Characterization of water-soluble oligomers formed during the emulsion polymerization of styrene by means of isotachophoresis

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Characterization of Water-Soluble Oligomers Formed during the Emulsion Polymerization of Styrene by Means of Isotachophoresis

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SYNOPSIS

The concentrations and probable nature of charged oligomers formed by aqueous-phase termination in the persulfate-initiated emulsion polymerization of styrene were measured by isotachophoresis. Isotachophoresis has some advantages over other techniques (e.g., GPC, UV spectroscopy) in that it separates species according to their molecular weight, geometry, and charge. The charged water-soluble oligomeric species were detected in experiments in which particles were nucleated in a surfactant-free environment. Identification of the moieties present was made by comparison with model compounds. Evidence was found for bimolecular combination as a major mechanism of termination in the aqueous phase, although the possibility of disproportionation could not be ruled out. The species formed in the aqueous phase under saturated monomer conditions were found to be subject to further reaction towards the end of polymerization. The surface adsorption characteristics of the compounds formed were compared with those of known surfactants and showed good agreement with the assumptions in the model of Maxwell et al. ([Macromolecules, 24, 1629 (1991)]) for initiator efficiencies in emulsion polymerization. The relatively large concentrations of nonradical aqueous-soluble oligomeric compounds demonstrate conclusively that initiator efficiencies are not 100%, as is often assumed in such systems. © 1993 John Wiley & Sons, Inc.

Keywords: emulsion polymerization • isotachophoresis • oligomer • free radical • aqueous phase • styrene • termination

INTRODUCTION

Recently Maxwell et al. developed a model for the process of the entry into latex particles of free radicals derived from thermal decomposition of water-soluble initiator in emulsion polymerization. Simply stated, this model follows the early ideas of Priest in recognizing that the radical species formed by the thermal decomposition of a water-soluble initiator (persulfate) are unlikely on thermodynamic grounds to transfer spontaneously to the particle phase. It requires the radical species to propagate with water-dissolved monomer, thereby becoming surface active species, which "instantaneously" enter the latex particle phase. Initiator efficiencies less than 100% result from bimolecular termination of radicals which are propagating in the aqueous phase. The rate-determining step for entry of radicals into latex particles is simply the rate of growth of these radicals to a degree of polymerization that imparts them with surface activity. The length at which oligomers formed in the aqueous phase become insoluble has been postulated to be of the order 60 units by Fitch et al. for methyl methacrylate, while other monomers have been measured to give similarly long chain lengths before aqueous phase solubility has decreased. Most of these measurements were designed to detect the insoluble limit of particular oligomers, which may differ substantially from the length required for entry into preformed latex particles. The
The chain length for styrene oligomers with sulfate head groups was postulated by Maxwell et al. to be approximately 2–3 monomer units before irreversible entry into existing latex particles and this has not been directly measured by previous experimental techniques.

Ammerdorffer et al. pioneered the use of isotachophoresis (ITP) to directly monitor the aqueous phase termination products of persulfate-initiated emulsion polymerization of butadiene. ITP has some advantages over other techniques (e.g., GPC, UV spectroscopy) for analyzing those products which are charged oligomers. First, the species are separated before detection according to their molecular weight, geometry, and charge. Second, by effectively suppressing electro-osmotic (back) flow, noncharged components stay at the injection point and do not interfere in the detection. This is contrary to other electrophoretic techniques such as capillary electrophoresis. In this article we apply ITP techniques in a study of the emulsion polymerization of an otherwise well-characterized system, styrene. In particular, we wish to probe the aqueous phase free radical chemistry.

**ISOTACHOPHORESIS**

ITP is a method that allows discrimination between water-soluble species based upon their electrophoretic mobility, which is a function of charge and a parameter involving geometric and interactive components. Within a homologous series with the same ionic group, the mobility is approximately proportional to molecular weight; thus, ITP should be a reliable method for separating water soluble oligomers according to size and number of ionic endgroups.

