

## ABSTRACT

AKYILDIZ, HALIL IBRAHIM. Effect of Styrene Sulfonic Acid on Solubility of Poly (acrylic acid-co-styrene-co-styrene sulfonic acid). (Under the direction of Dr. Stephen Michielsen).

In this study we have tried to improve the solubility of poly (acrylic acid-co-styrene) polymers by adding styrene sulfonic acid as third monomer. We expected styrene sulfonic acid to contribute to the solubility of the polymers since it has a strong polyelectrolyte nature. We saw that as we increase the styrene content we need to increase the styrene sulfonic acid content more. We have achieved to produce water soluble polymers with 5 and 10 mole styrene content as polymerized. We also investigated the solubility of the polymers after removing solvent and redissolving them at different pH levels. We saw that at higher pH polymers are soluble at higher concentrations. However we could not reach the concentrations of the polymerization batch after removal of the solvent. This is probably caused by hydrophobic clustering effect of the styrene units, because as the styrene content is increased clear solution concentrations decrease significantly. For characterization of the polymers size exclusion chromatography, intrinsic viscosity measurements for molecular weight determination, and Fourier Transform Infrared Spectrometer (FTIR) used for qualitative composition determination. We also investigated the kinematic viscosity of the polymer solutions at various pH levels and concentrations using Ubbelohde capillary viscometer.

© Copyright 2011 by Halil Ibrahim Akyildiz

All Rights Reserved

Effect of Styrene Sulfonic Acid on Solubility of Poly (acrylic acid-co-styrene-co-styrene sulfonic acid)

by  
Halil Ibrahim Akyildiz

A thesis submitted to the Graduate Faculty of  
North Carolina State University  
in partial fulfillment of the  
requirements for the Degree of  
Master of Science

Textile Engineering  
Raleigh, North Carolina

2011

APPROVED BY:

---

Dr. Richard Kotek

(Member of Advisory Committee)

---

Dr. David Hinks

(Member of Advisory Committee)

---

Dr. Stephen Michielsen

(Chair of Advisory Committee)

---

Dr. Saad Khan

(Member of Advisory Committee)

## **DEDICATION**

This thesis is dedicated to my parents and my wife Elif

## **BIOGRAPHY**

The author was born in Iskenderun, Turkey, in August 2<sup>nd</sup>, 1985. He received his Bachelor of Science in Textile Engineering, from Uludag University, Turkey, in 2007. In August 2009 he joined College of Textiles at North Carolina State University to pursue a Master of Science in Textile Engineering. He is planning to pursue a PhD degree in Fiber and Polymer Science after getting his Master of Science degree. He is married to Elif Akyildiz and they have a handsome baby boy named Mustafa Bilal.

## **ACKNOWLEDGEMENTS**

I am grateful to Dr. Michielsen for his sincere help and encouragement throughout my research. This thesis would not be possible without his endless and kind support. He as an advisor guided me during my research by showing right direction every time I needed. It was a chance to me to have him as an advisor.

I also acknowledge the members of my committee Dr. Kotek, Dr. Hinks, and Dr. Khan for their interest. I would like to thank Dr. Beck for his help during size exclusion chromatography experiments. I would like to thank also College of Textiles' staff who helped me during my research.

I also wish to express my appreciation to Textile Engineering, Chemistry and Science department, Laam Science, and Republic of Turkey Ministry of National Education for funding this research.

I thank my wife Elif for her endless support throughout my study in the United States. I should mention her great patience and sacrifice for this study. She has been the first who supported me in every obstacle I faced. I also thank my parents for their support throughout my life and during my study in the United States from overseas.

## TABLE OF CONTENTS

LIST OF TABLES .....	vii
LIST OF FIGURES .....	viii
1. INTRODUCTION .....	1
2. LITERATURE REVIEW .....	3
2.1. Polymer Synthesis .....	3
2.1.1. Monomers .....	4
2.1.2. Polymerization Techniques .....	6
2.1.3. Redox Initiation .....	9
2.1.4. Copolymerization .....	12
2.2. Polymer Characterization .....	15
2.2.1. Fourier Transform Infrared (FTIR) Spectroscopy .....	15
2.2.2. Molecular Weight Determination of Polymers .....	17
2.2.3. Solubility of Polymers .....	27
2.2.4. Viscosity of Polymer Solutions .....	28
3. EXPERIMENTAL .....	30
3.1. Polymer Synthesis .....	30
3.1.1. Chemicals .....	30
3.1.2. Tools .....	32
3.1.3. Polymerization procedure .....	33
3.2. Solvent Removal .....	34
3.3. Characterization .....	35
3.3.1. FT-IR Spectroscopy .....	35
3.3.2. Molecular Weight Determination .....	35

3.3.3. Solubility Determination .....	38
3.3.4. Viscosity Measurements.....	39
4. RESULTS AND DISCUSSIONS .....	40
4.1. Determination of Polymer Composition.....	40
4.2. Molecular Weight Determination.....	51
a. Dilute Solution Viscosity Measurements .....	51
b. Size Exclusion Chromatography (SEC) .....	54
4.3. Solubility of Polymers.....	60
a. Solubility of the polymerization batch .....	60
b. Solubility of Polymers at Different pH and Concentrations.....	62
4.4. Viscosity of the Polymer Samples at Various pH and Concentration Values .....	65
5. CONCLUSION .....	68
6. RECOMMONDATIONS FOR FUTURE RESEARCH.....	71
7. REFERENCES .....	72

## LIST OF TABLES

<b>Table 2.1</b> Reactivity ratios found in the literature.....	14
<b>Table 2.2</b> Nomenclature of solution viscosity.....	21
<b>Table 3.1</b> Monomer concentrations of polymerizations.....	31
<b>Table 3.2</b> First recipe used for acrylic acid polymerization.....	34
<b>Table 3.3</b> Parameters of intrinsic viscosity measurements and Mark-Houwink-Sakurada coefficients.....	36
<b>Table 3.4</b> Molecular weight of the standard polymers.....	37
<b>Table 4.1</b> Monomer feed compositions of polymer samples.....	44
<b>Table 4.2</b> Regression line equations of the lines in Figure 4.7.....	53
<b>Table 4.3</b> Intrinsic viscosity measurement parameters and results.....	54
<b>Table 4.4</b> Retention times of the standard polymer in SEC.....	55
<b>Table 4.5</b> Summary of the SEC results.....	58

## LIST OF FIGURES

<b>Figure 2.1</b> Skeletal chemical structure of acrylic acid.....	4
<b>Figure 2.2</b> Skeletal chemical structure of styrene.....	5
<b>Figure 2.3</b> Skeletal chemical structure of 4-styrenesulfonic acid sodium salt hydrate....	6
<b>Figure 2.4</b> Typical molecular weight distribution of a polydisperse polymer.....	19
<b>Figure 2.5</b> A schematic of size exclusion chromatography system.....	26
<b>Figure 4.1</b> FTIR spectra of monomers.....	45
<b>Figure 4.2</b> FTIR Spectra of the Poly (acrylic acid) samples.....	46
<b>Figure 4.3</b> Comparison of the FTIR spectra of acrylic acid homopolymer and copolymers with styrene.....	47
<b>Figure 4.4</b> Comparison of the three samples that consist of 90 mole% acrylic acid, 5 mole% styrene, 5 mole% styrene sulfonic acid.....	48
<b>Figure 4.5</b> Comparison of FTIR spectra of copolymers that has 5 mole % styrene and 0, 5 and 7 mole % styrene sulfonic acid.....	49
<b>Figure 4.6</b> FTIR spectra of copolymer including 10 mole% styrene and 0, 15 and 20 mole % styrene sulfonic acid.....	50
<b>Figure 4.7</b> Intrinsic viscosity measurements of the poly acrylic acid samples.....	52
<b>Figure 4.8</b> The $\log_{10}$ of the molecular weight is plotted vs. the retention time. A third degree polynomial SEC calibration curve was fit to the data in Table.....	56
<b>Figure 4.9</b> Size exclusion chromatography result for 10AA100I23 sample.....	57
<b>Figure 4.10</b> Comparison of SEC and intrinsic viscosity results.....	59

<b>Figure 4.11</b> Solubility dependence of the copolymers on styrene sulfonic acid amount as they were polymerized.....	61
<b>Figure 4.12</b> 5 mole% styrene polymer samples' solubility at various pH and concentrations.....	63
<b>Figure 4.13</b> 10 mole% styrene polymer samples' solubility at various pH and concentrations.....	64
<b>Figure 4.14</b> Viscosity measurements of sample 10AA88S5SSA7I23 at various concentrations and pH values.....	66

## 1. INTRODUCTION

As a protective textiles application, antimicrobial textiles is a part our modern daily life. They have great importance in healthcare applications and in preventing the spread of diseases. There are several proposed antimicrobial finishing processes in the literature. All these finishings are required to have some properties in common such as durability, effectiveness to a broad spectrum of bacteria and viruses with low toxicity, and process feasibility.(1)

Durability to laundering is one of the largest challenges in most of the applications. An important solution is surface modification of the materials via polymer grafting. In order to attach antimicrobial molecules permanently to nylon surfaces, S. Michielsen et al. proposed grafting a copolymer that includes antimicrobial agent attached to nylon surface.(2) This process basically proposes synthesis of an antimicrobial dye attached monomer, and copolymerization of this monomer with acrylic acid, subsequently grafting the copolymer to nylon surface. Acrylic acid here provides side groups that can attach to nylon surface. It also provides solubility in water.(3)

This process uses a dye that generates singlet oxygen when exposed to light to kill the bacteria and viruses. The dye is a non-toxic material. In this way the process aims to meet the first two requirements. However the feasibility of the process is the most important requirement and is possible with practical process time, temperature and low toxic solvents. S. Michielsen et al. conducted their experiments in aqueous solutions, (2,3) which limited them in dye attached monomer content in the copolymer, because this specific monomer is

insoluble in water and makes the copolymer insoluble as well when incorporated at levels above a few mole percent.

This problem leads to another problem which is about effectiveness of the process. Since antimicrobial dye photo bleaches after a certain amount of the time, this problem eventually causes another durability problem. It is expected that more dye attached monomer in the copolymer will make the copolymer more durable. However because of the solubility restriction it is not possible to achieve it with the present technique.

The aim of this study is to increase the solubility of the antimicrobial copolymer as much as possible. In order to do so we have added another monomer (styrene sulfonic acid) to the system to increase the solubility, and characterized the copolymers that we have produced. We polymerized acrylic acid and styrene to imitate the behavior of the previous studies since the dye attached monomer is a styrene based monomer and their solubility behavior in water is very similar. Later we have added styrene sulfonic acid to the system to increase the solubility of the copolymer.

Characterizations of the copolymers were made in order to determine the molecular weight and the composition of the copolymer. Ubbelohde viscometer, FTIR, and size exclusion chromatography (SEC) are used for characterization of the polymers. Viscosity and solubility behavior of the copolymer at different concentrations and pH values are observed as well.

## 2. LITERATURE REVIEW

Polymer synthesis and characterization are the two main focus points of our study and related work in the literature is reviewed and a brief summary is provided in this chapter.

### 2.1. Polymer Synthesis

Polymers are macromolecules that are made of smaller molecules called monomers. The synthesis of macromolecules using monomers is called polymerization. There are a couple of important classifications of polymerization methods. The older classification was done by Carothers based on polymer structure as condensation and addition polymerizations. Another classification based on polymerization mechanism was more commonly used today instead; step growth and chain growth polymerizations. Even though sometimes they are used interchangeably these classifications are based on different interests.(4)

Step growth polymerization occurs in a stepwise manner and monomers can react with each other or macromolecules of any size in the batch. This can be achieved by using monomers that have highly reactive functional groups. In order to get high average molecular weight values conversion of the reaction should be very high in this method. However it is still a very important method in production of very common polymers such as polyamides, polyesters, polycarbonates and polyurethanes.(5)

Chain growth reactions are achieved by the reactions of the monomers that have active centers. Monomers in the polymerization batch only can react with active centers. That's why a rapid increase of the molecular weight is observed in chain growth polymerizations even at low conversion rates. These active centers can be free radicals, ionic

centers or polymer catalyst bonds.(4) Active centers need to be activated by an external source and this step is called initiation. This step doesn't exist in step growth polymerization mechanism. Chain growth polymerization is the most widely used method polymer production. It is employed for polymerization of commonly used polymers such as polyethylene, polypropylene, and polystyrene.

### **2.1.1. Monomers**

Monomers build the repeat units in a monomer by polymerization. They are the prominent source of the properties of polymers. That's why for copolymer applications it is important to know the monomer properties in order to interpret copolymer properties in advance.

#### **a. Acrylic Acid**

Acrylic acid is very reactive monomer that goes under polymerization readily. It is a water soluble monomer and creates water soluble polymers. COOH group is the characteristic functional group and forms H bonding in monomer form. Acrylic acid is heavily used for superabsorbent polymer production as a crosslinked polymer.(6)

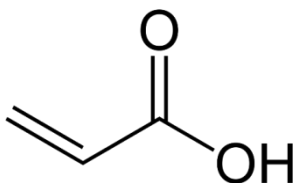


Figure 2.1 Skeletal chemical structure of acrylic acid (7)

Carboxyl group is very effective in terms of polymer properties. Poly(acrylic acid) is considered as a polyelectrolyte since it creates moderate acidity when dissolved in water. Also, reactivity of COOH group provides relatively easy modification of polymer. For example Tobiesen and Michielsen explained the amidization of carboxylic acid with an amine using a coupling agent.(3) This reaction allows poly(acrylic acid) to be grafted onto a nylon surface.

### **b. Styrene**

Styrene is an organic compound which is also known as vinyl benzene. It is a very commonly used monomer for polystyrene and copolymer applications. It is well known especially for synthetic rubber applications. Because of bulky phenyl side group, polystyrene is tough polymer and when used as a comonomer it increases toughness of the polymers.(8)

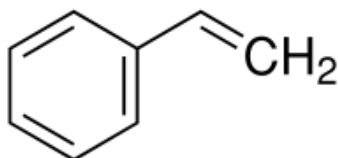


Figure 2.2 Skeletal chemical structure of styrene (9)

Styrene is not a water soluble monomer and decreases the solubility in the copolymers. However it is easy to derive new monomers from styrene monomer. We can add functionality to styrene monomers by adding functional molecule to phenyl ring. For instance as explained in following section styrene sulfonic acid is styrene derived monomer.(8)

### c. Styrene Sulfonic Acid

Styrene sulfonic acid is a styrene derived monomer which is more soluble than styrene monomer in water and creates water soluble polymers.(10) Commercially they are available as powders of sodium styrene sulfonic acid.

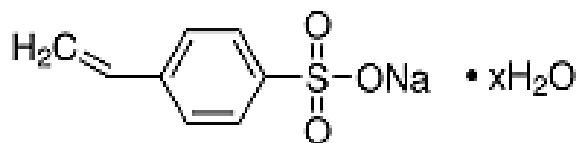


Figure 2.3 Skeletal chemical structure of 4-styrenesulfonic acid sodium salt hydrate(11)

Sulfonic acid group in the polymer is a stronger acid group than carboxylic acid groups. Polymer of styrene sulfonic acid has anion nature and readily dissolves in water. Adding styrene sulfonic acid into polymer composition might increase the solubility of the polymer.(12)

#### 2.1.2. Polymerization Techniques

There are different techniques that can be employed in the polymerization of the free radical polymerizations: bulk, solution, suspension and emulsion.(13) The sophistication of the technique increases in the same order. They all have their own advantages and disadvantages.

