

# Studies of Water-Soluble Oligomers Formed in Emulsion Copolymerization

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## SYNOPSIS

A polymer chain transfer agent was synthesized by the reaction between poly(vinylbenzyl chloride) latex particles and 2-aminoethanethiol in a basic environment. In subsequent emulsion polymerization reactions, low molecular weight species were formed when water-born oligomeric radicals diffused to the surface of these seed particles. These low molecular weight oligomers were separated by membrane filtration and their composition and molecular weight were analyzed by FTIR and mass spectroscopy. The measured composition results were compared with those that were calculated from the copolymerization equation. The molecular weights were compared with earlier experimental results that were obtained by isolation of oligomers formed when a water-soluble inhibitor was added to a reacting emulsion.

Three seeded emulsion copolymerization systems, that is, styrene-acrylic acid, styrene-methacrylic acid, and styrene-methyl methacrylate, were investigated. The distribution of monomer in the water phase and in the copolymer particles was analyzed. The results show that the oligomer compositions for different copolymerization systems can be approximated reasonable well by the copolymerization equation, using the reactivity ratios obtained from bulk copolymerization. The length of the oligomer radicals formed depends on their composition and the properties of the polymer particles, such as surface charge, composition, size, and concentration. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Emulsion polymerization is an important commercial process for the production for coatings, adhesives, synthetic rubbers, and other products. Emulsion polymerization theory, from nucleation mechanisms to particle morphology, has advanced significantly.<sup>1-3</sup> The conversion of monomer to polymer is known to take place primarily in the monomer-swollen polymer particles for most systems. However, the oligomer radicals, formed in the water phase, can play an important role in particle nucleation, stabilization, morphology, and in the characteristics of copolymer products.<sup>4-7</sup> Most studies of water-phase oligomers have been concerned with single monomers. The size of oligomers, which

nucleate new primary particles or enter existing polymer particles, has been calculated or measured, but the results obtained from different laboratories are not in agreement.<sup>6,7</sup> Hence, additional study is necessary, especially for systems that contain two or more monomers.

In a previous article, the authors have studied the water-soluble oligomers formed in acrylic acid-styrene emulsion copolymerization systems.<sup>8</sup> The radicals, formed in the water phase, were terminated by adding water-soluble inhibitor in order to obtain the critical oligomer size for particle entry. There is some uncertainty, however, that the oligomers obtained by this method are those that have achieved the critical length for entry. In order to examine this question, a new latex, which contained mercaptan chain transfer functional groups, has been synthesized. When the surface-active radicals, formed in water phase, enter these polymer particles, the transfer reaction to the mercaptan on the surface

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**Table I Recipe and Reaction Conditions for the Synthesis of SVBC Seed**

Recipe:	
Styrene	133.4 g
Vinylbenzyl Chloride	122.0 g
Sodium 4-Vinyl-Benzenesulfonate	2.00 g
Potassium Persulfate	6.00 g
Water	2000 g
Reaction conditions:	
65°C for 12 h, 75°C for 7 h, 85°C for 4 h	

**Table II Synthesis of Polymer Chain Transfer Agent, S-VBC-SH**

Recipe:	
S-VBC Latex	2005 g
Ethyl Alcohol	501 mL
2-Aminoethanethiol Hydrochloride Acid	168.3 g
Sodium Dodecyl Sulfate	12 g
Sodium Hydroxide	to pH 10
Reaction Conditions and Conversion:	
80°C for 54 h, conversion 68.3%	

will take place and the real critical length for entry should be measurable. Two copolymerization systems, styrene-methacrylic acid and styrene-methyl methacrylate, were studied in addition to acrylic acid-styrene copolymerization. The monomer distributions in the water phase and in the polymer particles were determined. A method was developed

for characterization of the composition and size of the critical-length radical oligomers.

## EXPERIMENTAL

### Materials

Styrene, acrylic acid (AA), methacrylic acid (MAA), and methyl methacrylate (MAA) (all from Aldrich) were used after distillation under reduced pressure. Vinylbenzyl chloride (VBC) (Aldrich) was washed with sodium hydroxide before use. 4-Vinylbenzenesulfonic acid sodium salt (VASA) (Fluka Chemika, Switzerland), sodium dodecyl sulfate (BDH England), potassium persulfate, hydrochloric acid (both from Fisher), and 2-aminoethanethiol (Aldrich) were used as received. The water was deionized.

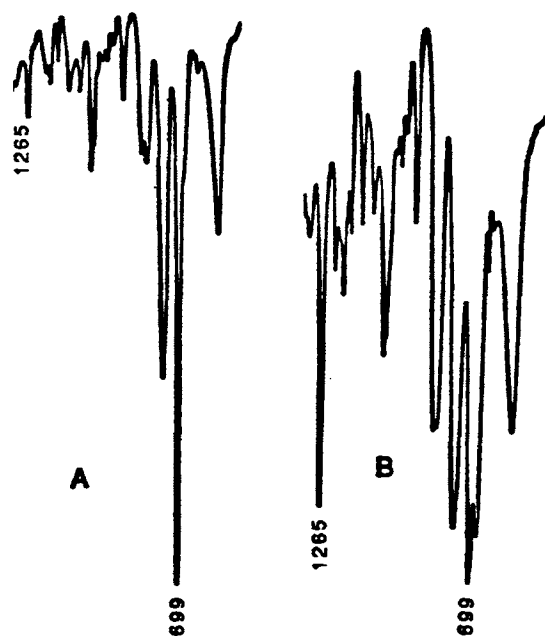
### Synthesis of SVBC Seeds and Polymer Chain Transfer Agent

Monodispersed styrene-vinylbenzyl chloride (SVBC) seeds were synthesized in a three liter, four-neck, round-bottomed flask, equipped with a glass stirrer, thermometer, nitrogen inlet tube, and condenser. The recipe and reaction conditions are presented in Table I. The reaction conversion was greater than 99%. The number-average seed diameter was 188 nm, with a polydispersity of 1.09 (measured by light scattering, Malvern Autosizer II c, England).

