Ion Containing Copolymers via the Emulsion Copolymerization of Polar and Ionic Vinyl Monomers

by

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(ABSTRACT)

The synthesis of ion containing copolymers by emulsion copolymerization of polar vinyl monomers with ionic vinyl monomers has been studied. The copolymerization of n-butyl acrylate with sodium-p-styrene sulfonate proved to be particularly rapid. With the proper choice of chain transfer agent soluble polymers with enhanced rubbery plateaus have been synthesized. The best conditions for the polymerizations were a reaction temperature of 70°C and reaction times up to 8 hours with TWEEN 20 used as the emulsifier.

Analysis of the copolymer composition by UV spectroscopy, and potentionmetric titration was not possible due to the vastly different solubility characteristics of the coponents of this system. This prevented the use of homopolymer blends as standards for these techniques.

The study of the copolymerization kinetics of this system was very difficult due to the coagulation of the polymer latex. The rate of copolymerization was nevertheless shown to be very rapid.

The synthesis of the sulfonated styrene monomer by a literature procedure led to the formation of a covalent sulfonamide instead of the desired ionic sulfonate. This product was substantiated by ^{1}H and ^{13}C NMR infrared, mass spectral, and melting point data.

Study of the physical properties of these polymers by differential scanning calorimetry and thermal mechanical analysis showed them to have only a low temperature acrylate glass transition with an enhanced rubbery plateau due to the ionic pseudo crosslinking. Stress-strain measurements showed that this pseudo crosslinking gives enhanced tensile properties (modulus, tensile strength) in the ion-containing polymers.

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I. INTRODUCTION

In the past ten years studies of ion-containing polymers have increasingly become a subject of academic and industrial interest. The extent of interest in ion-containing polymers can be seen by the number of papers dealing with the subject and by a number of conferences and symposia which have been devoted to ion-containing polymers, which have included a 1981 Gordon Research Conference.[1] This interest is due to the broad range of properties available from ion-containing polymers. These range from the water soluble polyelectrolytes to copolymer systems which have interesting bulk properties due to the presence of a low concentration of ions.

A particularly interesting class of ion-containing polymers has come to be known as "ionomers." The term ionomer in current usage refers to those ion-containing polymers which contain a low ion content (generally less than 10 mole % of the repeat units), with the remainder of the polymer chain structure being nonionic. Ionomers are of particular interest because of the unique property modifications which can be imparted to a covalent polymer by low levels of ionic groups attached to the polymer chain. These properties have been covered quite extensively in two books[2,3] and a number of review articles[4-7] on ion-containing polymers. Generally, these polymers displayed improved mechanical properties. Of particular interest are the rubbery ionomers, which have shown potential for use as elastoplastics and thermoplastic elastomers.[8]

In the synthesis of ionomers two approaches are available: introduction of the ionic group by a post polymerization reaction, or copolymerization of an ion-containing monomer with a nonionic "covalent" monomer. Both approaches have been used in the literature and each has its own merits. The preparation of ionomers containing different types of ionic groups on an identical backbone is best achieved by a post-polymerization approach.(9) In preparing a series of ionomers with different backbone chains and the same ionic group, direct copolymerization may be the preferred approach.

The major objective of this research was to synthesize a series of ionomers by direct copolymerization of acrylic (and methacrylic) esters with salts of p-styrene sulfonic acid. The physical properties of the ionomers thus prepared were characterized by DSC, TMA, and stress strain tests. These studies were then used in an attempt to understand the properties of ionomers and the structural factors which affect them.

II. SURVEY OF THE LITERATURE

This section will be divided into three parts: an overview of the physical properties of ionomers, a discussion of the syntheses of sulfonate containing ionomers, and a review of emulsion polymerization.

A. Physical Properties of Ionomers

The physical properties of ionomers are most strongly influenced by the presence of ionic groups which associate to form multiplets and clusters. This association of ionic groups has been treated theoretically by Eisenberg.[10] In this paper it was proposed that in media of low dielectric constant, the association of ion pairs to yield ionic multiplets is very favorable. These ionic multiplets may grow to the maximum size allowable without steric crowding of the ionic groups or the incorporation of covalent material into the multiplet regions. Multiplets can then aggregate further via dipole-dipole attractions to form clusters. Eisenberg derived equations which estimate the size of these clusters by balancing the electrostatic work of cluster formation against the work of chain extension. The most important of these is equation 1 which shows the factors which should affect the formation of clusters in ionomers.[10]

Eq. 1 (from ref.10, Eq. 19)

$$n = \frac{\rho N_{AV}}{Mc}\left[\frac{4}{3kTc}\,\frac{1^2}{}\,\frac{h^2}{ho^2}\,\frac{Mc}{Mo}\,\frac{k'}{K}\,\frac{1}{4\pi Eo}\,\frac{e^2}{r} + 2\,\frac{No\,Mc}{P\,N_{AV}}\right]^{2/3} 3/2$$

where:

n is the cluster size, number of multiplets/cluster;

ρ is the density of the polymer;

N_{AV} is 6.02×10^{23};

Mc is the average molecular weight between ionic groups;

l is the length of a backbone bond;

k is Boltzman's constant;

Tc is the critical temperature above which the cluster breaks up;

$\overline{h_2}$ is the mean square end to end distance of a free chain;

$\overline{ho^2}$ is the mean square end to end distance of a freely jointed chain;

Mo is the molecular weight per repeat unit;

k' is a parameter calculated for the assumed cluster geometry;

K is the dielectric constant of the polymer;

$1/4\pi Eo = 1$ dyn $cm^2/statcoulomb^2$,

e is the electronic charge in ion pair;

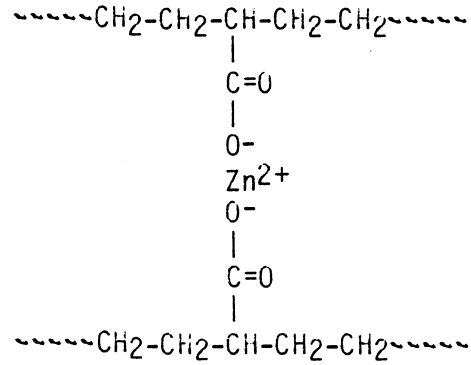
r is the distance between positive and negative charge centers.

The parameters which can be controlled are the concentration of ionic groups, the dielectric constant of the polymer and ratio of the charges on the ion pairs to distance separating their centers. The other factors are calculated theoretically, except for Tc which can be determined experimentally. Even this simplified treatment shows clustering to be a complex phenomenon which is not totally understood.

The idea that ions in polymers aggregate to form multiplets and clusters has lead to the development of a number of models which

attempt to describe the structure of ionic clusters.

The first model was proposed by Bonotto and Bonner[11] and is illustrated in Figure 1. No quantitative aspects were given in this model, but it clearly shows the exclusion of ionic groups as well as the unneutralized acid groups into small ionic domains which the authors referred to as "pockets". They also pointed out that their model could explain the effectiveness of monovalent counter ions which previous workers could not explain, since they believed divalent ions such as zinc acted as "crosslinks" by intermolecular association with two carboxylate anions, as depicted below:



The intermolecular crosslink could not occur with monovalent counter ions. In this respect this model was a significant advance in the understanding of ionomers even though it is rather basic when compared to later models.

Later models were developed based on experimental results from small angle x-ray scattering studies. These models were much more sophisticated than that proposed by Bonotto and have been reviewed recently by MacKnight and Earnest.[12]

The first of these models was proposed by Longworth and

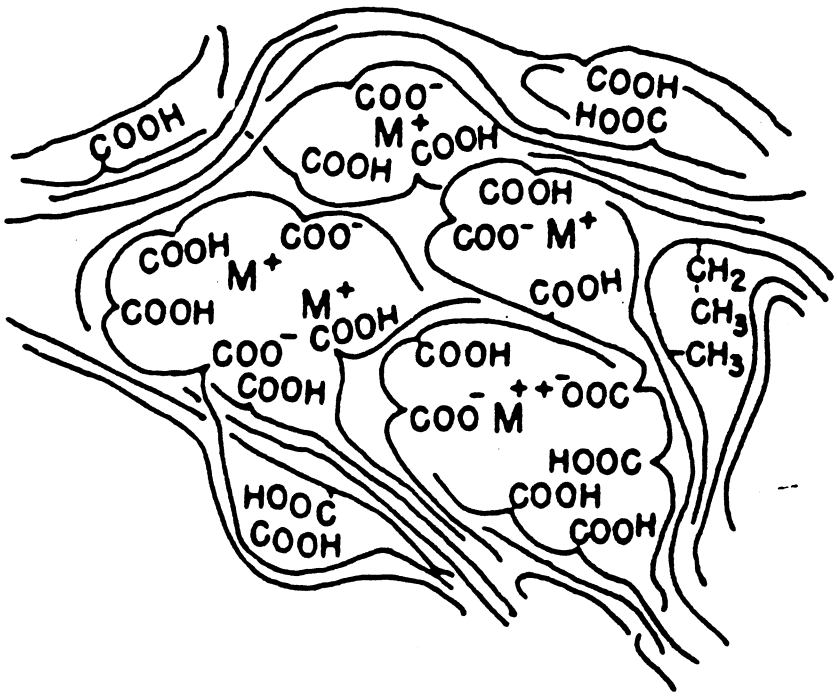
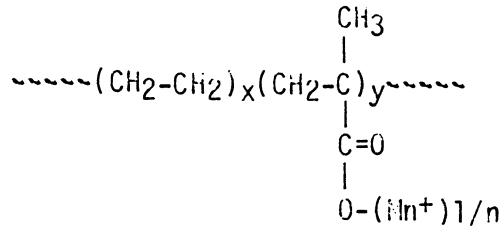


Figure 1. The Model of Bonotto et. al. for Ionic Aggregation. [From Bonotto and Bonner (1968) Ref. 11]

Vaughan[13] to describe ethylene-methacryclic acid ionomers which have the structure shown below.



(1)

This model, which is depicted in Figure 2, assumed that the "ionic" peak in the x-ray diffraction pattern shown in Figure 3[14] was due to the ordering of the hydrocarbon chain material imposed by the ionic aggregates at repeat distance of 20Å. This model is supported by the fact that even the lithium ionomer shows an "ionic" peak. This would not be expected if they were due to the ionic groups since lithium is known to scatter relatively weakly. The model also agrees with Eisenberg's theoretical treatment, with the exception that Longworth and Vaughan believed that a cluster will be derived from coordinated metal ions instead of multiplets. They pointed out that the the alkali metal ions used usually exhibit sixfold coordination.

MacKnight summarized a number of difficulties with this picture in his review[12] of the models of ionic clustering. For this model to show the ionic x-ray scattering peak at least five repeat units must be present, which requires a cluster size of at least 100Å. A cluster of this size would be expected to effect the degree of crystallinity of the ionomer. This was not observed for these ionomers, where it was observed that the well-annealed ionomers exhibited about the same degree of crystallinity as the acid form of the copolymers. A further

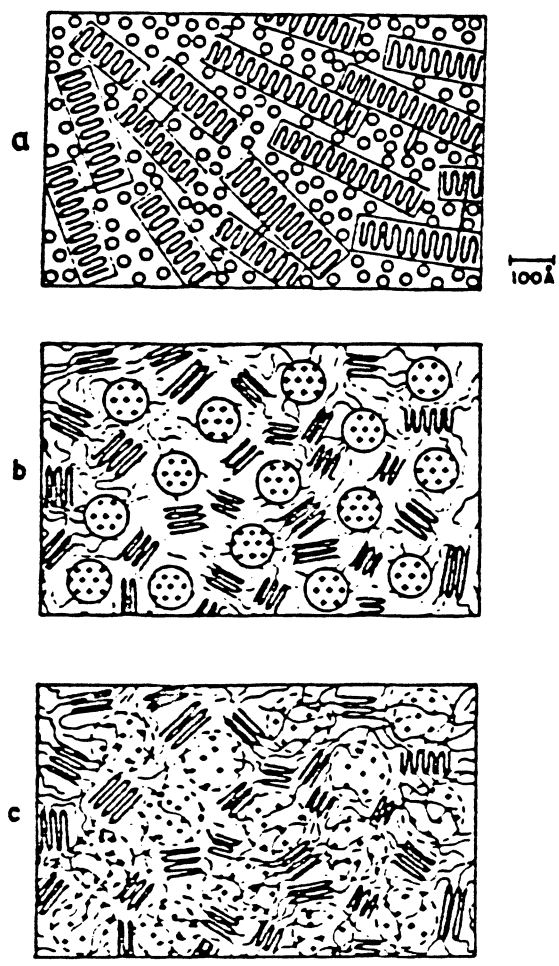


Figure 2. The Ionic Aggregation Model of Longworth and Vaughan. [From Longworth and Vaughan (1968) Ref. 13]

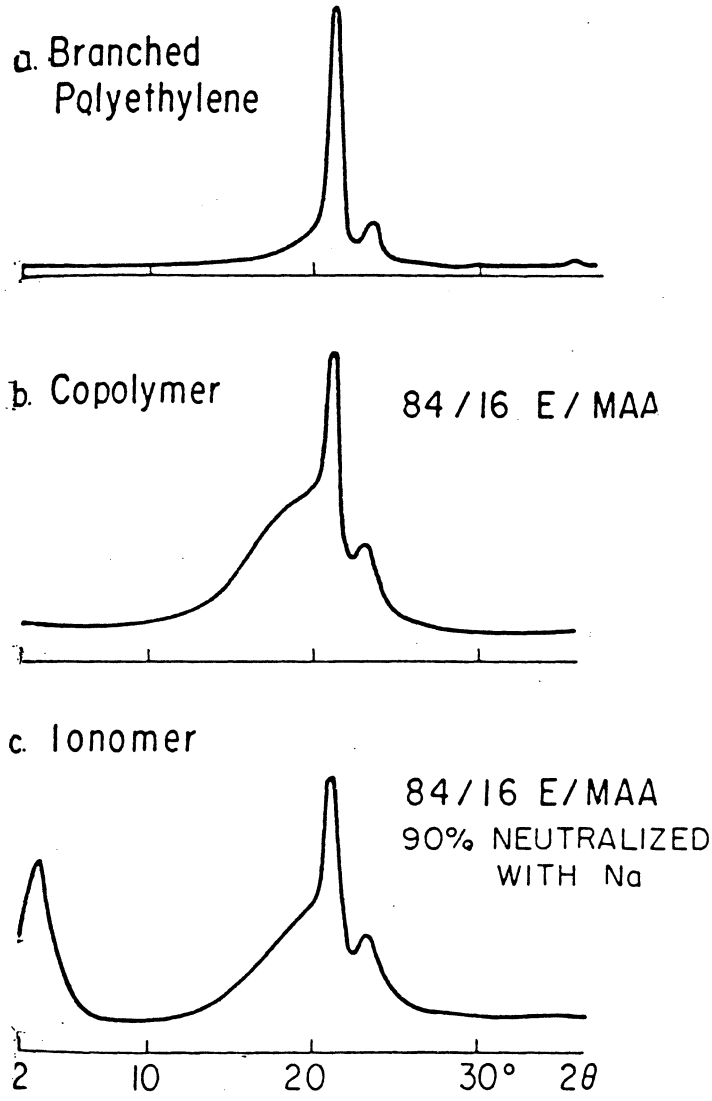


Figure 3. X-Ray Diffraction Patterns Polyethylene, Ethylene-Methacrylic Acid Copolymer, and the Ethylene Ionomer. [From Longworth and Vaughan (1968) Ref. 14]

difficulty with this model is that it is hard to explain how the regular repeat distance of 20Å can be imposed by ionic groups which are randomly distributed along the polymer chain.

Two other models have been developed which assume the ionic peak is due to electron density differences between the cations and the hydrocarbon material. These are very similar and MacKnight gives only brief mention of the model of Binsbergen and Kroon[15] with the model of Marx, Caulfield, and Cooper[16] being discussed much more thoroughly. Marx et. al. assumes the cations to be point scatters uniformly distributed in a paracrystalline lattice with no phase separation and only the formation of small aggregates. These aggregates contain both salt and acid forms of the carboxylate group.

One of a number of difficulties with this model is that it can not explain why a lithium salt ionomer shows an ionic saxs peak while the acid form of the copolymer does not. Since the electron density difference between the lithium carboxylate and the acid form is very small and both forms show the same degree of aggregation, both the lithium ionomer and the acid copolymer should show similar ionic peaks, which was not observed. A further difficulty pointed out by MacKnight with this model is that assignment of the ionic groups as point scatters in a paracrystalline lattice requires a considerable degree of regularity. It is difficult to envision how this regularity can be imposed in an amorphous random copolymer.

The last model discussed is that of MacKnight, Taggart, and Stein.[17] This model, depicted in Figure 4, was proposed after an

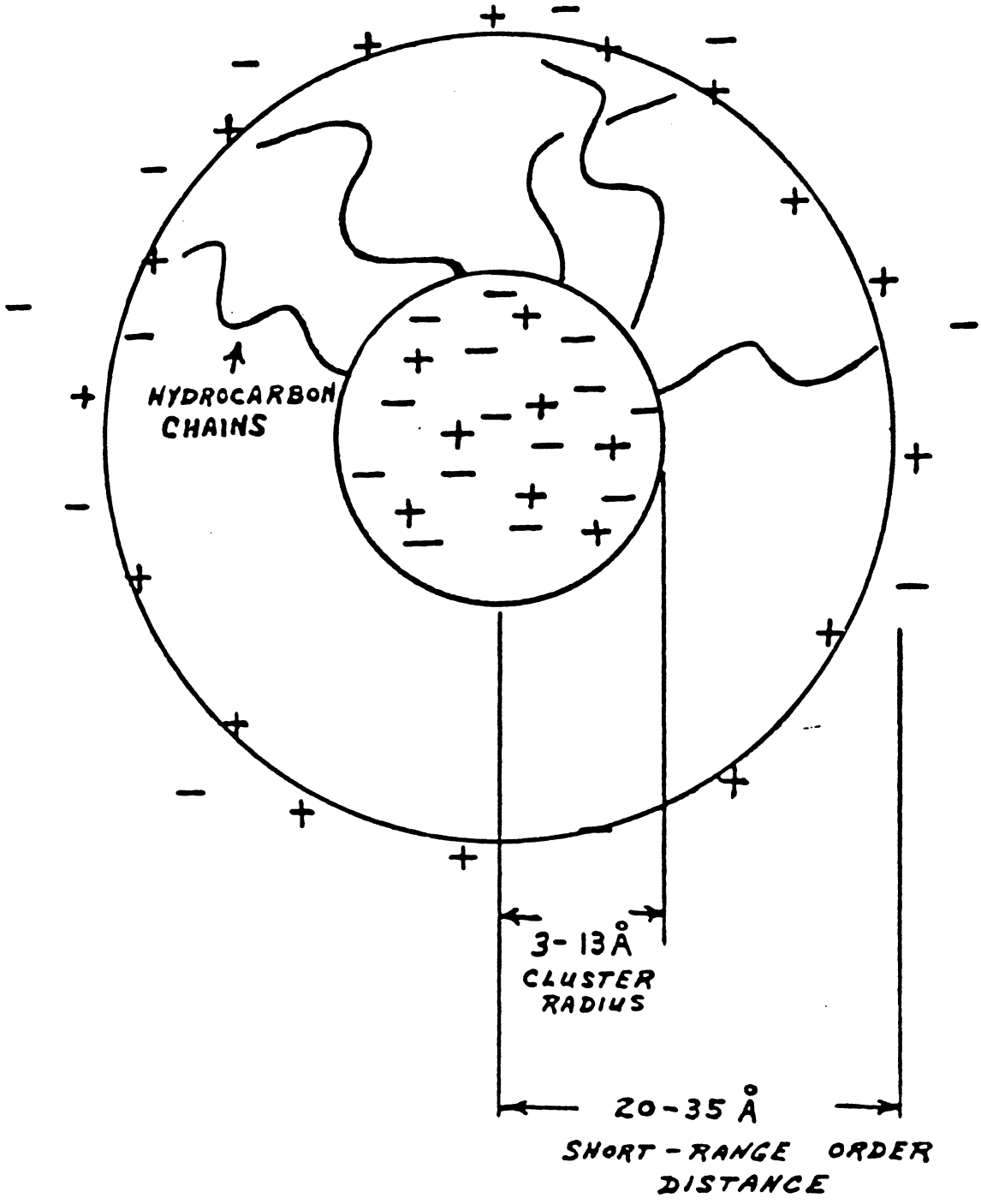


Figure 4. Schematic Drawing of the Ionomer Clustering Model of MacKnight et. al. [From MacKnight, Taggart, and Stein (1974) Ref. 17]

extensive analysis of small angle x-ray scattering data using the methods of Porod and Guinier[18,19] as well as a radial distribution function analysis of x-ray diffraction data. The model shows a cluster of 3-13Å radius separated from the matrix ions by shell of hydrocarbon material. This establishes a preferred distance of about 20Å for the matrix ions to the center of the cluster. Clusters built from coordinated metal ions will have a tendency toward charge imbalance which would establish a strong electrostatic attraction for the surrounding matrix ions. The matrix ions are limited in their approach by the hydrocarbon skin. This establishes a preferred distance of about 20Å for the matrix ions which is the origin of the ionic peak. This model gives the best agreement with the currently available x-ray scattering data and is consistent with the tendency of the metallic ions toward coordination.

