

Swelling Properties of Copolymers of Styrene and Divinylbenzene Containing Sulfonic and Carboxylic Acid Groups

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ABSTRACT: Copolymers of styrene, divinylbenzene, and acrylic acid that have undergone sulfonation exhibited good water absorbency properties. Removal of the lower molecular weight fraction in the surface region of the copolymer particles by toluene extraction before sulfonation has further increased the water swelling capacity of the sulfonated copolymers. The extent of swelling of the UV-irradiated copolymer could be related to the ratio of divinylbenzene to styrene. The less crosslinked copolymers were shown to absorb more water. The incorporation of more carboxylate groups in the copolymer could further increase its swelling capacity. Without UV irradiation, the

carboxylate containing copolymer was found to absorb more water than the sulfonated copolymer. UV irradiation has induced more effective crosslinking in the carboxylate containing copolymer, hence impairing its water absorbency. By replacing styrene and divinylbenzene partially with butyl acrylate, whereby the amount of crosslinking was reduced, the copolymer was able to absorb water 110 times of its dry weight. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1185–1189, 2009

Key words: crosslinking; emulsion polymerization; particle size distribution; polyelectrolytes; swelling

INTRODUCTION

Polyelectrolyte networks, a subclass of hydrogels, which are capable of swelling in contact with water, have received considerable attention in recent years because of their potentials in biomedical and biotechnological applications.¹ Other applications of such materials are as effective moisture absorbents in agricultural technology,^{2,3} packaging, and public works.^{3,4} In these applications, the degree of crosslinking plays an important role in the performance of the water absorbency of the copolymer.⁵ The networks were formed by free-radical copolymerization of at least two vinyl monomers, one of which contained an additional polymerizable double bond. This process introduces random crosslinks between chain segments.^{6,7}

The absorption of a liquid by a crosslinked polymer network depends on the nature of both the liquid and the polymer. The rate of absorption depends on the maximum amount of liquid that can be absorbed, which provides the driving force for the swelling process. Lower crosslink density pro-

vides larger swelling capacity. Other factors include the particle size and the particle size distribution in the polymer emulsion, and the density of the polymer and specific surface area of the particles.³

A high-swelling superabsorbent polymer can exhibit a phenomenon called gel blocking whereby the surfaces of the particles swell rapidly due to the large driving force and small diameter. The surface layers of neighboring particles quickly become soft and sticky owing to the inevitable presence of some soluble polymer in the particle. The individual polymer networks may entangle with each other, forming large-sized agglomerates of partially swollen gel.³ As a result, a dramatic reduction in the absorption rate is observed. The crosslinking reaction at the particle surface reduces the concentration of toluene soluble polymer in the surface region and presumably prevents gel blocking and increases the overall rate of swelling of the particle mass.³

This article presents a study on the swelling properties of polyelectrolyte networks which contain both the sulfonic and carboxylic groups. The objective of this work is to study the effects of divinylbenzene (DVB) to styrene ratio, the incorporation of carboxylate group and butyl acrylate, toluene extraction and UV irradiation on the swelling capacity of sulfonated styrene copolymers.

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TABLE I
Formulations of Polymers I and II

Ingredient	Polymer I (g)	Polymer II (g)
Distilled water	560.0	490.0
NP40 ^a	0.7	3.2
Sodium lauryl sulfate	3.5	3.5
Potassium persulfate	1.2	1.0
Seed latex (Polymer 1)	–	87.5
Styrene	–	106.5
Methyl methacrylate	35.0	3.7
Butyl acrylate	84.0	0.0
Methacrylic acid	21.0	2.5
Acrylic acid	–	1.2
Hydroxyethyl methacrylate	–	3.0
Divinyl benzene	–	5.6
Total charge	705.4	707.7

^a Nonyl phenol ethoxylate (40 units of ethylene oxide).

