition time 0.4 s, flip angle 45°, pulse delay 1.6 s, and number of scans 512. DMSO was used as locking agent for all NMR spectra. The sequence distribution at the triad level was characterized by the sensitive resonances of the carboxylic and the C1 carbons of phenyl in the copolymer (Fig. 1). The split peaks of the carboxylic carbon were assigned as AAA, AAS, and SAS and those of the C1 carbon of phenyl were assigned as SSS, SSA, and ASA, respectively. The integration under the area of every split peak represents the fraction of the corresponding triad.

RESULTS AND DISCUSSION

Composition Analysis of Oligomers

The composition of styrene–acrylic acid copolymer can be determined by ^{1}H or ^{13}C–NMR, in which the area of a resolution peak is used to measure the quantity of one kind or proton or carbon. The amount of acrylic acid and styrene in water-soluble oligomers cannot be calculated from the ^{1}H–NMR spectra, because the proton in the carboxylic group cannot be detected. Although the carbon in carboxylic and phenyl groups can be measured by ^{13}C–NMR, the presence of impurities, consisting mainly of quinone and emulsifier, strongly influences the accuracy. Hence, FTIR was used for composition analysis.

Figure 2 shows an FTIR spectra of oligomer, obtained from the SA-40 latex. There is a strong absorption peak at 1731 cm^{-1}, which is a result of the asymmetrical and symmetrical C $=$ O stretching vibrations of the carboxylic group and a middle absorption peak at 701 cm^{-1}, which is attributed to out-of-plane ring bending of phenyl. Another strong absorption, at 1199 cm^{-1}, can be attributed to absorption of three groups: carboxyl, sulfate, and quinone. Comparison of this spectra with the spectra of small organic molecules shows that the bands at 1512, 1449, 830, and 760 cm^{-1} are due to hydroquinone.
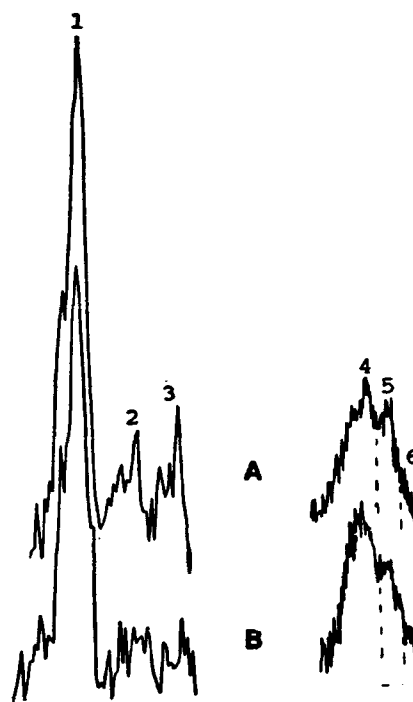
Figure 1 ^{13}C–NMR spectra of carboxyl carbon (1, 2, 3) and C1 carbon of phenyl (4, 5, 6) in SA-40 copolymer. Sequence and chemical shift (ppm): (1) SAS, 176.1; (2) AAS, 175.6; (3) AAA, 175.3; (4) SSS, 144.2; (5) SSA, 143.6; (6) ASA, 143.2. SA-40 copolymers at different conversion: (A) 26.32%, (B) 91.95%.