From the above discussion one can see that clustering in ion-containing polymers is a complex problem which has not been completely elucidated. A more complete understanding of the nature of clustering in ion-containing polymers and the factors which affect it would allow a better understanding and control of the physical properties of ionomers.

The first ionomers to be thoroughly studied were copolymers of ethylene with methacrylic acid. DuPont markets these materials under the trade name "Surlyn". The copolymers have either zinc or sodium counter ions and have the structure shown previously. The first extensive study of this class of ionomers was reported by Rees and

Vaughan.[20,21] They studied a series of copolymers of ethylene with metacrylic acid which were partially neutralized to the sodium salt. The most striking properties of these polymers were their optical clarity and greatly increased tensile strengths as shown by haze and stress-strain measurements. This is illustrated in Figures 5 and 6. The clarity was attributed to a reduction in the size of the crystalline spherulites and the increased tensile strength was attributed to the increased in interchain forces due the presence of the ionic groups.

Stress-relaxation experiments by Ward and Tobolsky[22] indicated that these forces do not totally compensate for the reduction in the degree of crystallinity. In these experiments the high initial moduli produced by the ionic groups rapidly decayed in stress-relaxation as shown in Figure 7. These stress relaxation observations agree with those observed earlier for carboxylic rubbers and have been attributed variously to ionic bond exchange[23] and to a sparsely cross-linked network.[24] The authors [22] point out that neither theory completely describes the properties of the ionomers. They believed that the model proposed by Bonotto and Bonner[11] best explained the properties of these ionomers. This model was illustrated earlier in Figure 1 and predicts small domains containing the ionic material dispersed among the crystalline lamellae. The authors believed that these domains acted both as crosslinks and reinforcing filler for the crystalline regions.

The second most studied ionomer systems are those based on

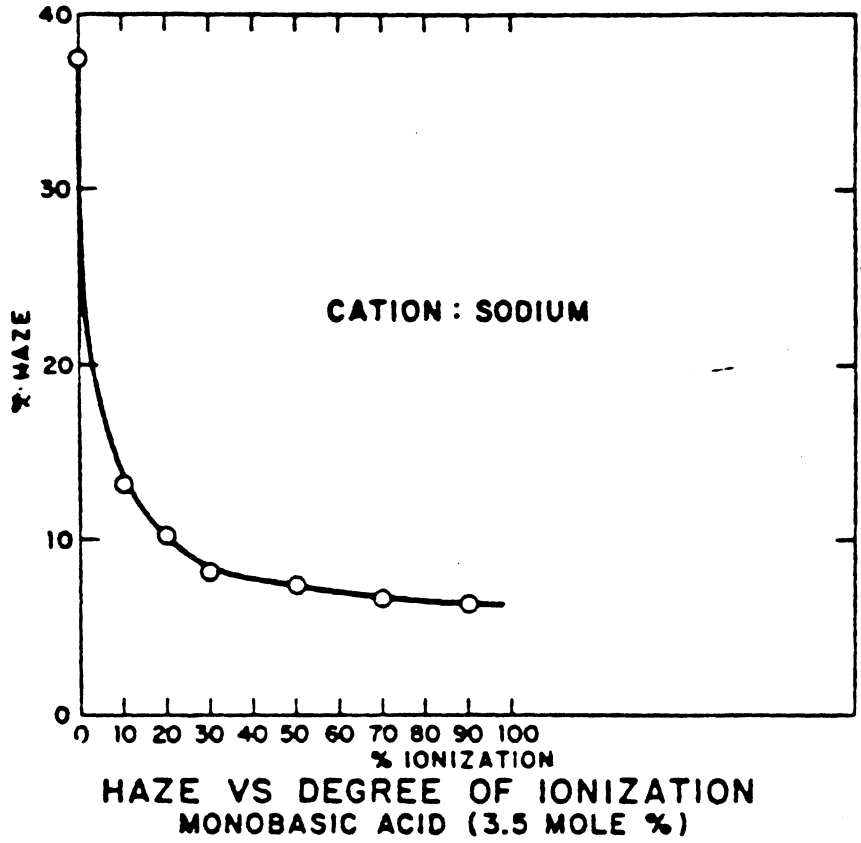


Figure 5. Haze as a Function of the Degree of Neutralization of a Ethylene-Methacrylic Acid Ionomer. [From Rees and Vaughan (1965) Ref. 20]

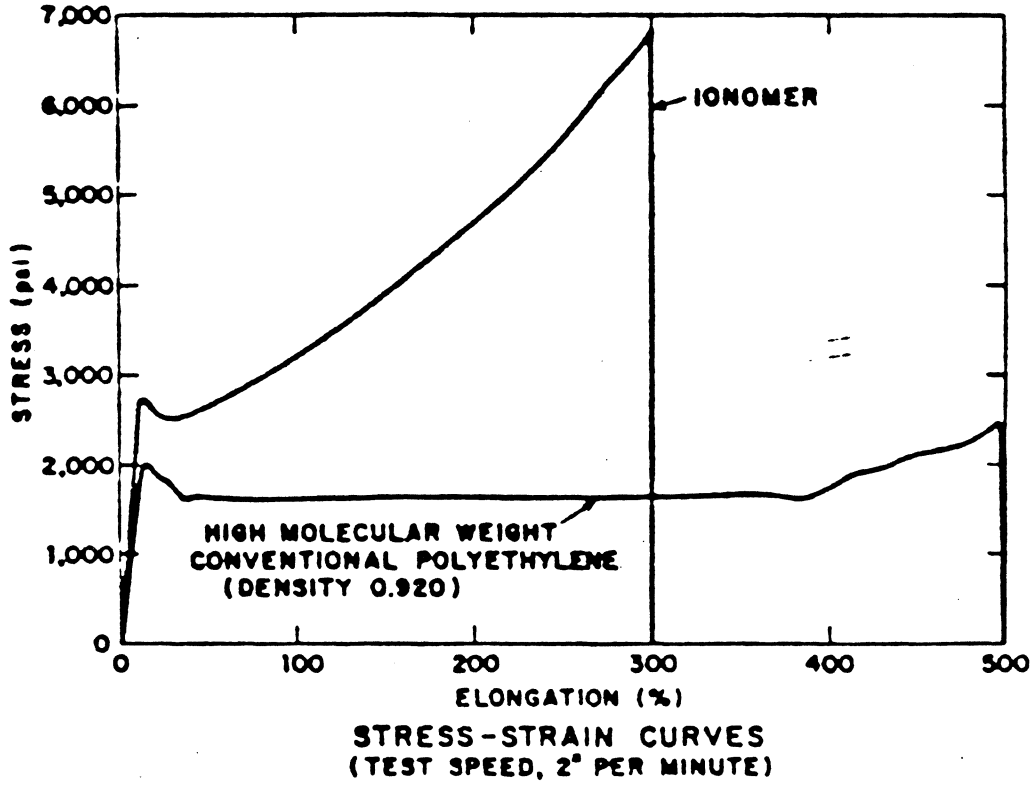


Figure 6. Stress-Stain Curves for Polyethylene and Ethylene Based Ionomer. [From Rees and Vaughan (1965) Ref. 21]

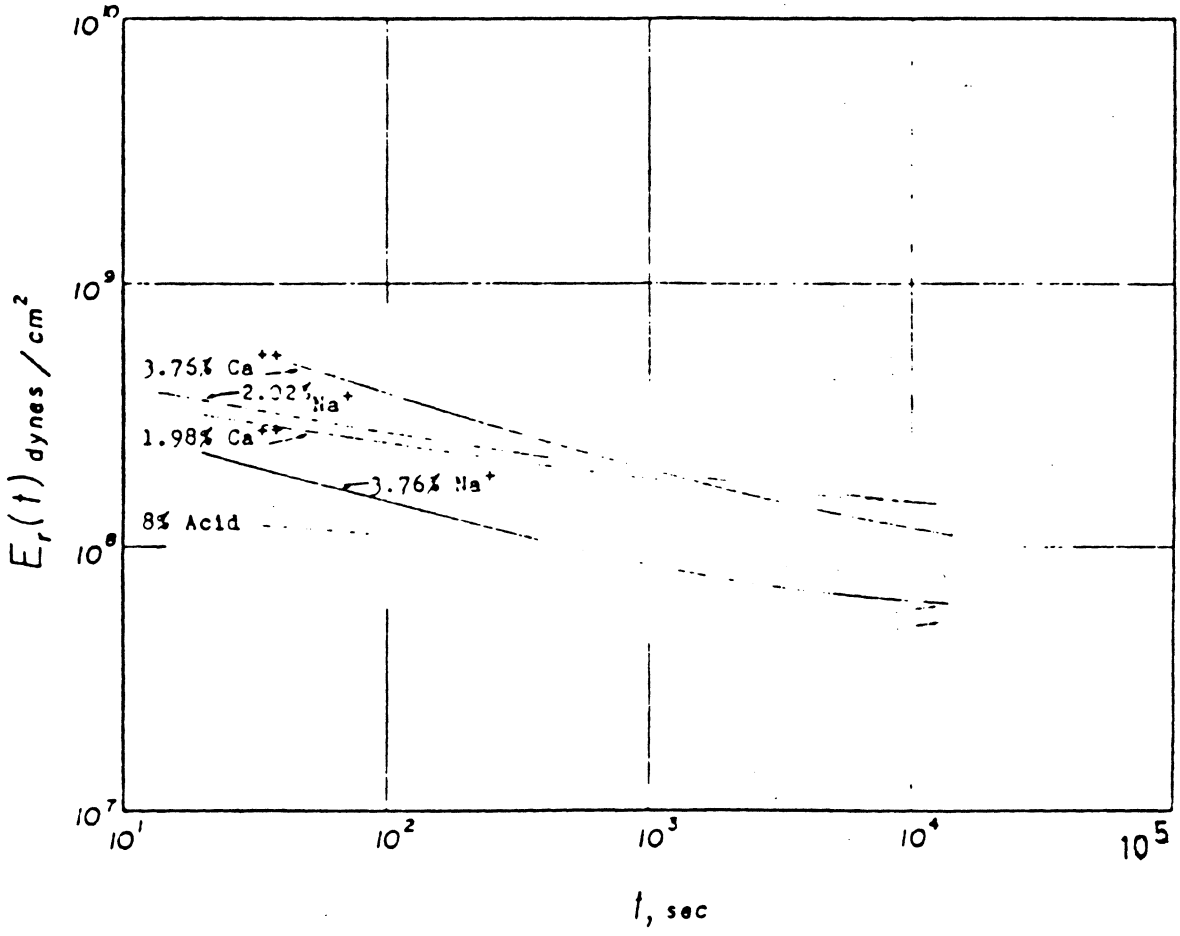
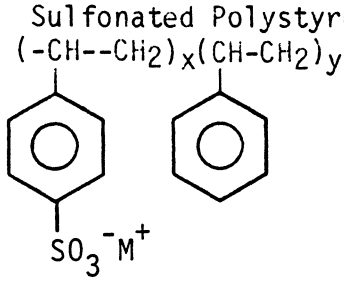


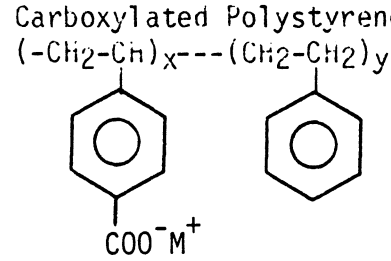
Figure 7. Stress-Relaxation Curves for Various Polyethylene Based Ionomers, Quick-Quenched and Run at 50°C. [From Ward and Tobolsky (1967) Ref. 22]

polystyrene. Most of these studies support the observations made on the ethylene methacryclic acid ionomers. One study which is of particular interest is a comparison of the carboxylate and sulfonate ionomers based on polystyrene.[25] In this case, carboxylate and sulfonate groups were introduced onto identical polystyrene chains with the structures shown below.

Sulfonated Polystyrene



Carboxylated Polystyrene



The introduction of either ionic group introduced a rubbery plateau and raised the glass transition temperature (Tg) of the ionomer as shown by thermal mechanical analysis (TMA) and as illustrated in Figure 8. However, the effect of the sulfonate group was observed to be much stronger than the carboxylate group. This was shown by the very well developed rubbery plateau of the sulfonate ionomer which persisted 75-100° above that shown in the carboxylate ionomer. Observations of melt rheology and solution viscosity also show a stronger ionic association for the sulfonate group. This strength was assumed to be due to the greater degree of polarization of the sulfonate group compared to the carboxylate group.

Perhaps the most interesting class of ionomers are the rubbery systems. These were, in fact, the earliest known ionomers and much of the early work was reviewed by H. P. Brown.[26] The early rubbery ionomers were known as carboxylic rubbers and were prepared by

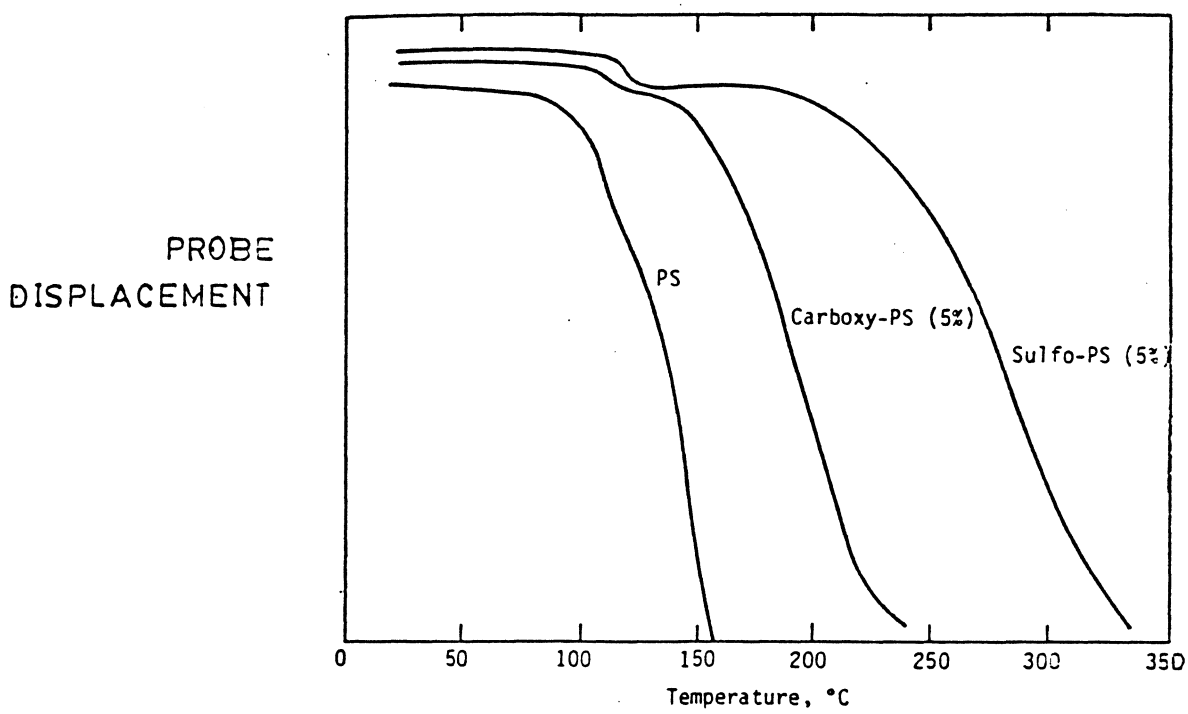
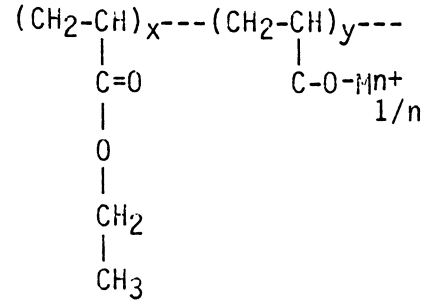


Figure 8. Thermal Mechanical Analysis Curves of Polystyrene(PS) Carboxylated Polystyrene (Carboxy PS) and Sulfonated Polystyrene (Sulfo-PS). [From Lundberg and Makowski (1980) Ref. 25]

copolymerizing carboxylic acid containing monomers with monomers such as butadiene or the acrylic esters. These ionomers showed increased tensile strengths, hardness, abrasion and oil resistance when compared to the rubbery homopolymers. Unfortunately these enhanced properties were also accompanied by poor permanent set compared to sulfur cured vulcanizates. Mixed (eg. Ionic or Sulfur) vulcanization systems have recently been reviewed.(27)

A particular study by Eisenberg et al.(28) is of particular interest to this thesis. Eisenberg studied the viscoelastic properties of ethyl acrylate - acrylic acrylic acid ionomers, the structure of this ionomer is shown below.



It was found that ionic clustering took place at about 12 mole % acrylic acid, as indicated by the failure of time temperature superposition in stress-relaxation experiments as illustrated in Figure 9. The non superposability of the individual stress relaxation curves for 16.3 and 24.7 mol % acrylic acid ionomers indicates that more than one stress-relaxation mechanism exists and that each have different temperature dependencies. This is attributed to the onset of ionic clustering above 12 mole % acrylic acid. This is also the region where

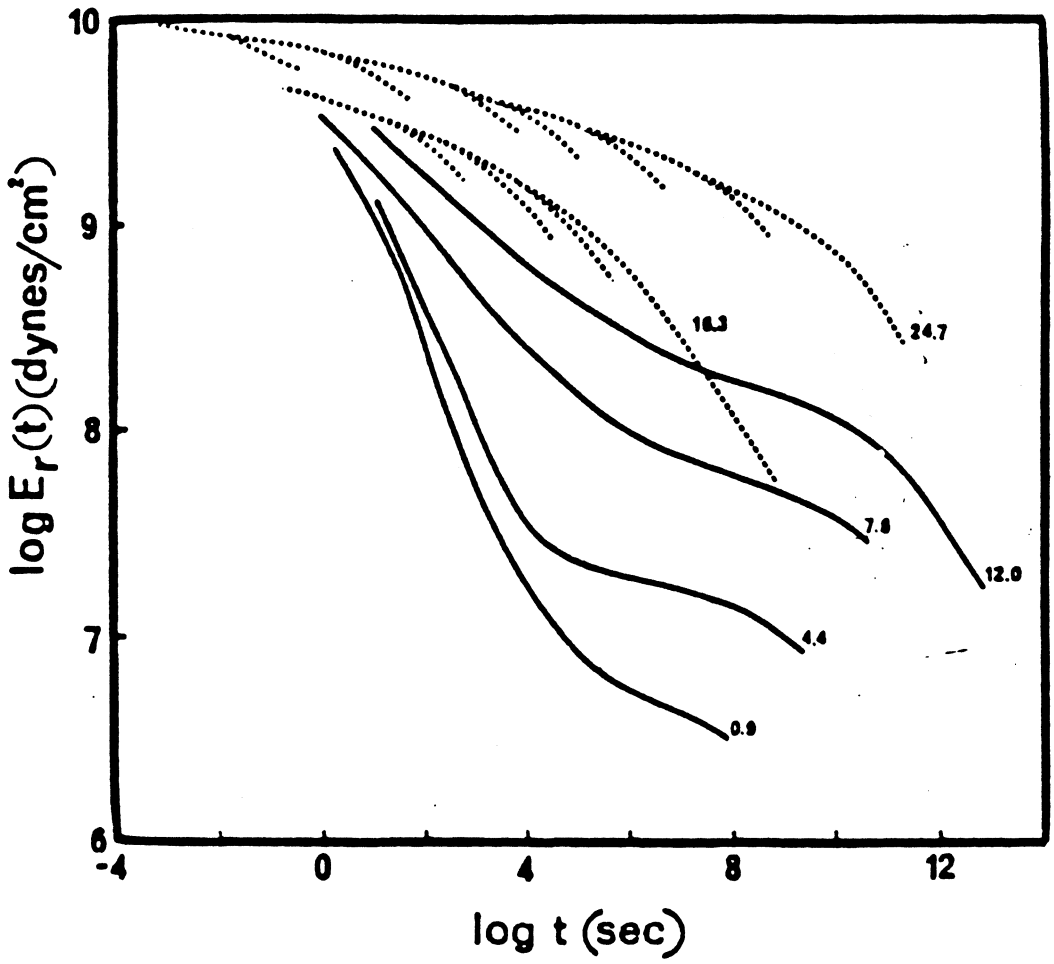
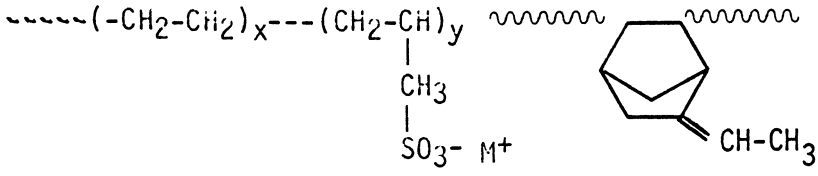


Figure 9. Attempted Stress-Relaxation Master Curves for Ethyl Acrylate Ionomers. [From Eisenberg, Matsuura, and Tsutsui (1980) Ref. 28]

a change was observed in an earlier study[29] of the effect of water absorption on the glass transition temperature. Thus, ion clustering in ionomers seems to be dependent on the dielectric constant of the medium, since clustering was of observed in styrene ionomers containing more than 6 mole % methacryclic acid.[30]

Another type of rubbery ionomer which is of interest is the ionomers prepared by sulfonation of random ethylene-propylene diene terpolymers[31] (EPDM). The diene monomer used in these ionomers was ethylidene norbornene (ENB) and the copolymers were sulfonated to the desired level of sulfonation with the resulting ionomers may have structure as shown by W. Thaler[32].