Bulk polymerization only requires the solubility of the initiator in the monomer. However it is not easy to control reaction temperature and polymer molecular weight.(4)

Solution polymerization eliminates prominently the temperature control problem of the bulk polymerization. Stirring the polymerization batch is much easier compared to bulk polymerization. Solubility of the initiator in the solvent is required as well as solubility of the monomer. If the polymer is soluble in the same solvent, a solvent removal step is required after polymerization. It is important that solvent has the required chain transfer properties. Also another important point is that polymerization temperature must be lower than boiling point of the solvent.

Omidian et al. (14) studied aqueous solution of neutralized acrylic acid in order to produce poly(sodium acrylate) under atmospheric conditions (unlimited access to oxygen). They used a water soluble redox pair as initiator. They investigated the effect of monomer concentration, initiator concentration, pH, and temperature on the rate of polymerization. They concluded with decreasing monomer and initiator amount, the rate of the polymerization decreases significantly. They observed a rapid increase in viscosity of the polymer solution with low starting temperature even though it lowers the polymerization rate. According to Omidian et al. pH 8.7 – 9 range causes reduction in the batch viscosity and polymerization rate. However the effect of atmospheric conditions is not discussed in the paper.

Bokias et al. (15) published a study that polymerized acrylic acid using water soluble redox initiators. They investigated the effect of pH, monomer concentration and concentration of redox units on  $M_w$  of the polymer. They concluded that ionic strength of the

polymerization solution does not affect the final product  $M_w$  significantly. Monomer concentration has an inverse relationship with molecular weight.

Scott et al. (16) studied the kinetics of the solution polymerization of acrylic acid. They concluded that polymerization kinetics with ammonium persulfate initiator is highly dependent on solution pH, initial monomer concentration, initiator concentration and polymerization temperature. They also showed that crosslinking agent concentration also effect on polymerization kinetics.

Cutié et al. (17) studied the kinetics of acrylic acid polymerization with a sodium persulfate initiator. They found similar results as Scott et al. found. Unlike Scott et al. and Bokias et al. they claimed the ionic strength of the solution affects the molecular weight of the polymer.

In suspension polymerization both initiator and monomer are not soluble in the solvent. With stirring the system, small droplets of the monomer and initiator are created and polymerization occurs in these droplets like bulk polymerization in small droplets. But the heat problem is eliminated by the continuous solvent medium.(13)

Different from the suspension polymerization, in emulsion polymerization initiator is soluble in the solvent unlike monomer and polymerization occurs at the interface of the emulsified droplet and solvent. Also droplet sizes are smaller in emulsion polymerization. Very high molecular weight polymers can be produced in this method by controlling the droplet size. (13)

Suspension and type of polymerization is common for copolymerization of monomers that show different solubility behaviors. Styrene and acrylic acid comonomers are studied by Wang et al. (18) in an emulsifier free emulsion copolymerization, by Liu et al. (19) in inverse dispersion copolymerization using redox initiators, and by Wang and Poehlein (20) in emulsion polymerization. Shoaf and Poehlein explained emulsion copolymerization kinetics of acrylic acid. (21)

Since we decided to use solution polymerization technique after literature review, we don't discuss the details about suspension and emulsion polymerization here.

### **2.1.3. Redox Initiation**

One of the most common free radical generation methods is achieved by redox reaction of organic or inorganic compounds. This method is well known for its high effectiveness in mild conditions. (5,22) Also because components of the redox couple are stable when they are separate, initiator feed can be controlled very easily and catalyst can be delivered in a long period of time if needed.

Redox initiation can be divided into two groups according to free radical formation mechanism.(22) In the first mechanism the free radical generation is achieved by dissociation of covalent bonds by energy absorption. The energy can be provided as light or thermal energy. Other mechanism of redox initiation employs ions or atoms in order to transfer electrons from them.(22)

Thermal homolysis decomposition energy of the most practical initiators is in the range of 125-160 kJ/mol.(22) Above or below this range initiator compounds show either very slow or very rapid generation of radicals at reaction temperatures. For redox couples this range of dissociation energy can be met by only certain covalent bonds; these are; oxygen – oxygen, oxygen – nitrogen, and sulfur – sulfur bonds.(22)

There are four different types of redox initiators based on the chemistry of the initiators. (5)

- Peroxides are one of the most common used types of redox initiators in combination with a reducing agent. For example, some typical organic peroxide radical generation with ferrous ion is given below.



Ferrous sulfate is a very common reductant however there are other reductants such as  $\text{Cr}^{+2}$ ,  $\text{V}^{+2}$ ,  $\text{Ti}^{+3}$ ,  $\text{Co}^{+2}$ , and  $\text{Cu}^{+2}$  can also be used instead. This type of initiation is used mostly in emulsion and aqueous solution polymerizations. In organic solvents acyl peroxides can be used in combination with amine reductants as well.(5)

- Secondly there are varieties of inorganic redox couples that can initiate free radical polymerizations. For example ammonium persulfate (initiator) and sodium metabisulfite (oxidizing agent) redox couple is a common pair in this group.

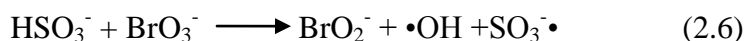
- Also organic – inorganic couples can be used as redox initiators.
- Some monomers also can be used as a component of redox pair. For example methacrylic acid and acrylamide monomers with thiosulfate initiation.(5)

Redox initiators are mostly water soluble and used in emulsion polymerizations very extensively. Redox initiators are dissolved in the aqueous phase of the emulsion and monomers are emulsified in the non-aqueous phase. Polymerization occurs at the interface between the emulsions and solvent.(5)

Ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and sodium metabisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) pair is very commonly used redox pair for polymerization of acrylic acid and acrylic acid copolymers [1,2]. (14) Even though there are several opinions on the reaction steps of redox pairs mostly ammonium persulfate (APS) is accepted as the initiator in the system and sodium metabisulfite (SMBS) is the reductant. The reaction is often described as in Eq. (2.4)



Also in some studies ammonium persulfate is used as initiator by itself. (16) Similarly Cutié et al. (17) used sodium persulfate as initiator. Liu et al. (19) used potassium bromate with sodium metabisulfite and explained the redox initiation reactions in a different way as in Eq. (2.5) and (2.6)



#### 2.1.4. Copolymerization

All polymers have some advantages and disadvantages for certain applications. Copolymerization of more than one monomer in free radical polymerization is a highly versatile method in order to balance the polymer properties as needed. It provides flexibility to polymer engineers and scientists.

Copolymers can be classified as random, alternating, block and graft copolymers.(4) Each of them has their own unique properties. We can balance the polymer properties by changing the copolymer type in different ways and monomer ratios. Mostly the type of copolymer that we can produce is governed by nature of the comonomers. Especially the reactivity difference of the monomer towards its own species and the other species defines the type of the copolymer that we will produce.(4) Since the tendencies of the monomers in the copolymerization reaction is different, homopolymerization rates are not useful to understand the copolymer composition. Instead we need to use different concepts to understand the change in the reactivity of monomers. This is defined with reactivity ratios and copolymer equation.

Copolymerization equation (2.7) is derived to predict the behavior of the monomers in copolymerization and the composition of the copolymer.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])} \quad (2.7)$$

Left hand side of the equation gives the ratio of the monomers in the copolymer ( $d[M_1]/d[M_2]$ ). Right hand side of the equation gives the relation between copolymer

composition and monomer concentrations ( $[M_1]$ ,  $[M_2]$ ) with the reactivity ratios ( $r_1$ ,  $r_2$ ). From the equation we understand that reactivity ratios are the most important parameter for copolymer composition. Rate constant of a propagating species adding the same kind of monomer over the rate constant of adding the comonomer type gives the reactivity ratio of the monomer.(4) Reactivity ratios are calculated for specific monomer pairs. Higher the reactivity ratio of a monomer means higher the tendency to add its own species in a monomer couple.

There are several reactivity ratio values reported in the literature for acrylic acid and styrene copolymerization. For styrene and sodium styrene sulfonic acid copolymerization we could not find any reported reactivity ratios in the literature. Instead we found a similar structure styrene sulfonic acid fluoride in meta- and para- configuration. For acrylic acid and styrene sulfonic acid pair we found only one reference. Reactivity ratio values found in the literature is given by Table 2.1.

When we look at the table we can see that reactivity ratios of the monomers changes in a wide range. This can be due to polymerization method, temperature of the polymerization, and reactivity ratios calculation method. But to get a general idea we can see that most of the values for acrylic acid and styrene pair shows that styrene species shows higher tendency to add its own species. However, most of the values are less than 1 this means copolymerization of these species will show a tendency of randomness.

For styrene and styrene sulfonic acid case sulfonic acid shows a tendency to add its own species rather than styrene. This increases the chance of creating styrene sulfonic acid

blocks when they are copolymerized. Styrene sulfonic acid shows same tendency to add its own species and acrylic acid whereas acrylic acid shows a strong tendency to add styrene sulfonic acid rather than its own species.

**Table 2.1 Reactivity ratios found in the literature**

<b>Monomer 1</b>	<b>Monomer 2</b>	<b>r<sub>1</sub></b>	<b>r<sub>2</sub></b>	<b>Reference</b>
Acrylic Acid	Styrene	0.05	0.25	(23)
Acrylic Acid	Styrene	0.08	1.1	(23)
Acrylic Acid	Styrene	0.25	0.15	(23)
Acrylic Acid	Styrene	0.35	0.22	(23)
Acrylic Acid	Styrene	0.136	0.253	(23)
Acrylic Acid	Styrene	0.15	0.25	(23)
Acrylic Acid	Styrene	0.45	0.25	(23)
Acrylic Acid	Styrene	0.25	0.15	(23)
Acrylic Acid	Styrene	0.07	0.25	(24)
Acrylic Acid	Styrene	0.13	0.75	(24)
Acrylic Acid	Styrene	0.14	0.9	(24)
Acrylic Acid	Styrene	0.15	0.7	(24)
Acrylic Acid	Styrene	0.15	1.03	(24)
Acrylic Acid	Styrene	0.05	1.6	(24)
Acrylic Acid	Styrene	0.13	0.3	(24)
Acrylic Acid	Styrene	0.13	0.38	(20)
Acrylic Acid	Styrene	0.25	0.93	(25)
Styrene	Styrene m-sulfonic acid Fluoride	0.788	1.268	(23)
Styrene	Styrene p-sulfonic acid Fluoride	0.171	1.372	(23)
Acrylic acid	Sodium styrene sulfonate	0.1	1.0	(10)

## **2.2. Polymer Characterization**

Polymer characterization is one of the most important aspects of the polymer science and engineering applications. Since copolymers are produced for this study it is important to determine the composition of the samples. Also molecular weight determination is important because it affects the polymer properties. Determination of solubility and viscosity of polymers are necessary for polymer processing.

### **2.2.1. Fourier Transform Infrared (FTIR) Spectroscopy**

Infrared spectroscopy is a useful qualitative tool to determine composition of molecules which studies the interaction of the light with matter. (26) Infrared is a part of electromagnetic spectrum which corresponds to between visible and microwave regions. (27) When a molecule is exposed to light, molecule shows different absorption at different wavelengths. Like a fingerprint depending on the nature of the molecule.(26-28)

The output of the measurement in infrared spectroscopy is a plot of transmittance or absorbance of the infrared light versus wavenumber of the light. Instrument that is used for this measurement is called infrared spectrometer and Fourier Transform Infrared Spectrometer (FTIR) is the most commonly used type.(27)

When we measure infrared spectrum of a sample we start the measurement by measuring the background spectrum without putting the sample. This is necessary since the absorbance and transmittance values are the ratio of the light intensities without and with the sample. When we expose a sample to light, it will vibrate the chemical bonds in the sample

that makes change in the spectrum since functional groups of a molecule absorbs the light at the same wavenumber regardless of the rest of the molecule.(27)

$$A = \log (I_0/I) \quad (2.8)$$

$$T = I/I_0 \quad (2.9)$$

Absorbance (A) and transmittance (T) is given by equations (2.8) (2.9) where I is the light intensity with a sample in the infrared beam, and  $I_0$  is the light intensity measured with no sample in the infrared beam.(27) It is easy to relate the transmittance to absorbency.

$$A = \log (1/T) \quad (2.10)$$

It is possible to quantitatively determine the concentration of the functional groups in the sample by using Beer's law;

$$A = \epsilon lc \quad (2.11)$$

Where A is absorbance,  $\epsilon$  is absorptivity, l is pathlength, and c is concentration. When this equation is used spectrum must be plotted absorbency vs. wavenumber.(27)

Monomers that we have used have different functional groups and expected to show a significant effect on the polymer spectra as they are polymerized. Acrylic acid has a carbonyl group which shows very significant peak at around  $1700 \text{ cm}^{-1}$ . Styrene and styrene sulfonic acid has phenyl group which shows a significant peak at around  $690 \text{ cm}^{-1}$ .(27) Sulfonate group also shows different peak positions but most characteristic ones are usually observed

1100-1000  $\text{cm}^{-1}$  range due to symmetrical  $\text{SO}_3\text{H}$  groups and 1200-1000  $\text{cm}^{-1}$  range for unsymmetrical  $\text{SO}_3\text{H}$  groups.(29)

It is expected to qualitatively understand whether monomers participated into polymerization using these characteristic behaviors of the functional groups of the monomers.

### **2.2.2. Molecular Weight Determination of Polymers**

Many properties of polymers are highly dependent on the length of the macromolecular chain. Therefore, size determination of the polymer chains is very important from polymer characterization aspect. Since most of the polymerization techniques produce polydisperse samples, average molecular weight definitions are used in order to characterize a polymer samples. Most common average molecular weight definitions are number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ).

$M_n$  is calculated by using the molar fraction of the chains that has the same molecular weight. Sum of the products of molecular weight and molar fraction, gives the number average molecular weight of the polymer. If we consider molar fraction of the chains that has molecular weight of  $M_i$  is  $x_i$ , then number average molecular weight of the sample can be calculated by equation (2.12).

$$M_n = \sum x_i M_i \quad (2.12)$$

$M_n$  can also be written in terms of number of the molecules ( $N_i$ ) as in equation (2.13)

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad (2.13)$$

Weight average molecular weight is different from number average molecular weight by basically using weight fraction ( $w_i$ ) of the molecules that has molecular weight of  $M_i$ . So the  $M_w$  can be calculated using equation (2.14)

$$M_w = \sum w_i M_i \quad (2.14)$$

If we write weight fraction in terms of  $N_i$ , as in equation (2.15), then we can revise equation (2.14) and get equation (2.16)

$$w_i = \frac{N_i M_i}{\sum N_i M_i} \quad (2.15)$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (2.16)$$

Then  $M_w$  can be written in terms of  $M_n$  as in equation (2.17)

$$M_w = \frac{\sum x_i M_i^2}{M_n} \quad (2.17)$$

Using these two average molecular weights, we can estimate the molecular weight distribution of a polymer. If we consider a continuous polymer molecular weight distribution which is usually rightly skewed, then  $M_n$  represents the median of the distribution and  $M_w$  represents the average of the distribution. That's why these two molecular weights are very important especially when it comes to understanding the polydispersity of the polymer. For synthetic polymers, polydispersity index of the polymer, which is the ratio of  $M_w$  to  $M_n$ , is

usually greater than unity. A typical molecular weight distribution of a polydisperse polymer is given by Figure 2.4

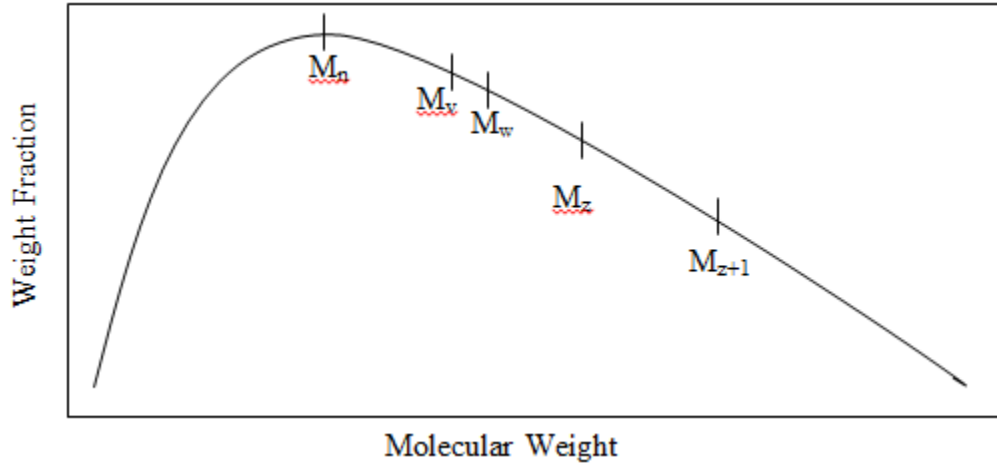


Figure 2.4 Typical molecular weight distribution of a polydisperse polymer (30)

As seen in the Figure 2.4 there are also different average molecular weight definitions such as viscosity average molecular weight ( $M_v$ ), z-average molecular weight and other higher degree average molecular weights. All higher degree average molecular weights are also used for understanding the distribution of the molecular weight from different aspects, whereas viscosity average molecular weight is used for different purpose. Basically viscosity average molecular weight is very close to  $M_w$  and best estimate for it. It is going to be given more details in following sections.