If one assumes that: (1) the same type of groups in molecules, having similar molecular structures, have the same absorption behavior and (2) the same kind of molecules in different states also have the same absorption, the small organic molecules can be used as standard compounds to quantify the amount of carboxyl and phenyl groups in the oligomer. Hence, the composition can be calculated. Ethylbenzene and propanoic acid were used as the standard compounds for this purpose. The two compounds, in different ratios, were used for FTIR measurements. The mole ratio of carboxyl to phenyl groups was plotted vs. the absorbance ratios at 1731 cm^{-1} and 701 cm^{-1}, and at 1199 cm^{-1} and 701 cm^{-1}, as shown in Figure 3. Figure 3(B) shows a linear relationship between the functional group ratio and the absorbance ratio at 1199 cm^{-1} to that at 701 cm^{-1}, that is, agreement with the Beer–Lambert's law (A = ELC, where A is absorbance, E is an extinction coefficient, L is the length of sample pool, and C is sample concentration). Figure 3(A) shows that a linear relationship exists when A_{1731}/A_{701} is between 2 and 8.
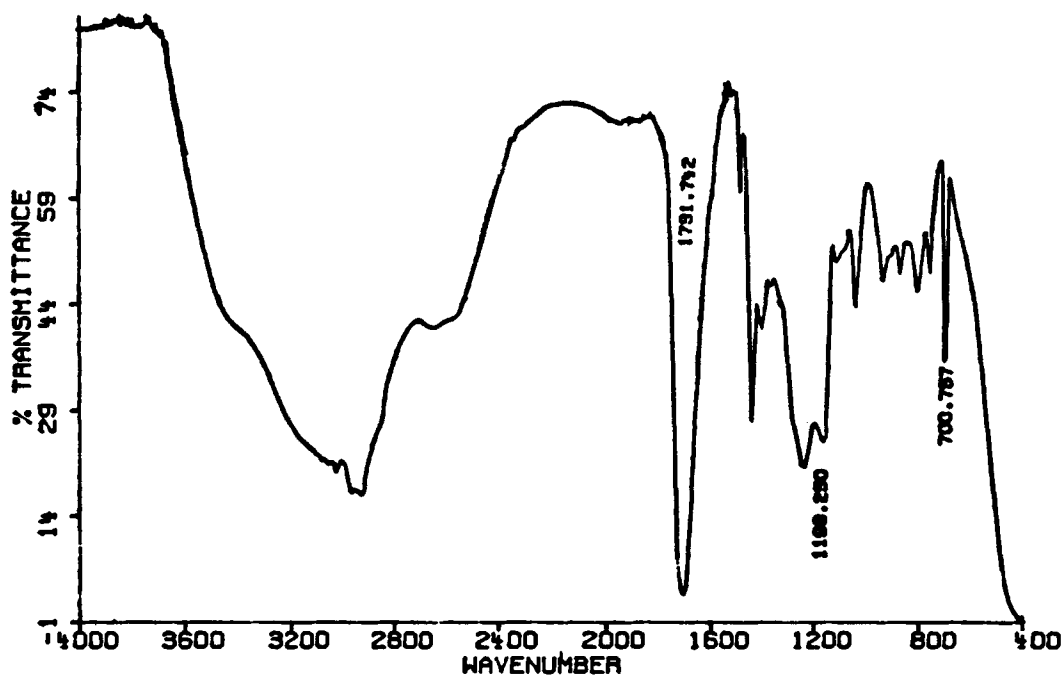
Figure 2 FT–IR spectra of oligomer in sample of SA-40.

The presence of sulfate groups and hydroquinone in the copolymerization system influences the correlation shown in Figure 3(B). Hence, for this experimental system, only Figure 3(A) can be used in the quantitative analysis of the monomer composition of oligomer. The ratio of acrylic acid to styrene was calculated according to following formula, derived from the data shown in Figure 3(A).

$$M_{AA}/M_S = 1.7532\ A_{1731}/A_{701} - 2.5356, \quad (1)$$

when A_{1731}/A_{701} is 2 to 8, and

$$M_{AA}/M_S = -0.03609(A_{1731}/A_{70})^3$$
$$+ 0.60191(A_{1731}/A_{701})^2$$
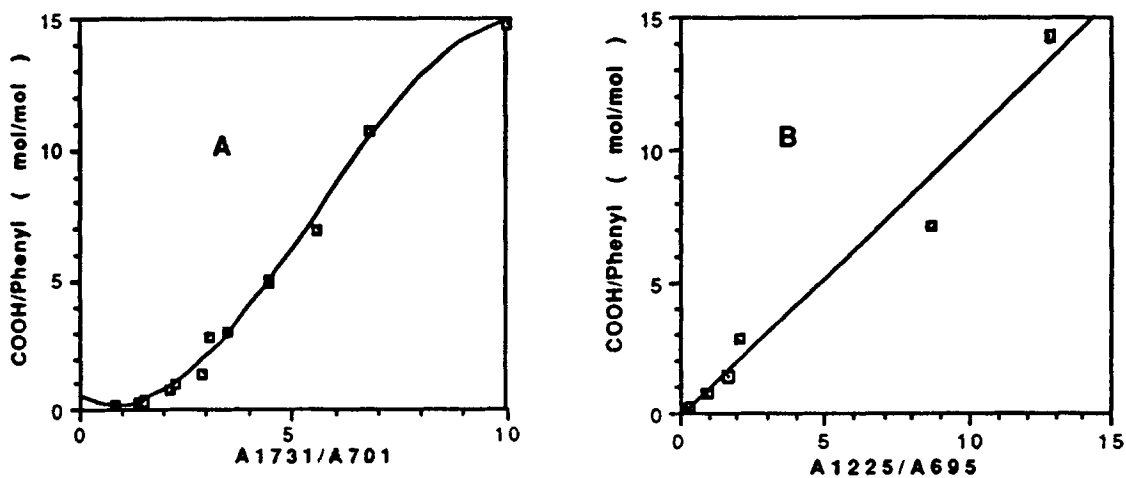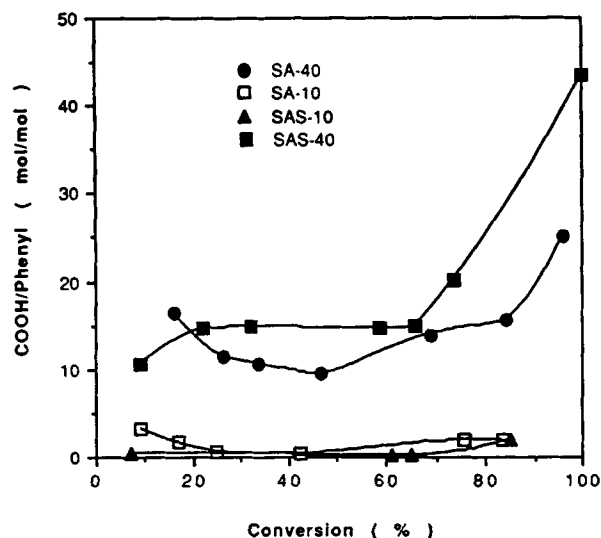$$- 0.98034A_{1731}/A_{701} + 0.57177, \quad (2)$$