The sulfonate groups in these ionomers were shown to give strong ionic "crosslinking". This crosslinking which affects the tensile strength and dilute solution and melt viscosities is influenced significantly by the nature of the counter ion as shown in Table 1.[33] Table 1 also shows the effect of plasticization of the ionomer with zinc stearate, which selectively plasticizes the ionic interactions. By proper selection of the counter ion and plasticizer level, ionomers with mechanical properties and melt viscosities in the proper range for

Table I

Effect of Cation and Zinc Stearate on Flow and Physical Properties[a]

Metal	Apparent Viscosity[b] (poise x 10^{-5})	Tensile Strength (psi)	Elongation (%)
	Unplasticized		
Hg	--	--	--
Mg	55.0	320	70
Ca	53.2	410	90
Co	52.3	1180	290
Li	51.5	760	320
Ba	50.8	340	70
Na	50.6	960	350
Pb	32.8	1680	480
Zn	12.0	1480	400
	Plasticized[c]		
Hg	12.7	400	160
Mg	5.7	2130	510
Ca	6.0	1900	470
Co	6.1	2020	490
Li	3.4	1970	480
Ba	10.7	1710	480
Na	5.0	1690	500
Pb	3.0	2312	460
Zn	1.5	2470	480

[a] Base Polymer; sulfonate content - 31 meq/100g EDPM; dissolved 100 g of free acid in 1000 ml hexane - 150 ml isopropanol; neutralized with 90 meq acetate in 25 ml water.

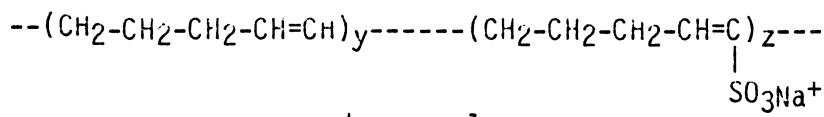
[b] At 200°C and 0.88 sec^{-1}.

[c] With 90 meq of zinc stearate/100 g of polymer.

[From Makowski and Lundberg (1980) Ref. 33]

thermoplastic elastomers could be produced. More recently Lundberg et al. have studied the viscoelastic dynamic mechanical properties[34] of these ionomers. They found the properties to be dependent on the degree of sulfonation as well as the type of counter ion.

The only other sulfonated rubbery ionomer which has been studied in depth are the polymers prepared by sulfonation of polypentenamer[35] as shown below. Interestingly, only the cis isomer was easily sulfonated.



random copolymer

The major difference noted in this ionomer compared to sulfonated EPDM is that clear evidence of ionic clustering was shown by a change in the slope of a plot of glass transition temperature versus mole percent sulfonation as shown in Figure 10. These ionomers showed increasing strength with increasing percent of sulfonation as do sulfonated EPDM's and appear quite similar except for the observations of the onset of clustering. This difference may be due to the difference in the sulfonate contents of the two types of ionomers studied.

In the past few years the dilute solution properties of ionomers have been studied[36-38]. Their solution behavior is indeed one of the interesting aspects for future ionomer study.

From the studies discussed above one can see that ion-clustering

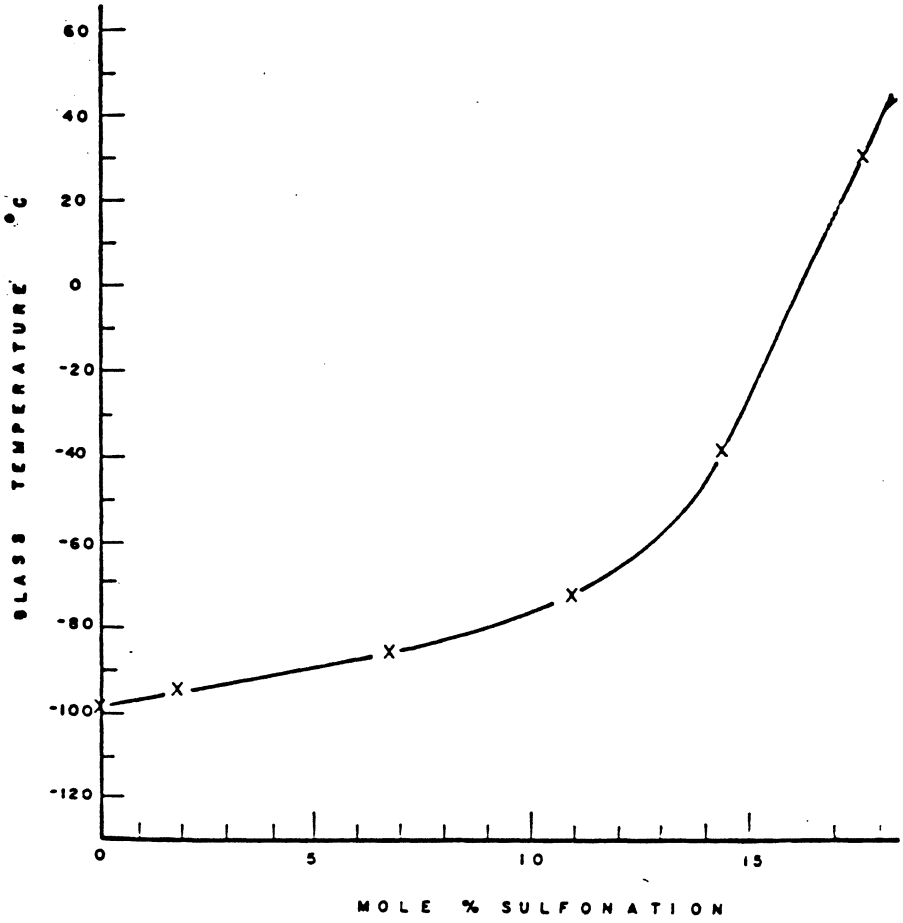


Figure 10. Glass Transition Temperatures as Function of Sulfonate Content. [From Rahrig and MacKnight (1980) Ref. 35]

has a strong influence on the properties of ionomers. The rubber based ionomers are of particular interest for their possible applications as thermoplastic elastomers.

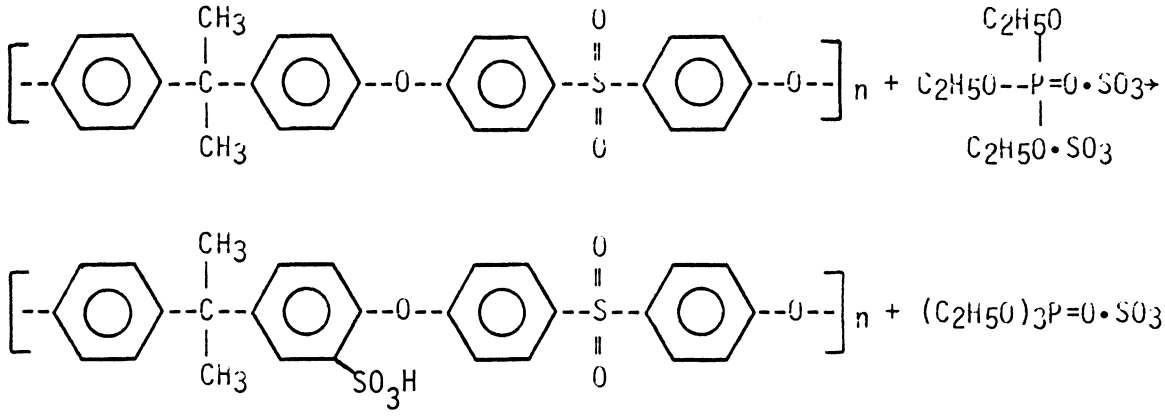
B. Synthesis of Sulfonated Ionomers

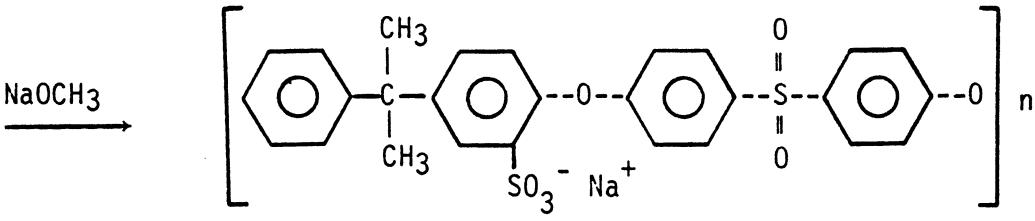
Two major routes have been used in the literature for the synthesis of sulfonated ionomers. These are post polymerization sulfonation and direct copolymerization of sulfonated monomers with a covalent comonomer.

Post polymerization sulfonation has found application in the preparation of ion exchange resins from styrene-divinyl benzene networks, and has been used to prepare sulfonated polystyrene polyelectrolytes.

More recently an ionomer has been prepared by the post-polymerization sulfonation of bisphenol A polysulfone[39] by the route shown in Scheme 1.

Scheme 1

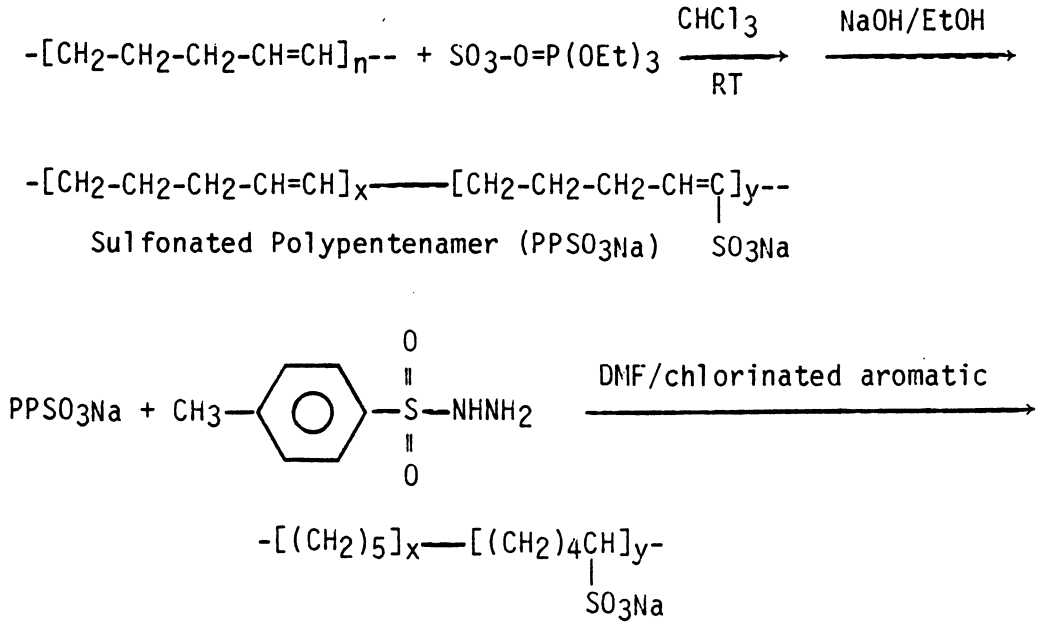




The triethyl phosphate-sulfur trioxide (TEP-SO_3) complex used in this scheme allowed high degrees of sulfonation which could be controlled by the amount of complex used. These sulfonated polysulfones are under study for reverse osmosis desalination membranes, and work has continued in our laboratories on the preparation of sulfonated polysulfones using a number of sulfur trioxide complexes.(40)

Post polymerization sulfonation has also been used for the preparation of sulfonated polypentenamer and its hydrogenated derivative as shown in Scheme 2.(41)

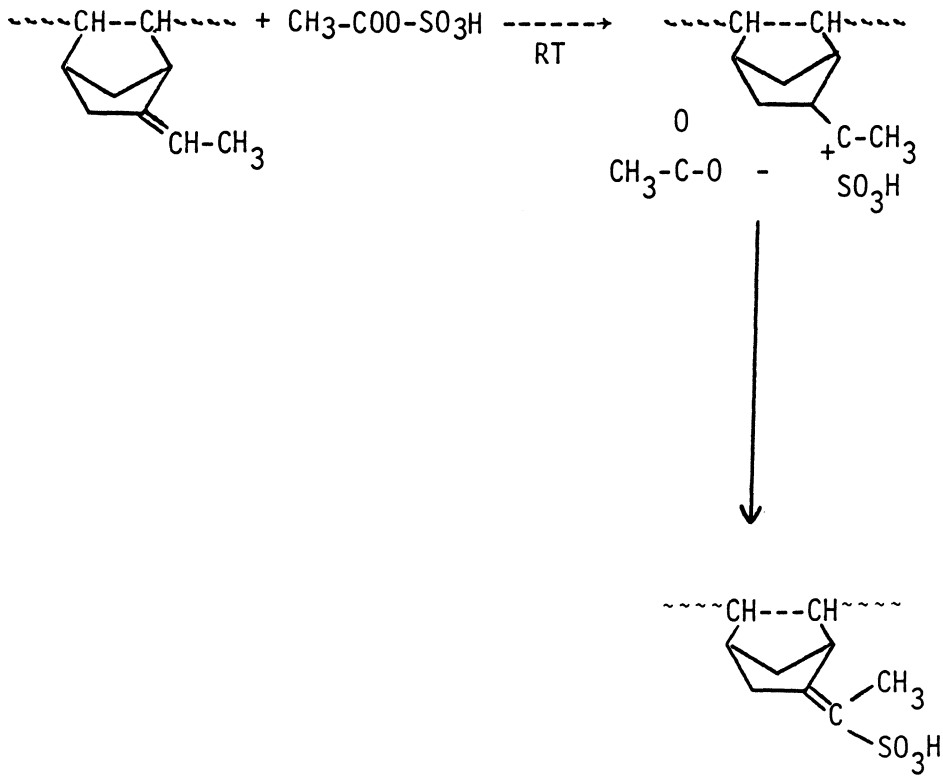
Scheme 2



The major difference between this sulfonation reaction and the one used for the sulfonated polysulfones was the use of a 1:1 SO_3-TEP complex. This complex did not give efficient sulfonation of the polysulfone which required a 2:1 complex.

Another group of ionomers prepared by post polymerization sulfonation were the sulfonated EPDM's[42] by the route shown in Scheme 3.

Scheme 3



This route used the mixed anhydride formed by the reaction of sulfuric acid with acetic anhydride as the sulfonating agent. This reagent sulfonated EPDM in hydrocarbon solvents "rapidly and

reproducibly according to the authors.

The remainder of the sulfonated ionomers have been prepared by direct copolymerization of a monomer containing sulfonic acid or sulfonic acid derivative groups with a covalent vinyl monomer. In order to understand these copolymerization studies a brief review of copolymerization reactivity ratios and the Price-Alfrey Q-e scheme will be provided.

In any chain copolymerization there are at least four possible propagation steps each with its own rate constant as shown in the scheme below outlined by Odian.(43)

$$\sim\sim\sim\sim M_1^* + M_1 \xrightarrow{k_{11}} \sim\sim\sim\sim M_1 - M_1^*$$

$$\sim\sim\sim\sim M_1^* + M_2 \xrightarrow{k_{12}} \sim\sim\sim\sim M_1 - M_2^*$$

$$\sim\sim\sim\sim M_2^* + M_1 \xrightarrow{k_{21}} \sim\sim\sim\sim M_2 - M_1^*$$

$$\sim\sim\sim\sim M_2^* + M_2 \xrightarrow{k_{22}} \sim\sim\sim\sim M_2 - M_2^*$$

Where Ma^* depicts an active chain end of monomer type a. The reactivity ratios are defined as.

$$r_1 = \frac{k_{11}}{k_{12}} \text{ and } r_2 = \frac{k_{22}}{k_{21}}$$

There are three types of copolymerization behavior as defined by the values of r_1 and r_2 and their product as outlined by Odian.(43)

In the first types of copolymerization, termed "ideal"

copolymerization, $r_1r_2=1$, both propagating species M_1^* and M_2^* show the same reactivity toward one or the other of the monomers. This leads to the relatively random incorporation of monomers into the copolymers, although one of the monomers may still be consumed more rapidly. In the special case where $r_1=r_2=1$ then the monomers are incorporated into the copolymer at the ratio of the monomer feed composition and in a perfectly random placement.

The second type of copolymerization termed alternating copolymerization, occurs when $r_1=r_2\cong 0$. This occurs when neither of the active chain ends M_1^* or M_2^* can easily add to a monomer of its own type and indeed, prefers to add to the second monomer. This leads to the perfectly alternating incorporation of the two monomers into the copolymer.

The third type of copolymerization, termed block copolymerization takes place when $r_1>1$ and $r_2>1$. This results when both chain ends prefer to add their own type monomer. This tends to cause the formation of block copolymers with blocks of both types of monomer sequences, assuming the growing species has a long lifetime. It is important to note that in free radical polymerization the short radical lifetimes and transfer processes usually prohibit the formation of block copolymers by this method, and instead undesirably produce homopolymer mixtures.

These three types of behavior are only limiting cases of copolymerization. In fact most copolymerizations show an intermediate type of behavior, being somewhat random with tendencies towards

either alternation or block formation. Because of the importance of reactivity ratios in controlling the copolymer composition, various attempts have been made to develop schemes to predict reactivity ratios.

One of the most successful of these is the Semi-empirical Price-Alfrey Q-e scheme.[44] This approach allows the calculation of the reactivity ratios from the Q and e values for the two monomers by equations 2 and 3.

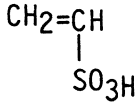
$$(2)\quad r_1 = \frac{Q_1}{Q_2} \exp\left[-e_1(e_1-e_2)\right]$$

$$(3)\quad r_2 = \frac{Q_2}{Q_1} \exp\left[-e_2(e_2-e_1)\right]$$

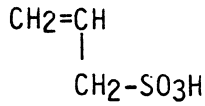
The Q and e values are determined by experimental copolymerizations and are related to the standard values for styrene assigned as Q=1 and e = -0.80. The Q value is a factor related to the reactivity of the monomer; the larger the value, the more reactive the monomer. The e value is a factor related to the polarization of the double bond in the monomer. The same value is also assumed for the radical as for the corresponding monomer. A negative e value indicates a relatively negative polarization and a positive value suggests a relatively positive polarization. This approach deals with only the reactivity of the monomer and the electrostatic attraction of the monomer to the chain end.

Despite obvious deficiencies, the Q,e scheme has been proved to be fairly successful in many copolymerization systems.

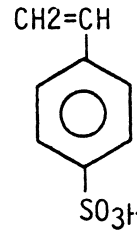
About half a dozen different significant sulfonated monomers have been reported in the literature in copolymerization systems. The most extensively studied of these are the vinyl, allyl, and p-styrene sulfonic acids shown below.



vinyl sulfonic acid (VSA)



allyl sulfonic acid (ASA)



p-styrene sulfonic acid (SSA)

The most important of these is p-styrene sulfonic acid. This monomer is particularly interesting, since it can be quite readily synthesized and is potentially useful for copolymerization with a variety of comonomers. This interest has been shown by extensive numbers of publications in the literature of copolymers containing this monomer. It is now commercially available from DuPont, and elsewhere.

The vast majority of these publications are patents for copolymers and terpolymers containing sulfonated styrene. These patents unfortunately do not provide any details of copolymerization reactivity ratios of this monomer nor do they extensively study the physical properties of the resultant polymers. The sulfonated styrene was generally used to impart some particular property to the polymer for

such applications as coatings and fibers. The patent literature never-the-less suggests the feasibility of copolymerizing sulfonated styrene with a range of different vinyl monomers.

More recently sulfonated sytrene has been studied in a number of papers in the literature which describe its copolymerization reactivity ratios with a range of vinyl monomers.

The first of these papers describes the copolymerization of styrene with potassium p-styrene sulfonate.[45] This copolymerization was carried out in dimethyl formamide solution at 90° and 110° using t-butyl hydroperoxide as initiator. The conditions of the copolymerization were such that the copolymer precipitates as it forms. Surprisingly, this did not seem to affect the composition of the copolymers which were charged high in styrene content (80 mole % styrene in monomer feed) and which gave reproducible compositions as determined by potassium analysis. The copolymers of low styrene charge content (30 mole % in the feed) however did not give reproducible copolymer compositions. Rather there were two distinct sets of copolymer compositions obtained. This may have been due to absorption of sulfonated styrene onto the precipitated polymer. For this reason and the fact that only two monomer feed compositions were used (80 and 30 mole % styrene) no serious emphasis should be placed on the copolymerization reactivity ratios reported in this paper for the styrene-potassium p-styrenesulfonate system. This paper does however demonstrate the copolymerizability of potassium-p-styrenesulfonate.

A later paper by Izumi et. al.[46] describes the copolymerization kinetics of acrylonitrile (AN), ($\underset{\sim}{2}$) with sodium p-styrene sulfonate (NaSS) in DMSO at 45° using azobisisobutyronitrile (AIBN) as initiator.

$$CH_2 = \underset{\underset{C\equiv N}{|}}{CH}$$

$\underset{\sim}{2}$

The authors reported no difficulty in determining reactivity ratios in this study and values of $r_{(AN)} = 0.15$ and $r_{(NaSS)} = 0.55$ were reported. This indicates a tendency of both the acrylonitrile and sulfonated styrene radical chain ends toward crossover propagation. There would therefore be a tendency toward forming an alternating copolymer in this system.