**Table III Results from SVBC Seed Synthesis**

	A	B	C	D	E
Recipe:					
Styrene (g)	6.25	6.25	6.25	6.25	6.25
VBC (g)	6.11	6.11	6.11	6.11	6.11
VSAS (g)	0.000	0.100	0.100	0.200	0.200
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g)	0.300	0.100	0.300	0.150	0.300
Water (g)	100.00	100.00	100.00	100.00	100.00
Reaction:					
Temperature (°C)	65	65	65	65	65
Reaction Time (h)	15	17	15	15	15
Results:					
Conversion (%)			89.7		> 78.3 <sup>a</sup>
Diameter (nm)	Heavy Coagulation	Heavy Coagulation		Light Coagulation	190
Polydispersity			1.06		1.09

<sup>a</sup> Some solids were deposited on the stirrer.

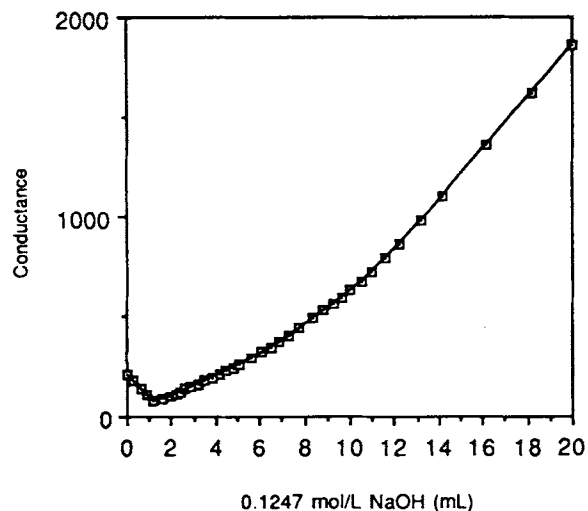


**Figure 1** IR spectra of SVBC-SH (A) and SVBC (B).

The polymer chain transfer agent was synthesized with this seed latex in the same reactor. The recipe and reaction conditions are provided in Table II. The residual 2-aminoethanethiol and emulsifier in the final latex was removed by serum replacement with water filter, containing an 80 nm pore diameter membrane.

#### Oligomer Synthesis and Separation

Emulsifier-free copolymerization reactions were carried out in a 250 mL reactor with the polymer mercaptan seeds. The reactions were stopped by cooling in dry ice. The latex samples were washed with water by serum replacement, as described above. The volume of wash water was five times that of the latex and the solution containing the water-



**Figure 2** Conductometric titration curve of SVBC-SH latex.

soluble oligomers was evaporated in a rotary evaporator under reduced pressure to obtain a dry sample for further analysis.

#### Measurement of Oligomer Composition and Its Molecular Weight

The composition of oligomer was analyzed by FTIR. The dry samples were dissolved in reagent alcohol and the solution containing oligomer 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  $\text{cm}^{-1}$  for the SAA and SMAA systems and at 1732 and 698  $\text{cm}^{-1}$  for the SMMA system.

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

**Table IV** Reaction Between SVBC Seeds and 2-Aminoethanethiol

Reaction Time (h)	Reaction Temperature (°C)	Ethyl Alcohol Added (mL/g Latex)	$A_{1265}/A_{699}$	Conversion (%)
0	65	0.00	0.4913	0.00
16	65	0.00	0.4245	13.60
40	65	0.00	0.3369	31.43
40	80	0.00	0.2311	47.05
43	80	0.25	0.1422	71.06