Figure 3 Relationship between the ratio of carboxyl to phenyl groups (mol/mol) and the ratio of their absorbance at different wave numbers.

Figure 4 Oligomer composition in four polymerization reactions at different conversion levels.

when A_{1731}/A_{701} is less than 2, and where M_{AA} and M_S are molar amounts of acrylic acid and styrene in the oligomers, respectively.

The compositions of oligomers in the four polymerization systems were measured at different conversions. The results are shown in Figure 4. The content of acrylic acid in the oligomer increases significantly when the amount of acrylic acid in the monomer feed increases. Larger variations in composition of the oligomer take place at low conversion (< 20%) and at high conversion (> 80%). The composition of the oligomer is nearly constant from 20 to 70% conversion. The water-soluble free radicals, formed at low conversions, contain more acrylic acid in the unseeded reaction. Some water-soluble homopolymers of acrylic acid or copolymers, having low styrene content, are produced at high conversion. The amount of these water-soluble polymers increases as the acrylic acid content in the feed increases. The ratio of acrylic acid to styrene in oligomer or polymer increases with conversion in the seeded reactions. The results of these seeded and unseeded experiments confirm the common belief that when acrylic acid is used, latex stability can be derived from both reactions. First, short hydrophilic chains are produced in the water phase and then are chemically anchored to a hydrophobic polymer. Then, the hydrophilic polymer that is formed and adsorbed on the particle surfaces remains in the water phase.

The content of water soluble oligomer or polymer in the latexes was measured and is shown in Figure

5. As described in the experimental section, all of the oligomer, emulsifier, and salts remained in water when the oligomer–copolymer–dioxane solution was dispersed in water. The amount of oligomer and emulsifier, adsorbed on the precipitated polymer, can be neglected, because an excess of water was used for the precipitation and the polymer was washed three times by water. Hence, the content of oligomer was calculated by subtracting the amount of salts and emulsifier from the solids content of the water solution. Figure 5 shows that more water-soluble oligomers are produced in the reactions with the higher acrylic acid content and the amount of water-soluble oligomer (or polymer in the final reaction) increases with conversion. Oligomer content in the unseeded emulsion polymerization reactions was higher than that in the seeded reactions. These results can be explained by the facts that the seed particles adsorb water-borne free radicals and that the amount of monomer, used in the seeded emulsion system, is relatively lower than that in the unseeded emulsion system (Table II). These results also confirm the presence of water-soluble homopolymer in the final latex.