The Price-Alfrey Q-e values for sodium p-styrenesulfonate calculated from the reactivity ratios and the known Q and e values for acrylonitrile (1.20 and 0.44) are Q = 0.44 and e = -0.38. This would suggest that this monomer is less reactive than styrene, and that the double bond of NaSS is somewhat less strongly negatively polarized than in styrene. This may explain why the copolymerization of acrylonitrile appears to be more alternating with NaSS than with styrene, since the strong electrostatic attraction of oppositely polarized monomers is decreased.

The initial rate of polymerization as a function of monomer feed composition was also investigated in this paper. At approximately 90 mole % NaSS in the monomer feed, the initial rate of polymerization was higher than in alternative composition regions as shown in Figure 11.

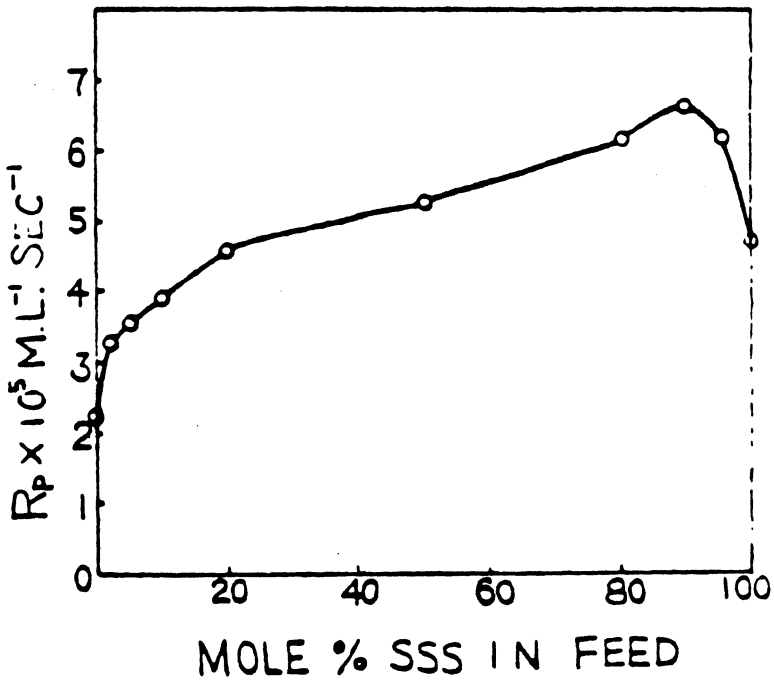


Figure 11. The Initial Rate of Polymerization as Function of Sodium Styrenesulfonate, for the Acrylonitrile-Sodium p-Styrenesulfonate, in DMSO Solvent System. [From Izumi et. al. (1965) Ref. 46]

Under microscopic observation, two liquid phases were observed at the temperature of polymerization for this feed composition. The authors felt that this may have been the cause of the higher rate of polymerization.

The same workers[47] had earlier reported the copolymerization of acrylonitrile with sodium p-styrenesulfonate in aqueous media at pH values of 3 and 7 at 45°C. In this paper they show that the media has a significant influence on the copolymerization of NaSS with acrylonitrile. This is shown by the different reactivity ratios exhibited for this system at pH 3 and 7 namely, r_{AN} = 0.10 and r_{NaSS} = 1.20 at pH 3, and r_{AN} = 0.05 and r_{NaSS} = 1.40 at pH 7. From these reactivity ratios and the known Q and e values for acrylonitrile, the Q and e values for NaSS were calculated.

The Q and e values reported for NaSS in aqueous solution are; Q = 0.76 and e = -0.26 at pH 3 and Q = 1.24 and e = -0.43 at pH 7. These values combined with those found in DMSO solution indicate a strong influence of the medium on the copolymerization reactivity of NaSS.

In studying the initial rates of polymerization of these systems the authors noted a similar behavior to their DMSO solution study. In particular the rate of polymerization was shown to have a maximum at about 5 mole % NaSS in the monomer feed as shown in Figure 12. This maximum occurred at low NaSS content while the maximum in DMSO solution occurred at high NaSS content. The behavior was similar in that the

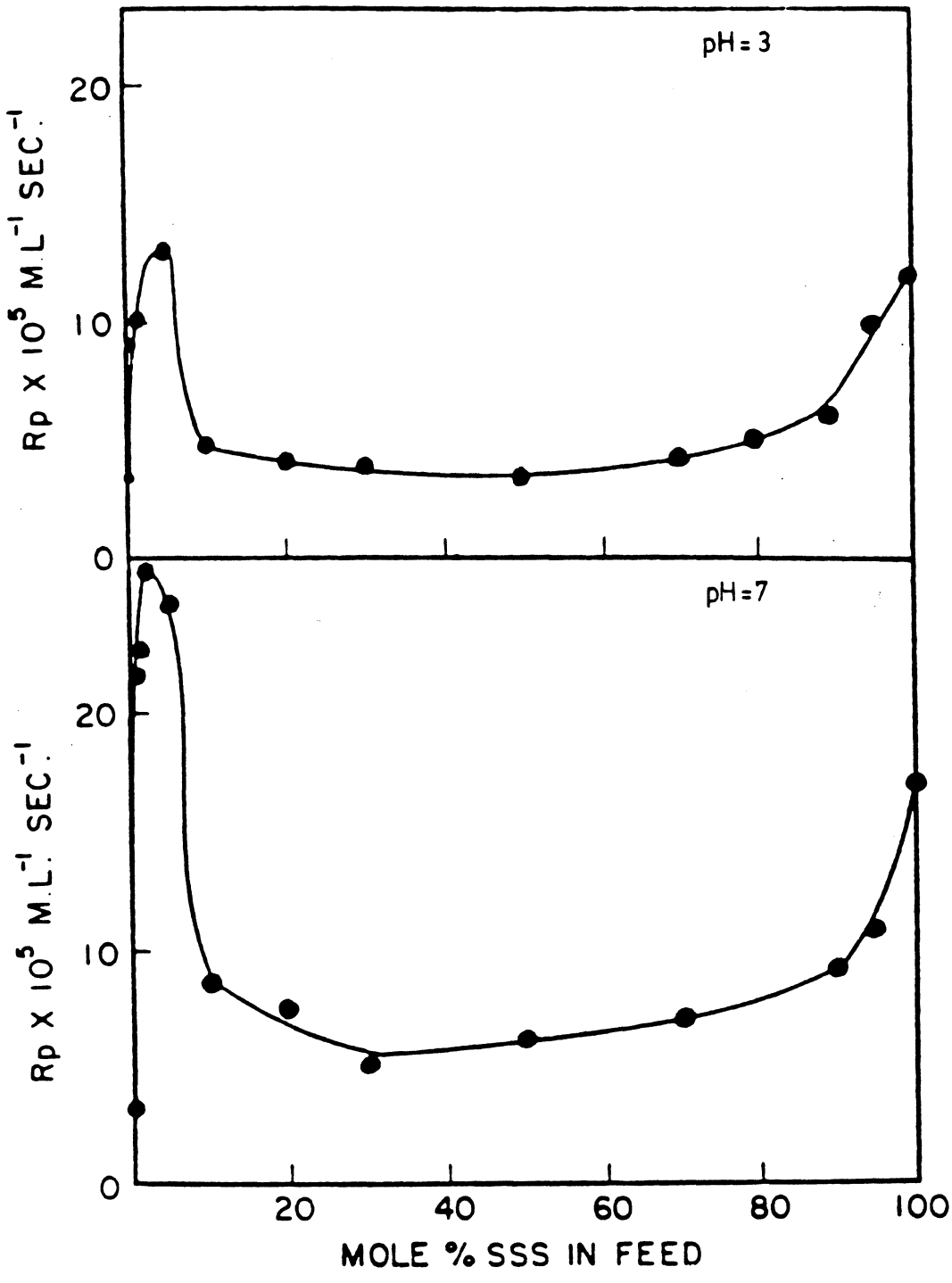
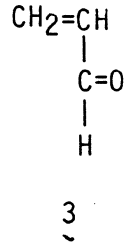


Figure 12. The Initial Rate of Copolymerization for the Acrylonitrile-Sodium P-Styrenesulfonate System in Aqueous Media. [From Izumi et al. (1963) Ref. 47]

authors attributed it to the multi-phase nature of this polymerization.

An earlier paper by Grabiel and Decker[48] also studied the copolymerization of sodium p-styrenesulfonate in aqueous media at pH 7 and 40°C. The authors reported identical reactivity ratios within experimental error to those later reported by Izumi et al. The authors also studied the acrylonitrile-potassium p-styrenesulfonate system under identical conditions to the AN-NaSS system. They found that changing the counter ion from sodium to potassium had no effect on the copolymerization under these conditions. The authors also report on the copolymerization of NaSS with acrylic acid at 70° in water solution of pH 7. This copolymerization gave an ideal copolymerization ($r_1r_2=1$).

A study on the copolymerization characteristics of acrolein (structure 3) in aqueous solutions used sodium p-styrenesulfonate as one of the comonomers.[49] This study found an increaing tendency



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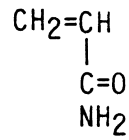
toward alternation in these systems with increasing pH as evidenced by the decreasing r_1r_2 values of 0.106 at pH 3, 0.012 at pH 5, and 0.0065 at pH 7. The reactivity ratios were also used to calculate Q and e values for acrolein using the Q and e values for NaSS at pH 3 reported by Izumi et al., these were then used to calculate Q and e values for NaSS at pH 5 and 7.

The Q and e values found for NaSS are; Q = 0.51 and e = -0.87 at pH 5, and Q = 0.39 and e = -1.00 at pH 7. This indicates a strong influence on the double bond polarization with changes in pH, and only a slight influence on the monomer reactivity. The influence on polarization being to increase negative polarization with increased pH. This change in polarization is consistent with the conclusions of a later study by Kurenkov and Myagchenkov[50] of the copolymerization of sodium and potassium p-styrenesulfonate.

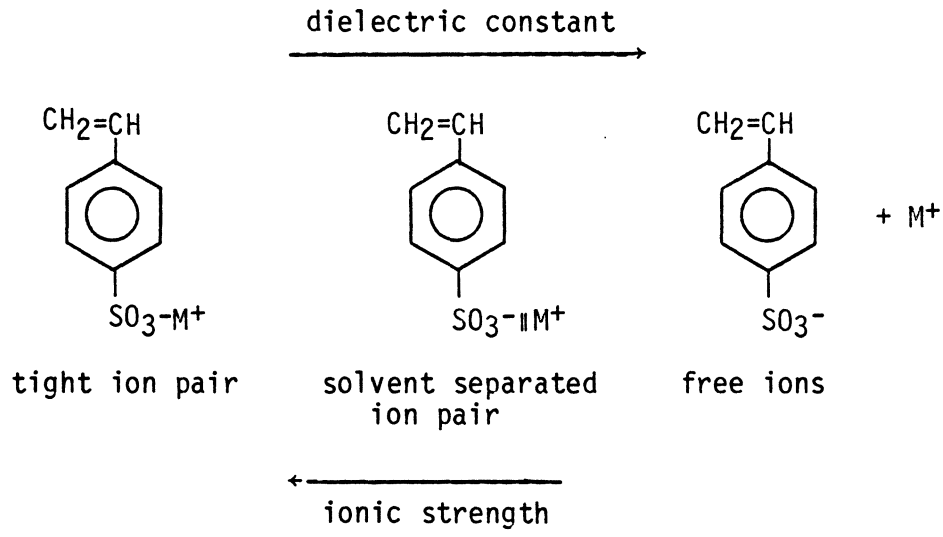
These authors[50] studied the copolymerization of sodium p-styrenesulfonate with acrylamide (structure 4) in water-salt and water-DMSO mixtures. They concluded that the reactivity of styrene-



4

sulfonate salts is dependent on the dielectric constant of the medium and on the ionic strength of the solution in which it is being polymerized. This was attributed to a shift in the monomer dissociation equilibrium shown in Scheme 3. Because of this influence the authors believed reactivity ratios and Price-Alfrey Q and e values

Scheme 3

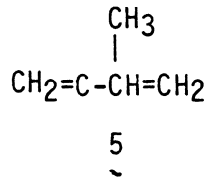


for these systems were only useful at constant ionic strength and constant dielectric constant.

In a recent paper Lundberg et. al.[51] studied the emulsion copolymerization of butadiene with sodium styrenesulfonate using hydrocarbon soluble initiators. They found the emulsifier played an important role in copolymerizing NaSS with butadiene. The emulsifier influenced both the rate of polymerization and the incorporation of NaSS into the copolymer. The concentration of NaSS monomer also influenced the rate of polymerization and the sulfonate content of the copolymers.

Thus, sulfonated styrene salts can be copolymerized with a range of different comonomers in various media. The factors which affect this copolymerization are however not totally understood, although dielectric constant, ionic strength and possibly the sulfonated styrene salt concentration play important roles in controlling the copolymerization.

The only other approach used to synthesize ionomers containing styrenesulfonate groups was the emulsion copolymerization of esters of styrenesulfonic acid with isoprene (structure 5).[52] This was followed by hydrolysis of the sulfonate ester groups in the copolymer



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to produce styrenesulfonate salt groups. This approach allowed the synthesis of soluble copolymers of isoprene with high sulfonate ester contents which could be hydrolyzed to sulfonate salt groups. This approach can not be used however with comonomers containing easily hydrolyzable groups such as the acrylic esters. Also the sulfonate esters are believed to be considerably more toxic than the salts.

C. Review of Emulsion Polymerization

Emulsion polymerization has proved to be one of the most useful methods of polymerizing vinyl monomers. The major advantages of emulsion polymerization are faster polymerization rates, higher molecular weights, good heat transfer (to remove the heat of polymerization), and the possibility of using the emulsion directly as formed. These advantages are accompanied by the disadvantages that recovery of the solid polymer may be more difficult when compared to other polymerization techniques, and that is often difficult to remove all of the emulsifier from the polymer formed. The unique advantages

and disadvantages of emulsion polymerization are due to the special character imparted to the polymerization kinetics by application of this technique.

The unique kinetics of emulsion polymerization result from the particular components used in emulsion polymerization. A typical emulsion formula would consist of one or more water insoluble monomers, water, emulsifier, a water soluble initiator, a chain transfer agent, and possibly a buffer. The way in which these components interact is well dicussed in a review of the kinetic features of emulsion homopolymerization by Alexander and Napper.[53] Two recent books have also been published[54,55].

In the initial stages of polymerization the monomer is present in three forms; in large (1μ diameter) droplets which are stabilized by emulsifier, inside the emulsifier micelles, and dissolved in the aqueous phase to its limiting solubility. During this early stage of polymerization, known as Interval I, all of the latex particles are generated. The number of latex particles determines the rate of polymerization in the later stages. Therefore Interval I has a very strong influence on the overall rate of emulsion polymerization, even though only 10-15% or less of the monomer is polymerized during this stage.

The latex particles are produced in Interval I when a free radical produced by decomposition of the initiator in the aqueous phase, diffuses into one of the monomer swollen micelles. This initiates the polymerization of the monomer in the micelles, which grows into a

monomer swollen polymer particle stabilized by emulsifier. These components of the emulsion stystem are illustrated in Figure 13 as depicted by Odian.[56] The monomer swollen polymer particles continue to grow absorbing both monomer and emulsifier from the micelles. Thus in Interval I., micelles are consumed, by initiation by free radicals and by absorption into the growing polymer particles, until there are no more micelles remaining. At this point no more latex particles can be formed and Interval I has ended.

Smith and Ewart[57] derived an equation to estimate the number of latex particles produced in Interval I. This is shown below as equation 4. The most important points to note here

$$\text{Eq. (4)} \quad N = k(\rho^*/\mu)^{2/5}(AsS)^{3/5}$$

where: N = number of latex particles (l^{-1})

k = constant $0.37<k<0.53$

ρ^* = rate of entry of radicals into the micelles and particles (l^{-1} sec^{-1})

μ = particle volume increase per unit time (cm^3/sec)

As = area occupied by unit weight of surfactant (cm^2/g)

S = weight of surfactant per unit volume (g/l)

are that the number of particles is proportional to the initiator concentration to the 0.4 power and to the emulsifier concentration to the 0.6 power. Thus the number of latex particles produced in Interval I can be controlled by varying the concentration of the initiator and

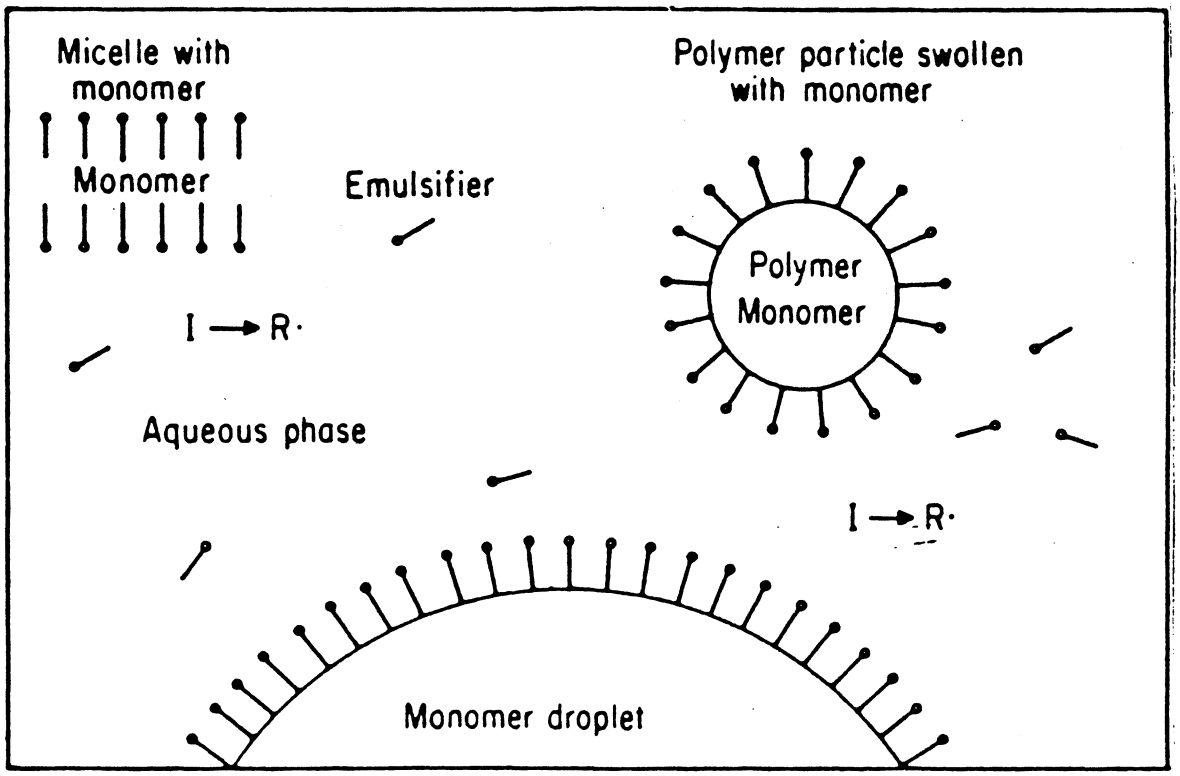


Figure 13. A Schematic Representation of the Components of an Emulsion Polymerization [From Odian (1981) Ref. 56

the concentration of the emulsifier.

The latex particles produced in Interval I continue to polymerize and grow in Interval II. It is assumed that all of the polymerization takes place in these polymer particles which are swollen with about 50% monomer. It is also assumed that the concentration of monomer in the polymer particles is constant, since as the particles grow they are continually swollen with about 50% monomer from the aqueous phase. The monomer in the aqueous phase is likewise replenished with monomer from the monomer droplets. This leads to a pseudo zero order kinetics with regard to the macroscopic monomer concentration.

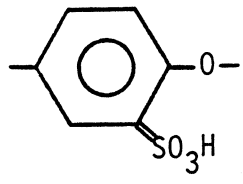
Each monomer swollen polymer-particle continues to polymerize in Interval II until it is terminated. This is assumed in Smith-Ewart case 2 kinetics to take place only by diffusion of another radical into the particle, which instantaneously terminates the propagation of the first radical. Polymerization is then reinitiated in the particle by diffusion of a third radical into the particle. Therefore on average, half of the latex particles contain one radical and half contain no radicals at any given time. These polymerization processes continue until all of the monomer droplets have been consumed.

Interval III commences when the monomer droplets have been consumed. In this stage the monomer which is swelling the polymer particles is polymerized. This polymerization continues until of the monomer has been consumed. Thus the rate of polymerization during the later stages is controlled by the number of active latex particles

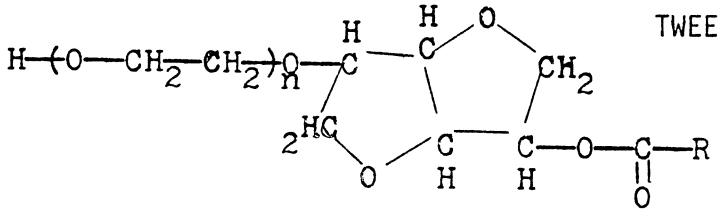
produced in Interval I.