**Table V** Oligomer Synthesis in Styrene–Acrylic Acid and Styrene–Methacrylic Acid Emulsion Copolymerization

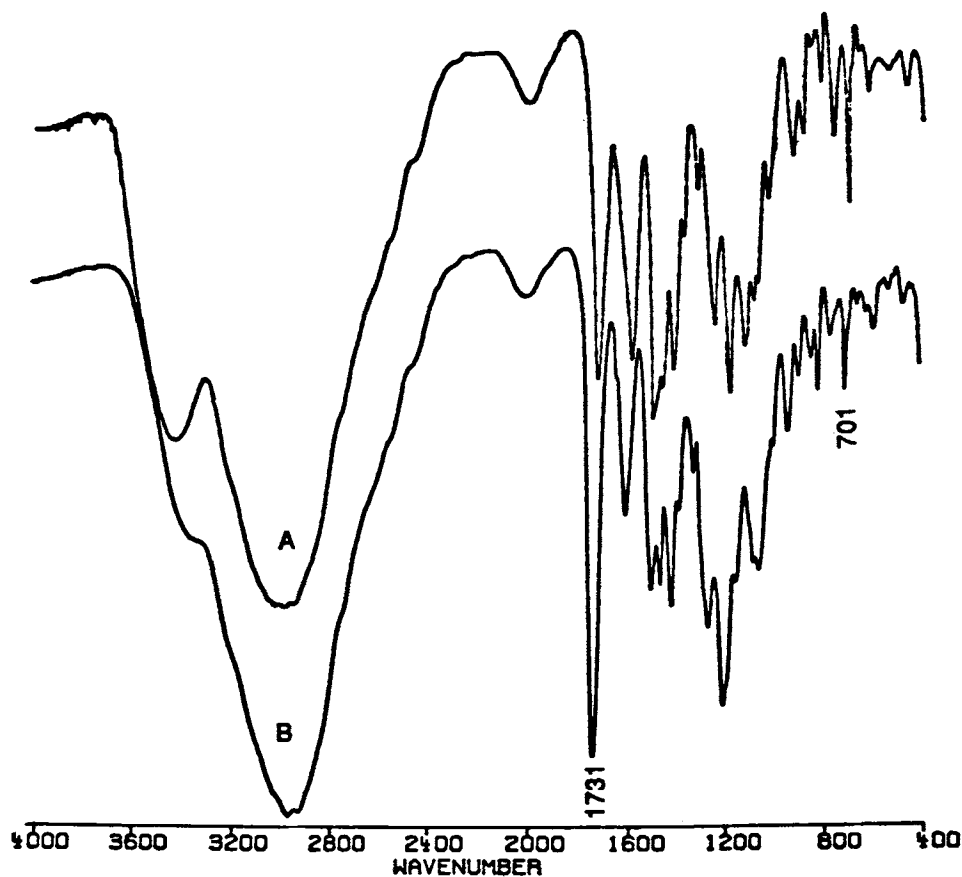
	SAA-5 or SMAA-5	SAA-10 or SMAA-10	SAA-20 or SMAA-20	SAA-30 or SMAA-30
SVBC-SH Solid (g)	10.00	10.00	10.00	10.00
Styrene (g)	10.00	10.00	10.00	10.00
Acrylic Acid or Methacrylic Acid (g)	0.525	1.110	2.500	4.300
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g)	0.150	0.150	0.150	0.150
Water (g)	21.12	21.12	21.12	21.12
35% Hydrochloride Acid (g)	1.00	1.00	1.00	1.00

spectroscopy recording conditions were: energy, 8 KV; mass range, 330–2000; resolution, 1000; ion model, positive; data system, 1–250 J; matrix, m NBA; EB geometry. The organic molecular weight of the oligomer was obtained from the largest peak by deducting the weight of the sulfate end group.

## RESULTS AND DISCUSSION

### Synthesis of SVBC Latex and Polymer Chain Transfer Agent

Two latex formulations are frequently used in subsequent chemical reactions. One is poly(vinylbenzyl



**Figure 3** IR spectra of SAA oligomers. (A) SAA-5, (B) SAA-30.

**Table VI Oligomer Composition and Size in SAA Copolymerization System**

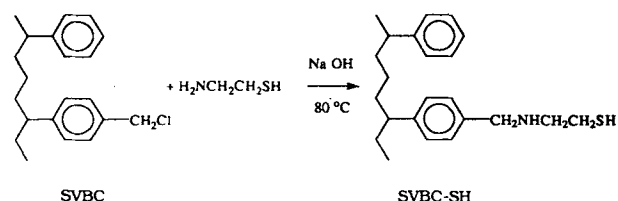
	SAA-5	SAA-10	SAA-20	SAA-30
Molecular Weight	592	621	747	822
Acrylic Acid Units/ Styrene Unit (mol/mol)	3.371	7.458	13.208	14.807
Acrylic Acid Units				
Measured	5.76	7.22	9.34	10.39
Rounded	6	7	9	10
Styrene Units				
Measured	1.71	0.97	0.71	0.70
Rounded	2	1	1	1
Oligomer Units	8	8	10	11

chloride), another is poly(glycidyl methacrylate) or their copolymers.<sup>9</sup> A latex, containing mercaptan groups, has been synthesized by a reaction of poly(glycidyl methacrylate) with sodium sulfite.<sup>9</sup> This reaction can coagulate because a significant amount of salt is needed<sup>10</sup>; a problem that has been confirmed in this laboratory. When hydrogen sulfite was used instead of sodium sulfite, the reaction was too slow.

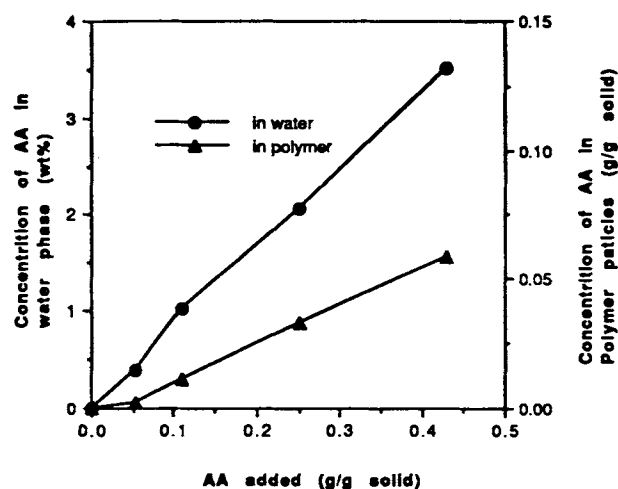
Poly(vinylbenzyl chloride) can be synthesized in a normal emulsion system.<sup>11</sup> Emulsifier-free seeds were preferred in this research in order to facilitate the characterization of oligomers obtained in different copolymerization systems. The synthesis re-

sults for the emulsifier-free SVBC seeds are presented in Table III. The amount of vinylbenzene sulfonic acid sodium salt (VSAS) has a significant effect on final latex stability. If the VSAS content is small, the latex is unstable, due to fewer sulfate groups on the surface of the polymer particles. If the VSAS content is high, the latex is also unstable, because VSAS contains salt. Table I shows a useful recipe and shows reaction conditions.