In order to measure the molecular weights defined above there are several techniques. Those techniques are mainly divided into two groups as, absolute and relative methods.

Commonly in the literature, absolute is used interchangeably with primary and relative is used as secondary methods.(30)

Most common absolute methods are light or neutron scattering, osmometry and mass spectrometry. Intrinsic viscosity and size exclusion chromatography (SEC) methods are the most common relative methods. It is not possible to obtain the all molecular weight types from one method. Actually each method provides one type of the molecular weight that is defined above except SEC. It is possible to obtain the whole distribution with this method; so we can obtain both  $M_w$  and  $M_n$  at the same time.(4,30)

Since in our research, we employed intrinsic viscosity and size exclusion chromatography more information will be provided about them.

#### **a. Intrinsic Viscosity Measurements**

It is also called dilute solution viscosity test in the literature. This method is based on the effect of the polymer chains on the solution viscosity. It is well known that polymer solutions have significantly higher molecular weights than solvents. There are some factors affecting the viscosity increase of polymer solutions such as, nature of the polymer (linear or branched, flexible or rigid, ionic or nonionic, etc.), nature of the solvent, temperature, concentration, and size of the polymer chains. (4)

**Table 2.2 Nomenclature of solution viscosity**

Name	Symbol	Definition
Solution Viscosity	$\eta$	
Solvent Viscosity	$\eta_0$	
Relative Viscosity	$\eta_r$	$\eta/\eta_0$
Specific Viscosity	$\eta_{sp}$	$\eta_r - 1 = \eta/\eta_0 - 1$
Reduced Viscosity	$\eta_{red} = \eta_{sp}/c$	$(\eta_r - 1)/c$
Inherent Viscosity	$\eta_{inh}$	$(\ln \eta_r)/c = (\ln (\eta/\eta_0))/c$
Intrinsic Viscosity	$[\eta]$	$[\eta] = \lim_{c \rightarrow 0} \frac{1}{c} \left( \frac{\eta - \eta_0}{\eta_0} \right)$

So the molecular weight of a sample can be estimated from its contribution to solution viscosity since it is dependent on the size of the molecular chains. This average estimation is defined as viscosity average molecular weight ( $M_v$ ). Before giving how we calculate the viscosity average value it is necessary to explain the theory of increase in the viscosity.(4,30)

So the question is why and how the polymer in the solution increases the viscosity? In order to understand this phenomenon, we can first consider small suspended particles in a solvent instead of polymer chains. When a solvent flows through a tube there will be a velocity gradient; the velocity is zero at the walls of the tube and reaches its maximum at the center of the flow. So the velocity of the flow will be different layer by layer. This is because of the retarding forces between the molecules of different layers. A suspended particle in this flow will cause collision of the liquid to its surface and rotational movement of the particle.

This effect will lead to a change in the velocity of the layers and in the viscosity of the suspension subsequently.(4)

Einstein related the change in the viscosity with the volume fraction of suspended particle ( $\phi$ ) and a factor that depends on the shape of the particles ( $\omega$ ) as shown in equation (2.18)

$$\frac{\eta}{\eta_0} = (1 + \omega\phi) \quad (2.18)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the suspension and solvent respectively.

It was shown by Einstein that for spherical particles and polymer random coils  $\omega$  is equal to 2.5. With relating the volume fraction  $\phi$  to molecular weight of the polymer we can relate the relative viscosity of the polymer ( $\eta/\eta_0$ ) to molecular weight of the polymer molecular weight.(4)

When it comes to polymers, in a solvent random coil shaped polymers act like suspended particles, because the solvent in the coil moves slower than the rest. Since most of the synthetic polymers are flexible chains and form random coil shape in the solvent this theory can be used to understand the viscosity increase in the polymer solutions.(4,30)

If we assume there is no overlapping and entangling of the polymer chains in solution we can write  $\phi$  of solvent swollen polymer at a concentration  $c$  as in equation (2.19)

$$\phi = \frac{LcV}{M} \quad (2.19)$$

where  $L$  is Avogadro's number,  $M$  is molecular weight of the polymer (assuming polymer is monodisperse), and the  $V$  is the volume of the each coil. If we insert all of these in equation (2.19), then we can get the equation (2.20)

$$\frac{1}{c} \left( \frac{\eta - \eta_0}{\eta_0} \right) = \frac{2.5LV}{M} \quad (2.20)$$

The ratio in the parenthesis, which is viscosity increase due to solute over the solvent viscosity, is also called specific viscosity. Specific viscosity divided by concentration actually gives increase in the viscosity free of concentration effect. But still this value does not give the effect of a single chain because it is not possible to get dilute enough to isolate any chain's flow from disturbance of others'. Even we can get very dilute solutions as we assumed, possibly we won't be able to measure the  $\eta - \eta_0$  difference. So in order to get this value we extrapolate our experimental data to find the addition of one single polymer chain to the solution viscosity. This value is called the intrinsic viscosity  $[\eta]$ .

$$[\eta] = \lim_{c \rightarrow 0} \frac{1}{c} \left( \frac{\eta - \eta_0}{\eta_0} \right) = \lim_{c \rightarrow 0} \frac{2.5LV}{M} \quad (2.21)$$

Flory and Fox, both theoretically and experimentally showed that under theta conditions relationship between molecular weight of the polymer and intrinsic viscosity is

$$[\eta]_{\theta} = K_{\theta} M^{0.5} \quad (2.22)$$

where  $K$  is a constant and depends on the polymer solvent pair. This is accurate for theta conditions only. However a theta condition is not necessarily the most practical

condition for intrinsic viscosity measurements. Then at a certain temperature and a solvent, equation (2.22) can be modified to equation (2.23)

$$[\eta] = KM^a \quad (2.23)$$

where  $a$  is constant that depends on the flexibility of the chain in a particular solvent at a particular temperature. This empirical equation is also known as Mark-Houwink-Sakurada (MHS) equation. This method is a very practical and easy method for homopolymers. For a variety of polymer solvent pairs Mark Houwink Sakurada constants are given in the literature. Using an Ubbelohde viscometer we can easily determine the intrinsic viscosity of the sample by measuring specific viscosity of several dilute solutions (as a rule of thumb concentrations less than 2 g/dL). By plotting specific viscosity over concentration vs. concentration and extrapolating concentration to zero we can obtain intrinsic viscosity of the sample and using equation (2.23) we can calculate viscosity average molecular weight of the sample.

#### **b. Size Exclusion Chromatography**

Size exclusion chromatography also known as gel permeation chromatography, is a very common technique that is used for molar mass measurements. Actually a chromatograph that is obtained by size exclusion technique provides the whole molecular weight distribution. Based on the distribution we can calculate number, weight and higher order molecular weight averages of polymer samples.(4,30,31)

Pioneering work on size exclusion chromatography was done by Porath and Flodin.<sup>(31)</sup> Using water soluble polymers and polydextrane gels they defined the separation porous gel medium. After these gel mediums were commercialized, a lot of study was made on the filtration of biopolymers, especially proteins. In 1964 separation of synthetic polymers in polystyrene gels by Moore from Dow Chemical. Since then size exclusion chromatography became a standard method for determination of molecular weight distribution of polymer samples.<sup>(31)</sup>

A basic schematic of size exclusion mechanism is given in Figure 2.5. As seen in the figure size exclusion mechanism consists of a solvent (also called mobile phase), injection system (pump), column(s), detectors, and software.

Initially a constant mobile phase flowing through the column is created. Via high precision pumps a dilute polymer sample solution, which is prepared with mobile phase, is injected into columns. These columns are filled with stationary phase which is basically bed of various sizes of pores. When polymer flows through these pores with mobile phase smaller molecules enter smaller pores while larger molecules can only enter larger pores. By entering smaller pores small molecules travels longer ways. Larger molecules are excluded faster than smaller molecules. As polymer chains exits the column a detector is used to detect the concentration.<sup>(30,31)</sup>

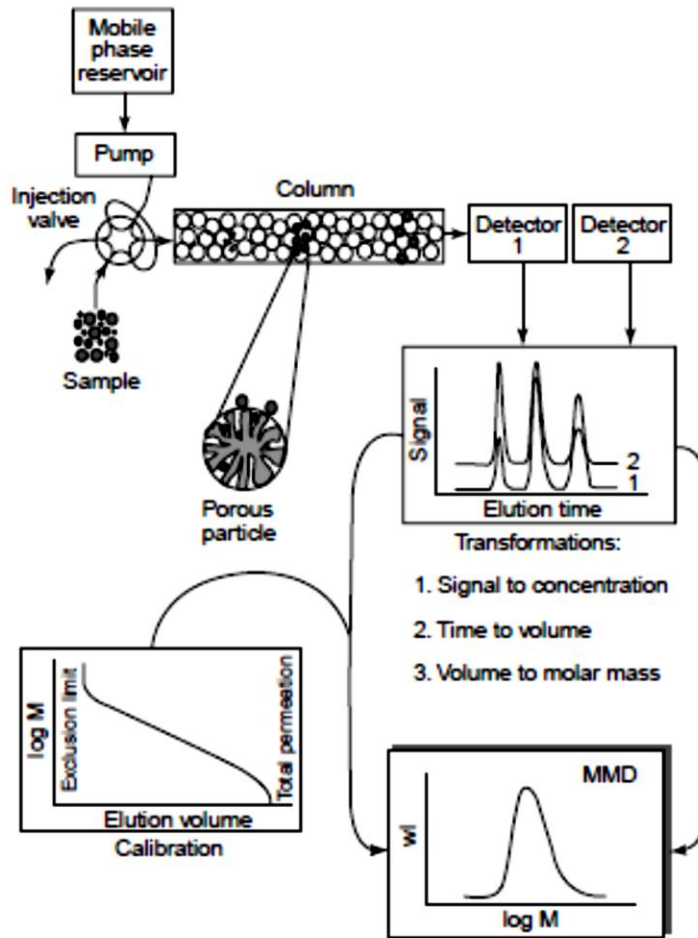


Figure 2.5 A schematic of size exclusion chromatography system (31)

Elution time of the chains can be used for interpretation of the molecular weight of the sample using either converting elution time to elution volume and calculating molar mass by elution volume or using a calibration standard polymer sample. (31)

Using a standard polymer sample for calibration curve, can lower the errors that might be caused by calculation of molar mass with elution volume. However it is important to choose an appropriate standard polymer. Since the volume in the solvent is highly

dependent on nature of the polymer that also can cause some error. Solvent should be a good solvent for both sample and standard species, to eliminate non-exclusion effects.(31)

Also to avoid errors it is important to use high quality pumps to create constant and reproducible flow rates since size exclusion experiments are highly dependent on exclusion time.(31)

Kato et al. (32) calculated Mark-Houwink-Sakurada coefficients for neutralized poly(acrylic acid) in aqueous NaCl solutions at 25 °C using size exclusion chromatography method for calculating the weight average molecular weights of the polymer samples.

### **2.2.3. Solubility of Polymers**

Solubility of the polymers is different from the solubility of the small molecules. When small molecule is dissolved in the solvent it diffuses into the solvent very quickly. However this is not the case for polymers. Polymer dissolving process consists of several steps. First solvent wets the polymer molecules on the surface and wetted polymer molecules starts to open space for incoming solvent molecules eventually all the polymer should be wetted and swelled before polymer molecules can diffuse into the solvent. This step can take very long time depending on the chemical nature of the solute and solvent, crystallinity and molecular weight of the polymer, and temperature. If the polymer is crosslinked, the polymer will only show swelling and will not dissolve in the solvent.(30,33)

Polarity of the solvent and polymer dramatically affects the solubility. Acrylic acid and styrene sulfonic acid both exhibit anionic nature. They show very good solubility

behavior in water as polymers but they are not soluble in most of organic solvents. Styrene is not a polar monomer and is insoluble in water. (12)

Thermodynamically, solubility of the polymers is governed by free energy of mixing,

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (2.24)$$

A negative value of  $\Delta G_M$  will lead mixing of the solvent and solute. In the equation (2.24) entropy of mixing always is positive and it is obvious it is not the part that defines the solubility. In order to get a negative  $\Delta G_M$  enthalpy should be low enough to mix the solvent and solute. Most of the case heat of mixing is positive for polymers and this is why solubility of the polymers is usually limited.(30,33)

It is possible to balance the solubility of the copolymers by using electrolyte monomers such as acrylic acid and styrene sulfonic acid. Solubility these types of polymers are highly dependent on pH of the solution. By controlling the pH of the solvent it is possible to increase the solubility concentration.(12)

Also the temperature of the dissolving is very important because polymer and solvent interactions highly dependent on the temperature and heat enthalpy of the mixing can be changed by changing the temperature of the system.(34)

#### **2.2.4. Viscosity of Polymer Solutions**

One of the most important parameters in polymer processing is the viscosity of the polymer solutions and melts. Solution viscosity is a little bit different than melt viscosity since the concentration of the polymer in the solution is also effective on viscosity.

We have to consider two distinguished regime in the case of solution viscosity. First we need to consider the dilute regime where polymers are far away from each other and viscosity of the polymer comes only from chain size and quantity. We have discussed the theory of the viscosity of dilute solutions in section 2.2.2.a. At higher concentrations polymer starts to interact each other and much higher they start to entangle and this increases the viscosity dramatically.(30,35)

Also the solution viscosity of the polyelectrolyte polymers highly depends on the pH of the solution. This is because of the pH affects the size of the polymer coils and this causes either increase or decrease in viscosity.

In this study we investigated the effect of styrene sulfonic acid, pH, and concentration on the solubility of poly(acrylic acid-co-styrene) copolymers. We also investigated the effect of pH on viscosity of the solutions at different concentrations.

### 3. EXPERIMENTAL

#### 3.1. Polymer Synthesis

##### 3.1.1. Chemicals

Acrylic acid (anhydrous, 99%, containing 180-200 ppm monomethyl ether hydroquinone as inhibitor), styrene (ReagentPlus®, ≥99%) and 4-styrenesulfonic acid sodium salt hydrate were used in various molar ratios as monomers. Monomers were obtained from Sigma Aldrich and used as received without further purification. Ammonium persulfate (reagent grade, 98%) and sodium metabisulfite (ACS reagent, ≥97.0%) were obtained from Sigma Aldrich and used as a redox catalyst system. Ferrous sulfate heptahydrate (Sigma Aldrich) was used as a reducing agent before the addition of the catalysts to the system in order to capture any residual oxygen. Hydroquinone (Sigma Aldrich) was used as inhibitor at the end of the reaction. Deionized water was used throughout.