The assumptions made in the Smith-Ewart theory of emulsion polymerization do not hold for all emulsion polymerizations. In particular, the case where the monomer has a significant water solubility does not fit Smith-Ewart kinetics. This is attributed to the contribution of copolymerization in the aqueous phase. The polymerization is further complicated in the case of copolymerization of monomers with greatly different water solubilities. In this case, there can be homopolymerization of the less water soluble monomer in the polymer particles, homopolymerization of the more water soluble monomer in the aqueous phase, and copolymerization in the micelles or at the micelle water interface. Moreover, both water soluble and oil soluble initiator may be used. Thus the kinetics of emulsion copolymerization can be extremely complicated.

The unique characteristics of an emulsion polymerization are imparted by the isolation of the polymerization locus to the surfactant (emulsifier) stabilized micelles and polymer particles. Thus the surfactant plays an extremely important role in the emulsion polymerization system. There are three major types of surfactants; anionic, nonionic, and cationic with typical structures shown in Scheme 4. The anionic and nonionic surfactants being more commonly used. The type of surfactant has been found to have a strong influence on many of the characteristics of emulsion polymerization; such as the rate of polymerization, the emulsion stability, the latex particle size, and the emulsion viscosity. These factors are very important in determining the utility of an emulsion polymerization system for a



Nonionic Surfactant



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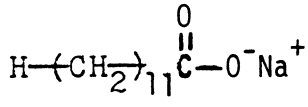
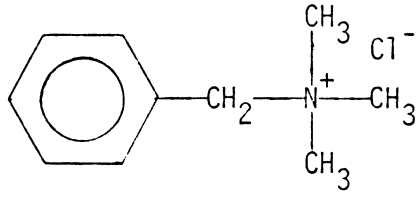
Anionic Surfactant



Sodium Laurate

Cationic Surfactant



Trimethylbenzyl
Ammonium Chloride

Scheme 4

particular application. Many of the characteristics of an emulsion system have been found to be correlated to a property of the surfactant known as the HLB in a study by Greth and Wilson.(58)

The HLB number of a surfactant is its "hydrophilic-lipophilic balance". In this system an HLB of one indicates oil solubility, and an HLB of twenty indicates extensive water solubility. The HLB can be determined by calculations based on structure,(59) solubility studies(60), cloud point determinations(61), or by measurement of the spreading coefficient of oil on a one percent solution of the emulsifier in water.(62)

In the study of Greth and Wilson it was found that the HLB of the surfactant had a significant influence on the rate of polymerization, emulsion stability, latex particle size, and emulsion viscosity for styrene and vinyl acetate emulsion homopolymerization systems. When the emulsilfier HLB was varied, by changing the ratios of a nonionic and anionic emulsifier in a blend, a maximum in the rate of polymerization, emulsion stability, and the emulsion viscosity which all fell at the same HLB for the same monomer was observed. This HLB was also found to give the smallest latex particle size and was taken to be the optimum HLB value for the polymerization. The general observations from this study were that it appears that the optimum HLB for many polymerization is probably in the range of 13 to 16, the HLB system is applicable to nonionic surfactants and to anionic nonionic surfactant blends, but for anionic or cationic surfactants the

applicability may be limited.

In the emulsion copolymerization of monomers with different water solubilities the HLB of the surfactant may be even more important in controlling the polymerization. In addition to the influences noted above the emulsifier might influence the local concentration of the water soluble monomer at the micelle (or polymer particle) water interface. In this way it may be possible to influence the copolymerizability of such a system by proper choice of surfactant.

The final component of the emulsion polymerization systems is the chain transfer agent. These are typically alkyl mercaptans which can donate a hydrogen to the growing radical chain end, thus forming a radical on the sulfur atom. This radical then reinitiates more monomers thus "transferring" the chain activity. It becomes clear from the above discussions that emulsion polymerization, and copolymerization, is a complex system which is not completely understood. This does not however necessarily restrict its utility in the preparation of a number of important polymers in industry and in preparation of new types of polymers and copolymers which may be of both academic and industrial interest such as the ionomers.

III. EXPERIMENTAL

A. Synthesis of Sulfonated styrene

Potassium styrenesulfonate was synthesized by using a slight modification of the procedure of Wiley et. al. (63). The procedure involves three steps as discussed below.

(1) β-Bromoethylbenzene Sulfonylchloride

A three necked 500 ml round bottom flask was equipped with an overhead stirrer, addition funnel and condenser. The flask was then charged with 99 ml (1.52 moles) chlorosulfonic acid (Aldrich Cat. No. 18, 630-9) and cooled with an ice-bath. Then 40.4 ml (0.29 moles) of β-bromoethylbenzene (Aldrich Cat. No. B6, 578-0) was added dropwise through the addition funnel. The addition caused the evolution of acid fumes and turned the color of the mixture from reddish brown to orange-brown. After the addition of the β-bromoethylbenzene was completed, the ice bath was removed and the mixture was allowed to warm to room temperature. After standing for one hour the mixture was poured onto a large quantity of ice which produced an off white precipitate. The aqueous mixture was then extracted with one 200 ml and three 100 ml portions of ether.

The ether extracts were combined and washed with a 5% sodium bicarbonate solution to neutralize the excess acid. They were next washed with water and dried over anhydrous sodium sulfate. The dried ether extract was then decanted from the sodium sulfate and the sodium sulfate was extracted with 75-100 ml of ether to recover all of the sulfonyl chloride. The ether extracts were combined and dried on a

rotary evaporator thus affording crude sulfonyl chloride.

(2) Potassium Styrene Sulfonate

The sulfonyl chloride from the previous step was placed in a 1ℓ three neck round bottom flask equipped with an overhead stirrer, addition funnel and condenser. The sulfonyl chloride was then dissolved in 210 ml of methanol. The solution was cooled with an ice bath during the addition of 300 ml of methanol containing 67.2 g KOH (Fisher 85% pellets). The addition of KOH produced a white precipitate. After the addition of KOH was completed the reaction mixture was heated to reflux and held for 1 hour. The mixture was then slowly cooled to approximately -20°C to precipitate the mixture of organic and inorganic salts which were then vacuum filtered onto a course frit glass funnel. The crude mixture of salts were then dried under vacuum at approximately 40° for 3-4 hours.

(3) Purification of Sulfonated Styrene as the p-toluidine Salt (TSS) and Recovery as the Potassium Salt

The mixture of salts from the previous step was dissolved in 450 ml of warm water, treated with decolorizing carbon and filtered through a cake of filter aide. The solution was then cooled in an ice-bath and treated with 144 ml of 1:1 conc. HCl/H_2O containing 30g of p-toluidine. After the addition of the p-toluidine was completed the soution was cooled with an ice bath to precipitate the p-toluidine styrenesulfonate. The salt was then isolated by vacuum filtration onto a fritted glass funnel. The toluidine salt was then dissolved in about 300 ml of warm distilled water, treated with Norit, filtered warm

through filter aide and then cooled with an ice-bath to precipitate the p-toluidine styrene sulfonate. The product was then isolated by vacuum filtration onto a fritted glass funnel and dried in a vacuum oven overnight at approximately 40°C.

After storage for several months, in the refrigerator, the p-toluidine salt of styrene sulfonic acid was purified prior to conversion to the potassium salt. It was dissolved in warm water, treated with decolorizing carbon, recrystallized by cooling in an ice-brine bath and vacuum filtered which allowed recovery of the pure salt.

The purified toluidine styrene sulfonate was converted to the potassium salt by slurrying 5.52g TSS in 30 ml distilled water and treated with 25 ml of 1 normal KOH solution. The slurry was then diluted with 100 ml of distilled water and extracted with 100 ml and four 50 ml portions of ethyl acetate. The ethyl acetate extracts were then evaporated on a rotary evaporator to yield the potassium styrenesulfonate which was then purified by recyrstallization from methanol. The overall yield of the monomer by this route was about 74% of the toluidine salt.

B. Synthesis of Copolymers and Homopolymers

(1) Materials

The acrylate monomers used for this study were purchased from Polysciences Inc., and were freed from inhibitor by passing through a column of neutral alumina prior to use in the synthesis of polymers. The butyl acrylate monomer used in the kinetic studies was purified by passage through a column of neutral alumina followed by vacuum

distillation.

The potassium styrene sulfonate used in this study was purchased from Polysciences, Inc. and was used without further purification. The sodium styrenesulfonate used in this study was a gift from Exxon Research and Engineering Co., and was used without further purification.

The potassium persulfate and sodium bisulfite initiators were obtained from Fisher Scientific Co., and were used without further purification. The potassium persulfate initiator for the kinetic studies was obtained from FMC Co., and was recrystallized from warm water prior to use.

The chain transfer agent, 1-dodecanethiol was obtained from Aldrich Chemical Company.

The emulsifiers were a gift from ICI Americas Inc., their trade names, chemical composition, and HLB numbers are given in Table II.

Water used for the emulsion polymerizations was distilled and deoxygenated. The water used in the kinetic studies was double distilled (second distillation over $KMnO_4$) and deoxygenated.

(2) Procedures

(a) Acrylate Copolymers and Homopolymers

The acrylate copolymers and homopolymers were synthesized using a variety of different procedures. The most satisfactory results were obtained when the following procedure was used.

The polymerization reactor consisted of a 250 ml four neck round-bottom flask equipped with an overhead stirrer, thermometer,

Table II

Emulsifiers

Trade Name	Chemical Composition	HLB
SPAN 20	Sorbitan Monolaurate	8.6
ATLAS G-1292	Polyoxyethylene fatty glyceride	10.8
ATLAS G-3300	Amine salt of Alkyl Arylsulfonate	11.7
ATLOX 8916-TF	Nonionic Surfactant	15.4
TWEEN 20	Polysorbate	16.7

nitrogen inlet and condenser as shown in Figure 13. In this apparatus one approach is to place the desired quantities of the emulsifier, potassium persulfate, sodium bisulfite, distilled deoxygenated water, dodecanethiol, and the sulfonated styrene and acrylate monomer. The flask was first purged with nitrogen for several minutes. Then a preheated temperature bath was raised and the polymerization was run for 5 to 6 hours at 65-75°C. An alternative approach would be to add the initiator last. The polymerization was terminated by pouring the latex into a 500 ml round-bottom flask and rinsing the reaction flask with approximately 100 ml of tetrahydrofuran which was combined with the latex. The latex was then evaporated on a rotary evaporator.

The relatively dry polymer was then dissolved in the necessary quantity of tetrahydrofuran to give a 5-10% solution weight polymer/volume solvent and coagulated in a tenfold or greater excess of 1:1 isopropanol-water mixture. The polymer was filtered, washed several times with approximately 200 ml of isopropanol-water, then with isopropanol, and dried in a vacuum oven overnight at 50-60°C. The yield of the polymer was determined gravametrically. In addition, high conversion samples were taken from selected kinetic runs.

(b) Sulfonated Styrene Homopolymer

A 250 ml four neck round bottom flask was equipped the same as for the acrylate polymerizations. In this flask was placed 7.5013g sodium styrenesulfonate, 0.025g $K_2S_2O_8$, 0.0148g $NaHSO_3$, and 75 ml of distilled deoxygenated water. The flask was purged with nitrogen, the preheated temperature bath was raised and the polymerization was run at 73-74°

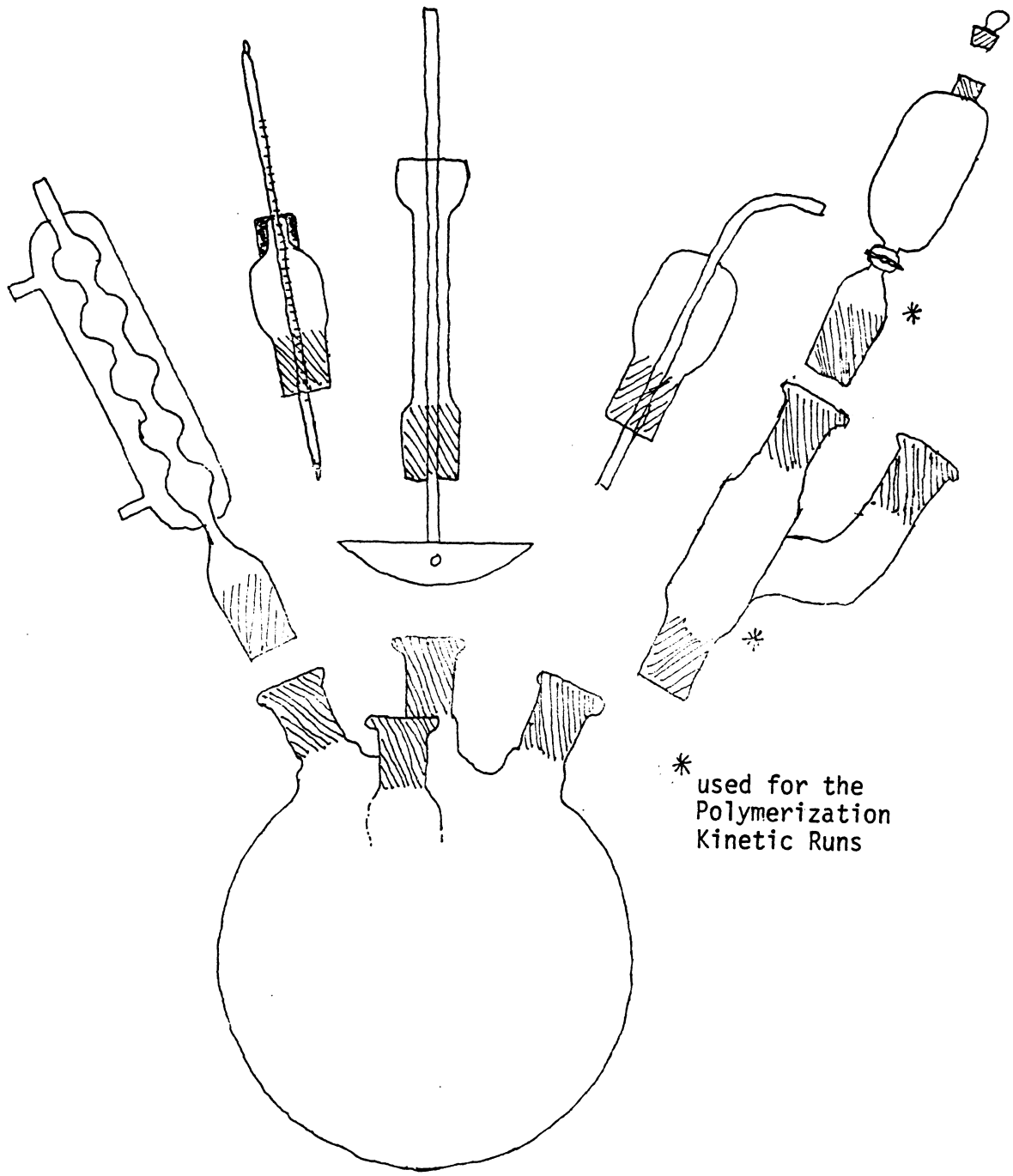


Figure 14. Apparatus for the Emulsion Polymerizations

for 5 1/2 hours. The polymer was then conaulated in 800 ml of isopropanol, suction filtered, washed with isopropanol and dried in a vacuum oven @ 50-60°C.

(c) Study of the Copolymerization Kinetics of the n-Butylacrylate/Sodium Styrene sulfonate System.

Time-conversion studies of the n-butyl acrylate/sodium styrene-sulfonate system were performed using the apparatus shown in Figure 13. The apparatus was set up in a constant temperature bath with an immersion heater and preheated to the reaction temperature of 70°C. The nonionic emulsifier TWEEN 20 (0.800 g) was dissolved in 30 to 50 ml of double distilled water in a 125 ml erlenmeyer flask, purged with nitrogen for several minutes and then transfered to the reaction flask. The overhead stirrer and the nitrogen purge of the reaction flask were started at this time. The potassium persulfate initiator was dissolved in 10 ml of double distilled water, purged with nitrogen for 2-3 minutes and then placed in the addition funnel. The sodium styrene sulfonate (NaSS) monomer was weighed into a separate erlenmeyer flask and dissolved in 20 to 40 ml of double distilled water. The NaSS solution was then purged with nitrogen and transfered to the reaction flask. Finally, the chain transfer agent (CTA) dodecanethiol (0.03 ml) was dissolved in the n-butyl acrylate monomer, which had been freshly vacuum distilled. The CTA/MONOMER solution was purged with nitrogen and transfered to the reaction flask. The reaction was then started by adding the $K_2S_2O_8$ solution from the addition funnel. Less than ten minutes elapsed from addition of the monomers until the start of the reaction. Aliquots were taken at selected time intervals in preweighed

sample vials. The latex was quickly weighed and then one to two milliliters of one percent hydroquinone solution were pipeted into the sample vial. The time of addition of the hydroquinone solution was taken as the time of termination of the reaction. The samples were then dried to constant weight, first in a vacuum oven with air flow @ 75-80° and then under vacuum at approximately 60°C. Finally high conversion latex samples were taken to study the physical properties of the polymers as well as the characteristics of the latex.

The percent conversion of the samples was calculated by comparison of the observed and theoretical weight percent of solids in the latex after correction for the contribution of the emulsifier and terminator weight.

C. Carbon-13 and Proton NMR

Carbon-13 nuclear magnetic resonance spectra of some of the vinyl monomers of interest were obtained in deuterated DMSO solution to characterize the monomers as well as to attempt to correlate the Price-Alfrey e values of the monomers. In addition the sulfonated styrene monomer which was synthesized was characterized by ^{1}H NMR, FTIR, mass spectral and melting point data.

D. Analysis of Copolymer Composition

(1) UV-spectrophotometry

Extensive attempts were made to use UV spectrophotometry to analyze the copolymer composition of the acrylate sulfonated styrene copolymers. These attempts were frustrated by the fact that the

absorption spectra of sulfonated styrene show shifts due to the nature of solvent used in preparation of the standard solution. Figure illustrates the effect of the solvent on the UV absorbance of potassium p-toluenesulfonate (K-p-TS), used as a model of the styrene sulfonate repeat unit, along with the UV spectrum of poly ethyl acrylate. Because of this and the fact that the two homopolymers are totally incompatible in solution it was unfortunately not possible to prepare a UV calibration curve for the analysis of copolymer composition.

(2) Potentiometric Titration

Attempts were also made to analyze the copolymer composition by potentiometric titration of the sulfonate group. These attempts were hindered by the inability to find a suitable solvent system for the titrations. Further efforts should be made.

(3) Elemental Sulfur Analysis

The copolymer compositions were analyzed by sulfur analysis on well purified samples. The sulfur analysis were kindly performed by the Exxon Research and Engineering Co., Corporate Research Laboratory.

E. Characterization of the Physical Properties of the Copolymers and Homopolymers

(1) Differential Scanning Calorimetry

The glass transition temperatures of the polymers produced were determined by analysis of DSC thermograms obtained on a Perkin-Elmer DSC model 2 at a heating rate of 10°/min.

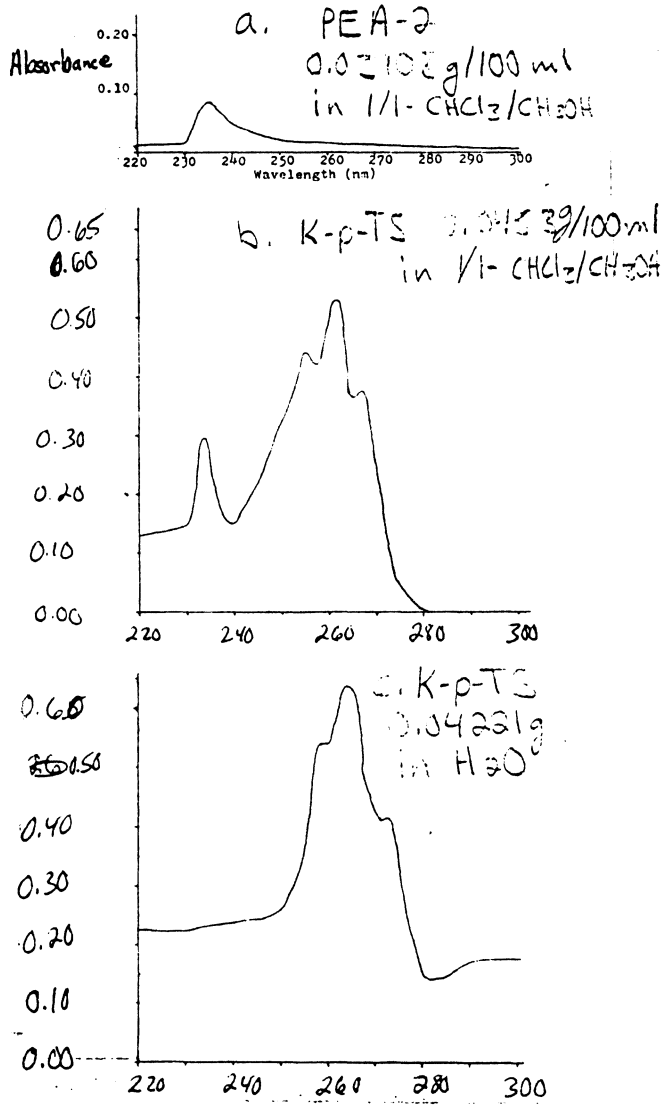


Figure 15. UV Absorbance Spectra of Poly Ethyl Acrylate and Potassium-p-toluenesulfonate

(2) Thermal Mechanical Analysis

The TMA penetration curves were obtained on a Perkin Elmer Thermal Analysis System 2 using different weights and a heating rate of 10°/min.