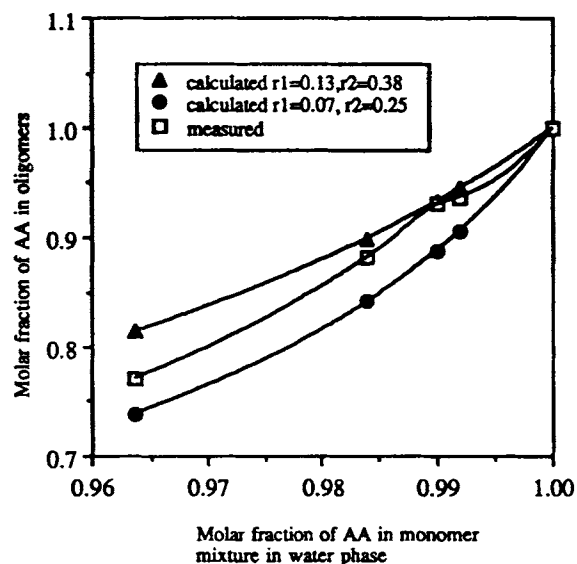
The reaction between SVBC seeds and 2-aminoethanethiol is illustrated as follows.



IR spectra of SVBC and SVBC-SH are shown in Figure 1. The chloromethyl groups in SVBC have strong absorbances at  $1265\text{ cm}^{-1}$ . The absorbance at  $1265\text{ cm}^{-1}$  decreased or disappeared after the reaction. The conversion can be calculated by the ratio of absorbance peaks at  $1265$  and  $699\text{ cm}^{-1}$ . Reaction conditions were investigated and some results are presented in Table IV. The amination reaction is not easy to complete because of the high water affinity of 2-aminoethanethiol. The addition of ethyl



**Figure 4** Distribution of AA in the water phase and the polymer particles. Styrene added: 1 g/g solid.



**Figure 5** Calculated and measured oligomer composition in SAA copolymerization system.

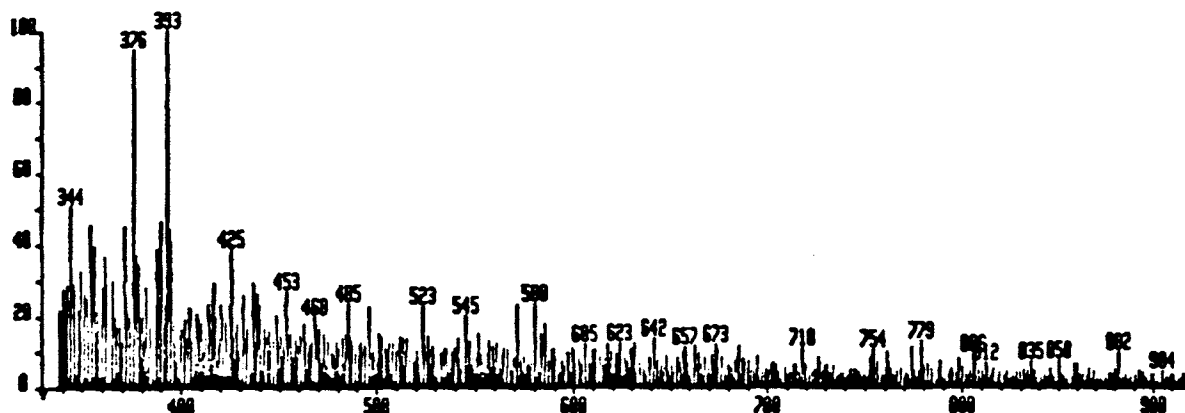


Figure 6 Mass spectra of SAA Oligomer.

alcohol causes swelling of the polymer particles and increases the distribution of 2-aminoethanethiol in the particles, so that the conversion can be increased. In the absence of ethanol, this reaction takes place primarily on the surface of the polymer particles; hence, complete conversion of buried chloromethyl to aminoethanethiol does not influence the concentration of mercaptan on the polymer particle surface.

The surface character of the SVBC-SH latex was

analyzed by conductometric titration. The SVBC-SH latex was treated with a strong cation exchange resin four times and then was titrated with 0.1247 mol/L NaOH. Figure 2 is the titration curve, in which two slope changes are shown. The first is due to the sulfate groups and the second is due to carbonate, produced by hydrolysis of sulfate and ammonium. The group concentrations, calculated from the titration curve, were sulfate 0.01347 mmol/g

