

Preparation of Ion-Containing Elastomers by Emulsion Copolymerization of Dienes with Olefinic Sulfonic Acid Salts

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Synopsis

Procedures were developed for the emulsion copolymerization of either butadiene or isoprene with several different water-soluble monomers containing sulfonic acid salt groups, primarily with sodium styrenesulfonate, for the preparation of ionomer elastomers. By the use of a nonionic surfactant and a two-component redox initiator, which was based on a water-soluble reducing agent and a hydrophobic peroxide, copolymers with sufficient amounts of the ionic monomer could be prepared. Unusual effects of conversion on rate, copolymer composition, and molecular weight were observed and attributed to special effects caused by the ionic monomers. The copolymers were soluble in mixed hydrocarbon-alcohol solvent systems.

INTRODUCTION

Incorporation of ions into a rubber matrix results in unusual physical and mechanical properties. For example, it was shown by Tobolsky and co-workers that the viscoelastic responses of metal salts of butadiene-methacrylic acid copolymers were similar to those observed with linear segmented elastomers in that both showed an enhanced and extended "rubbery plateau" region above a major glass transition temperature.¹ This behavior is believed to be a result of the presence of ionic aggregates in the rubber matrix which act as time-dependent crosslinks.²

Modification of partially unsaturated elastomeric hydrocarbon polymers by sulfonation has recently been reported by several investigators.^{3,4} The rheological and tensile properties⁵ of these sulfonated elastomers as well as their thermal and dynamic-mechanical responses have been characterized and described.⁶ The evidence shown in these recent studies^{6,7} indicates that pendent sulfonate groups on the elastomers aggregated to form microphase-separated ionic domains in the same manner as the carboxylate salts mentioned above.¹

It would be desirable, of course, to prepare such sulfonated elastomers by direct copolymerization of an appropriate monomer, such as isoprene, and a sulfonic acid salt comonomer. Indeed, the polymerization of olefinic sulfonic acid derivatives and their homogeneous copolymerization with various comonomers has been studied fairly extensively because of their utility in the preparation of ion exchange resins.⁸ However, most polymerization studies were carried out on the homopolymerization of the alkali metal salts of the sulfonate monomers

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in aqueous solution.⁹⁻¹¹ Solution polymerization of the acid form of the monomer is not usually carried out, although the homopolymerization of ethylene sulfonic acid has been reported.¹² Solution copolymerizations of olefinic sulfonic acid esters with nonpolar organic comonomers have also been reported.^{13,14}

Inclusion of ionic monomers in emulsion recipes is not uncommon,¹⁵ but their use has been mostly to impart colloidal stability to the resulting polymer particles and to improve latex resistance to coagulation rather than for modification of the properties of the polymeric product.¹⁶⁻²¹ Quite likely, the lack of extensive investigations in this area can be attributed to the limited extent of copolymerization of the ionic comonomer. Generally speaking, in order to affect the copolymer properties, a much greater amount of the ionic comonomer must be incorporated into the macromolecule than that required to enhance the colloidal stability of the latex.

Marvel and co-workers¹⁴ considered the emulsion copolymerization of vinylsulfonic acid and β -phenylvinylsulfonic acid and their salts with butadiene in order to improve the oil resistance of polybutadiene rubber. Their attempts were unsuccessful, and their failure was attributed to "the extreme differences in solubility between butadiene and vinyl sulfonic acid or its salts."

The present study was undertaken to evaluate the feasibility of preparing copolymers of isoprene or butadiene with several olefinic sulfonic acid salt comonomers by radical initiation in an emulsion polymerization process. Sodium styrene sulfonate (NaSS), sodium allyl sulfonate (NaAS), sodium 2-sulfoethyl methacrylate (NaSEM), and sodium 2-acrylamido-2-methylpropane sulfonate (NaAMPS) were successfully copolymerized with diene monomers, as shown by the data in Table I. Except for differences in reaction vapor pressure and polymer molecular weight, no major differences were observed between butadiene and isoprene in their emulsion copolymerization reactions with the same sulfonate comonomers. This investigation, however, was primarily concerned with the emulsion copolymerization reactions of either isoprene or butadiene with NaSS.

EXPERIMENTAL

Monomers

Isoprene of greater than 99% purity was obtained from Aldrich Chemical Co. and stored in the dark at -20°C . It was further purified by washing with a 0.5M solution of sodium hydroxide, followed by subsequent washings with distilled water and by fractional distillation at atmospheric pressure. NaSS was obtained from Columbia Organic Chemicals Co., AMPS from Lubrizol Co., SEM from Dow Chemical Co., and NaAS from Universal Oil Co. All sulfonate monomers were used as received.