Molecular Weight of Oligomer

Reactions and transport phenomena, in the water phase of emulsion polymerization, can include thermal dissociation of initiator, initiation, growth of oligomer radicals, entry and exit of free radicals from polymer particles, and termination between two
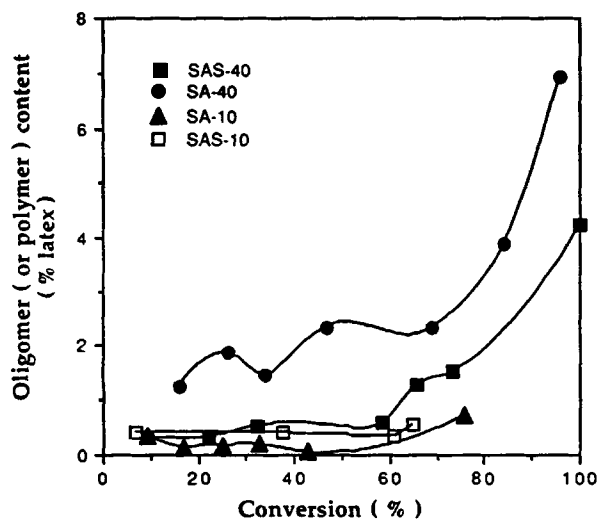
Figure 5 Content of water soluble oligomer or polymer in latex at different conversions.
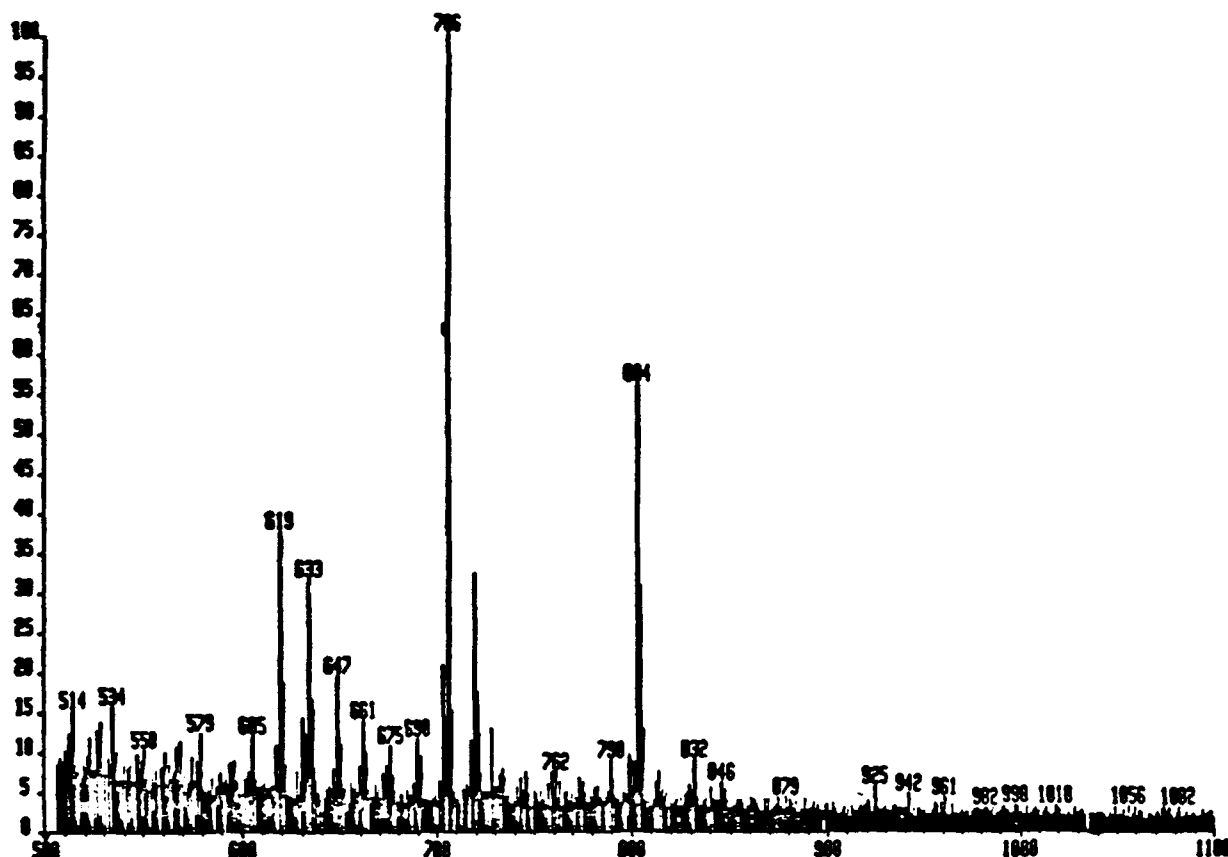
Figure 6   Mass spectra of oligomer in SA-10 system at low conversion.

similar or different radicals. The major reaction is initiation. Termination in the water phase can normally be neglected at low conversion.[9] When the reaction is stopped by hydroquinone, the oligomer remaining in the water phase will be derived mainly from the propagating free radicals. If no hydrolysis of the sulfate end groups occurs in the water phase, all oligomer obtained should have one sulfate and one quinone end group. With the development of new ionization methods, the most accurate technique for measuring the oligomer molecular weight is mass spectroscopy, which was used in this work. The largest M^+/e number was seen as the molecular weight, including the contributions of the two end groups.