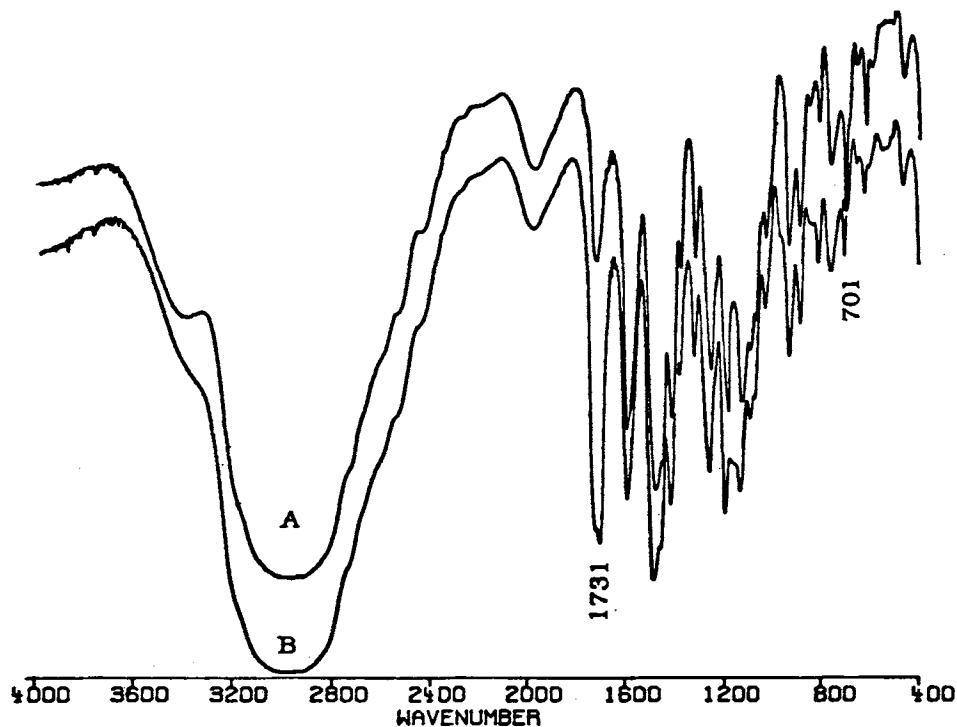


Figure 7 IR spectra of SMAA oligomers, (A) SMAA-10, (B) SMAA-30.

**Table VII Oligomer Composition and Size in SMAA Copolymerization System**

	SMAA-5	SMAA-10	SMAA-20	SMAA-30
Molecular Weight	477	479	491	562
Methacrylic Acid/Styrene (mol/mol)	0.923	1.385	6.506	18.220
Methacrylic Acid Units				
Measured	2.40	2.97	4.81	6.12
Rounded	2	3	5	6
Styrene Units				
Measured	2.60	2.14	0.74	0.34
Rounded	3	2	1	0
Oligomer Units	5	5	6	6

polymer and carbonate and ammonium 0.0839 mmol/g polymer particles. The titration result also confirms that the reaction postulated had taken place.

### Oligomers in the Styrene-Acrylic Acid Copolymerization System

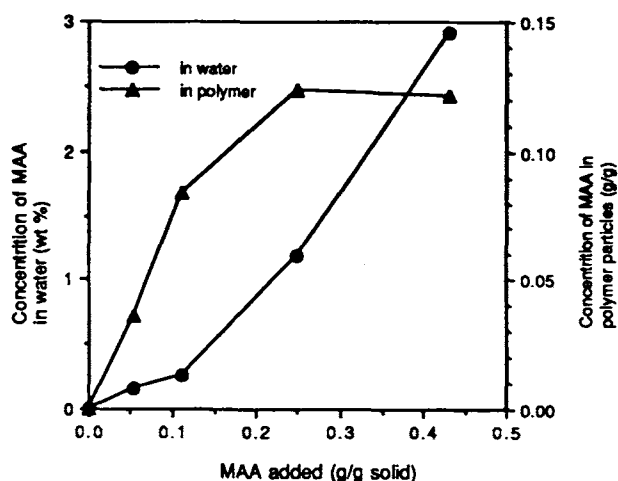
The recipe for the copolymerization of acrylic acid-styrene is presented in Table V. The oligomer composition was measured by FTIR and was calculated with the copolymerization equation. Figure 3 shows IR spectra of the SAA oligomers, in which the absorbance at 1731  $\text{cm}^{-1}$  is derived from the asymmetrical and symmetrical C=O stretching vibrations. The peak at 701  $\text{cm}^{-1}$  is attributed to the out-of-plane ring bending of phenyl. The compositions

of oligomers were calculated from their IR absorbance, using the following equation:

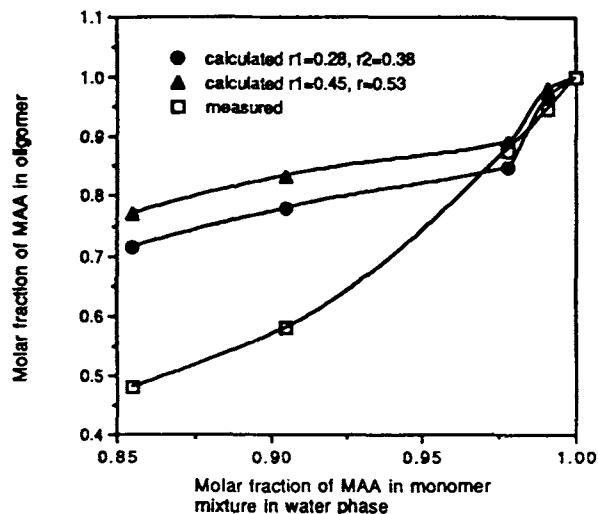
$$F_{AA}/F_S = -0.03609(A_{1731}/A_{701})^3 + 0.60191(A_{1731}/A_{701})^2 - 0.98034A_{1731}/A_{701} + 0.57177, \quad (1)$$

where  $F_{AA}$  and  $F_S$  are molar amounts of acrylic acid and styrene in the oligomers, respectively. This formula was obtained from IR spectra of the standard compounds ethylbenzene and propanoic acid.<sup>12</sup> Some results of the composition of the SAA oligomers are provided in Table VI.

The distribution of acrylic acid in the water phase and in the polymer particles was analyzed with a gas-liquid chromatograph (GLC conditions were:



**Figure 8** Distribution of MAA in the polymer particles and the water phase. Styrene added: 1 g/g solid.



**Figure 9** Calculated and measured oligomer compositions for the SMAA copolymerization system.



Figure 10 Mass spectra of SMAA oligomer.

injector temperature, 220°C; column temperature, 220°C; detector temperature 230°C), with dimethylsulfone as an internal standard (Fig. 4). The distribution coefficient (the ratio of the concentration in the polymer particles, g/g, to the concentration in the water, g/g), within the measured range, was approximately constant at 1.7408. A constant value is not always observed, especially when the AA concentration is high.