Polymerization Reactions

Conditions for all copolymerization reactions are listed in Tables I and II for the benzoyl peroxide-ferrous ion redox system (BP-Fe) and for the hydroperoxide-amine redox system (DIPBH-TETA), respectively. Detailed procedures for each system are described in the following sections.

TABLE I
Emulsion Copolymerization of Isoprene and Butadiene with Several Sulfonate-Containing Olefinic Monomers

Diene type	Monomer amount, g	Sulfonate type ^a	Monomer amount, g	Buffer g ^b	Initiator BP-Fe ^c	Emulsifier g ^d	Polymerization time, hr ^e	Polymer yield, %	Sulfur in copolymer, %
Isoprene	15.2	NaAs	1.60	0.156	0.0638/0.157	1.880	21.4	84.9	1.00
Butadiene	15.4	NaAs	1.61	0.160	0.0722/0.170	1.257	21.0	28.0	0.97
Isoprene	15.2	NaSEM	1.60	0.157	0.0647/0.164	1.841	23.7	48.5	2.14
Butadiene	15.6	NaSEM	1.62	0.169	0.0603/0.162	1.879	18.2	85.4	0.94
Butadiene	15.4	NaAMPS	1.60	0.104	0.0645/0.160	1.888	20.5	76.1	1.20
Butadiene	89.0	NaSS	9.6	0.94	0.37 /0.97	7.50	67.0	77.0	1.17

^a NaAs = Sodium allyl sulfonate; NaSEM = sodium 2-sulfoethyl methacrylate; NaAMPS = sodium 2-acrylamido-2-methylpropane sulfonate; NaSS = sodium styrene sulfonate.

^b Na₄P₂O₇·10H₂O.

^c Redox initiator consisting of benzoylperoxide (BP) and ferrous ammonium sulfate (Fe).

^d Sodium lauryl sulfate; all reactions were in 25 g water, except the last, which was in 160 g water.

^e At 25°C.

TABLE II
Emulsion Copolymerization of Isoprene and Butadiene with NaSS^a

NaSS, g	CTA, g ^b	Temperature, °C	Reaction time, hr	Conversion, %	Sulfur in copolymer, %
Recipe A					
0.6	0	20	21	13.0	0.27
0.88	0	20	21	23.6	0.81
1.19	0	20	21	32.7	1.06
1.19	0	20	21	78.0	0.70
1.19	0	20	21	78.0	0.49
1.79	0	20	21	62.7	1.21
—	0	20	21	32.6	0
0.35	0	22	21	61.0	0.39
0.35	0.08	22	21	1.5	—
0.7	0	25	17	71.0	0.40
0.7	0.03	25	17	39.0	0.30
1.4	0	0	21.5	0.5	—
1.4	0.04	0	21.5	1.0	—
1.05	0.04	20	21	49.0	0.38
2.1	0.04	20	21	19.0	1.60
2.1	0.03	25–30	47	76.0	1.16
4.2	0.03	25–30	23.5	37.0	3.53
1.4	0.03	15–21	26	87.0	0.71
1.75	0.03	15–21	26	84.0	0.95
Recipe B					
1.19	0.07	25	1.5	4.0	1.34
1.19	0.07	25	3.0	—	0.95
1.19	0.07	25	2.5	13.0	0.90
1.19	0.07	25	6.0	29.0	0.70
1.19	0.07	25	16.3	64.0	0.56
1.19	0.07	25	21.5	77.0	0.46

^a Recipe A: 17 g isoprene, 28 ml water, 1.73 g Tween 80, 0.24 g DIPBH, 0.25 g TETA, 0.15 g buffer. Recipe B: 17 g butadiene, 29 ml water, 1.36 g Tween 80, 0.3 g DIPBH, 0.03 g TETA, 0.17 g buffer.

^b Lauryl mercaptan as chain transfer agent (CTA).