EXPERIMENTAL

Materials

Butyl acrylate (BA, >99%, Fluka, Switzerland), methyl methacrylate (MMA, >99%, BDH, UK), styrene (St, >99%, R and M), hydroxyethyl methacrylate (HEMA, 97%, Aldrich), DVB (Fluka), methacrylic acid (MAA, >99%, Merck-Schuchardt, Germany), and acrylic acid (AA, >99%, Fluka) were used without further purification. Potassium persulfate (97%) from Avocado Research Chemicals (UK) was used as initiator. Sodium lauryl sulfate and NP-40, which is nonyl phenol ethoxylate with 40 units of ethylene oxide, were the surfactants used in the emulsion polymerization. Toluene was used for further treatment of polymer. Concentrated sulfuric acid and sodium hydroxide were used for the sulfonation and neutralization processes, respectively.

Preparation of copolymer latices

The emulsion polymerization was carried out in a glass reactor at 75°C by a semicontinuous process.

The seed latex was prepared according to the formulation of Polymer I, whereas the core-shell polymer was prepared by seeded emulsion polymerization according to the formulation of Polymer II in Table I, similar to the procedure described elsewhere.⁸ The core-shell copolymers with different weight ratios of DVB to styrene were prepared according to Table II.

Toluene extraction of styrene copolymer

Copolymer latex was dried in oven at about 65°C. The dried copolymer was ground to powder and placed in an extraction thimble lined with filter paper. The copolymer was then extracted with toluene in a Soxhlet extractor for 4 h, in a similar procedure described by Zhang et al.⁹

UV irradiation of polystyrene-DVB copolymer

About 2 g of dry copolymer was weighed into a glass tube with stopper, followed by 0.1 g of a 20% photoinitiator solution. Sufficient amount of toluene was then added, and the copolymer was soaked overnight to ensure better penetration of photoinitiator into the copolymer.

A thin layer of the viscous copolymer solution was spread on a glass panel and irradiated by UV light from a 400 W mercury lamp at wavelengths between 315 and 380 nm in the presence of air for 30 s, at a distance of 14 cm from the light source.

Sulfonation of polystyrene-DVB copolymer

Following the procedure described elsewhere,¹⁰ about 10 g of dry copolymer was weighed into a 500 mL round-bottomed flask, and about 15 g of dichloromethane was added to wet the copolymer thoroughly. The copolymer was sulfonated with 60 g of concentrated sulfuric acid at 120°C for 2 h. The sulfonated copolymer was cooled before being neutralized with 1 mol L⁻¹ NaOH solution. The product was washed thoroughly with plenty of distilled water and then stored in 10% brine solution.

Particle size analysis of emulsion copolymer

The latex particle diameter was determined by Coulter N4 Plus submicron particle sizer which applies the principle of multiple-scattering angle detection to measure intensity-weighted particle size.¹¹ The latex samples were diluted to suitable concentration with distilled water and adjusted from pH 2.3–9.1 (±0.2) with ammonia solution. The latex samples should be diluted to a concentration that gives an average of lower than 1.5 × 10⁶ counts per second as detected by the instrument.

TABLE II
Polymer II with Different Weight Ratios of DVB to Styrene Monomers

Monomer (parts by weight)	Copolymer				
	DS1	DS2	DS3	DS4	DS5
DVB	5.6	11.2	16.8	22.4	28.0
Styrene	106.5	100.9	95.3	89.7	84.1
DVB/styrene ratio	0.05	0.11	0.18	0.25	0.33

TABLE III
Particle Size of Polystyrene Copolymer Emulsion at pH 2.3

Emulsion	DVB/styrene weight ratio	Particle size/nm	
		Mean diameter	Standard deviation
DS1	0.05	142.5	34.6
DS2	0.11	142.6	13.4
DS3	0.18	142.8	22.0
DS4	0.25	139.2	42.0
DS5	0.33	148.8	17.6

Plastic sample cuvette was used to hold the diluted latex sample for the measurement. The angle of scattered-light detection was at 90°. For each particle size measurement, the equilibration time was 10 min, and run time was 120 s.

Swelling of the latex particles was calculated based on the volume change of the particles from pH 2.3–9.1.