The concentration of styrene in the water phase is too low to be detected. Hence, the corresponding saturated concentration of styrene in water-AA solutions, determined with a liquid-liquid distribution curve for styrene in the S-AA-water system, was used. The compositions of SAA oligomers were calculated, based on the data in Figure 4, according to the copolymerization equation.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (2)$$

where  $F_1$ ,  $f_1$  are monomer mole fractions of acrylic acid in the oligomers and in the water phase,  $f_2$  is the mole fraction of styrene in the monomer mixture in the water phase, and  $r_1$ ,  $r_2$  are the reactivity ratios of styrene and acrylic acid. Styrene is always designated as monomer 1 in this article. The  $r_1$  and  $r_2$  literature values used were 0.13 and 0.38,<sup>12</sup> or 0.07 and 0.25.<sup>13</sup> The measured and calculated results for the SAA oligomer composition are shown in Figure 5, which confirms that the calculated results agree reasonably well with the experimental measurements. Hence, in this case, the reactivity ratios measured in bulk can be used to estimate the composition of oligomer obtained in the water phase of an emulsion copolymerization. The major problem

is accurate calculation or measurement of the distribution of monomers in the different phases.<sup>14,15</sup>

Molecular weights of the oligomers were measured by mass spectroscopy. Figure 6 shows one mass spectra for the SAA oligomers. The molecular weight of the oligomer was assigned to the largest  $M^+$ /e peak after deduction of the weight of a sulfonate end group. Some results are presented in Table VI. The radical size for particle entry and the content, in terms of the different monomer units, can be calculated with the following equations:

$$N_2 = \text{int} \{ M_{w-o} / (M_{w1}G + M_{w2}) \} \quad (3)$$

$$N_1 = \text{int} [ N_2 \times G ] \quad (4)$$

$$G = N_1 / N_2 \quad (5)$$

$$Z = N_1 + N_2 \quad (6)$$

where  $N_1$  and  $N_2$  are the number of the units of first and second monomers in the radical, respectively,  $M_{w-o}$ ,  $M_{w1}$ , and  $M_{w2}$  represent the radical molecular

**Table VIII Oligomer Synthesis in Styrene-Methyl Methacrylate Emulsion Copolymerization**

	SMMA-20	SMMA-40	SMMA-60	SMMA-80
S-VBC-SH				
Solid (g)	10.00	10.00	10.00	10.00
Styrene (g)	8.00	6.00	4.00	2.00
MMA (g)	2.00	4.00	6.00	8.00
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g)	0.150	0.150	0.150	0.150
Water (g)	148.00	148.00	148.00	148.00



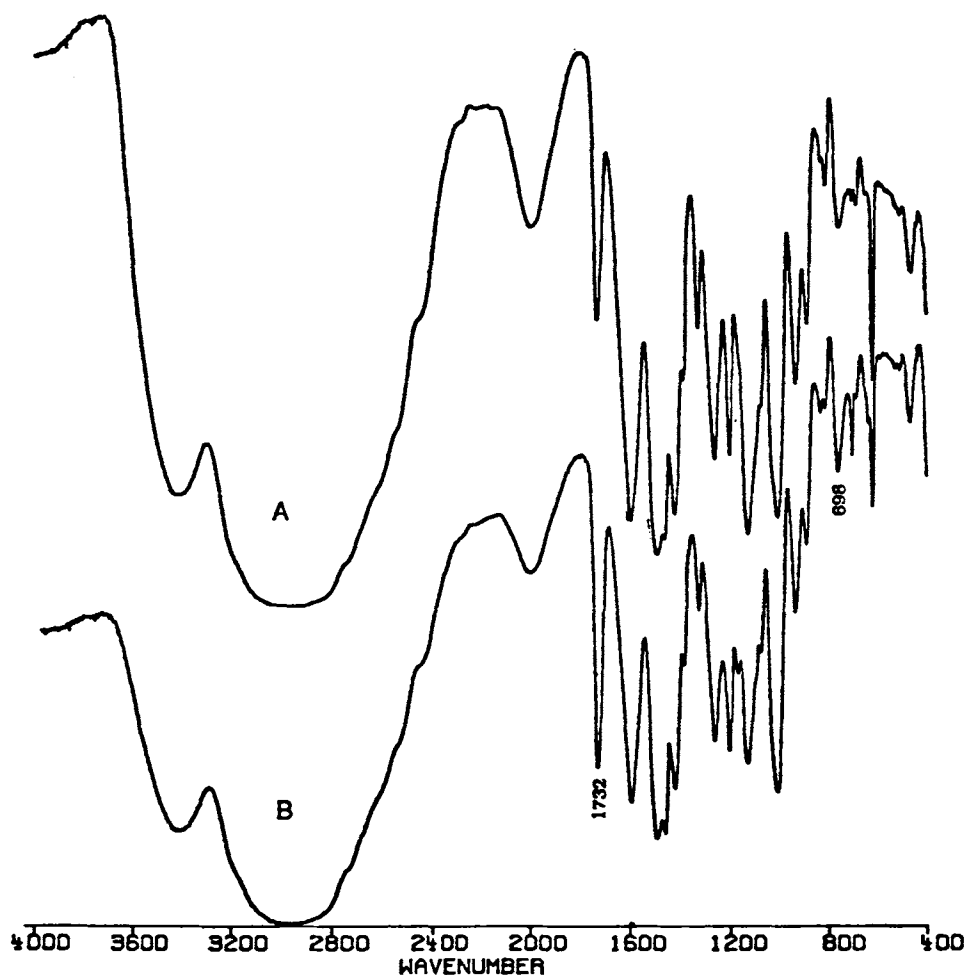


Figure 11 IR spectra of SMMA oligomers, (A) SMMA-20, (B) SMMA-60.

