Improving Water Solubility of Poly(acrylic acid-*co*-styrene) Copolymers by Adding Styrene Sulfonic Acid as a Termonomer

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ABSTRACT: Acrylic acid is often used to make water-soluble polymers while styrene is often modified to add special functions to polymers. However, when styrene and acrylic acid are copolymerized, the resulting polymer is much less water soluble. To regain water solubility, the effect of styrene sulfonic acid on solubility of poly(acrylic acid-*co*-styrene) copolymers was investigated. Even though acrylic acid polymers are known for their water solubility, the presence of styrene units within acrylic acid copolymers reduces the solubility of the copolymer substantially at the natural pH of the solutions. By adding styrene sulfonic acid as a termonomer, polymers that are water soluble at the natural pH of the polymerization could be obtained. The solubility of the polymer after removal of the solvent and by redissolving at different concentrations and pH levels is also reported. Solubility increases at higher pH especially with low styrene concentration in the copolymer. It was found that incorporation of as little as 5 mol % of styrene into poly(acrylic acid) reduced the aqueous solubility to less than 0.5 g dL^{-1} at pH 7. Upon adding 7 mol % styrene sulfonic acid as a termonomer, the water solubility increased to 5 g dL^{-1} at pH 7. At higher levels of styrene, more styrene sulfonic acid was needed, especially at low pH. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2208–2215, 2013

INTRODUCTION

Physical and chemical properties of polymers prominently depend on chemical structure. Thus, polymer properties can be predicted by using the chemical structure of the monomers that are used for polymerization.[1] For example, acrylic acid is a monomer that is well known for its water solubility, and it forms water-soluble polymers when polymerized with various initiator systems, such as free radical[2–4] and redox initiators[3,5,6] with solution bulk and inverse emulsion polymerization techniques. Poly(acrylic acid) (PAA) can be crosslinked and used for superabsorbent applications because of its polyelectrolyte nature, which allows PAA to absorb 30 times its weight of electrolyte solutions such as urine. Thus, it is often used for hygiene products.

Tobiesen et al.[7] previously studied grafting acrylic acid polymers onto nylon 6,6 film and fiber surfaces as a way to change the polymer surface properties. For instance, using this technique, the number of the functional groups on the surface of nylon can be increased dramatically because each repeat unit of PAA carries a carboxylic acid group while the only reactive groups in nylon are the acid and amino end groups. Thus, if PAA is grafted onto the amide groups on the surface of a nylon fiber or film, the number of functional groups on the surface is increased by a multiplicative factor nearly equal to the average degree of polymerization, n, of PAA. The original nylon has only two reactive groups per molecule, which is proportional to $1/n$, where this n is the average degree of polymerization of nylon. As each carboxylic acid functional groups in PAA can be used to attach new functional groups, the surface properties can be greatly altered, e.g., the antimicrobial and electrostatic properties,[8] as well as other properties can easily be changed.

Another way to change the surface properties of nylon is to use PAA for its water solubility and ability to graft to nylon, but to incorporate new functionality into PAA by adding comonomers. For instance, using derivatives of styrene, functional monomers can be created, and by copolymerizing these monomers, polymers with multiple functions can be produced. These modifications can be used for functional textiles as well as other functional polymer films and fibers.

For environmental reasons, grafting PAA onto nylon films is preferably conducted from water. Unfortunately, styrene and many of its derivative monomers such as 4-vinylbenzyl chloride are usually not soluble in water even at very low concentrations.

Table I. Monomer Ratios Used for Copolymer Synthesis and Measured Using FTIR

Acrylic acid (%)	Styrene		Styrene sulfonic acid	
	Feed ratio (%)	FTIR (%)	Feed ratio (%)	FTIR (%)
100	0	0	0	0
95	5	4	0	0
90	10	10	0	0
90	5	3	5	6
88	5		7	
75	10	9	15	16
70	10	13	20	19
65	10		25	

This makes the copolymer insoluble in water as well. In this study, we present a way to tailor solubility of styrene and acrylic acid copolymers, by adding styrene sulfonic acid as a termonomer to the system to increase the solubility of the copolymer. The sulfonic acid group is a stronger acid group then carboxylic acid groups; polymers of styrene sulfonic acid have an anionic nature and readily dissolve in water.[9]

Sui et al.[9] discussed tuning the solubility of random copolymers of diallyldimethylammonium and acrylic acid with poly(styrene sulfonate). They reported that stability of solubility highly depends on pH of the solution, which can be adjusted by polyelectrolyte complex concentrations. Following their lead, the effect of the pH of the solvent that is used to dissolve the polymers was also studied in the present work.