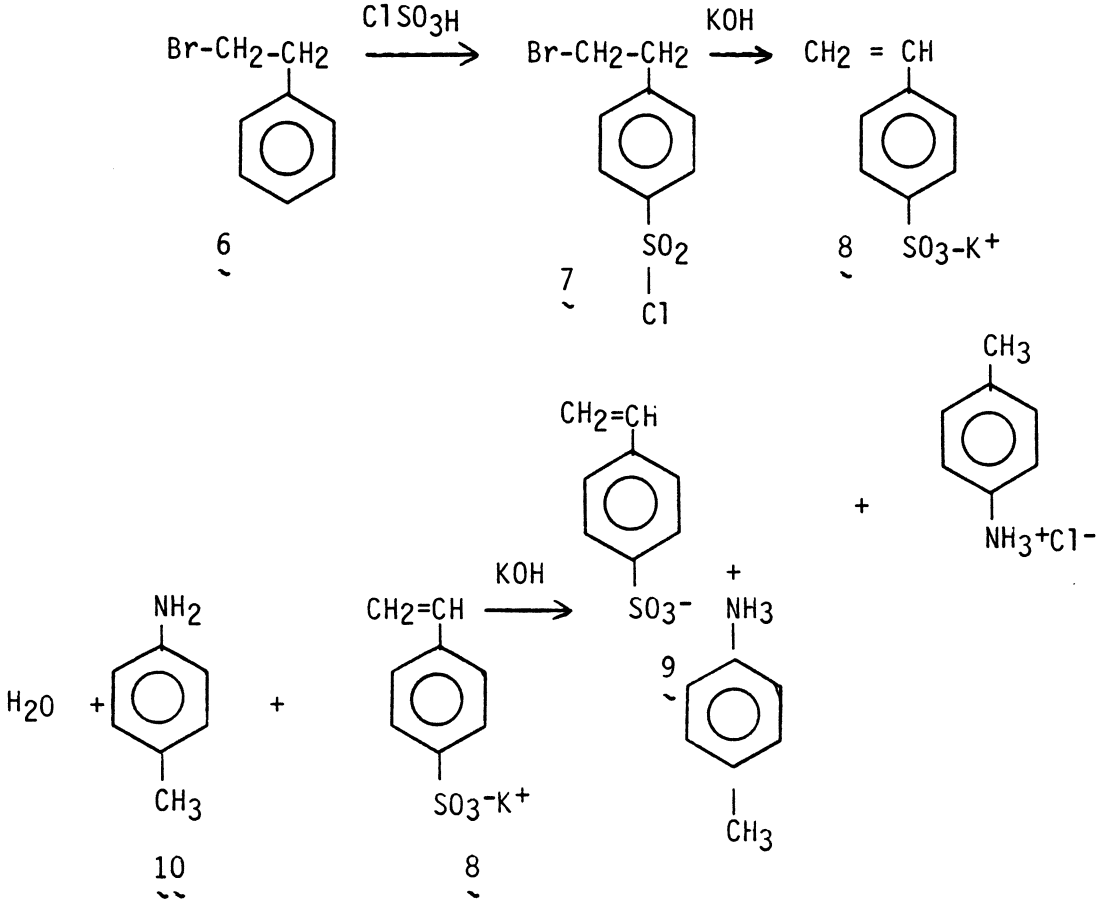
(3) Stress-Strain Measurements

Stress-Strain tests were carried out using an Instron 2211 tester. Dog-bone shaped samples 10 mm long were punched from compression molded films using special dies. The tests were performed at room temperature with a crosshead speed of 10 mm/minutes.

IV. Results and Discussion

A. Monomer Synthesis

The synthesis of sulfonated styrene monomer closely followed the procedure of Wiley et.al.[63] as mentioned previously. The only major modification of their procedure were in the use of ethyl acetate in place of ethyl ether for the extraction of potassium styrenesulfonate in the final purification, and also in the extended storage of the toluidine salt. This procedure is shown in the scheme below.



The first step of this procedure is the chlorosulfonation of β-bromoethylbenzene by a five fold excess of chlorosulfonic acid. The

excess chlorosulfonic acid serves to minimize the formation of sulfonic acid and sulfone side products(64).

The second step involves the simultaneous hydrolysis of the sulfonyl chloride to the sulfonic acid salt and the dehydrohalogenation of β-bromoethyl group. This step is very straight forward and presents no difficulties.

The final step; conversion to the p-toluidine salt, recrystallization, and conversion back to the potassium salt; should be eliminated since it only makes the isolation of pure potassium styrenesulfonate more difficult as will be discussed below. The product acutally isolated from the final step was the covalent 4'-methyl-N-phenyl-p-styrenesulfonamide in a 79% yield before recrystallization instead of the potassium salt. This compound which can be formed by the loss of water from the p-toluidine salt, was indicated by the ^{13}C and ^{1}H NMR spectra shown in Figures 14 a and b, with the most probable peak assignments. The ^{1}H NMR spectrum does not show the amide N-H proton, this could be due to the presence of proton exchange with water broadening the resonance and shifting it out of the spectral region. The ^{1}H NMR spectrum of sodium-p-styrenesulfonate monomer provided by Exxon and the potassium-p-styrenesulfonate monomer purchased from Polyscientific are shown in Figures 15 a and b for comparison.

The assignment of this structure to the product was also aided by comparison of the infrared spectra of KBr pellets of the sulfonated styrene synthesized in this laboratory and of authentic commercial sulfonated styrene monomers shown in Figure 16. The monomer synthesized in this laboratory had an infrared spectrum very similar to

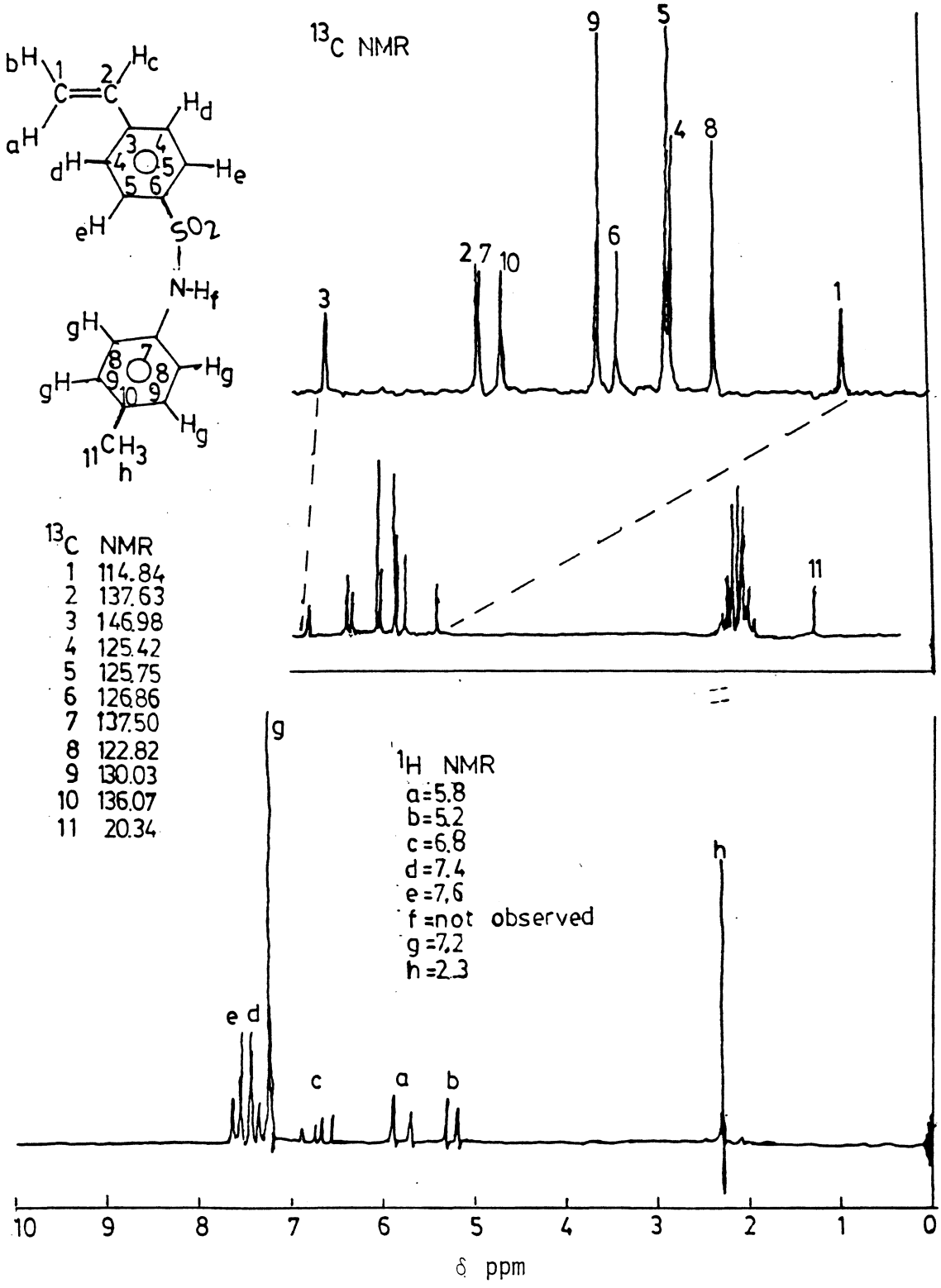


Figure 16. ^{13}C and ^{1}H NMR of 4'-methyl-N-phenyl-p-styrenesulfonamide

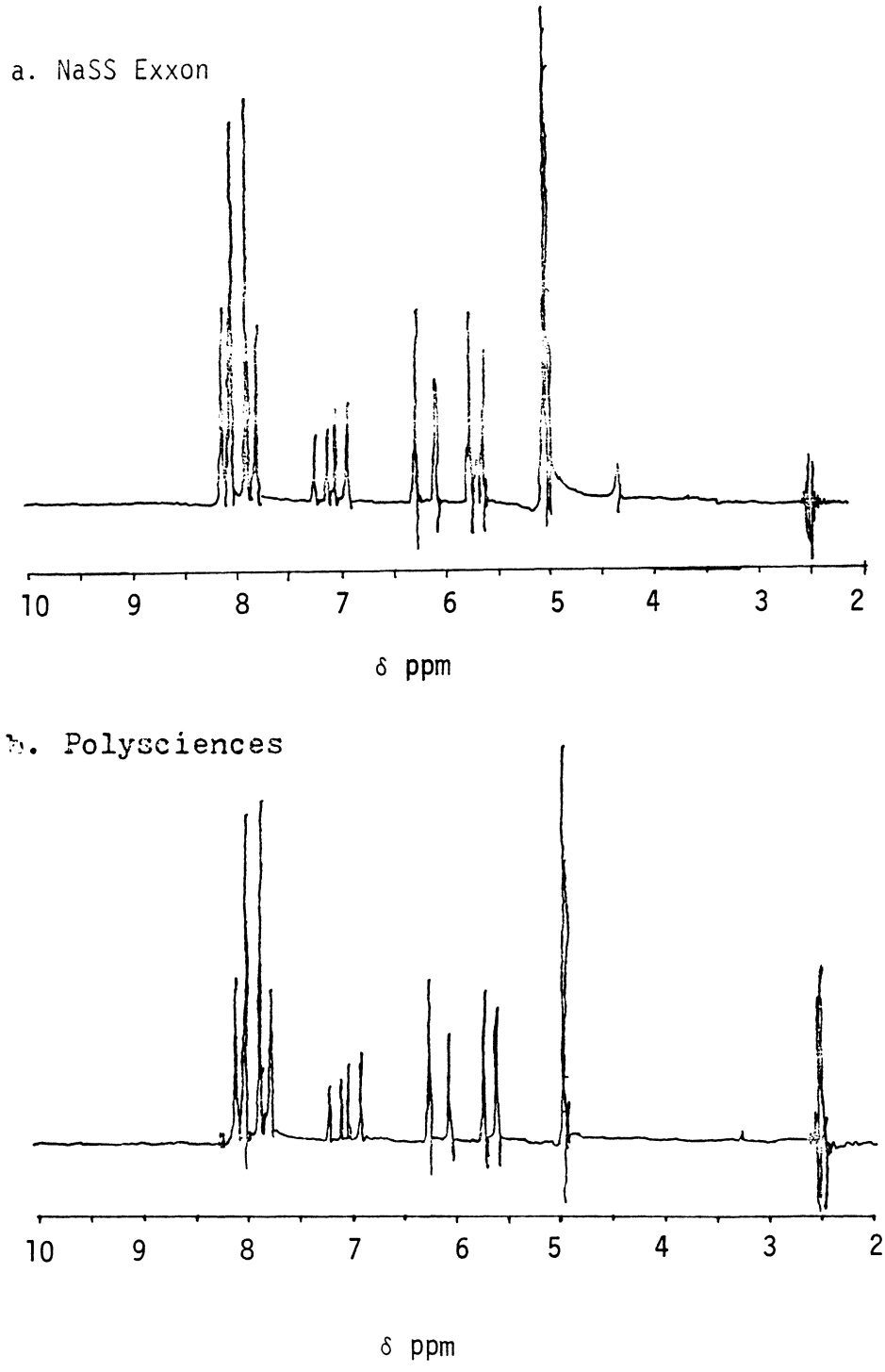
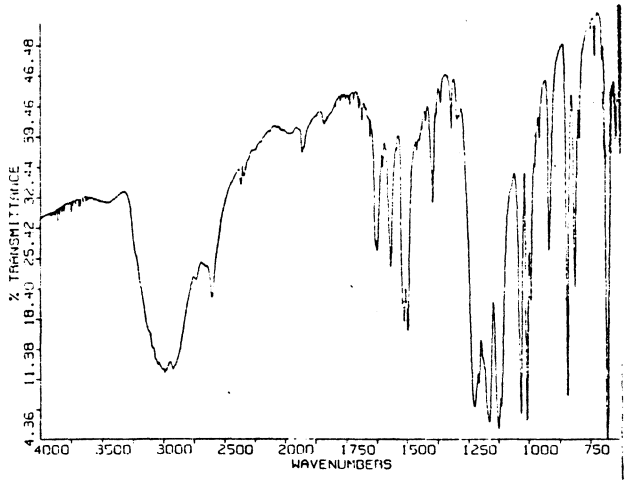
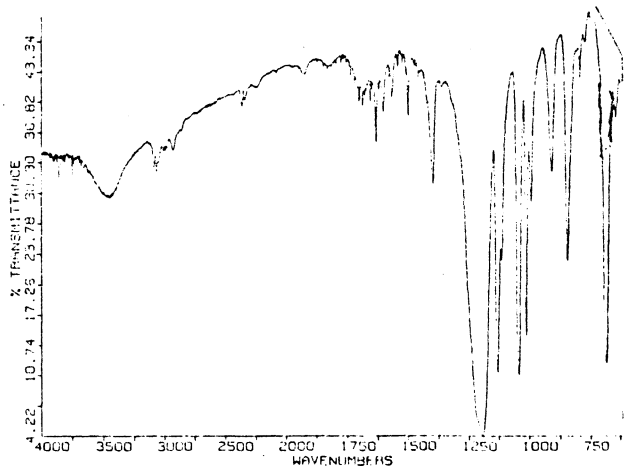


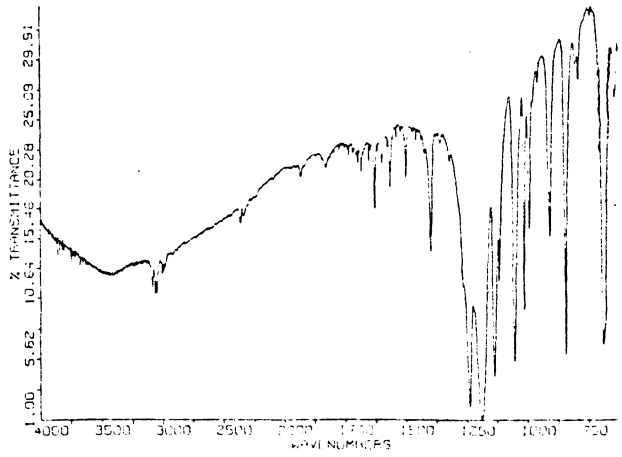
Figure 17. ^{1}H NMR of Sodium and Potassium Styrenesulfonate



a. potassium-p-styrenesulfonate
VPI



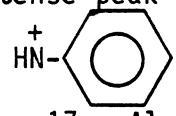
b. potassium-p-styrenesulfonate
Polyscientific



c. sodium-p-styrenesulfonate
Exxon

Figure 18. Infrared Spectra of Strenesulfonate Monomers

those of the commercial monomers, with the addition of an absorption at 1234 cm^{-1} due to the sulfonamide group.

Finally the structure of the monomer is substantiated by the presence of a very intense peak at m/e 106 due to the fragment ion from the toluidine group:  in the mass spectrum of the product shown in Figure 17. Also, the monomer melts at 181-186°C while the authentic monomer salts only discolor above 310°C and do not melt up to 400°C.

Wiley and coworkers have eliminated the use of the toluidine salt in one of their later papers(65), and its use is not recommended since it only makes isolation of the alkali metal salt more difficult. Because of the difficulties encountered in this synthesis and the tedious nature of the monomer synthesis, we chose to use the commercially available monomers in all polymerization experiments.

B. Polymer Synthesis and Kinetic Studies

A number of different polymers were synthesized in this study, some of these are summarized in Tables 3 and 4. The initial studies showed that the optimum emulsifier for both the ethyl acrylate and butyl acrylate emulsion polymerization systems was TWEEN 20. This emulsifier is a nonionic surfactant with an HLB number of 16.7 and is a polyethylene oxide sorbitan monolaurate type structure. It proved to be very effective for the polymerization of the acrylate monomers as evidenced by the high yileds and high molecular weights it produced in the polymers. This can be seen in Table 3 where the polymer polymerized using TWEEN 20 gave the highest yield and the highest