For each reaction the total monomer amount was always kept at 1.34 mole and all monomer fractions were calculated as mole percentage. The initiator amount was 0.45 g/L in the first three experiments then later to reach desired molecular weights it was reduced to half then quarter amount in subsequent reactions. Monomer fractions and initiator amounts of each reaction is given in the Table 3.1.

0.1% ferrous sulfate solution was prepared using ferrous sulfate heptahydrate. For each 1 L reaction, 3 ml was used, and 1 mL was used for 330 mL batches. To quench the

polymerization, 0.1 g hydroquinone delivered into 330 mL batch and 0.3 g hydroquinone delivered into 1 L batches.

**Table 3.1 Monomer concentrations of polymerizations.**

Sample	Volume	AA	St	SSA	Initiator	Inhibitor
3AA100I15	1/3 L	100%			0.15 g	0.1 g
10AA100I45	1 L	100%			0.45 g	0.3 g
10AA90S10I45	1 L	90%	10%		0.45 g	0.3 g
10AA100I23	1 L	100%			0.23 g	0.3 g
10AA95S5I23	1 L	95%	5%		0.23 g	0.3 g
10AA90S5SSA5I23-1	1 L	90%	5%	5%	0.23 g	0.3 g
10AA90S5SSA5I23-2	1 L	90%	5%	5%	0.23 g	0.3 g
10AA90S5SSA5I23-3	1 L	90%	5%	5%	0.23 g	0.3 g
10AA88S5SSA7I23	1 L	88%	5%	7%	0.23 g	0.3 g
10AA75S10SSA15I23	1 L	75%	10%	15%	0.23 g	0.3 g
10AA70S10SSA20I23-1	1 L	70%	10%	20%	0.23 g	0.3 g
10AA70S10SSA20I23-2	1 L	70%	10%	20%	0.23 g	0.3 g
10AA100I11	1 L	100%			0.11 g	0.3 g
10AA65S10SSA25I11	1 L	65%	10%	25%	0.11 g	0.3 g
10AA65S10SSA25I23	1 L	65%	10%	25%	0.23 g	0.3 g

### 3.1.2. Tools

Solution polymerization was carried out in 1500 ml ACE Glass Inc. jacketed cylindrical flask with a head that has three 24/40 joints. Agitation was done by a glass stirrer using an overhead mixer (Barnant mixer series 10, model: 700 – 5400) with a glass stirring rod (Chemglass CG-2075) and Teflon blade. The stirring shaft was lubricated with mineral oil. Catalysts and styrene were delivered by syringe pumps (SAGE™ ATI Orion model 361). For catalysts a Becton-Dickson 30 ml luer-lock plastic syringe was used with plastic tubing and pipetting needle (Popper 18x6” pipetting needle blunt end with standard hub). For styrene 30 ml popper micro-mate interchangeable luer-lock hypodermic syringe was used with Teflon tubing without a needle. Acrylic acid was fed with a 125 ml addition funnel (Chemglass with pressure equalizing arm and 24/40 joints) in initial experiments. Subsequently, a Fluid Metering Inc. (FMI) Q type lab pump with Q2CKC head module and Teflon tubing was used. When sodium styrene sulfonic acid was added to the system, it was dissolved in acrylic and water mixture and delivered together with the FMI pump. All reactions were conducted under nitrogen atmosphere at  $65 \pm 2^\circ\text{C}$  and temperature was continuously controlled by a thermal couple. The reactor was kept at the same temperature using a water circulator. Ferrous sulfate and hydroquinone were added using Becton-Dickson 30 ml plastic syringes and 18x6” popper blunt end pipetting needle with standard hub at the same time.

### **3.1.3. Polymerization procedure**

Deionized water was added to the reactor. Then using the circulator, the reactor was heated to  $65 \pm 2$  °C. When system reached about 60 °C, 0.1% ferrous sulfate solution was added and the nitrogen flow was started. As the system reached reaction temperature, 1/3 of the ammonium persulfate solution was injected into the reactor. Then monomer feed started and was set to deliver all monomers in 90 minutes. Subsequently 1/3 of sodium metabisulfite solution was injected and catalyst feed was started and set to deliver all catalyst system in 120 minutes. When the catalyst feed finished, the reactor kept at the reaction temperature for an additional 90 – 120 minutes. Then hydroquinone solution was injected and the reactor was allowed to cool. A summary table of the recipe that was used for acrylic acid polymerization is given below by Table 3.2.

**Table 3.2 First recipe used for acrylic acid polymerization**

<b>Chemical</b>	<b>Amount (g)</b>
<hr/> Initial Charge <hr/>	
D.I. Water	781
0.1 FeSO <sub>4</sub> solution	3.00
<hr/> Monomer(s) (90 min) <hr/>	
Acrylic Acid	96.85
<hr/> Initial Catalyst Charge <hr/>	
D.I. Water	2.82
APS	0.15
D.I. Water	2.82
SMBS	0.15
<hr/> Delay Catalyst Charge (120 min) <hr/>	
D.I. Water	56.32
APS	0.30
D.I. Water	56.32
SMBS	0.30
<hr/> Inhibitor <hr/>	
Hydroquinone	0.30

### **3.2. Solvent Removal**

After polymerization, the polymer solutions were placed into a Fisher Scientific (model 280) vacuum oven at 90 °C, house vacuum was turned on 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. %. In order to overcome phase separation while redissolving copolymers, the copolymers were dissolved in water at  $60 \pm 5$  °C with

agitation. Next the samples were freeze dried using a Labconco FreeZone<sup>®</sup> 1 liter benchtop (Model 7740020) freeze dryer system with a Welch<sup>®</sup> Freezedry Pump<sup>™</sup> direct drive vacuum pump (W series Model 8917A-80). Then polymers were granulated using an 8 oz. glass mortar.

### **3.3. Characterization**

#### **3.3.1. FT-IR Spectroscopy**

After the polymers were granulated, they were first characterized by FT-IR spectroscopy. FTIR spectra were obtained using a Perkin-Elmer Spectrum 100 Spectrometer after a background scan (eight scan) was made for each sample. To understand the nature of the monomers by themselves in FT-IR, we obtained their spectra first. Then each polymer's spectrum was compared to those of the monomers'.

#### **3.3.2. Molecular Weight Determination**

##### **a. Intrinsic Viscosity Tests**

Molecular weight of poly (acrylic acid) homopolymer samples were determined by the intrinsic viscosity of the samples. Using an Ubbelohde viscometer (Cannon) viscosity measurements were conducted in dilute solution regime. The first two samples from first reaction were measured with a 1 – L202 caliber Cannon Ubbelohde viscometer with a kinematic viscosity calibration factor of  $0.009529 \text{ mm}^2/\text{s}^2$ , reaction 2, 4 and 13 samples were measured with a 0C – C989 caliber viscometer with a kinematic viscosity calibration factor of  $0.002990 \text{ mm}^2/\text{s}^2$ . In first two experiments a 0.05 molar NaCl aqueous solution used as a solvent. Other experiments were done with 0.3 molar NaCl aqueous solutions. All

experiments were performed at 25 °C and the temperature was kept constant by keeping viscometer in water bath (Haake L) circulator (Haake D3). The intrinsic viscosity experiments' parameters and Mark-Houwink constants are given below in Table 3.3 (23).

**Table 3.3 Parameters of intrinsic viscosity measurements and Mark-Houwink-Sakurada coefficients (23)**

Sample	Viscometer	Aqueous		
		Solution	K (ml/g)	a
3AA100I15	1 - L202	0.05 M NaCl	$7.35 \times 10^{-3}$	0.88
10AA100I45	0C - C989	0.3 M NaCl	$16.9 \times 10^{-3}$	0.75
10AA100I23	0C - C989	0.3 M NaCl	$16.9 \times 10^{-3}$	0.75
10AA100I11	0C - C989	0.3 M NaCl	$16.9 \times 10^{-3}$	0.75

Using the data obtained from experiments we plot the data as specific viscosity over concentration versus concentration. Then extrapolated each set of data to zero concentration to get the intrinsic viscosity. We obtained the linear regression line equations and the standard errors for intercept by using JMP (Version 9 for Windows).

### **b. Size Exclusion Chromatography**

Molecular weight of the all samples determined using Size exclusion chromatography. Polymer solutions were prepared using 0.1 M sodium nitrate aqueous solutions as solvent. Sodium nitrate solution was prepared using 18 MΩ pure water which is purified by Siemens Pure Lab Ultra. Standard polymers were prepared with 2mg/mL concentrations and polymer samples were prepared with 1mg/mL concentration.

As a standard polymer a mixture of narrow molecular weight poly(ethylene oxide) (<23000) and poly(ethylene glycol) (>23000) used. Three different colored vials were prepared with standard polymer mixtures. Molecular weight information of polymer in vials are given by Table 3.4.

**Table 3.4 Molecular weight of the standard polymers**

<b>Vial</b>	<b>M<sub>p</sub> (g/mol)</b>
<b>RED</b>	1258000
	116300
	12140
	615
<b>YELLOW</b>	909500
	62100
	3930
	194
<b>GREEN</b>	442800
	23520
	1500
	106

Polymers injected into columns using Waters 2695 Separations Module. Polymer Labs Aquagel-OH 40 and 60 columns were employed for exclusion. Columns have 300 mm length and 7.5 mm diameter. 40 and 60 shows the pore size of the columns in Å. Both columns have 8 µm particle sizes.

Then using a Waters 2414 Refractive Index Detector we monitored the exclusion of the polymers by defining the retention time of the polymers. Data was analyzed using Empower Pro software.

### **3.3.3. Solubility Determination**

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

Second approach was conducted after removal of the solvent. Polymer was dissolved in solvent again at different concentrations. It was observed whether solution was clear, almost clear, slightly cloudy, or cloudy. Also it was observed whether there was any color change or particle aggregation. These experiments were done in deionized water at about pH 4-5, and buffer solutions of pH 7 and pH 10. This way any possible pH effect was investigated.

Buffer solutions were prepared with a recipe that was found in the literature.(36). pH 6.9 solution was prepared with 0.025 M potassium phosphate monobasic (Fisher Scientific (white crystals) BioReagents<sup>®</sup>) and 0.025 M sodium phosphate dibasic (Acros Organics, 99+%, for analysis, anhydrous). pH 9.93 solution was prepared with 0.05 M sodium bicarbonate (Fisher Scientific, certified A.C.S.) and 0.05 sodium carbonate (Sigma Aldrich, anhydrous ACS Reagent).

### **3.3.4. Viscosity Measurements**

Viscosity of the samples was investigated at different concentrations and different pH levels. Cannon brand Ubbelohde 1 – L202 and 2B – L739 caliber viscometers were used with kinematic viscosity constants  $0.00290 \text{ mm}^2/\text{s}^2$  and  $0.5298 \text{ mm}^2/\text{s}^2$  respectively. All the measurements were performed at  $20 \text{ }^\circ\text{C}$  using a Haake L water bath with Haake D3 circulator. Before every measurement sample, the viscometer was left in the circulator for 15 minutes in order to reach the desired temperature. After every measurement the viscometers were rinsed with water and before every measurement viscometers were rinsed with the samples that were going to be measured.

## 4. RESULTS AND DISCUSSIONS

In this section, we will present the results of polymer composition, molecular weight determination, water solubility and viscosity measurement experiments.

### 4.1. Determination of Polymer Composition

This step is very important for copolymer production in order to make sure that all the monomers joined copolymerization as expected. For basic and fast results the Fourier Transform Infrared Spectroscopy was utilized.

Using FTIR we first produced the spectra of monomers. This is helpful to understand what to expect and what not to expect in the polymer spectrum. Since each of the vinyl monomers have different substituted group they are expected to give their characteristic peaks at different wavenumbers. Spectra of the monomers are given by Figure 4.1.

Acrylic acid spectrum (blue spectrum) shows a very significant peak at  $1695\text{ cm}^{-1}$  which is due to C=O bond in the carboxylic acid substituent group. Also in the  $1300\text{-}1200\text{ cm}^{-1}$  wavelength band there are two significant peaks which are due to C-O bond. The intense and broad peak that observed at the wavelength range approximately between  $3500\text{-}2500\text{ cm}^{-1}$  is due to OH stretch in the carboxylic acid side groups. This is a very wide and intense peak because acrylic acid monomer forms hydrogen bonding between OH groups. Also in this range C-H stretches are effective but OH stretching masks the most of the peaks only the highest points are seen. We see a significant peak at the  $1635\text{ cm}^{-1}$  which is due to C=C bond in the vinyl monomer. Therefore it is expected that will disappear in the poly (acrylic acid) polymer.

When we look at the other monomers' spectra we see they have their own significant peak positions. Since they are all vinyl monomers they also show some similarities. For instance, since they all have C=C double bond, they all have a peak at 1660-1630 $\text{cm}^{-1}$  wavenumber range. However to understand whether they polymerized with other monomers we need to determine their characteristic peaks.

Styrene has a series of peaks at 3082, 3059, and 3027  $\text{cm}^{-1}$  wavenumbers. These peaks are due to C-H stretches in the phenyl ring. We see the same peaks on the styrene sulfonic acid spectrum as well since it has phenyl side group too. Also styrene spectrum shows the most significant peak at 690  $\text{cm}^{-1}$  wavenumber which is due to benzene ring bending. The same peak exists in the styrene sulfonic acid monomer as well but not as significant as styrene.

Styrene sulfonic acid shows similar behavior like styrene monomer except it has a series of peaks at the range of 1200-1150  $\text{cm}^{-1}$  wavenumber range due to sulfonate group attached to phenyl ring. This side groups the most significant peak of the monomer at 1190  $\text{cm}^{-1}$  wavenumber. So using all these characteristic peak position information we will be able to get a very basic idea about addition of the monomers to polymer very quickly.

If we analyze the spectra of the poly (acrylic acid) samples in Figure 4.2, we see that it is in agreement with the monomer spectrum. We have again a strong peak that is characteristic of carbonyl groups at 1700-1695  $\text{cm}^{-1}$  wavenumber range. Also the peak that was due to vinyl carbon – carbon double bond at 1635  $\text{cm}^{-1}$  wavelength has disappeared from the poly acrylic acid spectra and as expected we can still see the peaks due to OH groups, C-

O groups and C-H groups. The difference between the polymers is the initiator amount and they are not supposed to show any significant difference in the spectrum and as expected they are almost identical.

In Figure 4.3 we can observe the change in the spectrum that addition of styrene causes. Mostly the spectra show no significant difference than poly (acrylic acid) samples' except at the 690  $\text{cm}^{-1}$  wavenumber range. In that range acrylic acid styrene copolymers show a peak that is due to phenyl ring bending which is a characteristic peak position for styrene monomer as we mentioned above. We are not able to see the peaks due to C-H bending in the phenyl ring because O-H bending of the carboxylic acid group has a more intense and broad peak in the range.

We then decided to add styrene sulfonic acid to polymer. As a first step we polymerized 90 mole% acrylic acid, 5 mole% styrene, 5 mole% styrene sulfonic acid. We repeated this polymerization three times since first time we got a slightly cloudy solution and doubted there could be a small problem in the steadiness of the styrene flow. The spectra of these three samples are given in Figure 4.4 It is hard to say if they have really a significant difference in the styrene component without an overestimation but 3<sup>rd</sup> repeat has a more significant phenyl bending peak comparing to other two. Other than that we can see there is a significant change in the spectra at the wavenumber range 1200-1000  $\text{cm}^{-1}$  compared to spectra in Figure 4.3. This change is due to sulfonate addition to monomer.