EXPERIMENTAL

Acrylic acid (anhydrous, 99%, containing 180–200 ppm monomethyl ether hydroquinone as an inhibitor), styrene (ReagentPlus®, ≥99%) and 4-styrenesulfonic acid sodium salt hydrate were obtained from Sigma Aldrich and used as received without further purification. Monomers (mol %) used in these studies are given in Table I. Ammonium persulfate (reagent grade, 98%) and sodium metabisulfite (ACS reagent, ≥97.0%) were obtained from Sigma Aldrich and used as a redox initiator system. Initiator concentration was 0.23 g dL^{-1}. Ferrous sulfate heptahydrate (Sigma Aldrich) was used to prepare 3 mL of 0.1% ferrous sulfate solution, which was used as a reducing agent before the addition of the catalysts to the system to capture any residual oxygen. To terminate the polymerization, 0.3 g hydroquinone (Sigma Aldrich) was used as an inhibitor at the end of the reaction time. Deionized water was used throughout.

Solution polymerization was carried out in a 1500-mL (ACE Glass)-jacketed cylindrical flask with a head that has three 24/40 joints. Agitation was done using a glass stirrer with an overhead mixer (Barnant mixer series 10, model: 700–5400), a glass stirring rod (Chemglass CG-2075), and a Teflon® blade. The stirring shaft was lubricated with mineral oil. Initiators and styrene were delivered by syringe pumps (SAGE™ ATI Orion model

361). For delivery of the initiators, Becton-Dickson 30-mL Luer-lock plastic syringes were used with plastic tubing and a pipetting needle (Popper 18 gauge, 6″-pipetting needle blunt end with standard hub). Styrene was feed via a 30-mL popper micromate interchangeable Luer-lock hypodermic syringe with Teflon™ tubing without a needle. Acrylic acid was fed with a Fluid Metering (FMI) Q-type lab pump with Q2CKC head module through Teflon tubing. When sodium styrene sulfonic acid was added to the system, it was dissolved in an acrylic and water solution and delivered together with the FMI pump. Reactions were carried out under a nitrogen purge at 65 + 2°C. The temperature was continuously monitored by a thermal couple. The reactor was kept at constant temperature using a water circulator, which circulated hot water through the jacket of reactor. Ferrous sulfate and hydroquinone were added using Becton-Dickson 30-mL plastic syringes and 18 gauge 6″ popper blunt end pipetting needle with standard hub.

All polymers were made as follows. Approximately 800 mL of deionized water was added to the reactor. Then the reactor was heated to 65 ± 2°C using the circulator. When the system reached 60°C, 0.1% ferrous sulfate solution was added, and the nitrogen flow was started. As the system reached the reaction temperature, one-third of the ammonium persulfate solution was injected into the reactor. Then the monomer feed was started and was set to deliver all monomers in 90 min. Immediately after starting the monomer feed, one-third of the sodium metabisulfite solution was injected, the catalyst feed was started and set to deliver all catalyst to the system in 120 min. When the catalyst feed finished, the reactor was kept at the reaction temperature for an additional 90–120 min. Then, 0.3 g of hydroquinone dissolved in 10 mL of water was injected and the reactor was allowed to cool to ambient temperature.

After polymerization, the polymer solutions were placed into a Fisher Scientific (model 280) vacuum oven at 90°C, house vacuum was turned on, and a slow air purge was started. The samples were left in the oven overnight to dry. The polymer was then dissolved in deionized water at concentrations of 20–25 wt %. To overcome phase separation while redissolving copolymers, the copolymers were dissolved in water at 60 ± 5°C with agitation. Next, the samples were freeze dried using a Labconco FreeZone® 1-L bench top (Model 7740020) freeze dryer system with a Welch® Freezedry Pump™ direct drive vacuum pump (W series Model 8917A-80). Finally, the polymers were granulated using an 8-oz glass mortar.

After the polymers were granulated, they were first characterized by FTIR spectroscopy using a Perkin-Elmer Spectrum 100 spectrometer with background subtraction. The FTIR of the monomers were also obtained. Then each polymer's spectrum was compared to those of the monomers to qualitatively evaluate the composition of the copolymer. Polymer compositions were estimated from the FTIR absorbance.