Water swelling capacity of sulfonated polystyrene copolymer

The sulfonated copolymer stored in brine solution was rinsed with distilled water to remove the salt. Excess water was removed from the copolymer by filtering through a fine mesh wire sieve and blotted dry with filter paper. About 1 g of the hydrated copolymer was weighed accurately (W_1) into an aluminum cup. It was then dried in an oven at 140°C for 1 h. The dry copolymer was cooled in a desiccator before it was weighed again (W_0). The extent of swelling in water is proportional to the amount of water adsorbed; hence, the swelling capacity is estimated by the following equation:

$$\text{Swelling capacity (\%)} = \frac{(W_1 - W_0)}{W_0} \times 100$$

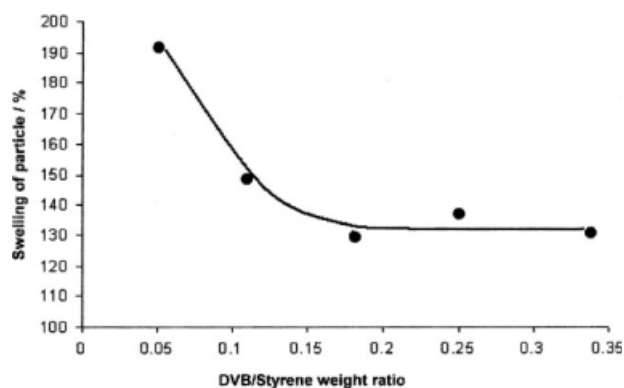


Figure 1 Effect of DVB/styrene ratio on the extent of swelling of copolymer particles in alkali medium (pH 9.1).

RESULTS AND DISCUSSION

Particle size analysis

The particle size of the copolymer prepared by seeded emulsion polymerization was between 140 and 150 nm in acidic pH (Table III). The finer particles possess larger surface area; hence, higher absorption rate of liquid into the polymer particles is expected.

Swelling of the copolymer particles in alkali solution

Copolymer with different DVB to styrene ratios were subjected to particle size analysis, both in acidic (pH 2.3) and alkali (pH 9.1) solution. Figure 1 shows that higher level of DVB in the copolymer has reduced the swelling of the particles in alkali solution. This is due to higher degree of crosslinking in the copolymer when higher level of DVB was incorporated. The results show that the swelling of the copolymer particles was restricted when the DVB to styrene weight ratios was above 0.15.

Water swelling capacity of polystyrene copolymer after sulfonation

The swelling capacity of the copolymer was determined after the copolymer has undergone each of the following treatments: (a) sulfonation, (b) toluene extraction followed by sulfonation, (c) UV irradiation followed by sulfonation, and (d) toluene extraction, followed by UV irradiation and then sulfonation.

The results in Figure 2 show that the UV-irradiated copolymers which have undergone sulfonation, especially those with lower DVB content, have better swelling capacity compared with their counterparts which were without sulfonation (Fig. 1). The sulfonation step has introduced sulfonate ion (SO_3^-) onto

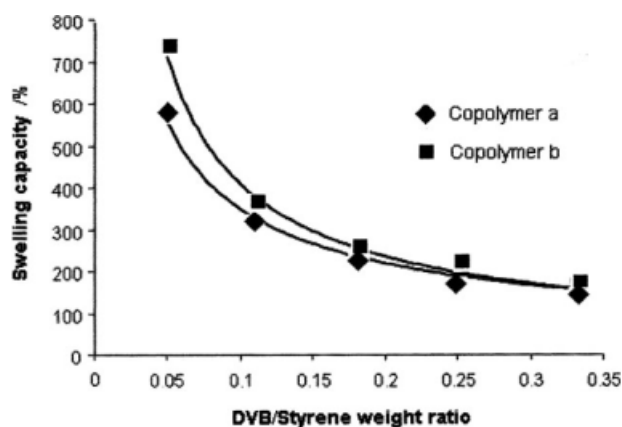


Figure 2 Water swelling capacity of copolymer that has undergone (a) UV irradiation followed by sulfonation and (b) toluene extraction, then UV irradiation and followed by sulfonation.

the aromatic ring.⁹ Thus, the polar sulfonic group created a stronger attractive force to draw water into the copolymer.