BP-Fe Recipe

A solution of 1.27 g sodium lauryl sulfate in 21.8 ml distilled, deionized water was prepared in a 10-oz. bottle, and to this was added 0.4 g ammonium ferrous sulfate hexahydrate and 0.4 g sodium pyrophosphate decahydrate dissolved in 5.4 ml distilled, deionized water. The solution was maintained at 60°C for 15 min and was then combined with 1.62 g NaSS and a solution of 0.06 g benzoyl peroxide in 23 ml freshly distilled isoprene in a beverage bottle. The bottle was sealed with a crown cap backed with Teflon-coated rubber liner and purged by an inert gas stream. The purging procedure consisted of evacuating to approximately 27 in. Hg vacuum, followed by repressurizing with pure nitrogen to 8–10 psig. The evacuation and inert gas purging were carried out three to four times, after which the reactor was maintained under 8 psig pure nitrogen pressure. Sufficient agitation was provided by the reciprocating shaking action of a shaker bath. Polymerization reactions were generally conducted at room temperature for 16–24 hr.

DIPBH-TETA Recipe

A solution of 2 g NaSS, 0.15 g sodium pyrophosphate decahydrate, and 0.25 ml triethylenetetramine (TETA) in 30 ml distilled, deionized water was placed in a 10-oz. beverage bottle. The bottle was capped and purged with pure nitrogen by the technique outlined in the recipe above. A solution of 1.6 ml Tween 80, 0.25 ml of a 14% solution of 1-dodecanethiol in benzene, and 0.25 ml diisopropylbenzene hydroperoxide (DIPBH) in 25 ml isoprene was added to the reactor under a pure nitrogen atmosphere through a needle inserted into the cap. The reactor was once again purged with pure nitrogen and allowed to remain under 8 psig pure nitrogen pressure. The polymerization was generally conducted at room temperature with sufficient agitation for 21 hr.

Determination of Latex Solid Content

Five milliliters of the latex was weighed in a tared aluminum weighing dish, and 1 ml of a 1% solution of hydroquinone in methanol was added to the weighing dish. The latex was dried at room temperature under reduced pressure followed by vacuum drying at 40°C for 24 hr. The solids content was determined as the ratio of the weight of the dried latex to that of the original latex.

Determination of Extent of Reaction

Reaction conversions were determined on the basis of the yield of the purified dried polymer and also on the basis of the solids content of the latex. Equations (1) and (2) give the relationships used between the extent of reaction and the solids content of the latex for both the BP-Fe and DIPBH-TETA recipes, respectively:

$$\% \text{ conversion} = 2.98 (\% \text{ solids}) - 23.98 \quad (1)$$

$$\% \text{ conversion} = 3.03 (\% \text{ solids}) - 23.53 \quad (2)$$

Copolymer Isolation and Purification

Copolymers were isolated by coagulation of the latex in methanol followed by subsequent washings by methanol and water in a Waring blender. The samples were further purified by extraction with methanol in a Soxhlet extractor for 48 hr. All isolation and purification steps were carried out under a nitrogen atmosphere using 2% solutions of 2,6-di-*t*-butyl-4-methylphenol with minimal exposure to light, and the samples were stored under vacuum away from light at 5°C.

Copolymer Composition Determination

Copolymer compositions were determined by sulfur analysis and from the infrared absorption spectra of the purified product. Prior to composition determination, each product was verified to be a true copolymer according to its solubility behavior.²² Sulfur analyses were carried out by the University of Massachusetts Microanalytical Laboratory. Equations (3) and (4) show the relationships between weight % and mole % of NaSS units in the copolymer and the amount of sulfur found by microanalytical techniques:

$$\text{weight \% NaSS in copolymer} = 6.44 (\% \text{ sulfur}) \quad (3)$$

$$\text{mole \% NaSS in copolymer} = \frac{3.1 (\% \text{ sulfur})}{1.47 - 0.064 (\% \text{ sulfur})} \quad (4)$$

IR spectra of the copolymers were recorded on a Perkin-Elmer model 283 IR spectrometer. Samples were prepared by casting films out of 1% solutions of the copolymer in a 95/5 volumetric mixture of toluene/isopropanol onto sodium chloride plates. Ratios of NaSS to isoprene units in the copolymer were determined from the ratio of the integrated intensities of the absorption peaks from the asymmetric S—O stretching mode at 1185 cm^{-1} and methyl group C—H bending vibration mode at 1445 cm^{-1} .^{23,24} Intensities of the reference beams were measured using a baseline method.²⁵ Figure 1 shows the relationship between the absorbance ratio and copolymer composition.

DISCUSSION OF RESULTS

An important factor in determining the suitability of an initiator for an emulsion polymerization reaction is its distribution between the two phases, that is, whether it is oil soluble or water soluble. Many water-soluble peroxides have found widespread application in emulsion polymerization systems, but in reaction systems containing both a water-soluble monomer and a water-insoluble monomer, such as the one studied here, they may not be desirable when a copolymer product is sought. Indeed, incorporation of persulfate initiators in the present recipes resulted in the formation of a mixture of two homopolymers and only a small amount of the desired copolymer.