Molecular weights of all samples were determined using size exclusion chromatography. Polymer solutions were prepared using 0.1M sodium nitrate aqueous solutions as solvent. The sodium nitrate solution was prepared using 18 MΩ deionized water, which was purified by Siemens Pure Lab Ultra. Standard

Table II. Molecular Weights of the Polymers in the Standard Polymer Mixture for Calibrating the Size Exclusion Chromatography

Vial	M_p (g mol^{-1})
Red	1,258,000
	116,300
	12,140
	615
Yellow	909,500
	62,100
	3930
	194
Green	442,800
	23,520
	1500
	106

polymers were prepared at 2 mg mL^{-1} concentration, and polymer samples made in this study were prepared at 1 mg mL^{-1} concentration. As a standardization polymer, a mixture of narrow molecular weight poly(ethylene oxide) (<23,000) and poly(ethylene glycol) (>23,000) was used. Three different colored vials were prepared with standard polymer mixtures as given in Table II. Polymers were injected into a size exclusion column using a Waters 2695 Separations Module. Polymer Labs Aquagel-OH 40 and 60 columns were used for exclusion. Columns had 300 mm length and 7.5 mm diameter. Both columns have 8-μm particle sizes. Then using a Waters 2414 refractive index detector, the exclusion of the polymers was monitored by determining the retention time of the polymers. Data was analyzed using Empower Pro software.

Two main solubility determinations were performed. The first determination was done immediately after cooling the reactor. The appearance of the polymer solution was considered as a measurement of the solubility, whether the solution was clear, cloudy, or milky. A clear solution indicates that the polymer is soluble in water right after reaction. At this time, the concentration of the polymer in the solution was ~10 wt %.

The second approach was conducted after removal of the solvent. Polymer was dissolved in solvent again at different concentrations and the solution was examined to see if it was clear, almost clear, slightly cloudy, or cloudy. Any color change or particle aggregation was also noted. Additionally turbidity of the solutions was examined at 500 nm wavelength using a Bio-tek Synergy HT spectrometer. These experiments were done in deionized water at pH 4–5, and buffer solutions of pH 6.9 and pH 9.93. In this way, pH effects were investigated.

The pH 6.9 solution was prepared with 0.025M potassium phosphate monobasic (Fisher Scientific (white crystals) Bio-Reagents®) and 0.025M sodium phosphate dibasic (Acros Organics, 99+%, for analysis, anhydrous). The pH 9.93 solution was prepared with 0.05M sodium bicarbonate (Fisher Scientific, certified ACS) and 0.05 sodium carbonate (Sigma Aldrich, anhydrous ACS Reagent). For clarity, these are referred to as the

natural pH (pH 4–5 as polymerized), pH 7, and pH 10 throughout the remainder of this article.

RESULTS

FTIR Results
The monomers used in this study are all vinyl monomers with different functional groups, which give different characteristic peaks in FTIR spectrum. The spectra of the monomers are given in Figure 1.

Acrylic acid shows a large peak at 1730 cm^{-1} due to carbonyl groups present in carboxylic acid groups. Also, it shows a very broad peak due to H bonding of OH groups. Styrene shows a large peak due to phenyl groups at ~ 690 cm^{-1}. This peak is also seen in the spectrum of 4-styrenesulfonic acid sodium salt hydrate since it has a phenyl group as well. Both monomers also show a series of peaks at ~ 3100–3000 cm^{-1} range due to CH stretch in the phenyl groups. However, these peaks are not expected to be seen in the spectra of the copolymer, because the wide and strong peak due to OH groups is expected to mask these peaks. 4-Styrenesulfonic acid sodium salt hydrate also shows a series of peaks at 1250–950 cm^{-1} range due to sulfonate groups. Besides these strong peaks, we also see a peak in each spectrum due to C=C bond present in the vinyl monomers near 1650 cm^{-1}, and this peak is expected to disappear from spectra after polymerization.

In Figure 2, FTIR spectra of the polymers with various ratios of monomers are shown. The dash-dot spectrum belongs to PAA and its largest peak is due to carbonyl group (1730 cm^{-1}). In the regions that styrene and styrene sulfonic acid show their largest peaks, PAA does not have any strong peaks. When we look at the solid line spectrum of the copolymer with 90% acrylic acid and 10% styrene, it shows nearly the same behavior as acrylic acid except for the 690 cm^{-1} region due to phenyl group bending, which suggests styrene is added into polymer. When styrene sulfonic acid is added to the copolymer (65% acrylic acid, 10% styrene, and 25% styrene sulfonic acid), the
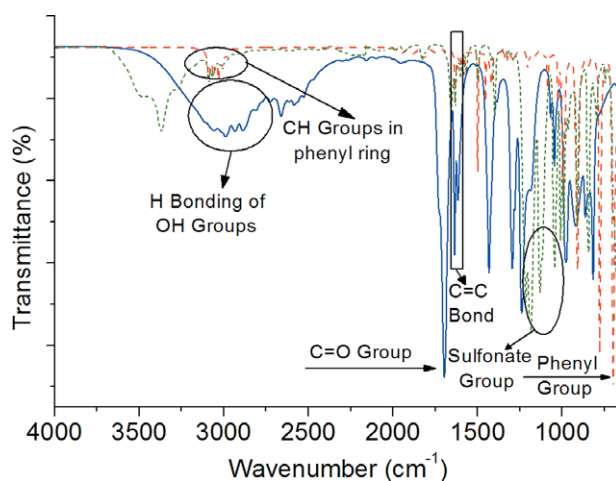