Also we can see the change caused by sulfonate group in Figure 4.5 more obviously since spectra of the polymers that have different amount of styrene sulfonic acid monomer

but the same amount of styrene. When we achieved to the synthesis of water soluble polymer with a content of 5 mole% styrene by adding SSA as a termonomer, subsequently we started to try to make a water soluble polymer with 10 mole% styrene and we added 15, 20 and 25 mole % styrene sulfonic acid to the system. When we compare the spectra of the 10 mole% styrene copolymers in Figure 4.6, we first realize that peaks due to sulfonate group increase its effect on the shape of the spectra especially in the 1200-1000  $\text{cm}^{-1}$  wavenumber range.

Overall we were be able to determine whether the polymers have the repeat units that we wanted by Fourier Transform Infrared spectroscopy. Even though we are not able to tell what the composition is quantitatively it is still a useful tool if we know the substituent group's typical behavior in FTIR.

**Table 4.1 Monomer feed compositions of polymer samples**

Sample	AA	St	SSA
3AA100I15	100%		
10AA100I45	100%		
10AA90S10I45	90%	10%	
10AA100I23	100%		
10AA95S5I23	95%	5%	
10AA90S5SSA5I23-1	90%	5%	5%
10AA90S5SSA5I23-2	90%	5%	5%
10AA90S5SSA5I23-3	90%	5%	5%
10AA88S5SSA7I23	88%	5%	7%
10AA75S10SSA15I23	75%	10%	15%
10AA70S10SSA20I23-1	70%	10%	20%
10AA70S10SSA20I23-2	70%	10%	20%
10AA100I11	100%		
10AA65S10SSA25I11	65%	10%	25%
10AA65S10SSA25I23	65%	10%	25%

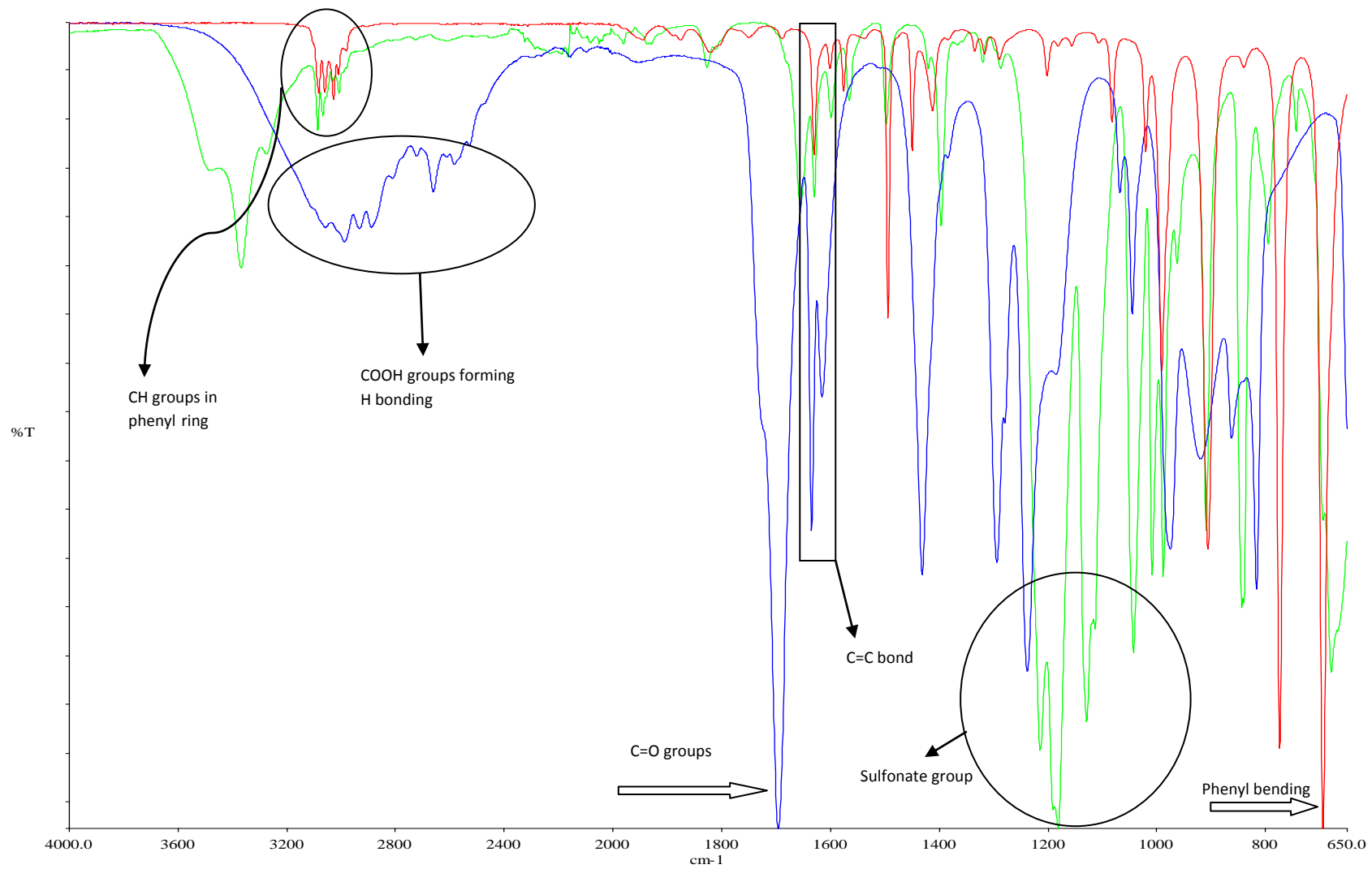


Figure 4.1 FTIR spectra of monomers (Blue: Acrylic Acid, Red: Styrene, Green: 4-vinylbenzene sulfonic acid sodium salt)

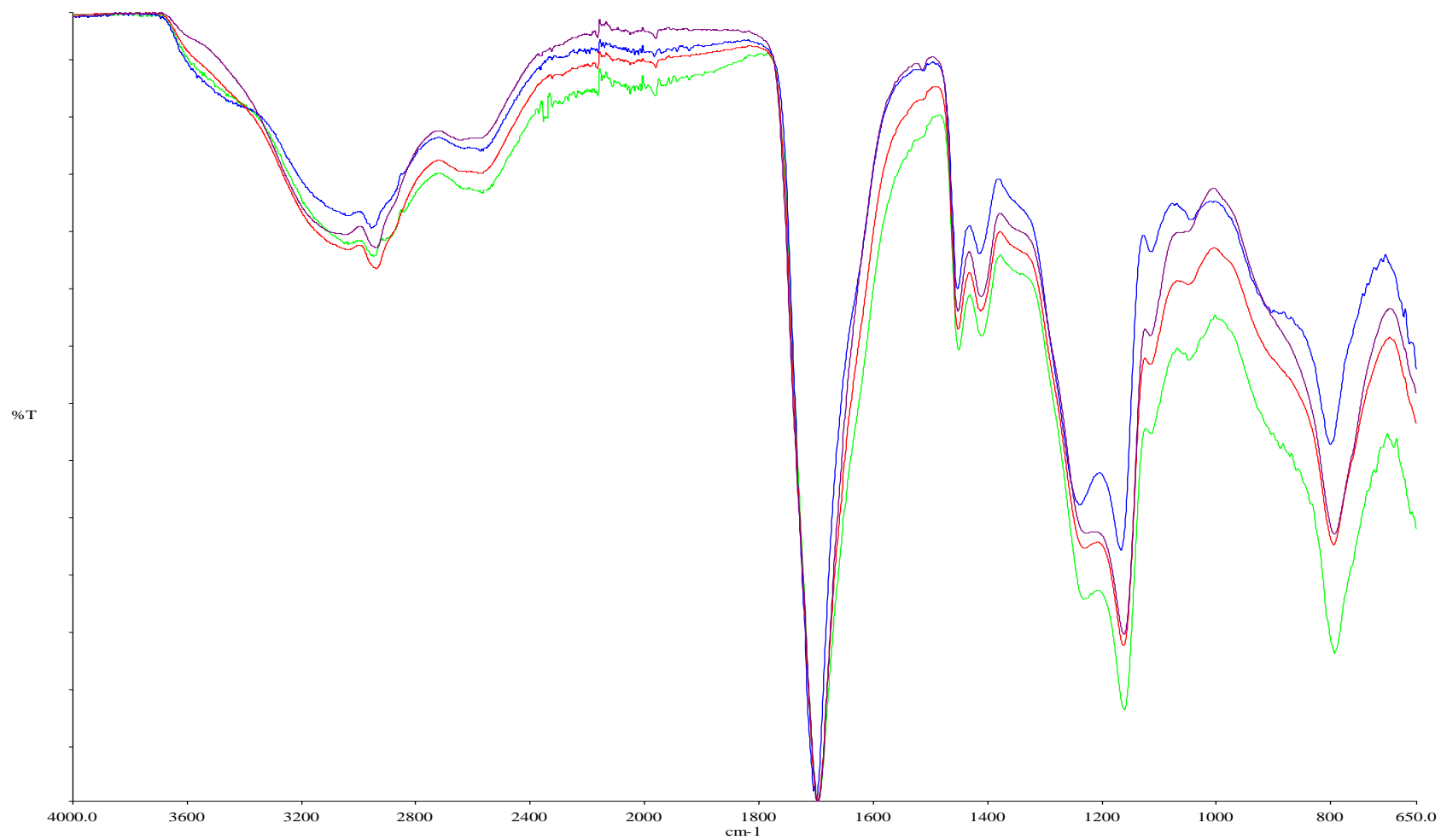


Figure 4.2 FTIR Spectra of the Poly (acrylic acid) samples (Green: 3AA100I15, Blue: 10AA100I45, Red: 10AA100I23, Brown: 10AA100I11)

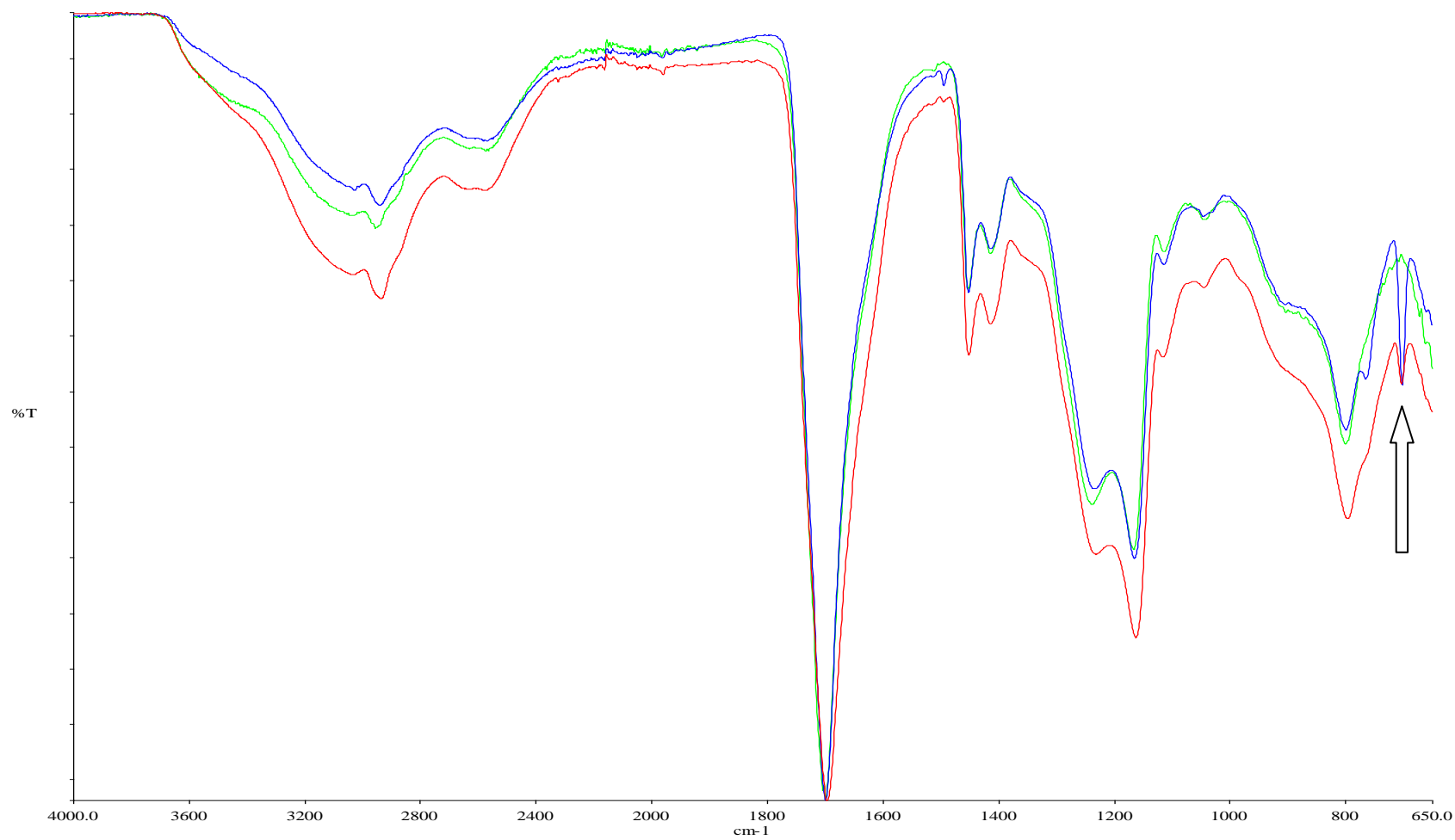


Figure 4.3 Comparison of the FTIR spectra of acrylic acid homopolymer and copolymers with styrene (Green: 10AA100I45, Blue: 10AA95S10I45, Red: 10AA90S5I45)