A typical mass spectra is shown in Figure 6. A molecular weight peak is shown at 804, with the largest peak at 706, which is attributed to a molecule of weight 804 losing a sulfate end group. The peak at 661 could be derived from the cleaving of a 706 ion, resulting in the loss of a carboxylic group. The 633 and 619 peaks could be attributed to the ion at

706 losing a propanoic acid and an isobutyl acid, respectively. These are illustrated as follows:
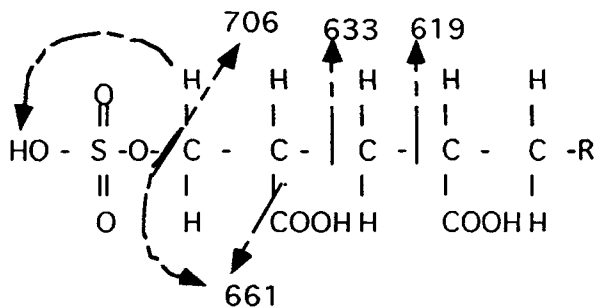
Proton transfer reactions could account for the 633, 619 M^+/e ion peaks. The peaks in Figure 6 do not seem to show molecules that contain two sulfate groups [no higher peak at 608 (706–98)]. Hence, termination is presumed not to be the main reaction in water phase. Some peaks in Figure 6 are a result of the cleavage of the largest oligomer ion, and some
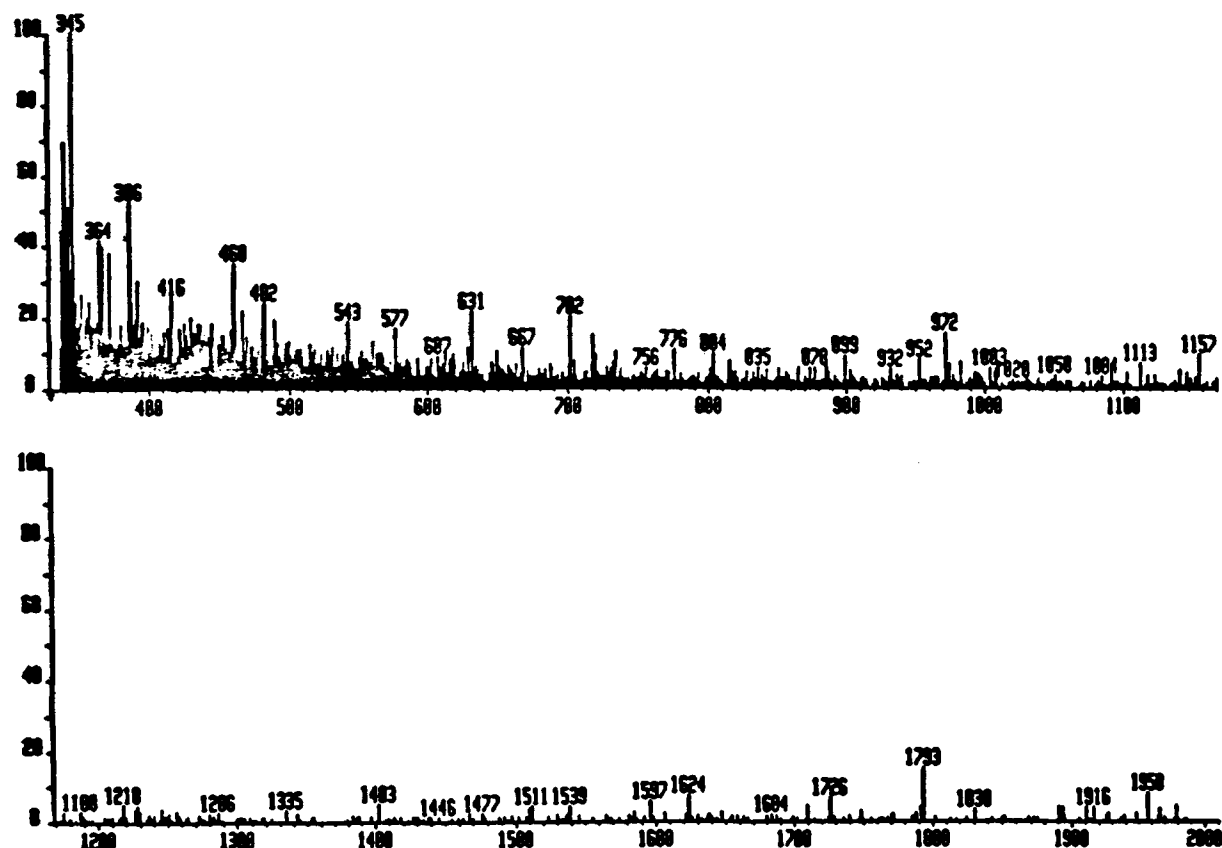
Figure 7 Mass spectra of oligomer with noise peak.