Figure 1. Spectra of the monomers (solid curve: acrylic acid; dashed curve: styrene; dotted curve: 4-styrenesulfonic acid sodium salt hydrate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
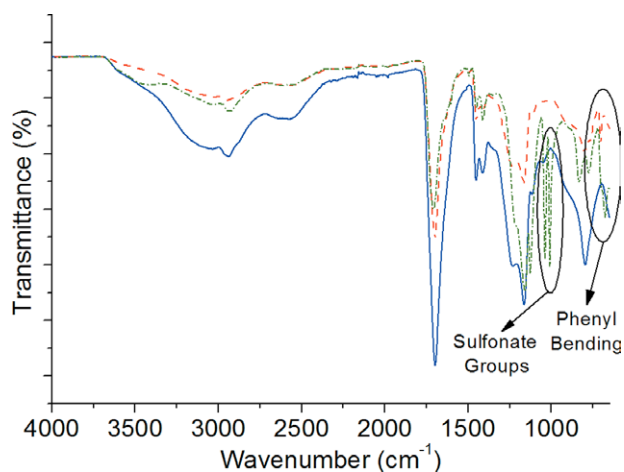
Figure 2. Spectra of some of the polymers (dash–dot curve: poly(acrylic acid); solid curve: poly(acrylic acid(90%)-*co*-styrene(10%))); dashed curve: poly(acrylic acid(65%)-*co*-styrene(10%)-*co*-styrene sulfonic acid(25%)).[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

largest peaks of the spectrum become the peaks between 950 and 1250 cm^{-1}, which are due to the sulfonate groups. The C=C stretching peak in the monomers' spectra at $\sim$ 1650 cm^{-1} has disappeared after polymerization. The FTIR results are qualitatively in agreement with the expected IR spectra of the copolymers and the estimated polymer compositions obtained by FTIR as shown in Table I, although the exact composition is not known.

Size Exclusion Chromatography Results

To measure the molecular weight and molecular weight distribution of the polymers described above, size exclusion chromatography was used. All of the polymers gave a bimodal distribution with a very large peak at high molecular weights

(M_w = 173,000–440,000) and a small peak at low molecular weights (M_w = 315–3786) as shown in Table III. A typical plot obtained from size exclusion chromatography is given in Figure 3. The polydispersity index of the intense peak of the distribution of polymers ranged between 1.65 and 3.54.

Solubility Evaluation Results

Solubility of Polymerization Batch as Polymerized. As the polymerizations were conducted in a glass reactor, it was possible to observe the clarity of the solution during and after polymerization. After cooling the polymerization batch, the appearance of the solution in the reactor was evaluated as clear, slightly cloudy, cloudy, or milky. To visualize the results, a bubble plot is shown in Figure 4.

It is obvious from the batch color that as the styrene sulfonic acid amount in the polymer was increased, clearer solutions were obtained. This is very good from the polymer-processing point of view if the polymer is to be used as polymerized. The calculated concentration of the solution in this form is $\sim$ 10 wt %.

Once clear solutions were obtained, no copolymers with higher SSA concentrations were made so it is unknown whether still higher SSA concentration would affect the solubility differently. However, these results by themselves showed the solubility of the polymer could be improved by adding styrene sulfonic acid.

After removal of the solvent, to further analyze the effect of SSA concentration on solubility of the polymer, turbidity measurements were performed at 500 nm by redissolving the polymers in deionized water. The results are shown in Figure 5. Both poly(acrylic acid-*co*-5- and 10-mol % styrene) samples show very high turbidity, even at very low concentrations. However, as the SSA concentration is increasing, the turbidity of the solutions decreases. In fact, the absorption values are approaching the absorption of deionized water, which is given by zero concentration in Figure 5.