In contrast, oil-soluble peroxides are generally unsuitable for emulsion polymerization because initiation occurs directly in both the monomer droplets and the monomer micelles. It was found, instead, that an initiating system most suitable for this emulsion copolymerization reaction was a redox system comprising an oil-soluble peroxygen compound and a water-soluble reducing agent. In this system it appeared that the monomer micelle (or monomer-polymer particle) interface was the preferred locus for radical formation, and this type of initiation strongly promoted the copolymerization reaction of the water-soluble and water-insoluble monomers, as shown in Tables I and II.

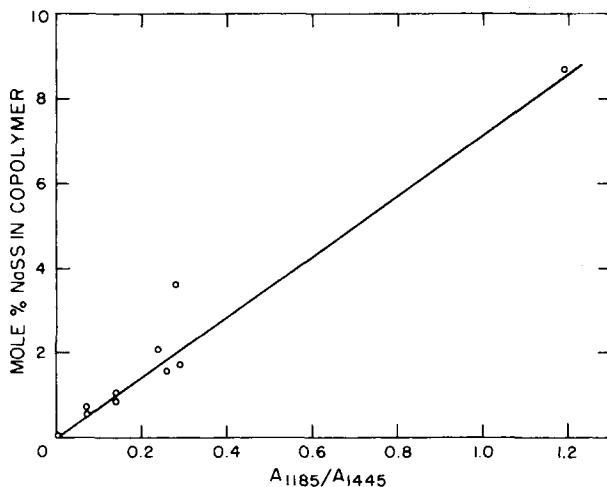


Fig. 1. Relationship between copolymer composition and IR absorbance ratio.

Effect of Emulsifier on Copolymer Composition

If initiation occurred at the micelle (or monomer-polymer particle) interface, the type of emulsifier used should have had a strong influence on the copolymer composition by its effect on the concentration of NaSS at the interface, particularly if NaSS was in direct competition with the emulsifier for adsorption on the surface of the micelle (or particle). That is, the adsorption energy of the emulsifier would determine the equilibrium concentration of NaSS at the interface. The data in Table III show the effect of the type of emulsifier on copolymer composition for systems based on either a nonionic emulsifier or an anionic emulsifier, respectively. For the former, a poly(oxyethylene) glycol ester of sorbitan monooleate (Tween 80) was used, while for the latter sodium lauryl sulfate was used in the copolymerization of isoprene and NaSS with a PB-Fe recipe.

As can be seen from the results in Table III, use of the nonionic emulsifier gave copolymers in which the NaSS unit content varied directly and uniformly with the NaSS monomer content in the feed. In contrast, use of the anionic emulsifier gave copolymers with higher NaSS unit contents at low NaSS ratios; but at increasingly higher NaSS monomer contents in the feed, the copolymer composition became independent of monomer composition. These results indicate that the NaSS monomer contents in both the monomer micelles and the monomer-polymer particles were lower in the presence of the anionic emulsifier at the higher NaSS contents, as would be expected if this anionic monomer were replaced or repelled by the anionic emulsifier.

Effect of Conversion on Copolymer Composition

It was generally observed in these copolymerization reactions that the copolymer composition decreased in NaSS content with reaction conversion in a uniform manner. An illustration of this effect is shown in Figure 2 for the copolymerization of NaSS with isoprene using a DIPBH-TETA initiator and the nonionic emulsifier. The observed decrease in NaSS content with reaction time

TABLE III
Variation in Copolymer Composition with Monomer Feed Composition for Different Emulsifiers in the Copolymerization of NaSS and Isoprene

Nonionic emulsifier ^a		Anionic emulsifier ^b	
NaSS in feed, mole %	NaSS in copolymer, mole %	NaSS in feed, mole %	NaSS in copolymer, mole %
1.15	0.58	0.67	1.85
1.68	1.78	1.71	1.97
2.26	2.36	3.30 ^c	2.85
3.36	2.71	3.36	2.92
3.92 ^c	3.63	5.50	2.78
7.54 ^c	8.71	7.63	2.62

^a Recipe in parts by weight: 17 isoprene, 28 distilled water, 1.73 Tween 80, 0.16 DIPBH, 0.25 TETA, 0.15 pyrophosphate, 0.6-4.2 NaSS; reacted at 20°C, except for the last reaction in table, which was at 23.5°C for 21 to 23.5 hr.