may be attributed by oligomers that have a different degree of polymerization. A few mass spectra peaks may result from noise. The peaks at 1113, 1157, 1403, 1624, 1726, and 1793 in Figure 7, for example, are not ion peaks because no isotopic peaks exist near them. The largest possible ion peak, that is, a molecular peak, was 972. The molecular weights, measured by mass spectroscopy, are listed Table III. The real radical weight due to propagation can be obtained by deducting the masses of the end groups. The data in Table III show that the oligomer weight is higher when the concentration of acrylic acid in the monomer mixture is high. The molecular weights in unseeded reactions are slightly lower than those in seeded reactions.

Higher concentrations of acrylic acid in the monomer mixture also lead to more acrylic acid units in the free radicals produced in the water phase (see Table IV), which raises the water solubility of these free radicals and extends their residence time in the water and permits them to grow larger. The reason that different polymerization methods (seeded and unseeded) produce different oligomer weights may

be because there are different surface characteristics of the polymer particles. The surface of the S-DVB particles can adsorb more emulsifier, but the surface of polymer particles, formed in the unseeded emulsion polymerization reactions, probably contains more carboxylic groups. The similar structure of the

Table III   Largest MS Ion Peaks of Selected Samples at Different Conversion

Sample Code	Conversion (%)	Largest M^+/e
SA-10	9.19	804
	16.99	716
SA-40	16.33	1251
	26.32	1205
SAS-10	7.00	992
	21.16	972
SAS-40	9.11	1318
	22.00	1380

Table IV   Critical Free Radical Size for Entry and Their Composition

Sample Code	Conversion (%)	M_w [a]	AA/S (mol/mol)	N_{AA}	N_S	Z
			Composition			
SA-10	9.19	599	3.26	6 (5.8)[b]	2 (1.8)[b]	8
	16.99	511	1.69	4 (3.8)	2 (2.3)	6
SA-40	16.33	1046	14.89	13 (13.2)	1 (0.9)	14
	26.32	1000	9.91	12 (12.1)	1 (1.2)	13
SAS-10	7.00	787	1.99	6 (6.3)	3 (3.2)	9
	21.16	767	1.93	6 (6.1)	3 (3.2)	9
SAS-40	9.11	1113	10.64	14 (13.6)	1 (1.3)	15
	22.00	1175	14.67	15 (14.8)	1 (1.0)	16

[a] $M_w = M^+/e - 205$, where M^+/e is the ion weight divided by its charge number in MS and 205 is added group weight of the sulfate and oxided hydroquinone in oligomer.

[b] The numbers bracketed are those calculated before conversion to an integer.

polymer surface and the free radicals in unseeded emulsion polymerization may allow easier free radical entry into the polymer particles. The surface charge differences between the particles could also play an important role in determining the free radical size for particle entry.

Table III also shows that in the same reaction, the oligomer size changes only slightly with conversion. This is a result of the different hydrophilic/hydrophobic properties of acrylic acid and styrene monomers. Most of the styrene exists in the polymer particles or monomer droplets, but most of the acrylic acid is present in the water phase. The monomer compositions in these phases change relatively slowly with conversion.

Composition and Sequence Distribution of Copolymer

The functional groups in a carboxylated latex may be present in three locations: (1) in the water phase as water-soluble polymer, (2) at the surface of the polymer particles as surface-active polymers, and (3) buried in the interior of the polymer particles as combined acid.[1] The presence of carboxyl groups in locations (1) and (2) has been confirmed by analysis of the composition of oligomers and the amount of oligomer in the latex. Measurements of the copolymer composition and sequence distributions will not only help to reveal the location of functional groups, but also help to establish the quantity of the functional groups in the different

locations. Figure 8 shows the overall composition of the corresponding copolymers. Their sequence distributions are shown on Figure 9. The data are for the unseeded reactions.