Table III. Molecular Weights of the Polymers in the Standard Polymer Mixture for Calibrating the Size Exclusion Chromatography

|			M_n	M_w	M_p	PDI
PAA	100% AA	First Peak	121,000	370,000	573,000	3.04
		Second Peak	941	2190	1422	2.33
PAA + S	90% AA + 10% S	First Peak	173,000	369,000	490,000	2.12
		Second Peak	790	3786	814	4.79
	95% AA + 5% S	First Peak	101,000	358,000	976,000	3.54
		Second Peak	1253	2954	1809	2.37
PAA + S + SSA	90% AA + 5% S + 5% SSA	First Peak	154,000	440,000	592,000	2.84
		Second Peak	734	1463	1292	1.99
	88% AA + 5% S + 7% SSA	First Peak	104,000	173,000	178,000	1.67
	75% AA + 10% S + 15% SSA	First Peak	138,000	267,000	357,000	1.93
		Second Peak	1892	2577	885	1.36
	70% AA + 10% S + 20% SSA	First Peak	156,000	283,000	350,000	1.81
		Second Peak	252	315	219	1.24
	65% AA + 10% S + 25% SSA	First Peak	131,000	217,000	170,000	1.65
		Second Peak	259	347	216	1.33
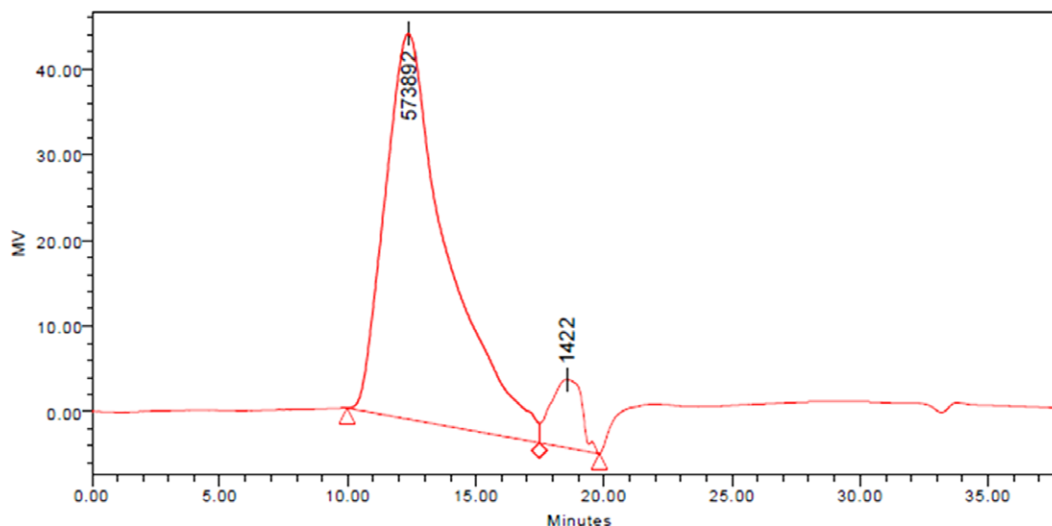
Figure 3. A typical plot obtained from size exclusion chromatography (poly(acrylic acid), intense peak: M_n: 121,000, M_w: 370,000 g mol^{-1}; small peak: M_n: 941, M_w: 1422 g mol^{-1}; polydispersity index of intense peak: 3.04). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Solubility of Polymers at Different pH and Concentrations

After polymerization, the solvent was removed, and an attempt was made to redissolve the polymer samples at different concentrations and pH values. This allowed a more complete investigation of the solubility of the polymers, even if they were not soluble immediately after polymerization. The same qualitative definitions were used as above: clear, slightly cloudy, cloudy, and milky. Turbidity measurements were also performed on the solutions.

Figure 6 presents the solubility of the polymer samples that have 5% styrene by mole at different concentrations and pH values. It is important to remember that the values on the plot are discrete numbers that were chosen for the polymerization and the highest concentration that gave a clear solution is shown as the solubility limit. As the pH of the solvent was
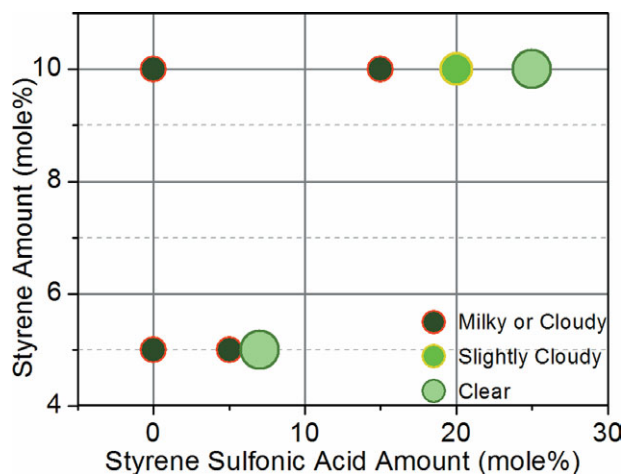