^b Recipe in parts by weight: 16.7 monomers (isoprene + NaSS), 25 distilled water, 0.625 sodium lauryl sulfate, 0.062 benzoyl peroxide, 0.157 ferrous ammonium sulfate, 0.156 buffer; reacted at room temperature for 17 to 24 hr.

^c Monomer contained lauryl mercaptan.

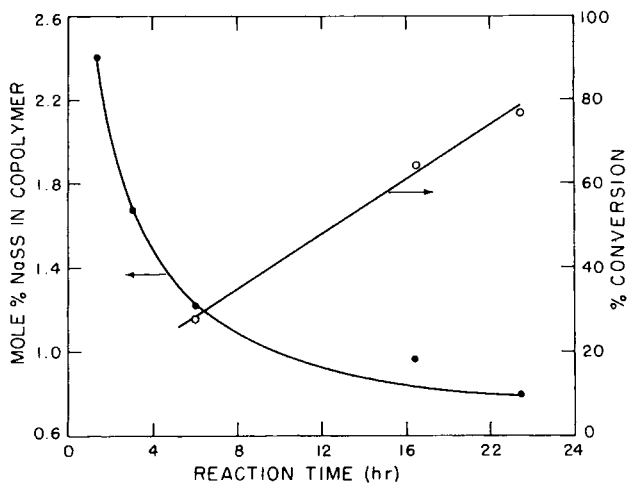


Fig. 2. Copolymer composition as function of reaction time or conversion.

(or conversion) is believed to be due to the repulsion of the anionic NaSS monomer by the anionic NaSS units in the copolymer, which were present on the surface of the monomer-polymer particles in increasing concentrations as the copolymer content of the particle increased.

Effect of Conversion on Molecular Weight

The molecular weight of the copolymer formed was observed to increase in a uniform manner with increasing reaction conversion as indicated by the solution viscosity of the product in xylene-hexanol solvent mixture.²⁶ The data obtained for the product of an NaSS-isoprene copolymerization with a nonionic emulsifier is shown in Figure 3. Similar studies carried out in this laboratory on the copolymerization of the nonionic methyl and butyl esters of styrene sulfonic acid showed no such effect.²⁷ It is believed that this observed increase in molecular weight for the ionic copolymers was caused by a "gel effect" resulting from immobilization of the polymer in the particles through ionic crosslinks with an

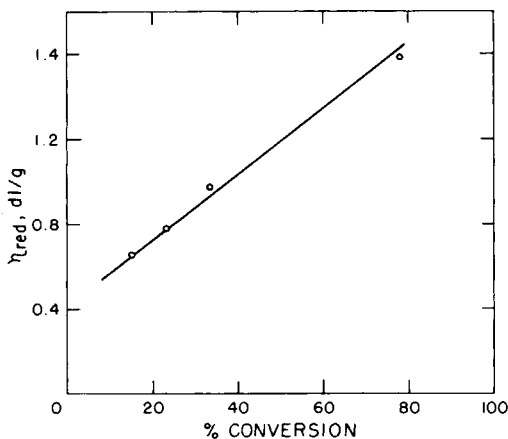


Fig. 3. Reduced viscosity of the copolymer formed as function of reaction conversion.

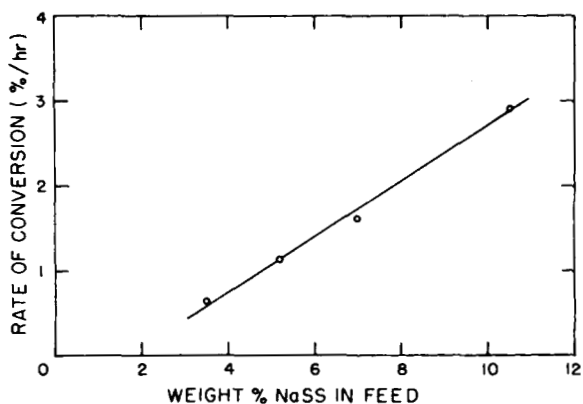


Fig. 4. Effect of comonomer feed composition on the overall rate of polymerization.

increasingly important contribution by diffusion control over the termination reaction.

It is also interesting to note that the overall rate of polymerization increased with increasing NaSS content in the monomer feed as seen in the data plotted in Figure 4. This result could be associated with an increase in the number of monomer micelles with increasing NaSS content, which would be expected if the anionic monomer acted as an emulsifier as discussed above.