Figure 8 indicates that the copolymer compositions follow the same trend as the water-soluble oligomers. The acrylic acid content in the copolymers decreases slightly as the reaction proceeds when the conversion is low, changes slightly during the 20–70% conversion interval, and then increases as the conversion approaches 80%. Unfortunately,
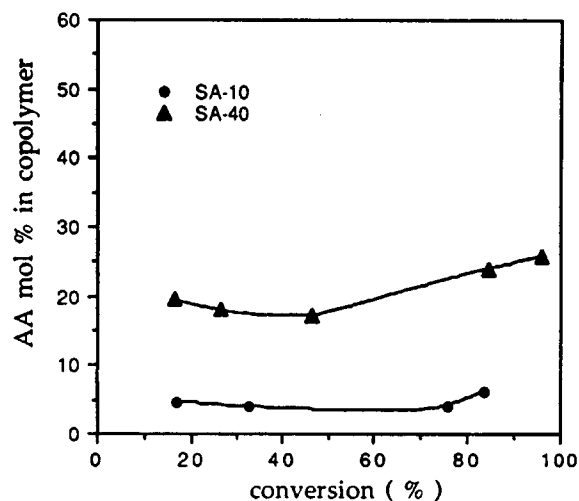
Figure 8   Composition of copolymers at different conversion. Initial AA mol % in monomer mixture: (SA-10) 13.83, (SA-40) 49.07.
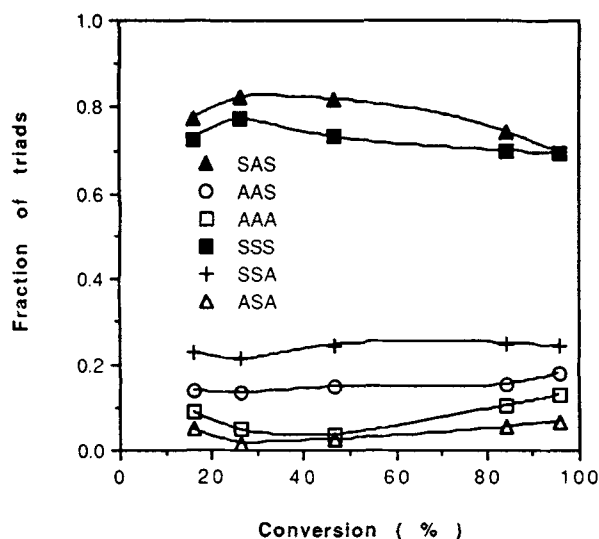
Figure 9 Triads sequence distribution of monomer in SA-40 at different conversions.

the composition of the copolymers from the seeded emulsion polymerization reactions could not be measured, because the copolymers were not easily separated from the seed polymers, even though low-crosslinked seeds were used.

The results in Figures 4 and 8 show higher AA content in the oligomers and copolymers at low conversion for unseeded emulsion polymerization. These results help to elucidate the nucleation mechanism for styrene–acrylic acid copolymerization. Nucleation takes place in the water-phase and more water soluble oligomers are formed at the beginning of the reaction to become the precursors, which further combine to nucleate the polymer particles. Hence, these reactions contain oligomers formed early with higher acrylic acid concentrations. The change of oligomer composition with conversion for seeded emulsion copolymerization (Fig. 4) also confirms this nucleation mechanism. No nucleation occurs in the seeded polymerization reactions, so the content of acrylic acid in the oligomer is high at low conversions, because little AA is partitioned into the seed particles.

Figure 9 shows that the fractions of AAA and ASA triads decrease with conversion at the beginning, change slightly as conversion increases from 20 to 70%, and then increase as conversion rises above 80%. The fractions of SSS and SAS triads show the opposite trend. The fraction of AAS and SSA triads hardly change with conversion. These results are in agreement with the data shown in Figures 4 and 8.

The fraction of acrylic acid, at different locations in the polymer particles, can be calculated with eqs. (3), (4), and (5), if the following three assumptions are made.

1. The triads AAA and AAS are derived from the water phase polymerization and SAS from polymerization in the polymer particle phase, according to the phase distribution of the two monomers.
2. The triads AAA and AAS, formed in the middle conversion range, are derived from an emulsifier "block copolymer," consisting of one primarily acrylic acid block formed in the water phase and located on the surface of the polymer particle and one styrene block formed in polymer particles and located in the interior of the polymer particles.
3. The AAA triads, at high conversion, come from this block copolymer and "homopolymer," adsorbed on polymer particles.

$$F_{h-s} = 3(F_{f-\text{AAA}} - F_{m-\text{AAA}})/$$
$$(3F_{f-\text{AAA}} + 2F_{f-\text{AAS}} + F_{f-\text{SAS}}) \quad (3)$$

$$F_{b-s} = (3F_{m-\text{AAA}} + 2F_{m-\text{ASS}})/$$
$$(3F_{m-\text{AAA}} + 2F_{m-\text{AAS}} + F_{m-\text{SAS}}) \quad (4)$$

$$F_e = F_{s-\text{SAS}}/(3F_{f-\text{AAA}} + 2F_{f-\text{AAS}} + F_{f-\text{SAS}}) \quad (5)$$