Figure 4. As polymerized solubility dependence of the copolymers on styrene sulfonic acid amount. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
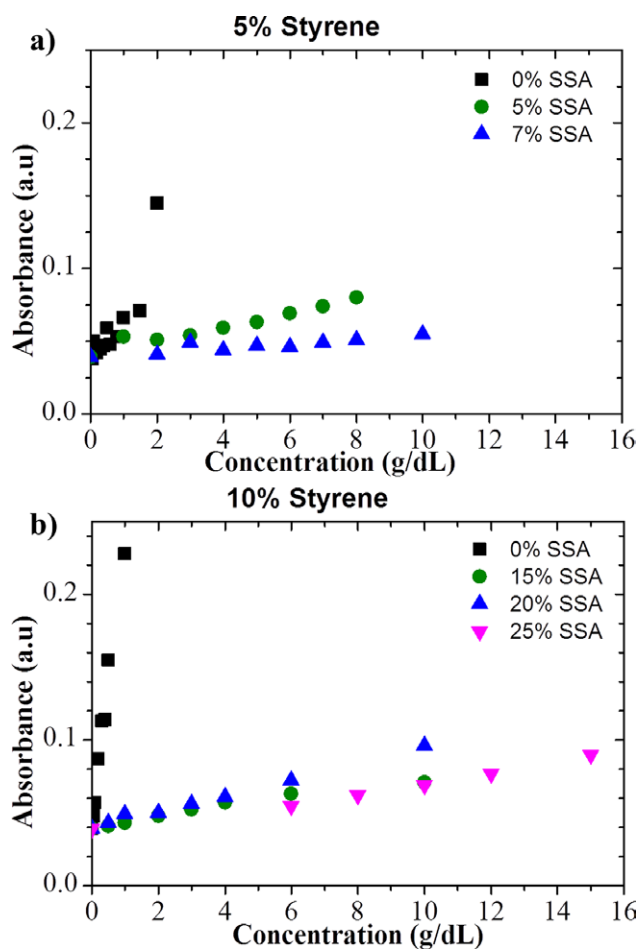

Figure 5. Results of turbidity measurements of (a) 5% and (b) 10% styrene samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
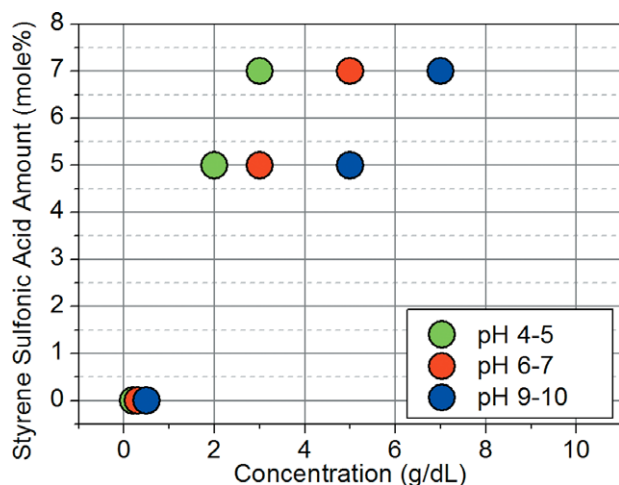
Figure 6. Solubility of 5-mol % styrene polymer samples at various pH and concentrations. Each point indicates the upper level of solubility. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased, the concentration in which the solutions appeared clear increased. As before, as we increase the SSA amount in the polymer, solubility increases.

For 10-mol % styrene copolymer samples, the solubility of the terpolymers clearly increases with increasing SSA, see Figure 7. However, after removal of the solvent and redissolving at different concentrations, clear solutions could not be obtained at high concentrations even though some of these polymer batches were clear right after polymerization. We believe this is caused by the formation of styrene clusters during drying. During the redissolving process, it may be difficult to break up these clusters.