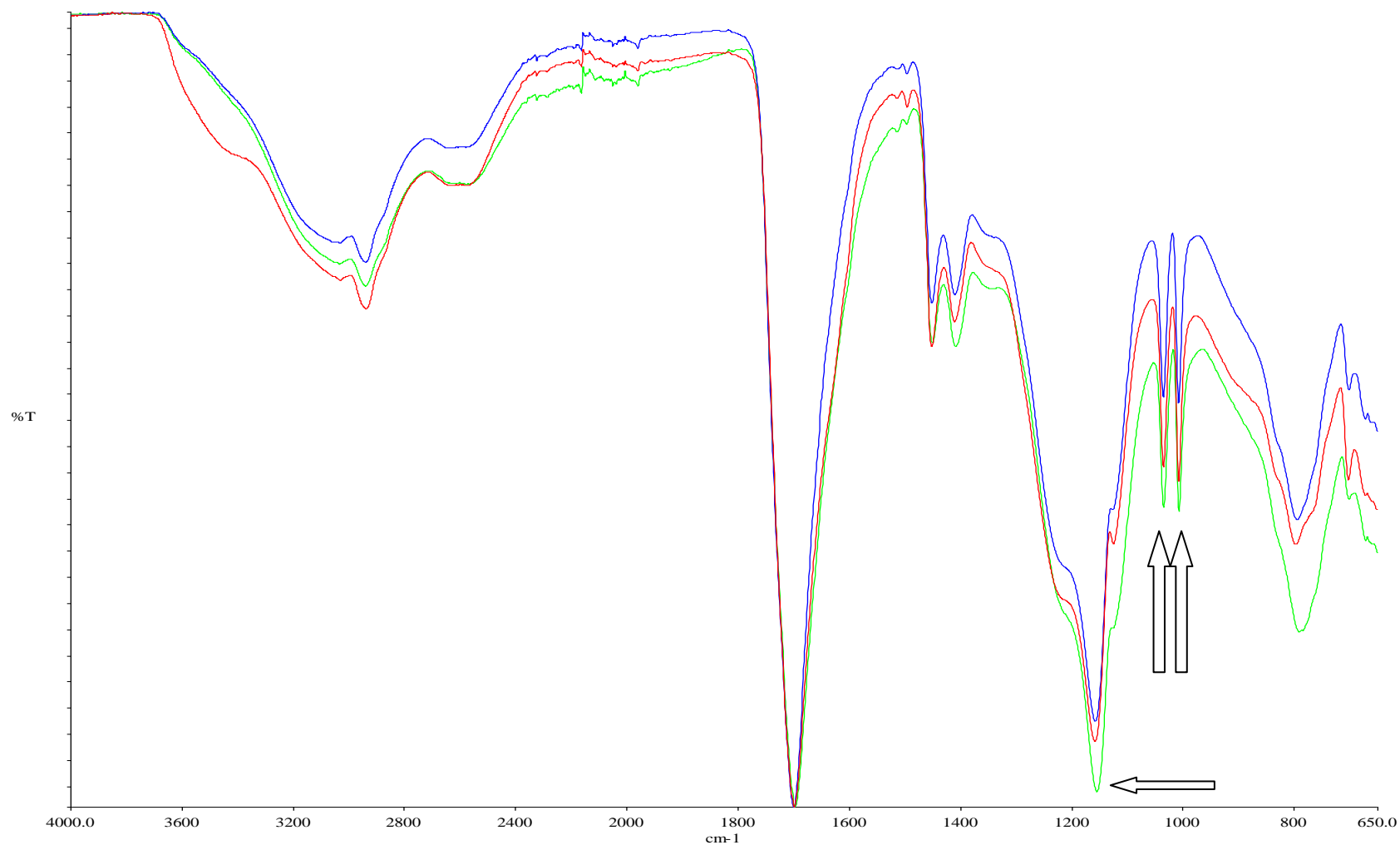


Figure 4.4 Comparison of the three samples that consist of 90 mole% acrylic acid, 5 mole% styrene, 5 mole% styrene sulfonic acid (Green: 10AA90S5SSA5I23-1<sup>st</sup>, Blue: 10AA90S5SSA5I23-2<sup>nd</sup>, Red: 10AA90S5SSA5I23-3<sup>rd</sup>)



Figure 4.5 Comparison of FTIR spectra of copolymers that has 5 mole % styrene and 0, 5 and 7 mole % styrene sulfonic acid (Green: 10AA95S5I45, Blue: 10AA90S5SSA5I23-3<sup>rd</sup>, Red: 10AA88S5SSA7I23)



Figure 4.6 FTIR spectra of copolymer including 10 mole% styrene and 0, 15 and 20 mole % styrene sulfonic acid (Green: 10AA90S10I45, Blue: 10AA75S10SSA15I23, Red: 10AA70S10SSA20I23)

## **4.2. Molecular Weight Determination**

It is well known that both thermodynamic and mechanical polymer properties are highly dependent on the average molecular weight and molecular weight distribution. That's why it is important to determine average molecular weight and distribution from characterization aspect.

Poly (acrylic acid) samples were synthesized in order to determine the average molecular weight of the polymers that can be produced by the recipe that is given before. Viscosity average molecular weights of these samples were determined by dilute solution viscosity measurements. Copolymer molecular weights could not be determined by viscosity measurements since the Mark-Houwink-Sakurada coefficients are not given in the literature. Therefore determination of copolymer molecular weights was done by size exclusion chromatography.

### **a. Dilute Solution Viscosity Measurements**

Using Ubbelohde viscometer, we measured the average flow time of solvent and the polymer solutions and calculated the specific viscosity of the samples and plotted the specific viscosity over concentration vs. concentration as given in the Figure 4.7. The intercept of the regression line gives the intrinsic viscosity. The equations of the regression lines are given in Table 4.2.

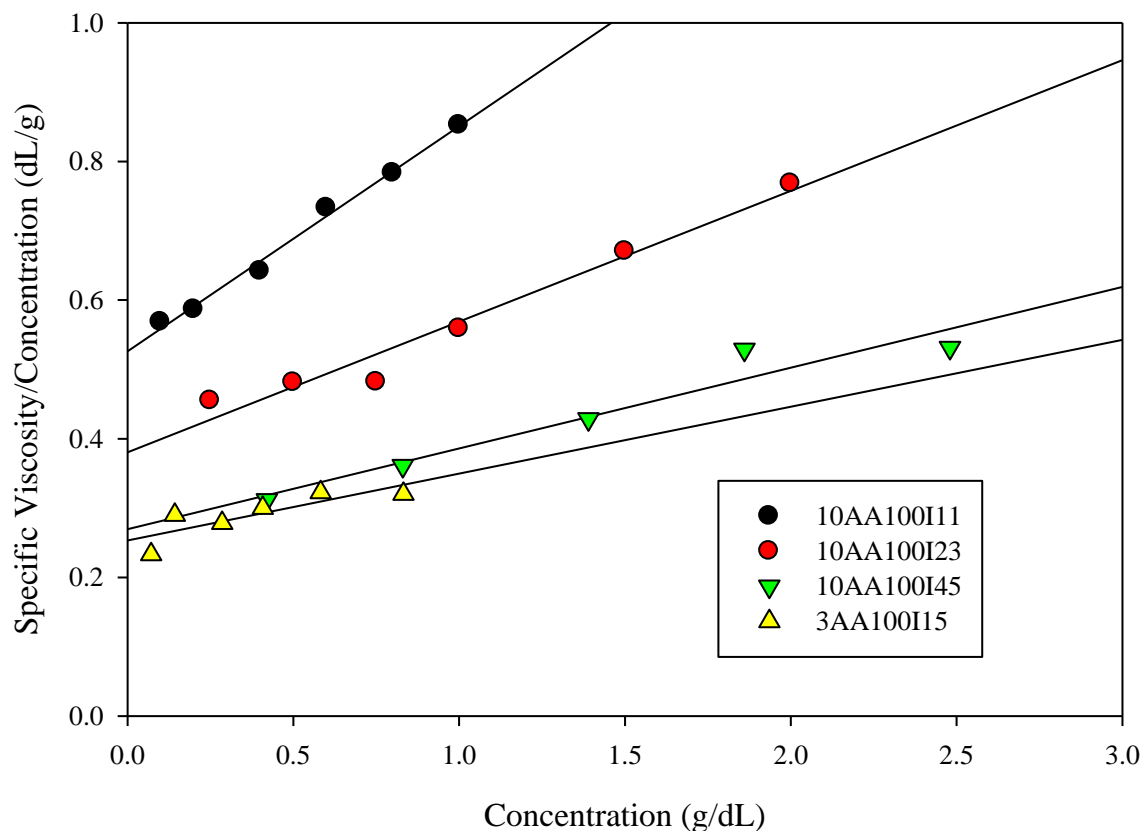


Figure 4.7 Intrinsic viscosity measurements of the poly acrylic acid samples

As seen in the plot, 3AA100I15 and 10AA100I45 samples give very close intrinsic values. They actually have the same initiator concentration but have different polymerization batch volumes. For first one we had some heating problems and it gave lower molecular weight as seen in the Table 4.3. We repeated the same recipe in 1 L batch and maintained the temperature constant, which resulted in higher molecular weight. Also for intrinsic viscosity measurements we used different concentrations of salt for these two samples. Even though they have very close intrinsic viscosity values they give quite different molecular weight. For

comparison of the samples on the plot it is important to note that all samples were measured in same solvent except 3AA100I15.

Sample 10AA100I45 is polymerized with the amount of the initiator of the initial recipe. Later we used half amount of initiator in 10AA100I23 and quarter in 10AA100I11. They showed significant differences in intrinsic viscosity values because molecular weight is expected to be related to initiator amount inversely. When we reduced the initiator amount to half we were expecting to get a double molecular weight but as seen in the Table 4.3, this is not the case.

**Table 4.2 Regression line equations of the lines in Figure 4.7**

<b>Sample</b>	<b>Equation</b>	<b>R<sup>2</sup></b>	<b>Standard Error of intercept</b>
3AA100I15	$y = 0.0969x + 0.2525$	0.6814	0.015
10AA10045	$y = 0.1169x + 0.2687$	0.9277	0.030
10AA10023	$y = 0.1917x + 0.3766$	0.9685	0.020
10AA10011	$y = 0.3183x + 0.5288$	0.9923	0.008

Using Mark-Houwink-Sakurada equation (2.23), which relates the molecular weight to intrinsic viscosity, we can calculate the viscosity average molecular weight  $M_v$ . Mark-Houwink-Sakurada constants and calculated molecular weights are given on Table 4.3.

**Table 4.3 Intrinsic viscosity measurement parameters and results**

Sample	Solvent	$K \times 10^3$ (mL/g)	a	$[\eta]$ (dL/g)	$M_v$
3AA100I15	0.05 M NaCl	7.35	0.88	0.25	10300
10AA100I45	0.3 M NaCl	16.9	0.75	0.27	18600
10AA100I23	0.3 M NaCl	16.9	0.75	0.38	29400
10AA100I11	0.3 M NaCl	16.9	0.75	0.53	45900

While doing size exclusion experiments we also ran these poly (acrylic acid) samples as well in order to compare the methods. However we saw that results from size exclusion are higher than viscosity measurements by an order of magnitude. This result was unexpected and we checked the procedure of Kato et al., (32) their procedure includes a neutralization step in order to eliminate the ionic forces in the solution. Since we have prepared the solutions using polymers as they are, they keep their polyelectrolyte nature in the solution. That's why Mark-Houwink-Sakurada coefficients reported by Kato et al. are not accurate for poly (acrylic acid) unless polymer is neutralized.

#### **b. Size Exclusion Chromatography (SEC)**

Even though intrinsic viscosity measurement is an easy and practical tool for homopolymers, it is not useful for copolymer samples. Size exclusion chromatography technique can be used for copolymer samples if a good standard polymer for calibration is available.

Since our samples are water soluble in the dilute regime we used water soluble polymer mixtures as standard. These mixtures consist of poly (ethylene glycol) and poly (ethylene oxide) at different molecular weights with very narrow distributions as given in details in Chapter 3. The retention time of the standard polymer mixtures are given by Table 4.4

**Table 4.4 Retention times of the standard polymer in SEC**

<b>Vial</b>	<b>M<sub>p</sub> (g/mol)</b>	<b>Retention Time (min)</b>	<b>Calculated Molecular Weight (g/mol)</b>
<b>RED</b>	1258000	11.777	1339475
	116300	14.332	103486
	12140	17.053	14513
	615	18.998	518
<b>YELLOW</b>	909500	12.033	901297
	62100	15.226	61229
	3930	18.059	3602
	194	19.358	201
<b>GREEN</b>	442800	12.619	422243
	23520	16.365	28019
	1500	18.64	1182
	106	19.5	134

Using the retention time of the standard polymer given on Table 4.4 we fit a third degree polynomial calibration curve as given in Figure 4.8.

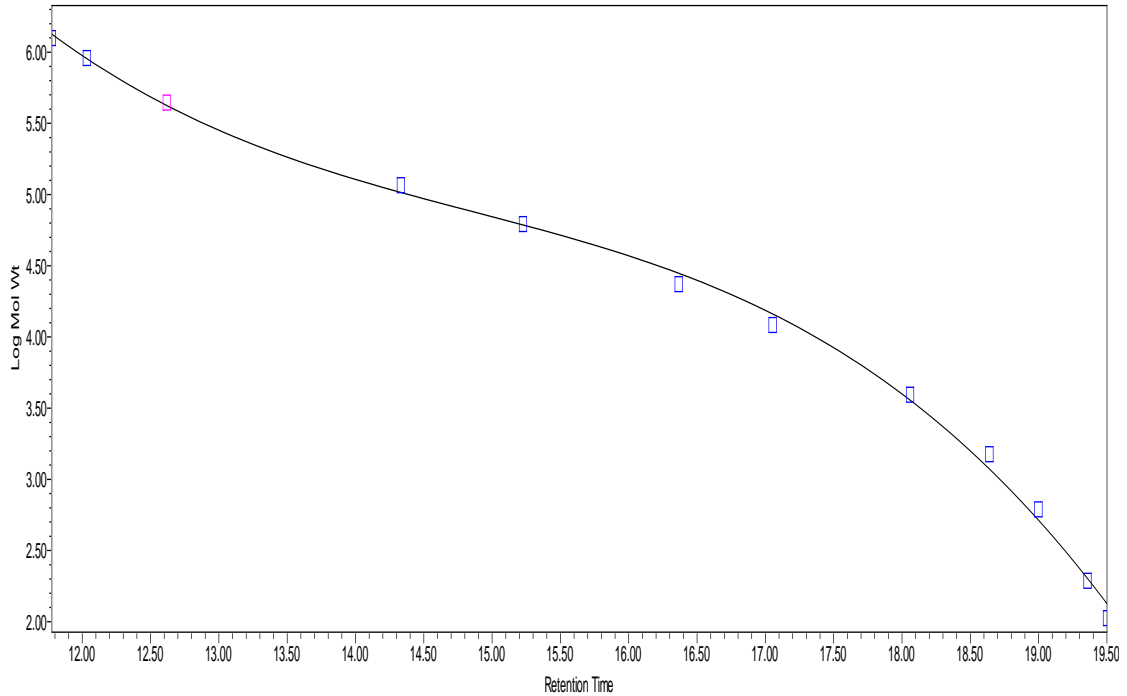


Figure 4.8 The  $\log_{10}$  of the molecular weight is plotted vs. the retention time. A third degree polynomial SEC calibration curve was fit to the data in Table 4.4.

Next we ran the samples using the calibration curve and obtained a bimodal distribution for all samples. As an example, the distribution of the sample 10AA100I23 is given in Figure 4.9. The intense peak in the distribution is the polymer portion and the smaller peak represents the oligomers that were present in the polymer sample. Excluding the small oligomer peak, our polymers samples gave high molecular weight.

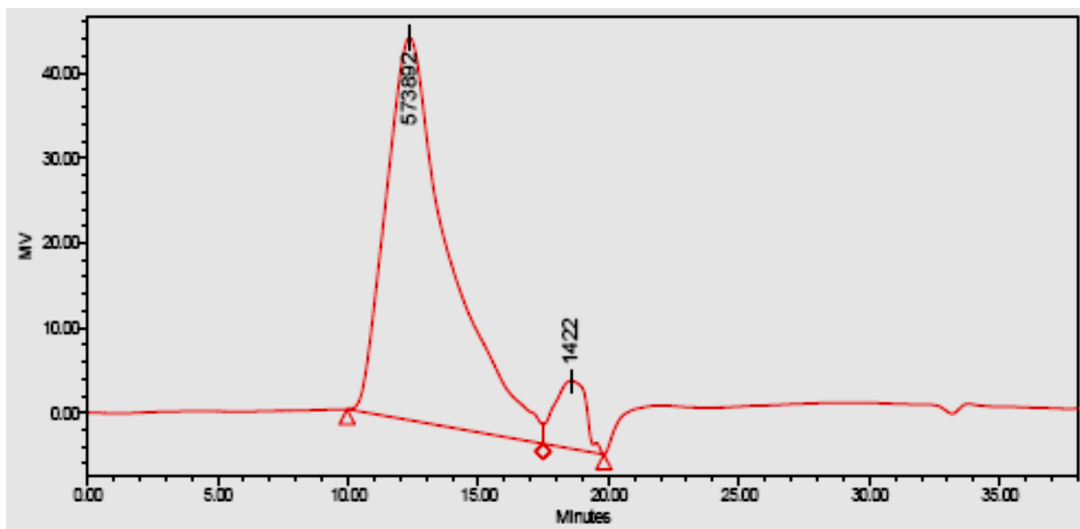


Figure 4.9 Size exclusion chromatography result for 10AA100I23 sample

Table 4.5 presents the molecular weight values of the samples that we obtained from SEC. Since we have two peaks in every sample we split two peaks for molecular weight calculations. So 1<sup>st</sup> peak means the intense peak and 2<sup>nd</sup> peak means the smaller peak corresponds to oligomers.