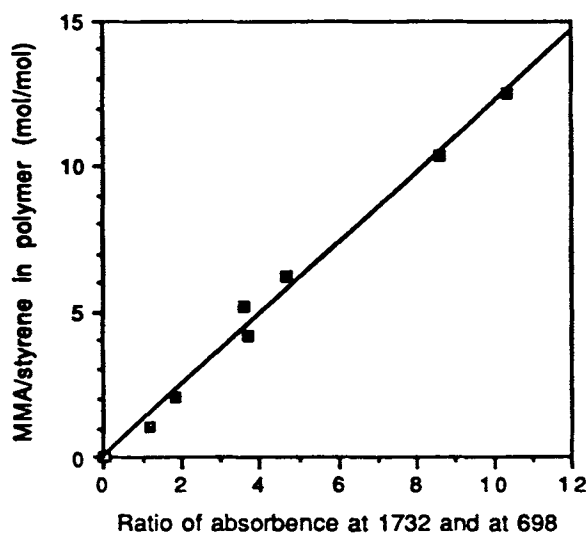


Figure 12 Absorbance-composition calibration for the SMMA system.

weights and the first and second monomer molecular weights,  $Z$  is the critical size for entry, and  $\text{int}$  means integrated value.  $G$ , which is the ratio of monomer 1 to monomer 2 in the oligomer, was obtained from FTIR spectra and  $M_{w-o}$  was calculated from the largest oligomer weight. The composition and size of the critical radical for entry in the different emulsion copolymerization reactions of SAA were obtained and are listed in Table VI. The SAA critical size oligomer radicals consisted of 1–2 styrene units and 6–10 AA units, with the total number of monomer units varying from 8 to 11.

Table VI shows that the size of the oligomer for entry increases with an increase of the molar fraction of acrylic acid in the monomer mixture. Higher concentrations of hydrophilic monomer in the feed increase the hydrophilic ratios of the oligomer radicals and this can delay the time for entry and permit the addition of more monomer units.

**Table IX Oligomer Composition and Size in SMMA Copolymerization System**

	SMMA-20	SMMA-40	SMMA-60	SMMA-80
Molecular Weight	274	290	374	413
MMA/Styrene (mol/mol)	3.274	4.385	5.712	10.651
MMA Unit				
Measured	2.08	2.34	3.16	3.76
Rounded	2	2	3	4
Styrene Unit				
Measured	0.63	0.53	0.55	0.35
Rounded	1	1	1	0
Oligomer Unit	3	3	4	4

### Oligomers in the Styrene–Methacrylic Acid Copolymerization System

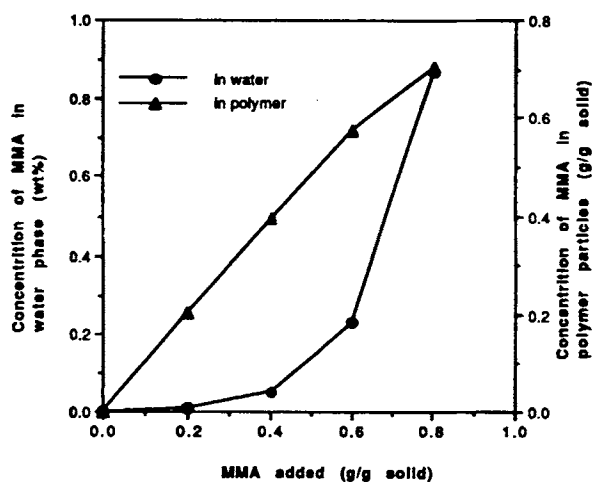
The recipes for the SMAA oligomer synthesis were same with those of corresponding SAA experiments and are shown in Table V. The IR spectra of the SMAA oligomers were also similar to those of SAA oligomers. Only the strength of various peaks changed (Fig. 7). Because MAA units in the oligomer have a structure that is similar to propanoic acid, the compositions of SMAA oligomers were calculated from their IR absorbance, using eq. (1), where  $F_{AA}$  was changed to  $F_{MAA}$ . The results are shown in Table VII. The ratios of MAA to styrene units in the SMAA oligomers were less than those in the AA reaction, when the acid monomer in the feed was lower. At higher concentrations of acid monomer, however, the results were reversed. These results are due to the differences in monomer distribution between the two phases and in the reactivity ratios.

The distribution of MAA in the two phases was determined and is shown in Figure 8. The concentration of MAA in the polymer greatly increases with the increased addition of MAA, and it eventually reaches a saturation concentration. The concentration of MAA in the water phase is lower than that of AA in the water phase. The ratio of MAA concentrations in the two phases was not a constant, so a distribution coefficient was not obtained.