Besides, Figure 2 shows that the sulfonated copolymers which have undergone toluene extraction before the sulfonation process (Copolymer b) have better swelling capacity than their counterparts which have not undergone toluene extraction (Copolymer a). This presumably is due to removal of toluene soluble fraction in the surface region of the particles, and gel-blocking was significantly reduced. With 5% wt of DVB in the polystyrene-DVB formulation (DS1), 1.0 g of the dry copolymer was able to absorb up to 7.5 g of water.

Swelling of modified polystyrene copolymer

The formulation of the copolymer that gave the highest swelling capacity (DVB/styrene = 0.05) (DS1) was further modified (Table IV). First, by replacing the styrene partially with acrylic acid (DS6) and second, by replacing all of the DVB with butyl acrylate and part of the styrene with acrylic acid and butyl acrylate (DS7). The replacement of DVB by BA would greatly reduce the amount of crosslinking, which would lead to increase in swelling. In addition, the soft segments of butyl acrylate in the copolymer have resulted in more flexible copolymer chains that could allow more water molecules to enter the polyelectrolyte networks. Table V summarizes the results of swelling capacity of the modified copolymers after different treatments.

The presence of more carboxylate ions ($-\text{COO}^-$) in the polyelectrolyte networks has increased the swelling capacity of the copolymers. For the sulfonated copolymer (DS6), where 15.8% of its styrene was replaced with AA, the swelling capacity has increased from 575% to almost 800%. For the sulfonated copolymer (DS6) that has undergone toluene extraction, the swelling capacity has increased from 433% to about 940%. These results showed that the carboxylate containing copolymers absorbed more water than the sulfonated copolymers. This was because acrylic acid is much more hydrophilic than styrene.

Further modification of copolymer DS6 was carried out by replacing some of its styrene and all of

TABLE IV
Modifications of Formulation DS1

Copolymer	Modification
DS6	15.8% wt of styrene was replaced by acrylic acid (AA).
DS7	15.8% wt of styrene was replaced by acrylic acid and another 12% wt of styrene by butyl acrylate; all of DVB was replaced by butyl acrylate (BA).

TABLE V
Water Swelling Capacities of Copolymers After Different Treatments. (a) Sulfonation, (b) Toluene Extraction and Sulfonation, (c) UV Irradiation and Sulfonation, and (d) Toluene Extraction, UV Irradiation, and Sulfonation

Sulfonated copolymer	Swelling capacity (%)			
	Treatment (a)	Treatment (b)	Treatment (c)	Treatment (d)
DS1	575	433	562	750
DS6	798	943	496	550
DS7	11,034	–	–	–

Copolymer DS7 contained no DVB. It did not undergo any crosslinking and was soluble in toluene. Hence, treatments (b), (c), and (d) were not applicable to this copolymer.

its DVB with butyl acrylate, the resulting copolymer (DS7) thus prepared was able to absorb water 110 times of its dry weight. The incorporation of butyl acrylate which has a 4-carbon alkyl group instead of an aromatic benzene ring of styrene has made the copolymer less rigid and less hydrophobic. Thus, allowing the copolymer to absorb more water.

Besides, the results in Table V show that the sulfonated copolymers that have undergone UV irradiation generally absorbed less water. UV irradiation has induced more crosslinking in the copolymer networks which contained divinyl benzene, and it was found more significant in DS6 than DS1. The reason could be that UV radiation can lead to crosslinking by an abstraction involving the aromatic ring, which reduces swelling by increased physical restriction of the polymer.

CONCLUSIONS

Copolymers of styrene, divinylbenzene, and acrylic acid have shown better water absorbency after sulfonation. The extent of swelling of the copolymer could be related to DVB to styrene ratio in the copolymer. The presence of more carboxylate group in the copolymer can enhance its swelling capacity. Without UV irradiation, the carboxylate containing copolymer was found to absorb more water than the sulfonated copolymer. However, with the presence of DVB in the copolymers, UV irradiation has induced higher amount of crosslinking in the copolymer networks and consequently reduced the swelling capacity of the copolymer. By reducing styrene and DVB and replacing them partially with butyl acrylate, the extent of crosslinking is greatly reduced, and more flexible copolymer absorbed water 110 times of its dry weight. Toluene extraction has increased the overall extent of swelling of the particle mass by the removal of lower molecular weight

fraction from the surface region of the polymer particles and thus reducing gel blocking.

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