**Table 4.5 Summary of the SEC results and comparison with intrinsic viscosity**

results

			$M_n$	$M_w$	$M_p$	$M_v$	PDI
PAA	<b>10AA100I45</b>	1st Peak	95000	284000	419000	18600	2.97
		2nd Peak	1004	2380	657		2.37
	<b>10AA100I23</b>	1st Peak	121000	370000	573000	29400	3.04
		2nd Peak	941	2190	1422		2.33
	<b>10AA100I11</b>	1st Peak	179000	403000	634000	45900	2.25
	PAA+S	<b>10AA90S10I45</b>	1st Peak	173000	369000	490000	
2nd Peak			790	3786	814		4.79
<b>10AA95S5I23</b>		1st Peak	101000	358000	976000		3.54
		2nd Peak	1253	2954	1809		2.37
PAA+S+SSA	<b>10AA90S5SSA5I23</b>	1st Peak	154000	440000	592000		2.84
		2nd Peak	734	1463	1292		1.99
	<b>10AA88S5SSA7I23</b>	1st Peak	104000	173000	178000		1.67
	<b>10AA75S10SSA15I23</b>	1st Peak	138000	267000	357000		1.93
		2nd Peak	1892	2577	885		1.36
	<b>10AA70S10SSA20I23</b>	1st Peak	156000	283000	350000		1.81
		2nd Peak	252	315	219		1.24
	<b>10AA65S10SSA25I23</b>	1st Peak	131000	217000	170000		1.65
2nd Peak		259	347	216		1.33	

It is obvious from the results that the weight average molecular weights of the samples are not significantly different than each other even though we decreased the initiator amount. Also as mentioned above, the SEC results conflict with intrinsic viscosity

measurements. In figure 4.10 we can obviously see that there is an order of magnitude difference between SEC and intrinsic viscosity results. To show that with changing the Mark-Houwink coefficients can give closer results we only take a lower a value which is 0.62 instead of 0.75. This estimate data set is given by the green series in figure 4.10. It is obvious that we can get closer values to SEC results by changing a values at natural pH.

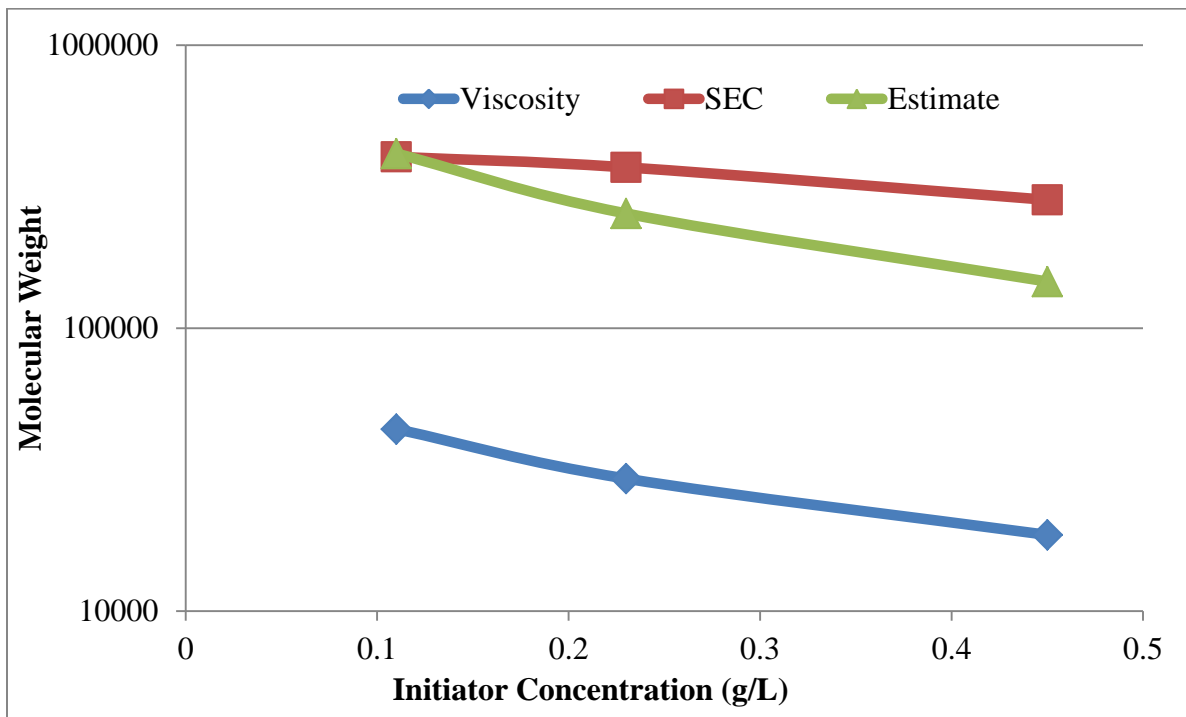


Figure 4.10 Comparison of SEC and intrinsic viscosity results

Since the reference from which we obtained the Mark-Houwink-Sakurada constants uses similar standard polymers in SEC it is expected to have similar results in viscosity test. However as we explained above Kato et al. neutralized the polymer and calculated the Mark-Houwink-Sakurada coefficients. That's why the coefficients didn't give accurate results.

Because of these it seems it is more reasonable to trust SEC results rather than viscosity measurement results.

### **4.3. Solubility of Polymers**

Solubility of the polymer samples are determined qualitatively by observing the color of the solutions. We followed two different identification methods to determine the solubility of the polymer samples as given in detail in section 3.3.3. Since polymer that we produced is used as it is polymerized in solution without further purification or solidification, the solubility in that state is very important in the first step. Secondly after removing the solvent and residual monomers, we dissolved polymers at different concentrations and pH levels and then determined solubility again.

#### **a. Solubility of the polymerization batch as polymerized**

After cooling the polymerization batch to room temperature, we defined them as clear, slightly cloudy, cloudy or milky. To visualize the results a bubble plot is prepared as in Figure 4.11.

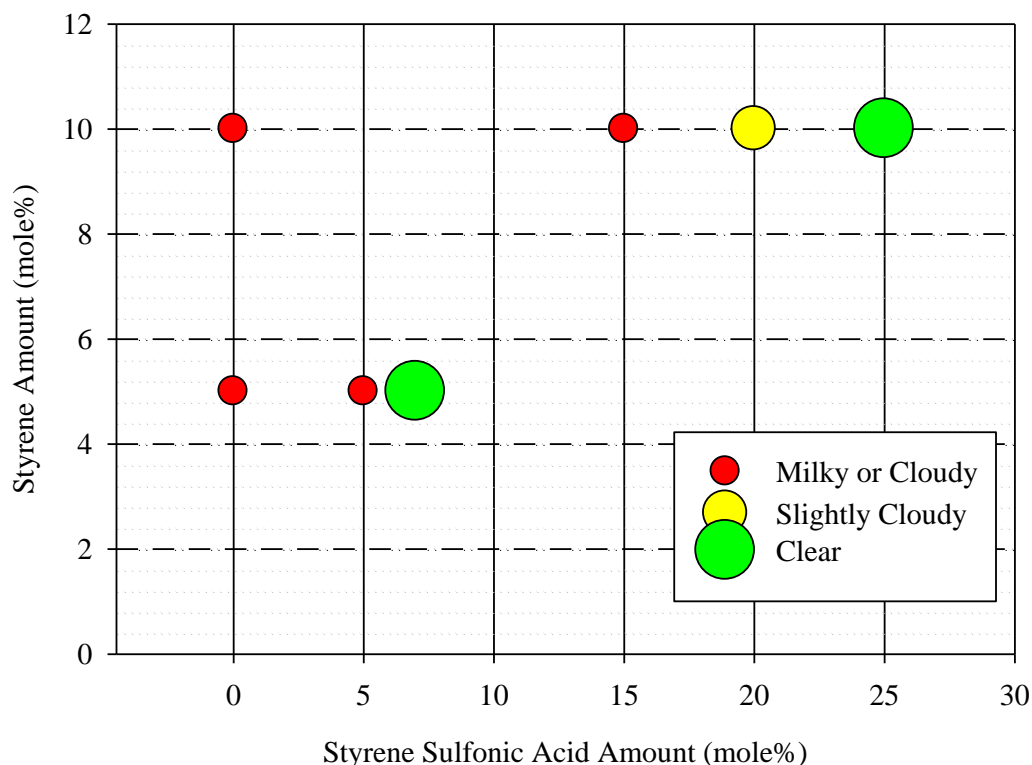


Figure 4.11 Solubility dependence of the copolymers on styrene sulfonic acid amount as they were polymerized.

It was very obvious from the batch colors that, as we increase the styrene sulfonic acid amount in the polymer, we obtained clearer solutions. This is very good for polymer processing since the polymer is used as it is synthesized, in solution. The calculated concentration of the solution in this form is approximately 10 weight%.

Once we obtained the clear solutions, we did not go further in SSA concentration so we don't know if there is a balance point that after that reduced acrylic acid amount inversely

affects the solubility. However these results by themselves showed us we can definitely improve the solubility of the polymer by adding styrene sulfonic acid to some extent.

### **b. Solubility of Polymers at Different pH and Concentrations**

After polymerization we removed the solvent and then tried to dissolve the polymer samples at different concentrations and pH values. This way we investigated the soluble concentration of the polymers, even though they are not soluble right after polymerization. Similar to polymerization batch evaluations we again used qualitative definitions; clear, slightly cloudy, cloudy and milky. Also since the polymers that we produced are classified as polyelectrolyte in the literature, we thought the pH of the solvent may change the solubility behavior of the polymers as well.

In Figure 4.12 we present 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 we have chosen and we put the highest concentration that gave a clear solution as the soluble point. As we increase the pH of the solvent, we see that the concentration in which solution is a clear, increases. We also mentioned previously we can see that as we increase the SSA amount in the polymer solubility significantly increases.

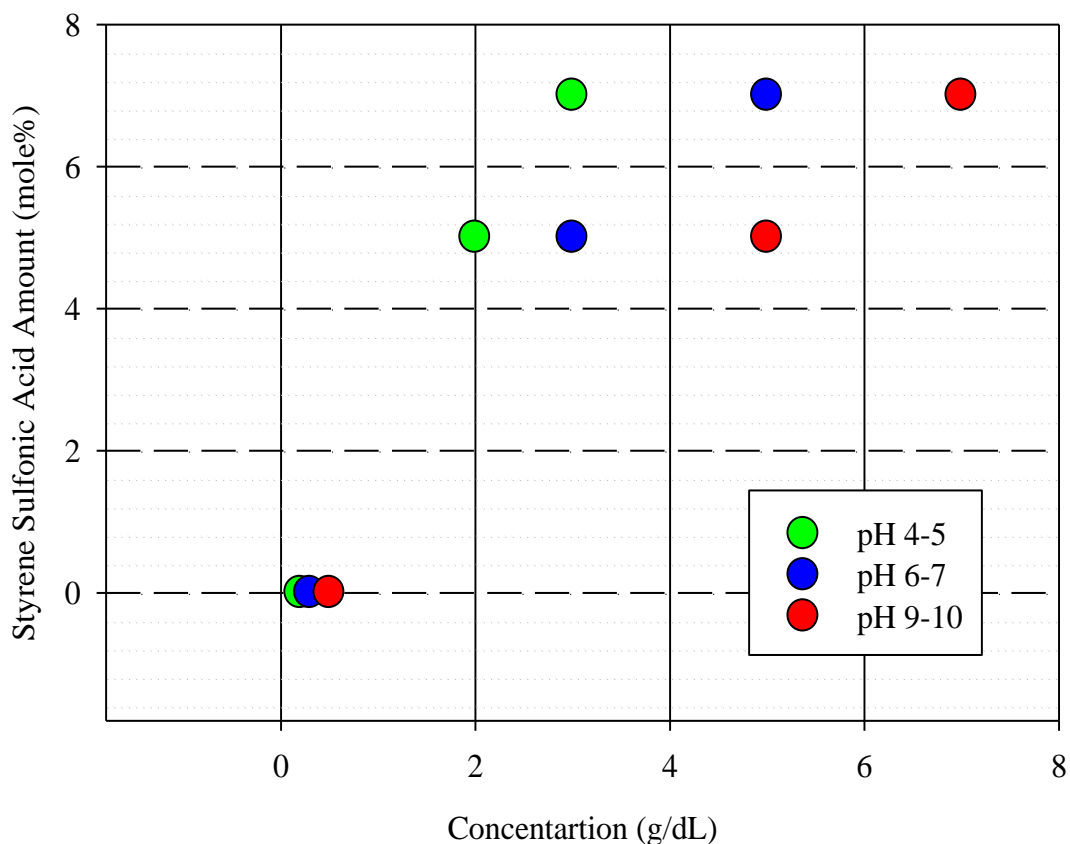


Figure 4.12 5 mole% styrene polymer samples' solubility at various pH and concentrations.

Each point indicates the upper level of solubility.

For 10 mole % styrene polymer samples, solubility of the polymers definitely increases with increasing SSA amount. However after removal of the solvent and dissolving at different concentrations we could not get clear solutions at higher concentrations as we had with 5 mole% styrene samples. Even the increasing pH of the solvent does not help as much as it did before. This can be because of the high styrene amount that causes insolubility in water. It can be due to the desire of the styrene units to form clusters to minimize their contact with water.

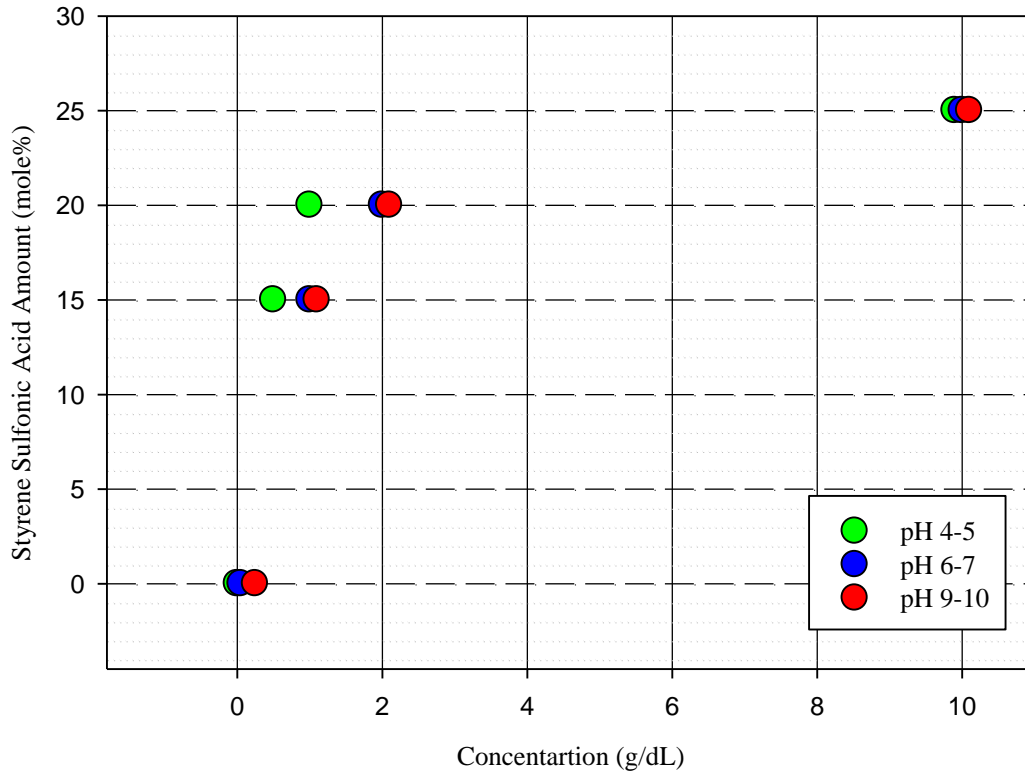


Figure 4.13 10 mole% styrene polymer samples' solubility at various pH and concentrations

Increasing styrene amount in the polymer always lead reduced solubility in water, but this is not enough to understand the phenomena since some of the polymer batches are clear right after polymerization. The concentration of the batch after polymerization is approximately 10 weight%. So there must be something else going on in the dissolving process. The nature of the polymers is strongly ionic. However, the styrene units are highly water insoluble and, might form clusters in the polymer when we remove the solvent. It is not easy to disperse these clusters when the polymer is redissolved without using high energy.