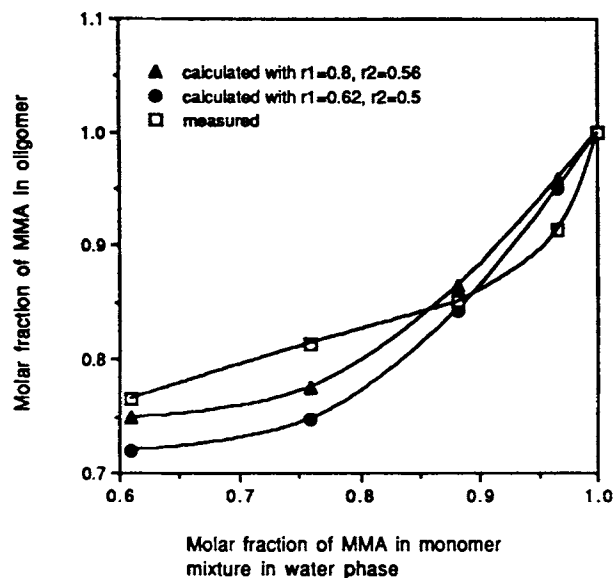
The compositions of SMAA oligomers were calculated with the concentration values of MAA in the water phase, the saturated concentration of styrene in water, 0.035%, and  $r_1 = 0.28$ ,  $r_2 = 0.38$ , as well as  $r_1 = 0.45$ ,  $r_2 = 0.53$ . The calculated and measured compositions of SMAA oligomers are shown in Figure 9. The calculated results were agreement with those measured when the concentration of MAA in the water phase was high. The calculated

and measured results at a lower MAA concentration did not agree. Several factors could be responsible for this lack of agreement: (1) the reactivity ratios are not suitable (temperature was not the same), (2) the MAA concentration measurements were inaccurate at low overall concentrations, and (3) the concentration of styrene in the water phase changes with the change of the concentration of MAA in the water phase.

Figure 10 is a mass spectra of the SMAA oligomer. The molecular weight of the SMAA oligomers are shown in Table VII. The critical size for particle entry was calculated according to eqs. (3)–(6), where monomer 1 was MAA, and monomer 2 was styrene. The results in Table VII show that the oligomers contain 2–6 MAA units and 3–0 styrene units, as the MAA concentration in the monomer mixture changes from 5 to 30%. The total number



**Figure 13** Distribution of MMA in the polymer particles and the water phase for SMMA system. Total amount of monomer added: 1 g/g solid.



**Figure 14** Calculated and measured oligomer compositions for the SMMA copolymerization system.

of monomer units in the oligomers was 5–6, which was less than the 8–11 units found with the SAA system. An oligomer radical, which contains only MMA, can enter the polymer particles in the SMAA system, but most of the oligomer radicals in the SAA system needed to add at least one styrene before they could enter the polymer particles.

#### Oligomers in the Styrene–MMA Copolymerization System

Most of the acid monomers in the SAA or SMAA systems are distributed in the water phase. Styrene concentration in water is small, compared with that

of the acid monomers, so that the amount of styrene used was not changed in the acid monomer systems. MMA, however, is less water soluble and, hence, mostly distributed in the polymer particles. The recipes for synthesis of SMMA oligomers contained a total monomer charge with an S : MMA ratio that varied (Table VIII).

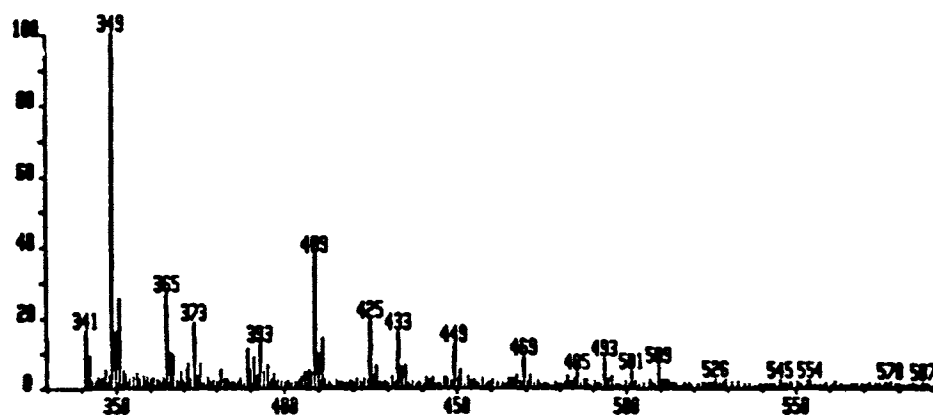
Figure 11 shows the IR spectra of the SMMA oligomer. The compositions of these oligomers were obtained from the absorbencies of carbonyl and phenyl at  $1732$  and  $698\text{ cm}^{-1}$ . The standard curve for the calculation of compositions of the SMMA oligomers was determined by IR spectra of polymer mixtures with different ratios of polystyrene and poly(methyl methacrylate). Figure 12 is the standard curve, which is fit by the equation:

$$M_{\text{MMA}}/M_{\text{S}} = 1.2203(A_{1732}/A_{698}) + 0.02371 \quad (7)$$

where  $M_{\text{MMA}}$  and  $M_{\text{S}}$  are the molar amounts of MMA and styrene in the oligomers, respectively. The molar ratios of MMA to styrene in the oligomers are listed in Table IX.

Figure 13 shows the distribution of MMA in polymer particles and in the water phase. The monomer molar fractions of MMA in the water phase were calculated, with 0.035% assumed as being the styrene concentration in water phase. The calculated and measured compositions of SMMA oligomers are compared in Figure 14. Reasonable agreement was obtained.

Figure 15 shows a mass spectra of the SMMA oligomers. The molecular weight of SMMA oligomers are presented in Table IX. The critical size for particle entry was calculated according to eqs. (3)–(6), where monomer 1 is MMA, and monomer 2 is



**Figure 15** Mass spectra of SMMA oligomer.

styrene. The results in Table IX show that the oligomers contain 2–4 MMA units and 1–0 styrene units, as the MMA concentration in monomer mixture changes from 20% to 80%. The total number of monomer units in the oligomers were 3–4, which is significantly less than the 8–11 units of the SAA oligomers and the 5–6 units of the SMAA oligomers. Half or more of the oligomer radicals, which enter the polymer particles, contain only MMA.

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