For example, the 5-mol % styrene samples with 7-mol % SSA formed a clear solution at pH 4–5 and about 10 g dL^{-1} concentration immediately after polymerization. After drying and
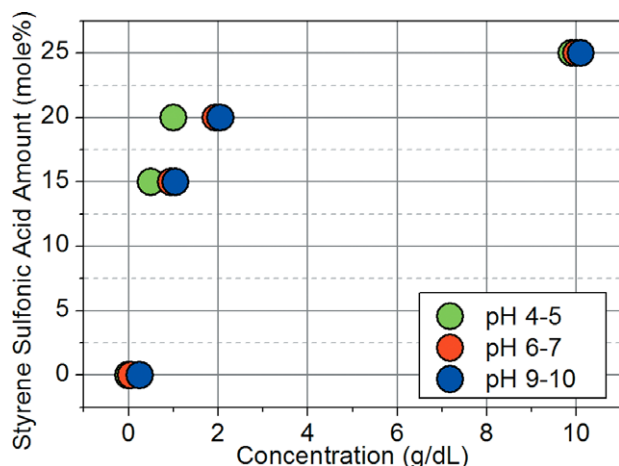

Figure 7. Styrene (10 mol %) polymer samples' solubility at various pH and concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
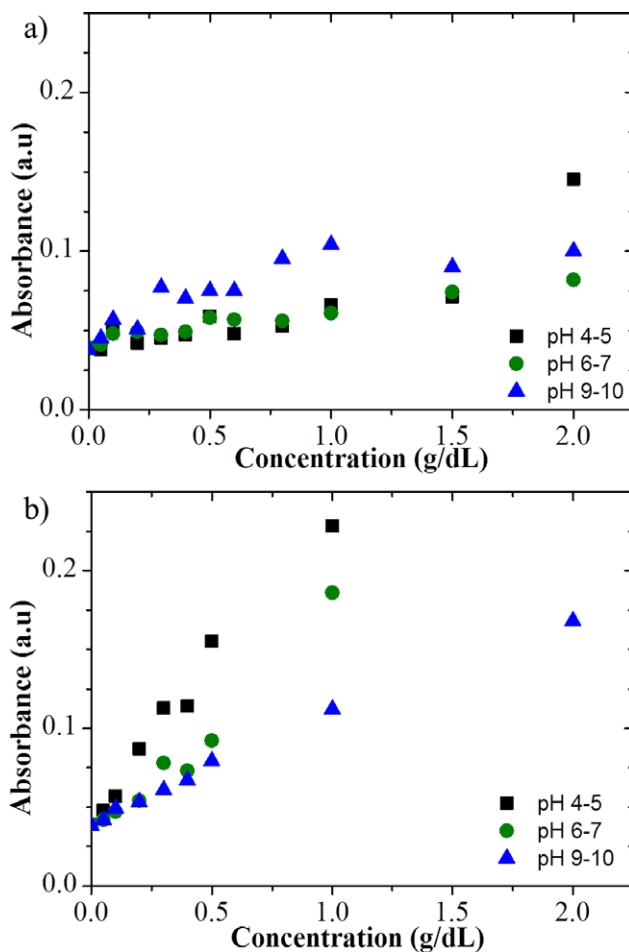

Figure 8. Effect of pH on solubility without presence of SSA. (a) 5% styrene, 0% SSA, and (b) 10% styrene, 0% SSA samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

redissolving this polymer, the maximum concentration that yielded a clear solution at pH 4–5 was 2 g dL^{-1}. This effect was even more pronounced at 10 mol % even when the concentration of SSA was increased 3× to 20 mol %.

Turbidity results of the poly(acrylic acid-*co*-5- and 10-mol % styrene) samples at different pH values are presented in Figure 8. It is clear that at higher pH, solubility increases significantly especially for 10% styrene samples. It was also observed for high styrene concentration samples; at pH 4–5, the samples showed small, visible particles, and although the particles dissolved at higher pH, the solutions remained cloudy, whereas the turbidity results of the SSA-containing samples do not exhibit as a dramatic effect on pH for the SSA concentrations studies, as shown in Figure 9. This is due to the increased solubility of the polymer by addition of the SSA.