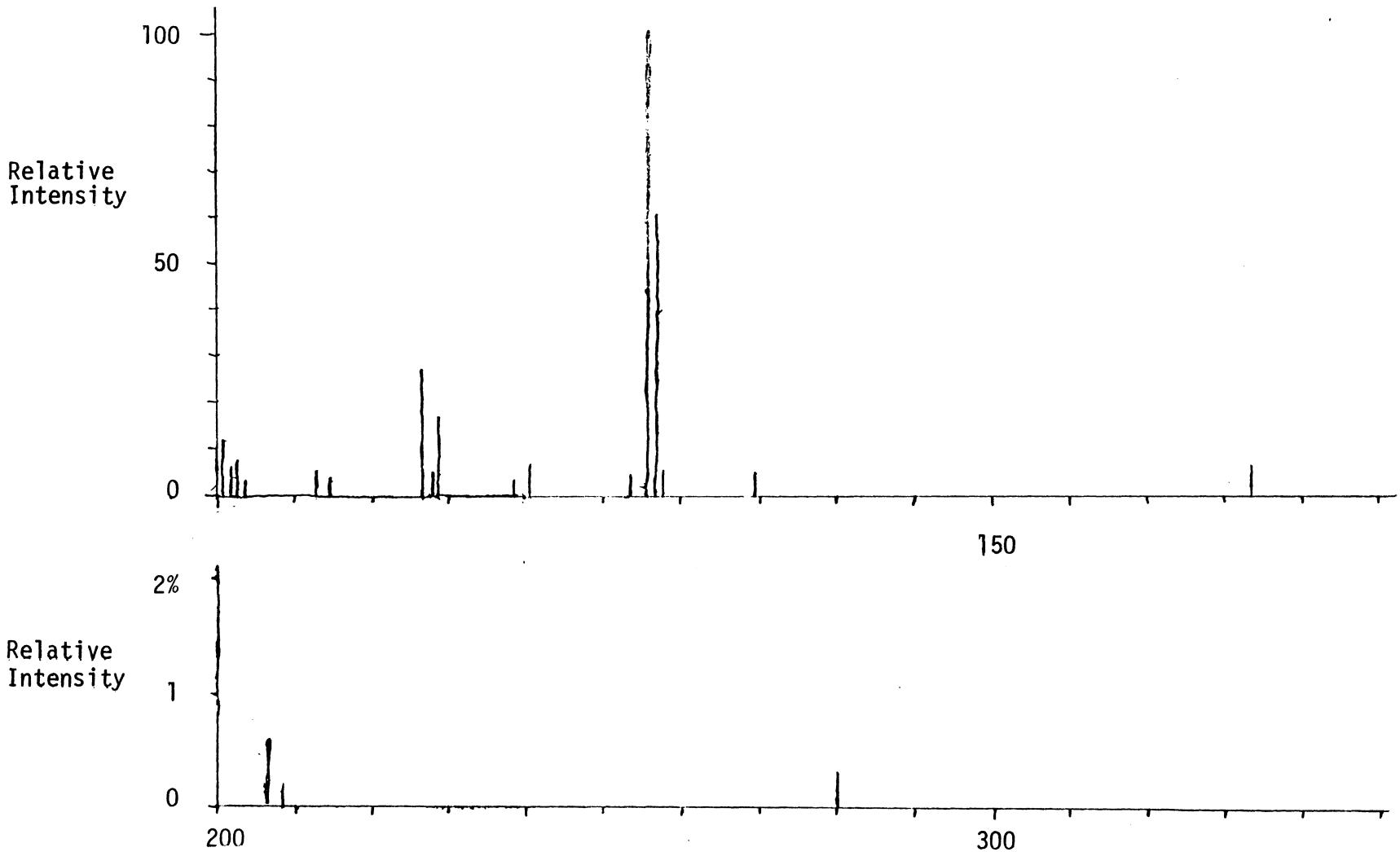


Figure 19. Mass Spectrum of 4'-methyl-N-phenyl-p-styrenesulfonamide

Table III

Synthesis of Acrylate-Sulfonated Styrene Copolymers and Homopolymers

Sample No	Acrylate Monomer, (moles/ Kg H_2O)	Sulfonated Styrene (moles/ Kg H_2O)	Mole % Sulfonated Styrene	Emulsifier, (g/100 ml)	$K_2S_2O_8$ Conc (moles/ Kg H_2O)	$NaHSO_3$ Conc (moles/ Kg H_2O)	Temperature	Time, Hours	Yield %	[η] 30° $CHCl_3$	Tg,°C
PEA-1	3.33 EA[1]	--	--	0.977 G[4]	0.00386‡[5]	0.00493	25°C	26	78	3.31	
PEA-2	3.37 EA	--	--	0.994 A	0.00374‡	0.00478	25°C	25	87.3	2.58	
PEA-3	3.18 EA	--	--	1.002 Na	0.00398‡	0.00482	25°C	24	--	--	
PEA-4	3.45 EA	--	--	1.018 T	0.00355‡	0.00495	25°C	24	87.6	3.97	-23
PEA-1-KSS-1	3.40 EA	0.0344 K	1.0	1.277 A	0.00401‡	0.00483	25°C	25	26.7		
PEA-2-KSS-1	3.16 EA	0.0707 K	2.2	1.026 A	0.00398‡	0.00487	25°C	25	43.8		
PEA-4-KSS-1	3.18 EA	0.1450 K	4.0	1.054 A	0.00393‡	0.00542	25°C	25	70.0		
PEA-3-QSS-1	2.90 EA	0.891 Q[3]	3.0	0.863 T	0.00323	0.00450	60-62°C	3.8	94.7		
KAP-II-24	--[2]	0.485 Na	100	--	0.00124	0.00170	73-74°C	5.5	84.2		
PBA-1	2.56 BA	--	--	1.010 T	0.00370	0.00541	25°C	25	~100.0		
PBA-1-KSS-1	2.56 BA	0.0218 K	0.9	1.015 T	0.00398	0.00500	25°C	25	91.9		
PBA-2-KSS-1	2.56 BA	0.0507 K	1.9	1.041 T	0.00350	0.00519	25°C	25	97.9		
n-BA-1	3.55 BA	--	--	1.818 A	0.00572	--	60°C	19	84.7		-50
n-BA-2	1.95 BA	0.0574 K	28.	1.075 A	0.00282	0.00351	65°C	9	95.1		-50
n-BA-3	1.95 BA	0.1136 K	5.5	1.050 A	0.00283	0.00339	65°C	9	93.2		-50
n-BA-4	1.95 BA	0.2137 K	9.8	1.000 A	0.00310	0.00353	60°C	5.5	93.4		-50

(1) EA, ethyl acrylate

(2) BA, butyl acrylate

(3) Q, Quaternary, tetramethyl ammonium counterion

(4) G, Atlas G-3300 A, Atlox 8916-TF Na, Na Laurate T, TWEEN 20 emulsifiers

(5) ‡, Fe_2SO_4 was also added

Table IV

Butyl Acrylate-Sulfonated Styrene
Kinetic Runs

Sample II	Acrylate Monomer Conc (moles/ Kg H_2O)	Sulfonated Styrene Conc (moles/ Kg H_2O)	Mole % Sulfonated Styrene	Emulsifier Conc (g/100 ml)	$K_2S_2O_8$ Conc (moles/ Kg H_2O)	Reaction Time (Hrs)	Dodecyl Mercepten Conc (moles/ Kg H_2O)	T,°C	Yield %
KAP-III-71	2.10 BA	--	--	1.000 T	0.00320	4	0.00157	69	95
KAP-IV-1	2.17 BA	--	--	1.000 T	0.00277	4	0.00157	69	55
KAP-IV-21	2.16 BA	--	--	1.000 T	0.00230	2.75	0.00157	69	~5
KAP-IV-9	2.17 BA	0.0220 Na	1.0	1.000 T	0.00277	4	0.00157	69	95
KAP-IV-11	2.17 BA	0.0446 Na	2.0	1.000 T	0.00274	4	0.00157	69	95
KAP-III-67	2.16 BA	0.0909 Na	4.0	1.000 T	0.00277	4	0.00157	69	45
KAP-IV-13	2.15 BA	0.1389 Na	6.0	1.000 T	0.00275	4	0.00157	69	99
KAP-IV-16	2.01 BA	0.8190 Na	8.6	1.000 T	0.00276	3	0.00157	69	82
KAP-III-57	2.19 BA	0.0908 Na	4.0	1.000 T	0.00368	4	0.00157	69	90
KAP-III-69	2.14 BA	0.0908 Na	4.1	1.000 T	0.00320	4	0.00157	69	50
KAP-IV-18	2.19 BA	0.0908 Na	4.0	1.000 T	0.00228	4	0.00157	69	100

All kinetic runs used TWEEN 20 emulsifier.

intrinsic viscosity for the ethyl acrylate homopolymer.

An initial study of the possible acrylate ionomers indicated that butyl acrylate was a particularly interesting monomer. This polymer has a glass transition temperature of -50°C and the pseudo crosslinking produced in ionomers offered the possibility of producing thermoplastic elastomers. For these reasons, most of the work was concentrated on the copolymers of butyl acrylate.

Polymers initially produced for this study were synthesized without the use of a chain transfer agent. These polymers were insoluble in common polymer solvents including mixed solvents. This may be due the combined effects of the high molecular weight, entanglement network and the ionic crosslinking. By using a chain transfer agent in the synthesis the molecular weight of the polymer can be decreased to a level which allows the polymer to be dissolved in polymer solvents such as tetrahydrofuran (THF) without sacrificing the solid state properties.

The emulsion copolymerization of monomers with significantly different water solubilities leads to very complex polymerization kinetics and makes a clear knowledge of the polymer composition more difficult. Because of this we studied the kinetics of copolymerization for the butyl acrylate/sodium-p-styrenesulfonate system. Typical conversion time curves for n-butyl acrylate homopolymerization and for the copolymerization with 4 mole % sodium-p-styrenesulfonate are shown in Figures 18 and 19.

The results from these kinetic unfortunately runs did not prove to be useful in studying the polymerization system. Many of the curves

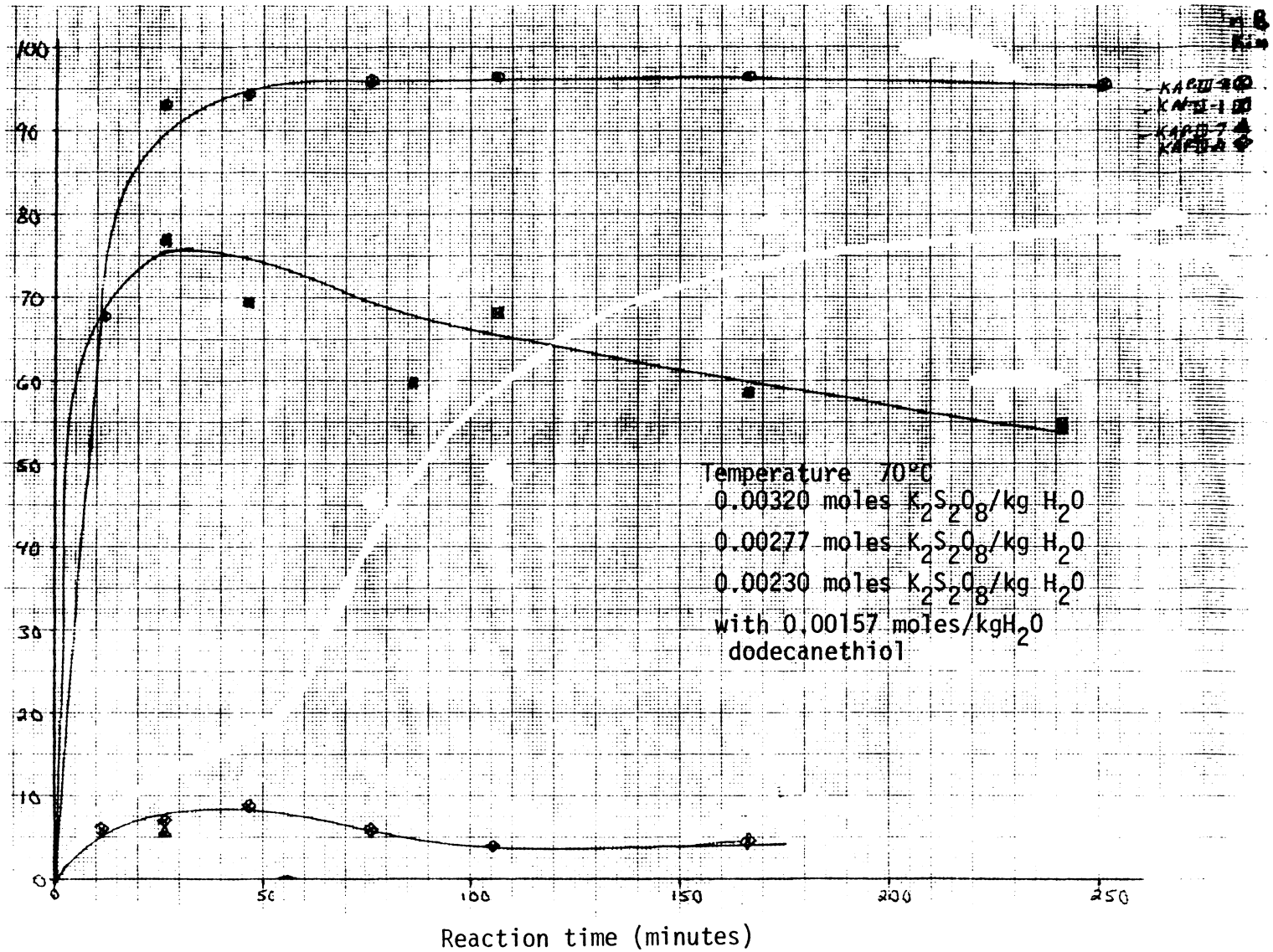
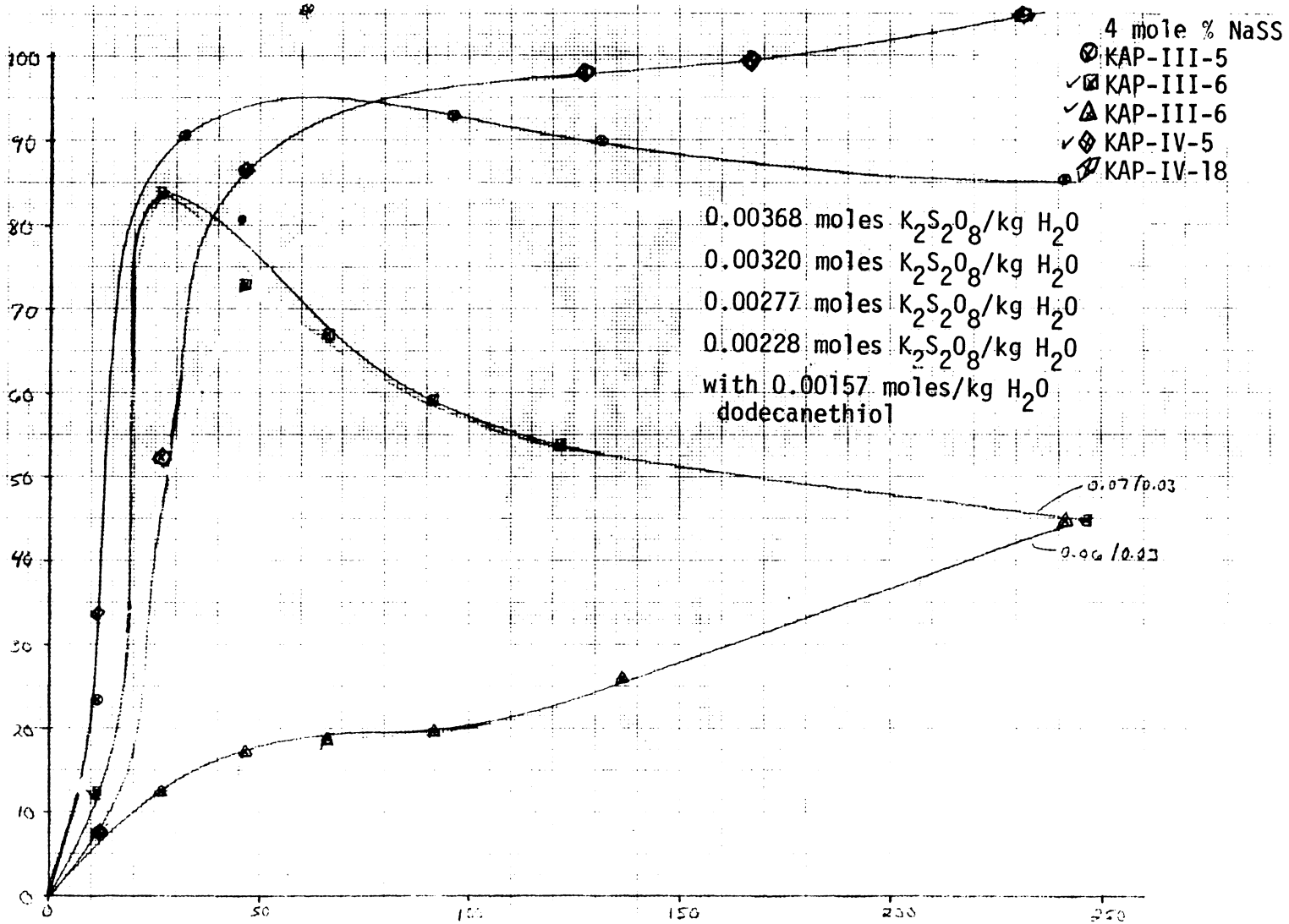


Figure 20. Typical Kinetic Curves for the n-butyl Acrylate Homopolymerization



Reaction time (minutes)

Figure 21. Typical Kinetic Curves for the n-Butyl Acrylate (4 mole %) Styrenesulfonate Copolymerization

show maxima in conversion beyond which time the conversion is seen to decrease. This is almost certainly due to the coagulation of polymer particles onto the walls of the flask. This effectively dilutes the latex which when sample aliquates are taken, giving the appearance of decreasing yield. This problem could be alleviated by running the polymerizations in sample bottles with serum caps and working up complete bottles at given time intervals. This requires the use of a thermostated shaker bath to provide constant temperature aggitation of the polymerizing latex. These facilities were not available so further kinetic studies were not pursued. Alternatively, lower monomer concentrations and lower temperature should be investigated. It is worth noting that copolymerization appears to be very rapid under the conditions of the kinetic studies, with a measurable exotherm being observed in many cases upon addition of the initiator solution.

C. Estimation of Price-Alfrey e Value from ^{13}C NMR

The possibility of predicting the copolymerizability of untried monomer combinations has been pursued for many years.(44) One recent development has been the observation that the ^{13}C chemical shift of the β carbon in vinyl monomers correlates to the e value in the Price-Alfrey Q and e scheme. This would allow the rapid analysis of the ^{13}C NMR spectrum of the new monomer to give at least a rough estimate of alternation tendency in the polymers of interest. Many of the early papers on this subject assumed a single line for the plot of this correlation(66), however a more recent paper by Herman and Teyssie(67) shows to correlations one for substituted styrenes and another for

other vinyl compounds. Using the equation reported in their paper for e values of substituted styrenes:

$$e = \frac{\delta C_\beta - 115.5}{3.5}$$

and the δC_β of 114.8 ppm for potassium-p-styrenesulfonate measured from the ^{13}C NMR (Figure 20) an e value of -0.2 can be calculated. The e value measured for the sodium salt of this monomer in DMSO solution at 45°C was reported by Izumi and coworkers[46] as -0.38. Using this e value found by NMR we find an $r_1 r_2$ product of 0.62 for sulfonated styrene/butyl acrylate copolymerization in DMSO. This value most probably does not hold under complex emulsion copolymerization conditions, but it does give a good indication that these two monomers can be copolymerized under homogeneous conditions with very little tendency toward alternation.

D. Analysis of Copolymer Composition

Initial attempts were made to analyze the copolymer composition by U.V. spectroscopy and by potentiometric titration. The use of U.V. spectroscopy to analyze the copolymer composition at first looked very promising because of the strong absorption band of the aromatic ring in sulfonated styrene in the region of 250 to 280 nm. This band is very intense and is not interfered with by the polyacrylate absorption bands. However in the ionic sulfonate this band shifts drastically with changes in the solvent type. This problem and the fact that the homopolymers of the two monomers are not compatible in solution or in the melt prevented the preparation of precise standards which are

needed to set up a calibration curve for the copolymer composition.

For the case of the potentiometric titration to determine the copolymer composition difficulty was encountered in finding a suitable solvent for the polymer. Solvents such as tetrahydrofuran or toluene which are good solvents for the polymer interfere with the potentiometric titration . They are too strong a base for use in titrating the extremely weak base, (the sulfonate salt) with perchloric acid or are too poor a conductor for the titration. Other solvents which are suitable for potentiometric titration which were also good solvents for the copolymer were not identified.

Because of these problems we chose to use elemental sulfur analysis to determine the styrenesulfonate content of the copolymers.

E. Physical Properties

The physical characteristics and mechanical porperties of the butyl acrylate-sulfonated styrene ionomers were evaluated by the use of thermal mechanical analysis, differential scanning calorimetry and stress strain measurements.

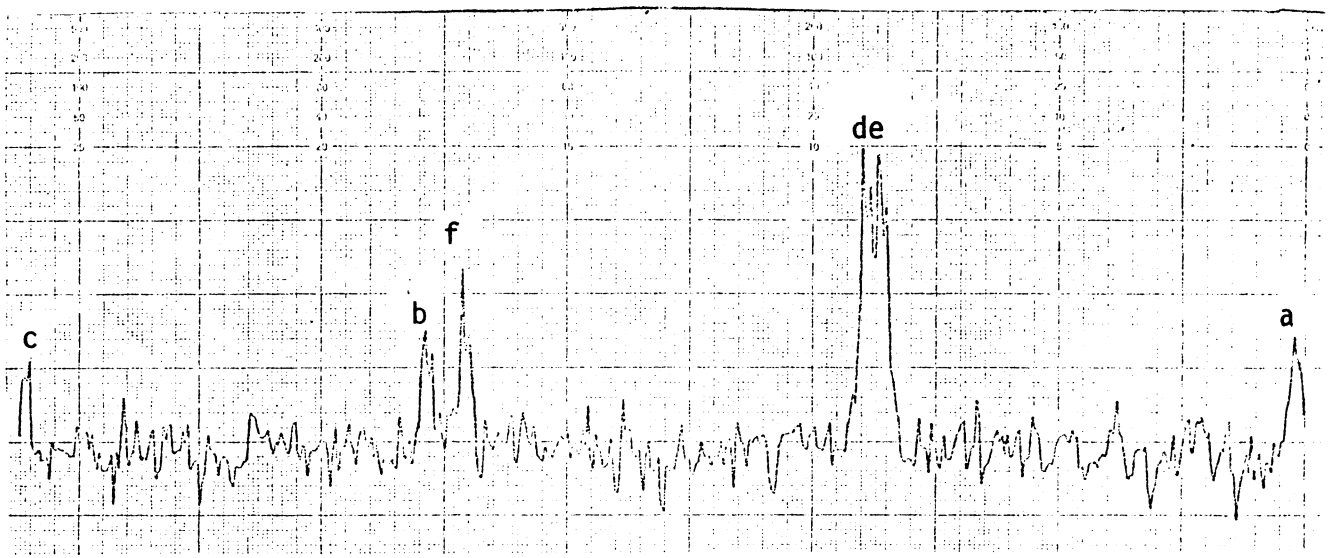
1. DSC and TMA Analysis

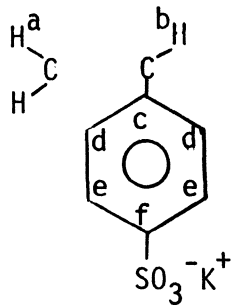
The butyl acrylate ionomers show a single Tg at -50°C which is independent of the copolymer composition. This contrasts with most previous ionomer studies[29,35] which have shown increasing Tg's with increasing ionic monomer content. This difference suggests that the ionic phase is better separated than in the previous ionomer studies. The fact that the transition temperatures of the ionic monomer are not seen could be due to its very low concentration in the copolymer.