When we look at the 5 mole% styrene samples again we see they cannot reach the batch concentration as well from solubility perspective. For instance the 7% SSA with 5% styrene sample formed a clear solution right after polymerization but the highest concentration that we reached after solvent removal was 3 g/dL in water. This value decreases significantly when we increase the styrene amount.

We had a similar problem when we tried to dissolve at high concentrations (20- 25 wt%) the polymer samples after vacuum oven drying. What we observed was that the solution formed different phases which had different viscosity. When we increased the temperature up to 65 °C we produced polymer solutions with more uniform viscosity distribution.

Another important result that we obtained from solubility experiments when we dissolved the samples in pH 10 buffer solvents we observed a color change in the solutions. A brownish color appeared. We don't know exactly what causes this scattering in the solution but it might be due to clustering effect of a few phenyl groups in that particular solvent.

#### **4.4. Viscosity of the Polymer Samples at Various pH and Concentration Values**

We have investigated the viscosity behavior of the polymer sample solutions at certain concentration and pH values. Our samples showed quite similar behavior at different pH values. As an example of typical graph is given in Figure 4.14

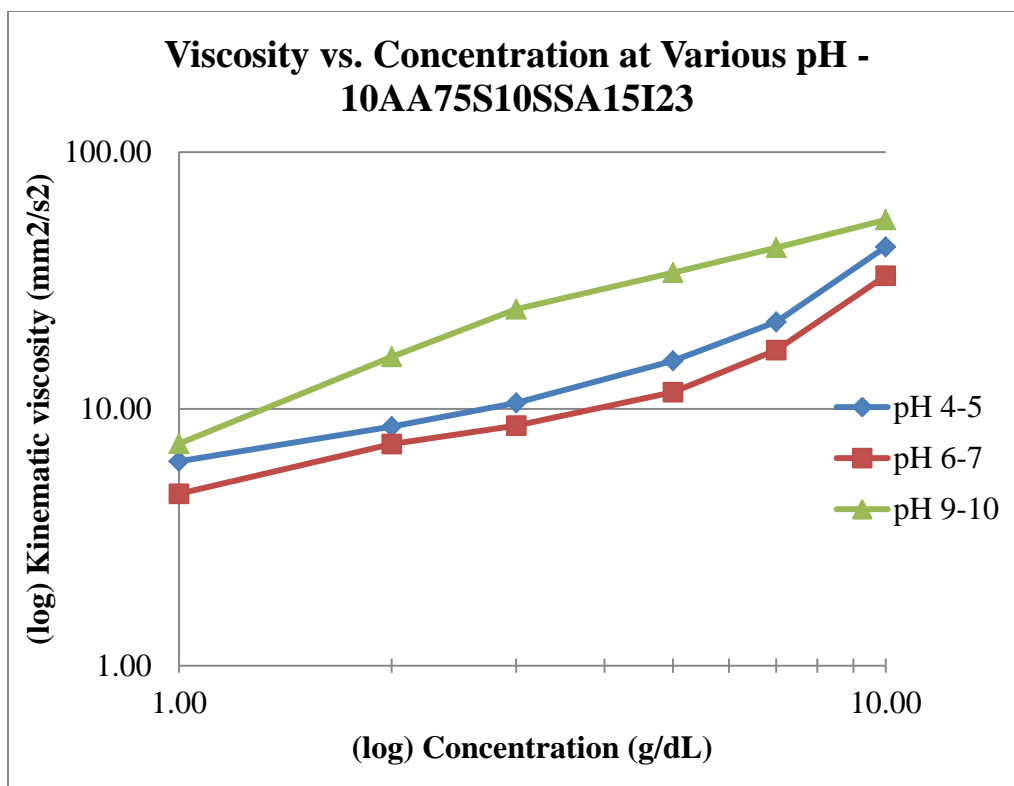


Figure 4.14 Viscosity measurements of sample 10AA88S5SSA7I23 at various concentrations and pH values

Solutions dissolved in water which gives pH of 4-5 and in pH 7 buffer solutions gives quite similar behavior. These solutions show increase in viscosity as we increase the concentration with an increasing slope. This increase is typical for most of the polymer and solvent couples. Basically this caused by the start of the interactions between the macromolecule chains. But this is not the case for the polymers in the pH 10 solvent. High pH and presence of the salt causes the polymer chains expand at low concentrations. That's why we see a rapid increase in the viscosity at low concentrations. Then once the polymer

chains get close enough to each other they start to repel each other and this leads shrinkage on the polymer chains.

## 5. CONCLUSION

In this study we tried to polymerize water soluble copolymers of acrylic acid, styrene and styrene sulfonic acid. We also tried to determine the molecular weight of the monomers using intrinsic viscosity and size exclusion chromatography methods. We determined polymer composition qualitatively with FTIR and investigated the solubility and viscosity of the copolymers at different pH levels and concentrations.

First and foremost the aim of this study is to improve the solubility of a polymer that contains styrene units. Since the polymer is going to be used for further applications as polymerized (without removing solvent and other residuals) the clearness of the polymer solution right after polymerization is the most important evaluation. We have achieved clear solutions with both 5 and 10 mole% styrene content by polymerizing 7 and 25 mole% styrene sulfonic acid, respectively, as polymerized (concentration is approximately 10 weight% in the polymerization batch). This is a significant improvement if we compare the solubility of 5 and 10 mole% styrene copolymers.

After polymerization, using FTIR we analyzed the spectra to observe the most significant side groups' behavior of monomers. Using the literature information we were able to tell qualitatively that we achieved polymerization of the monomers that we used.

Using intrinsic viscosity and SEC method we tried to determine the molecular weight of the polymer samples. We determined the intrinsic viscosity of the poly (acrylic acid) samples polymerized with different concentrations of initiator and calculated viscosity average molecular weight of the samples. We were able to see that different concentrations

gave different molecular weights. However when we run SEC for all samples, the molecular weight of samples didn't match with the intrinsic viscosity method. In determination of Mark – Houwink – Sakurada coefficients Kato et al. neutralized poly (acrylic acid) and then made measurements. Since we used the polymer without neutralization ionic strength of the solutions can be significantly different and this might cause the difference between molecular weights that we obtained from the two methods.

After removing the solvent and residuals of the polymerization we investigated the solubility of the polymers at different concentrations and pH levels of the solvent. For 5 mole % styrene containing polymers it was found that solubility of the polymer increases with increasing pH, because acrylic acid and styrene sulfonic acid are electrolyte materials their solubility behavior is highly dependent on the ionic nature of the solvent. For 10 mole% styrene monomers solubility of the polymers didn't change significantly. In both cases the highest soluble concentration was not as high as the concentration of as polymerized. This behavior was more influential for 10 mole% styrene content. It can be the hydrophobic clustering of styrene groups while solidifying the solvent that cause decrease in the solubility.

We investigated kinematic viscosity of the solutions at different pH and concentrations. Our result showed that pH of the solution significantly affects the viscosity of the solution. Especially when we dissolved the polymers at pH 10 viscosity increased with concentration with a decreasing slope. Behavior in pH 4 and pH 7 is reverse. This can be due to expansion of the polymer coils in pH 10 and as we increase the concentration effect of the

expansion decreases since polymer coils start to interact each other. Ionic strength of the polymer solution affects the viscosity of polyelectrolytes.

Overall we were able to increase the solubility of the polymer by adding an anionic monomer into system. We observed the functional groups of each monomer in the spectra of the polymers which means we successfully added all the monomers into copolymer. We also observed pH of the solutions has an effect on polymer solubility and viscosity of polyelectrolytes.

## 6. RECOMMENDATIONS FOR FUTURE RESEARCH

1) During the study we used styrene monomers in order to imitate the behavior of dye attached monomer (DAM) since DAM contains a styrene group. First step after this research should be the investigation of the solubility behavior of the polymers with dye attached monomer.

2) Solubility of the higher amount of styrene can be studied and a triangle plot of solubility depending on the concentration of three monomers can be drawn as map of solubility of poly (acrylic acid-co-styrene-co-styrene sulfonic acid) copolymers.

3) Mark-Houwink-Sakurada coefficients for acrylic acid in the literature are determined with neutralized poly (acrylic acid) and obviously don't work with poly (acrylic acid) without neutralization. If the solution pH values of poly (acrylic acid) is not significantly different at different concentrations in dilute regime. Using various molecular weight samples new coefficients can be determined.

4) Since we think the hydrophobic clusters form after solidification of the samples and this causes a decrease in solubility compared to polymerized polymers, dispersion of this clusters can be studied by dissolving the polymers at elevated temperatures. This way we can investigate whether our theory on hydrophobic clusters is true.

## 7. REFERENCES

- (1) Gao Y, Cranston R. Recent advances in antimicrobial treatments of textiles. *Text Res J* 2008;78(1):60.
- (2) Sherrill J, Michielsen S, Stojiljkovic I. Grafting of light-activated antimicrobial materials to nylon films. *Journal of Polymer Science Part A: Polymer Chemistry* 2003;41(1):41-47.
- (3) Tobiesen FA, Michielsen S. Method for grafting poly (acrylic acid) onto nylon 6, 6 using amine end groups on nylon surface. *Journal of Polymer Science Part A: Polymer Chemistry* 2002;40(5):719-728.
- (4) Rudin A. The elements of polymer science and engineering [electronic resource] : an introductory text and reference for engineers and chemists. San Diego, CA: Academic Press; 1999.
- (5) Odian GG, 1933-. Principles of polymerization. Hoboken, N.J.: Wiley; 2004.
- (6) Swift G. Acrylic (and Methacrylic) Acid Polymers. *Encyclopedia of Polymer Science and Technology*. 2002.
- (7) Available at: [http://en.wikipedia.org/wiki/Acrylic\\_acid](http://en.wikipedia.org/wiki/Acrylic_acid). Accessed 3/14, 2011.
- (8) Priddy D. Styrene Polymers. *Encyclopedia of Polymer Science and Technology*. 2002.
- (9) Available at:  
[http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=240869|ALDRICH&N5=SEARCH\\_CONCAT\\_PNO|BRAND\\_KEY&F=SPEC](http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=240869|ALDRICH&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC). Accessed 3/14, 2011.
- (10) Grabiell CE, Decker DL. Copolymerization characteristics of sodium styrenesulfonate. *Journal of Polymer Science* 1962;59(168):425-431.
- (11) Available at:  
[http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=328596|ALDRICH&N5=SEARCH\\_CONCAT\\_PNO|BRAND\\_KEY&F=SPEC](http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=328596|ALDRICH&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC). Accessed 3/14, 2011.
- (12) Sui Z, Jaber JA, Schlenoff JB. Polyelectrolyte complexes with pH-tunable solubility. *Macromolecules* 2006;39(23):8145-8152.
- (13) Carraher CE, Seymour RB. SeymourCarraher's polymer chemistry. 7th ed. Boca Raton: CRC Press; 2008.

- (14) Omidian H, Zohuriaan-Mehr MJ, Buhendi H. Aqueous solution polymerization of neutralized acrylic acid using  $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5$  as a redox pair system under atmospheric conditions. *Intern.J.Polymeric Mater* 2002.
- (15) Bokias G, Durand A, Hourdet D. Molar mass control of poly (N-isopropylacrylamide) and poly (acrylic acid) in aqueous polymerizations initiated by redox initiators based on persulfates. *Macromolecular Chemistry and Physics* 1998;199(7):1387-1392.
- (16) Scott RA, Peppas NA. Kinetic study of acrylic acid solution polymerization. *AICHE J* 1997;43(1):135-144.
- (17) Cutié S, Smith P, Henton D, Staples T, Powell C. Acrylic acid polymerization kinetics. *Journal of Polymer Science Part B: Polymer Physics* 1997;35(13):2029-2047.
- (18) Wang P, Pan CY. Preparation of styrene/acrylic acid copolymer microspheres: polymerization mechanism and carboxyl group distribution. *Colloid & Polymer Science* 2002;280(2):152-159.
- (19) Liu Z, Brooks B. A study of inverse dispersion polymerization of acrylic acid using water-soluble redox initiators. *J Appl Polym Sci* 1997;66(11):2191-2197.
- (20) Wang S, Poehlein GW. Investigation of the sequence distribution of bulk and emulsion styrene-acrylic acid copolymers by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR. *J Appl Polym Sci* 1993;49(6):991-1001.
- (21) Shoaf GL, Poehlein GW. Kinetics of emulsion copolymerization with acrylic acids. *J Appl Polym Sci* 1991;42(5):1213-1237.
- (22) Sarac AS. Redox polymerization. *Progress in Polymer Science* 1999;24(8):1149-1204.
- (23) Polymer handbook. New York: Wiley-Interscience; 1999.
- (24) Braun D, Czerwinski W, Disselhoff G, Tüdös F, Kelen T, Turcsányi B. Analysis of the linear methods for determining copolymerization reactivity ratios, VII. A critical reexamination of radical copolymerizations of styrene. *Die Angewandte Makromolekulare Chemie* 1984;125(1):161-205.
- (25) Lessard B, Schmidt SC, Marić M. Styrene/Acrylic Acid Random Copolymers Synthesized by Nitroxide-Mediated Polymerization: Effect of Free Nitroxide on Kinetics and Copolymer Composition. *Macromolecules* 2008;41(10):3446-3454.
- (26) Smith BC. Fundamentals of Fourier transform infrared spectroscopy. Boca Raton: CRC Press; 1996.

- (27) Smith BC. Infrared spectral interpretation : a systematic approach. Boca Raton: CRC Press; 1999.
- (28) Coates J. Interpretation of Infrared Spectra, A practical Approach. 2006; 2000.
- (29) Kabiri K, Azizi A, Zohuriaan-Mehr M, Marandi GB, Bouhendi H. Poly (acrylic acid–sodium styrene sulfonate) organogels: Preparation, characterization, and alcohol superabsorbency. J Appl Polym Sci .
- (30) Sperling LH. Introduction to physical polymer science. 4th ed. Hoboken, N.J.: Wiley-Interscience; 2006.
- (31) Trathnigg B. Size-Exclusion Chromatography of Polymers. 2006; 2000.
- (32) Kato T, Tokuya T, Nozaki T, Takahashi A. Molecular characterization of sodium poly (acrylate) by an aqueous gpc/LS method. Polymer 1984;25(2):218-224.
- (33) Eckelt A, Eckelt J, Wolf B. Solubility of Polymers. Encyclopedia of Polymer Science and Technology. 2002.
- (34) Blanks RF, Prausnitz JM. Thermodynamics of polymer solubility in polar and nonpolar systems. Industrial & Engineering Chemistry Fundamentals 1964;3(1):1-8.
- (35) Peterson JM, Fixman M. Viscosity of polymer solutions. J Chem Phys 1963;39:2516.
- (36) Gordon AJ. The chemist's companion: a handbook of practical data, techniques, and references. : New York, Wiley [1972]; 1972.