A schematic representation of the proposed structure of the monomer-polymer particle is offered in Figure 5. Shown in this figure are the suggested ionic crosslinks within the particle and the presence of the nonionic emulsifier as well as both the unreacted NaSS monomer and some of the NaSS copolymer units on the particle surface.

It should be noted that for copolymerization reactions in which either high NaSS monomer contents were used or the reactions were carried out to high conversions (above 30%), it was often necessary to use chain transfer agents to prevent the formation of insoluble, crosslinked polymer. The effective use of

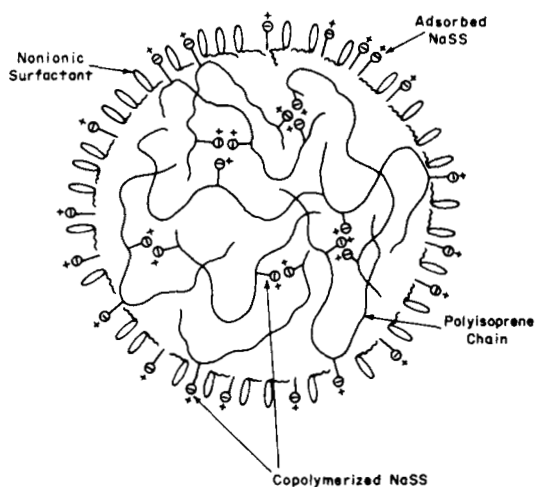


Fig. 5. Schematic representation of a monomer-copolymer particle during the emulsion polymerization.

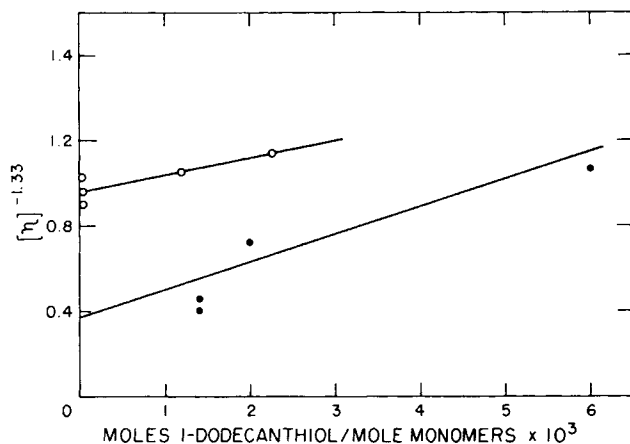


Fig. 6. Effect of addition of 1-dodecanethiol as chain transfer agent on copolymer molecular weight in the copolymerization of NaSS with either butadiene or isoprene: (●) butadiene copolymers; (○) isoprene copolymers.

dodecanethiol for this purpose is shown by the intrinsic viscosity data plotted in Figure 6 for NaSS copolymers of both butadiene and isoprene.

Copolymer Solubilities

The solubilities of the NaSS–isoprene copolymers prepared in these investigations are given in Table IV for a single solvent, which is a good solvent for polyisoprene itself (*p*-xylene), and also for a two-component solvent system, *p*-xylene–methanol. In the latter, methanol was added to solvate the sulfonic acid salt groups and thereby disrupt the ionic domains, which form effective crosslinks and prevent the copolymer from dissolving.²⁸

It can be seen from these data that the copolymers were increasingly insoluble in *p*-xylene with either increasing ionic unit content or increasing molecular weight, as would be expected from the formation of ionic aggregates in the copolymers which served as reversible crosslinks. All copolymers, however, were soluble in the polar–nonpolar solvent combination, except for the copolymer with the very high NaSS unit content in Table IV. Either this latter copolymer may have contained covalent crosslinks, or the ionic domain content may have been

TABLE IV
Solubility of NaSS–Isoprene Copolymers

NaSS in copolymer, mole %	Solubility, %		η_{red} , dl/g ^a
	In xylene	In xylene/methanol	
0.64	13.7	98.6	3.15
0.83	26.0	99.0	1.57
1.58	13.0	95.0	2.64
2.16	14.0	99.5	3.09
3.63	56.0	98.0	0.65
8.71	24.0	77.0	2.33

^a At a solution concentration of 0.2 g/l. in a mixed solvent of 95:5% by volume of *p*-xylene:methanol.

too high to be completely solvated, or *p*-xylene was no longer an effective solvent for the shorter isoprene sequences.

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