where F_{h-s}, F_{b-s}, and F_e are the acrylic acid fractions in homopolymer adsorbed on surface, in block copolymer, and entrapped in the polymer particles, respectively. $F_{f-\text{AAA}}$, $F_{f-\text{AAS}}$, $F_{f-\text{SAS}}$, $F_{m-\text{AAA}}$, $F_{m-\text{AAS}}$, and $F_{m-\text{SAS}}$ represent the fractions of triads AAA, AAS, and SAS at the final and middle conversion levels. If the values of F_{h-s}, F_{b-s}, and F_e are normalized, the fractions of acrylic acid at different polymer particle locations can be estimated. The normalized F_{h-s}, F_{b-s}, and F_e for SA-40 latex were 0.193, 0.325, and 0.481, respectively. Thus, 51.8% (32.5 + 19.3) of the acrylic acid that exists in the polymer particles acts as a surface–active agent. The entire distribution of acrylic acid, however, should include consideration of the oligomers in water phase (Fig. 5).

Critical Free Radical Size for Entry

Maxwell et al.[9] developed a model to calculate the free radical size for particle entry in the emulsion,

homopolymerization system. No theory or methods were published for understanding the critical size for entry in emulsion copolymerization. Based on the results obtained above, and some reasonable assumptions, the critical free radical size of emulsion copolymerization for entry can be calculated. The assumptions are:

1. The compositions of all radicals are the same, even though they have different molecular weights (equal reactivity of all radicals).
2. The size of the largest radical in water phase is the critical size for entry.

The critical size of styrene–acrylic acid free radical for entry can be calculated with the following equations:

$$N_S = \text{int}[M_w/(72.06G + 104.15)] \qquad (6)$$

$$N_{AA} = \text{int}[N_S \times G] \qquad (7)$$

$$G = N_{AA}/N_S \qquad (8)$$

$$Z = N_{AA} + N_S \qquad (9)$$

where N_{AA} and N_S are the number of acrylic acid and styrene units in the radical, respectively. M_w represents the radical weight, Z is the critical size for entry, and int means integer value. G was obtained from FTIR and M_w was calculated from the largest oligomer weight (Fig. 4 and Table III). The composition and size of the critical radical for entry in the different emulsion copolymerization reactions were obtained and are listed in Table IV.

These radicals consist of 2–3 styrene units and 4–6 acrylic acid units for SA-10 and SAS-10 reactions at low conversion, and one styrene unit and 12–15 acrylic acid units for SA-40 and SAS-40 reactions at low conversion. Z values increase with the increase of acrylic acid concentration in monomer mixture. The Z values do not change much when the conversion is low. The polarity, reactivity, and ratios of the different monomers in the monomer mixture influence the Z value. Polymer particle properties, ionic strength, and emulsifier property may also affect the Z value.

When the inhibitor, hydroquinone, is used in the termination of reaction in the water phase, one could question weather the oligomers obtained are the same size as the critical size for entry; that is, is assumption 2 correct? If the free radicals are terminated at the polymer surface by proton extraction

Table V   Critical Free Radical Size for Entry and Their Composition in the System Containing Polymer-Supported Chain Transfer Agent

Sample Code[a]	M_w	Composition			
		AA/S (mol/mol)	N_{AA}	NS	Z
SAS-SH-5	592	3.37	6 (5.75)	2 (1.71)	8
SAS-SH-10	621	7.46	7 (7.22)	1 (0.97)	8
SAS-SH-20	747	13.21	9 (9.34)	1 (0.71)	10
SAS-SH-30	822	14.81	10 (10.39)	1 (0.70)	11

[a] SAS presents seeded styrene-acrylic acid emulsion copolymerization, SH shows the polymer-supported mercaptan, and the number is the weight percent of acrylic acid in monomer mixtures.

chain transfer, rather than in the water phase by the inhibitor, would the oligomers detected have real critical size for entry?

This question was examined by the use of a specially prepared inhibition seed. Mercaptan groups were anchored onto the polymer particle surface by the reaction of poly(vinylbenzyl chloride) particles with 2-aminoethanethiol, and the groups used in styrene–acrylic acid emulsion copolymerization as seeds. The water soluble oligomers in this system were isolated out by low pressure cell filtration (serum replacement) or extracted with water and analyzed as described above. The results are listed in Table V. The synthesis of the polymer-supported chain transfer agent and its properties will be reported elsewhere. Comparing Table 5 with Table 4, similar results were obtained by the two different methods. These results seem to confirm that assumption 2 is reasonable and the real free radical oligomers, which have the critical size for entry, were obtained in the original experiments. Further work is clearly needed to develop a more detailed knowledge of these water phase phenomena in emulsion copolymerization.

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