Another important observation is that when the samples were redissolved in pH 10 buffer solvents, the color of the solutions changed to a brownish color. The visible spectra of these samples not show a significant peak, so we believe that this is due to light scattering from clusters of the phenyl groups in solution.
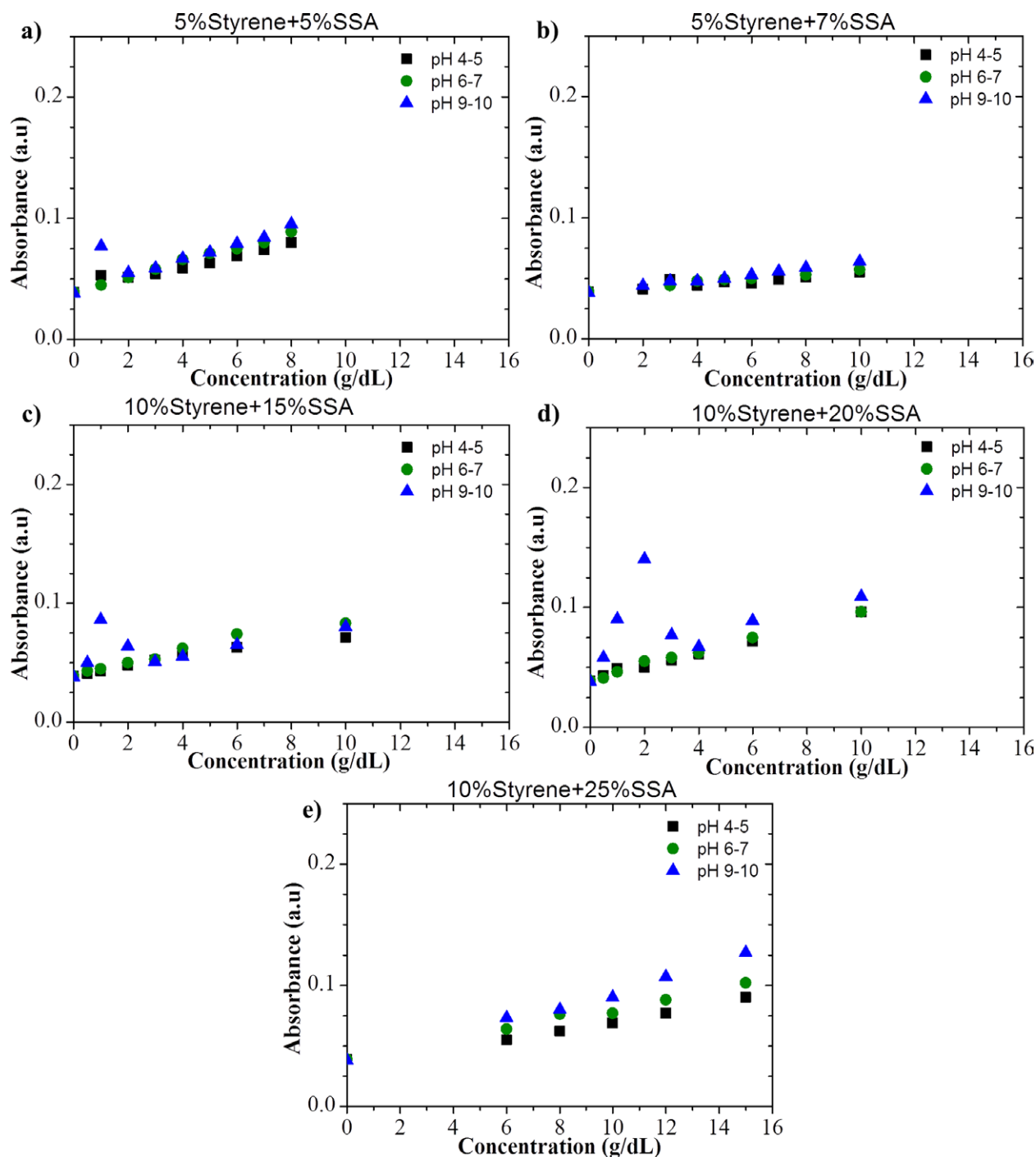
Figure 9. Turbidity measurement results of samples with SSA at different pH (a) 5% styrene + 5% SSA, (b) 5% styrene + 7% SSA, (c) 10% styrene + 15% SSA, (d) 10% styrene + 20% SSA, and (e) 10% styrene + 25% SSA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

Redox polymerization was used successfully to polymerize acrylic acid, styrene, and styrene sulfonic acid copolymers. FTIR results confirmed that by increasing the relative amount of the monomer in the feed, the intensity of the peak due to functional groups coming from that particular monomer increased. Size exclusion results indicated molecular weights of ∼ 200,000 g mol^{-1} and molecular weight distribution of 3. By adding

styrene sulfonic acid as a termonomer, the solubility in water of the acrylic acid and styrene copolymers was increased. The results also show that after removal of the solvent and redissolving the polymers at room temperature, hydrophobic clusters formed, and this reduced the highest soluble concentration of the polymer. Finally, by increasing the pH of the solution, it was possible to tailor the solubility of the polymer. These results indicate that even when incorporating a very water insoluble

monomer into PAA, water solubility can be retained by increasing the amount of SSA and by adjusting the pH.

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