The thermal mechanical analysis curves of the butyl acrylate homopolymer and two butyl acrylate ionomers (Figure 21) show strongly enhanced rubbery plateaus for the two ionomers. These plateaus which extend to 240 to 250°C suggest that there is a strong pseudo crosslinking effect due to the ionic aggregation into a well developed ionic phase. This suggests also a somewhat blocky nature to the polymerization.

2. Stress Strain Results

The stress strain curves for a n-butyl acrylate homopolymer and three n-butyl acrylate ionomers are shown in Figure 22. These curves show the marked increase in tensile strength demonstrated by even a small amount (2.8 mole %) of the styrenesulfonate ionic comonomer. Indeed in a plot of the stress at break versus the mole percent of sulfonated styrene in the copolymer (Figure 23) shows a definite sigmoidal shape. The step in the curve occurring somewhere between 3 and 5 mole % styrene sulfonate. This break can be attributed to the change in ionic association from multiplets to clusters as noted previously.[10] This onset of clustering at about 4 mole % compares to the onset at 12 mole % in an ethyl acrylate carboxylate ionomer[28] study by Eisenberg and coworkers. This behavior agrees with the observations of Lundberg et.a.[25] who found that the sulfonated polystyrene has stronger ionic interactions than the carboxylated polystyrene. Thus the mechanical properties indicate that these polar ionomers have significantly enhanced properties over that of the conventional homopolymer.





a 114.77
b 137.07
c 147.44
d 125.78
e 125.39
f 137.08

Figure 22. ^{13}C NMR of Potassium-p-styrenesulfonate

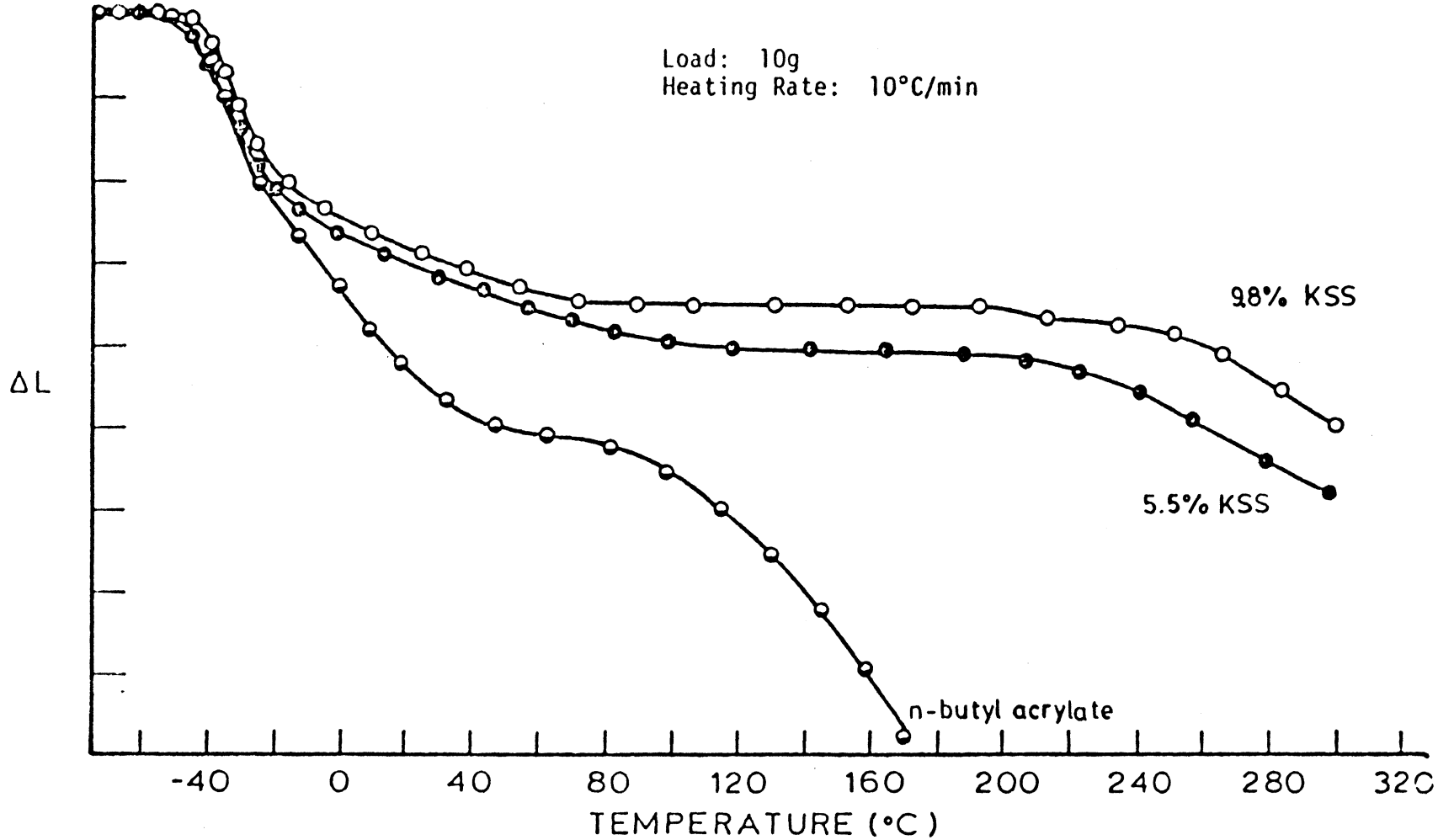


Figure 23. TMA Penetration Curves for n-Butyl Acrylate-Sulfonated Styrene Copolymers

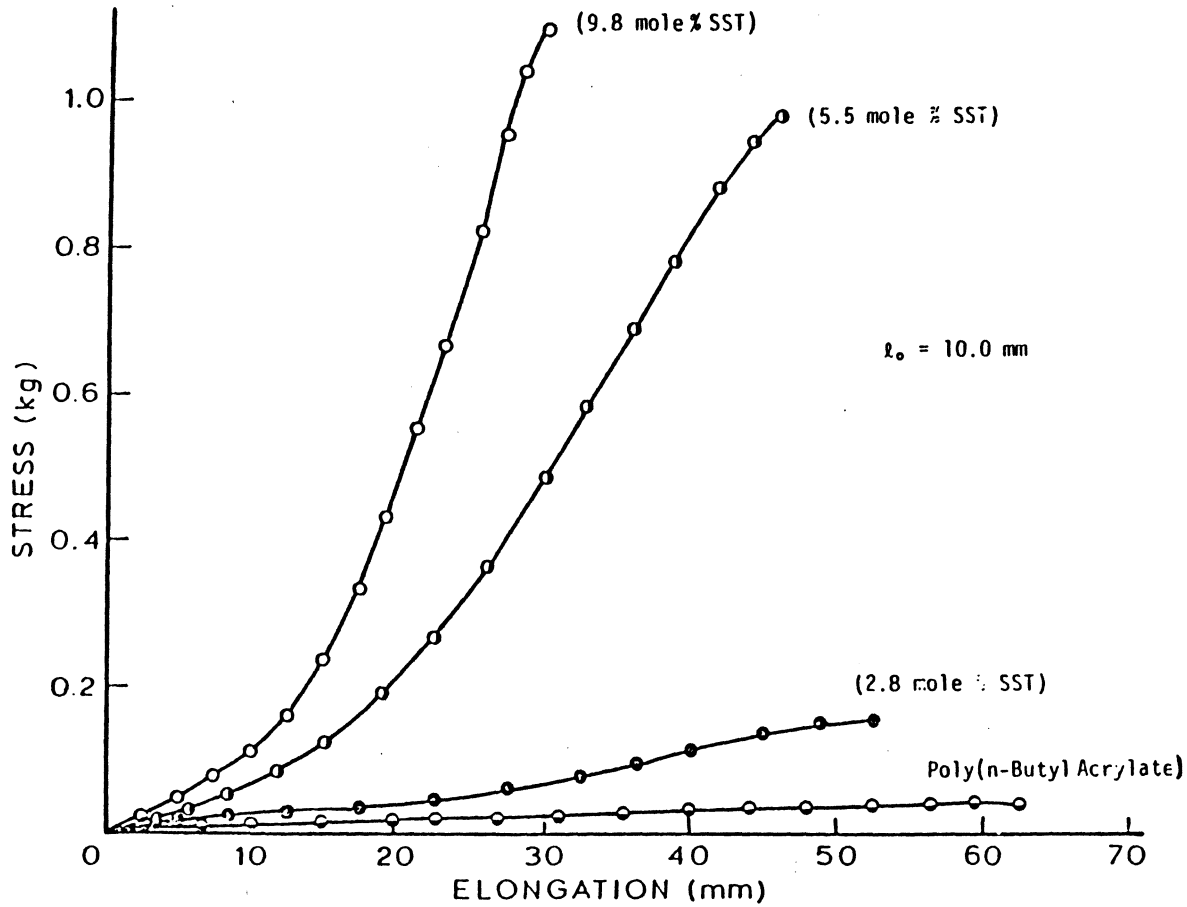


Figure 24. Stress-Strain Curves for n-Butyl Acrylate-Sulfonated Styrene Copolymers

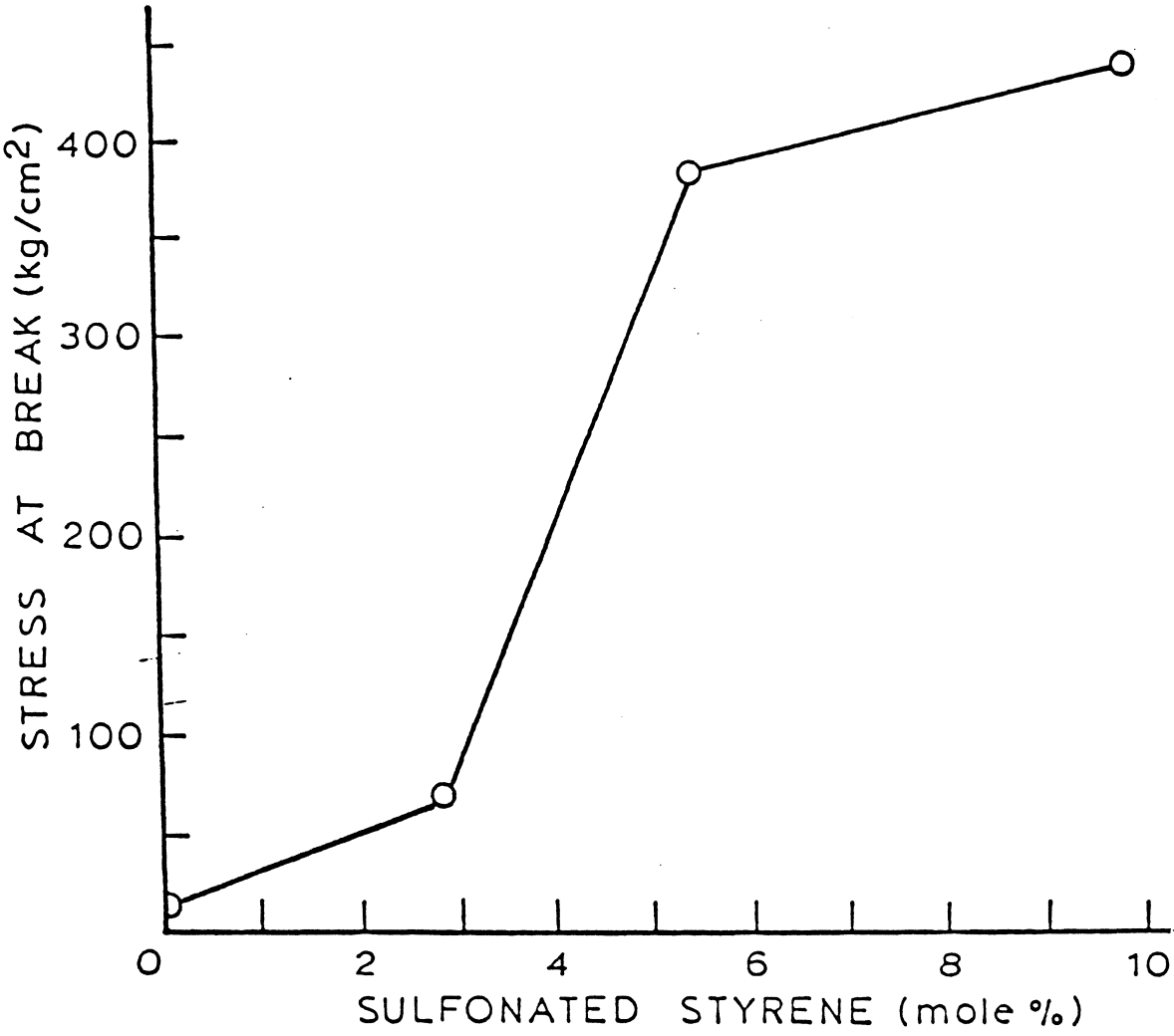
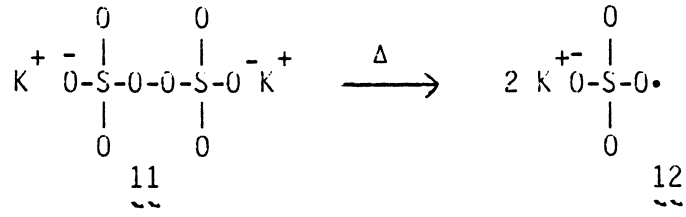


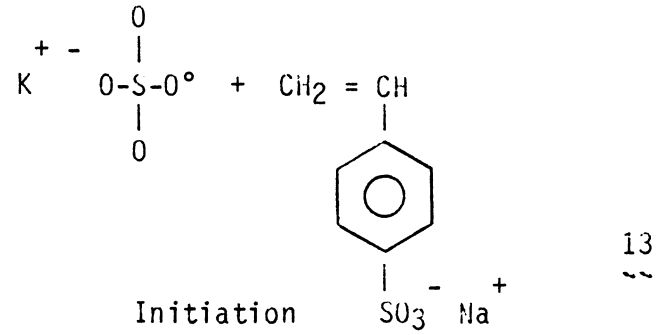
Figure 25. Stress at Break versus Sulfonated Styrene Content for n-Butyl Acrylate Copolymers

3. A Possible Model for the "Copolymerization"

It is proposed that the observed behavior is not only a function of the ionic sulfonate aggregation, but also due to the microheterogeneous, microstructure of the copolymer. Utilizing a water soluble initiator the polymerization must begin in the aqueous phase via attack of the persulfate radicals on the sulfonated sytrene.

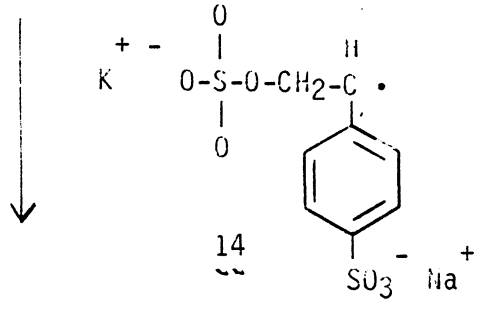


11 12



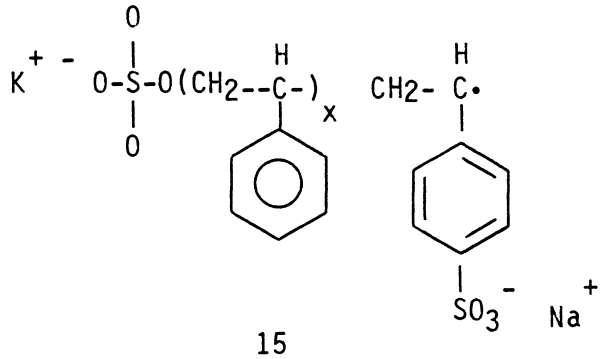
13

Initiation



14

More SST, Propagation



15

(a)

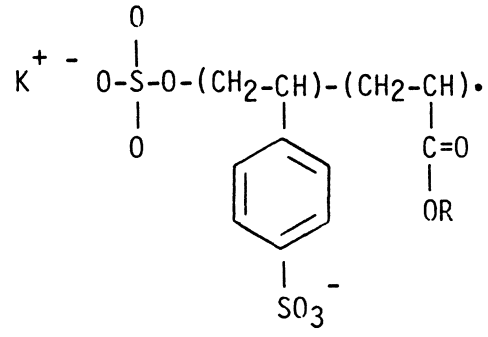
Termination

H_2O soluble
Homopolymer

16

(b)

Acrylate initiation,
micellar propagation



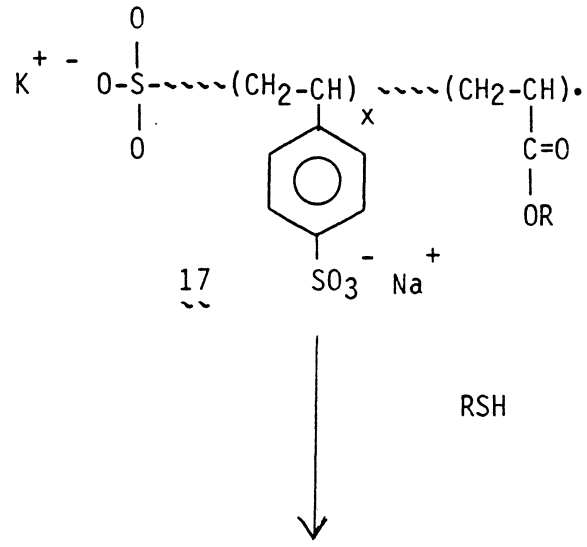
Transfer
Branching,
or Termination

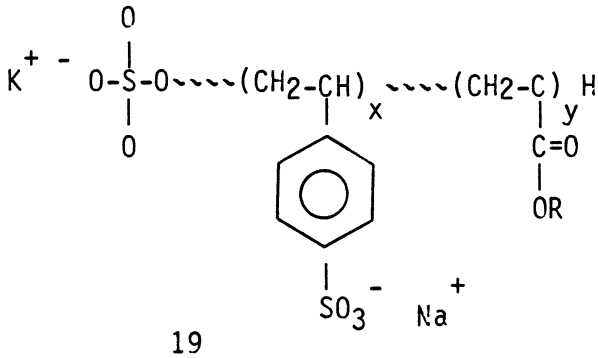
Copolymer

18

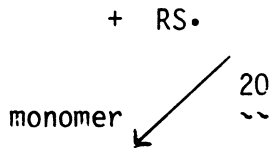
The resulting radical 14 should be highly stabilized and probably relatively long lived. It may add several units to form 15. Next, one

may visualize 15 either terminating to generate water soluble homopolymer 16 or initiationg the alkyl acrylate. The latter event possibly could take place in or around the micelles formed from the sufactant. Indeed, one must recall that the nonionic surfactant and the anionic SST "surfactant" are both present! In any event, as the alkyl acrylate polymerizes, the copolymer should become relatively hydrophobic and much more elastomeric. We speculate that the presence of the SST units near the end of the chain is important in that is provides a "blocky" character to the material. Moreover, the alkyl acrylate chain would be expected to terminate by combination, thus providing SST units near both ends of the chain! Note also that the terminal unit derived from the initiator may also be an ionic sulfate group. Interaction with the mercaptan transfer agent could disrupt the association and the pseudo "Triblock" structure as shown below. Such a mechanism may be important in improving THF solubility.

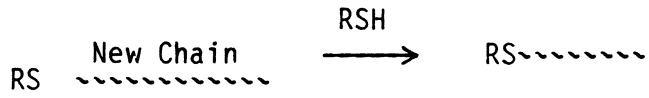




19



20



21 22

Thus, structure 19 could be pictured as a pseudo di-block structure that would probably be less associated than 18 (if termination by combination is postulated). The mercaptide radical 20 could reinitiate more monomer etc. Such a model is consistent with the results of Yilgor et al of our laboratory(68). He was able to generate conversion-time data from SST and 2-ethylhexyl methacrylate. The curves were somewhat sigmoidal. At low conversions, the polymer had a high Tg (~329°C) and was water soluble as the conversion proceeded, the copolymer became organic soluble and the Tg was much lower. Yilgor was also able to show that the reaction products, though no doubt

microheterogeneous, were completely different than simple physical blends of the two homopolymers.(68)

V. Conclusions

This work has demonstrated that novel ionomers can be synthesized quite readily by the direct copolymerization of covalent and ionic vinyl monomers in an emulsion system. The kinetics of this system are however very complex and deserve further study using more sophisticated techniques and equipment. This would require decreasing the rate of the polymerization by a factor about four times to allow for the measurement of low conversion data. This along with a technique which has less inherent error in the measurement of the extent of the conversion to polymer, due to the difficulty of polymer coagulation, would be very desirable. This could be done either by avoiding the conditions where coagulation occurs (high solids and high conversions), or by monitoring unreacted extractable monomer. The later technique while much more difficult to develop might provide the accuracy of data which would be desirable.

The composition of these copolymers, as well as ultimately the microstructure, needs to be studied in more detail after suitable techniques are developed.

The preliminary mechanical tests show that these polymers have very interesting properties. Most notable of these are the strongly enhanced properties such as modulus, and tensile strength which could provide use for these ionomers as elastoplastics. Further testing using such techniques as dynamic mechanical analysis and melt rheological study would further enhance the understanding of this unique class of materials.

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