The theory of ITP has been presented elsewhere. The following summary is given for the purposes of interpreting the experimental results. In an ITP experiment the sample is placed between two electrolytes of different compositions. The leading electrolyte (L⁻) contains the ion with the highest effective mobility and conversely, the terminating electrolyte (T⁻) contains the ion with the lowest effective mobility. When an electric current is applied, the leading ions migrate to the anode (Fig. 1). The sample ions with the highest effective mobility (A⁻) migrate immediately behind the leading zone. Consequently, a zone with only A⁻ ions is formed, followed by a mixed zone AB, the zone B (containing the sample ion with the second highest effective mobility), and so on until finally the terminating ion zone. After sufficient time, the sample zones separate and then all migrate with the same velocity. It is important to note that each zone contains only one species with a concentration which depends on that of the leading ion. The various components can be detected with a variety of detectors, most common of which is a conductivity cell. The linear signal zone height is characteristic of each component's mobility, and the length of the zones can be related to the quantity of each of the components. The apparatus used in this investigation has, just before the conductivity detector, a UV detector which gives useful additional information when identifying compounds. Analysis of an isotachopherogram usually involves calibration with model compounds that are similar to sample components. This provides zone heights, for qualitative analysis.

The concentration within each zone is related to the leading ion concentration by the following relationship:

$$[A^-]_2 = [L^-]_1 \frac{m_A (m_L + m_Q)}{m_L (m_A + m_Q)}$$

**Figure 1.** Diagram demonstrating the principle of anionic separation by isotachophoresis; (a) sample containing anions A, B, and C at the point of injection; (b) partial separation is achieved with the existence of mixed zones; and (c) complete separation.
Here $[A^-]_2$ is the concentration of sample species in the second zone, $[L^-]_1$ is the concentration of the leading (first) zone. The mobilities of the respective ions are given by $m$ and the subscript $Q$ refers to the background electrolyte, in this case $\beta$-alanine. The leading ion concentration thus determines the concentration of all other ions in solution. Absolute mobilities for the species present are unknown so the system must be calibrated. The signal of the conductivity detector is related to the mobility by:

$$\Lambda = z(m_A + m_Q)F$$

with $\Lambda$ = conductivity, $z$ = number of charge, and $F$ = Faraday’s constant. This dependency of conductivity and concentration on electrophoretic mobilities allows the calibration of the quantities of even unknown species with pure compounds of a comparable structure if the step heights are similar. In this work aliphatic sulfates or sulfonates are used.

The sensitivities of the method depends upon the concentration of the leading ion, the current used and the minimum detectable time increment. In our system 0.1 s is the lowest detectable time increment and for quantitative results 1 s a reproducible time increment. The conditions used are 60 $\mu$A and the concentration of leading electrolyte, $5 \times 10^{-3} M$. This leads to, for instance, a minimum reproducible quantity of the model compound octyl sulfate of 190 pmol. This means with a sample injection of 4 $\mu$L a minimum concentration of $4.8 \times 10^{-5} \text{ mol dm}^{-3}$ is possible.

**EXPERIMENTAL**

**Reaction Conditions**

A series of experiments were undertaken to: (1) identify the termination products in an emulsion polymerization and (2) investigate the effect of recipe on the observed species. All experiments carried out were unseeded surfactant free polymerizations initiated by sodium persulfate at various concentrations. The recipes are given in Table I. The polymerizations were carried out in this manner to avoid contamination by surfactant or other ionic species, which could have hampered detection by ITP or been involved in reaction.

The reactions were performed at 50°C in a 300 mL reaction vessel with propeller stirring (ca. 350 rpm). The styrene monomer was freshly distilled at room temperature under vacuum to remove inhibitor. Water was doubly distilled and other analytical grade reagents were used as received. Sampling was at irregular intervals over the course of the reaction, with conversion measured gravimetrically.

**Analysis**

The products were analyzed using ITP equipment developed by Everaerts et al. Detection was by means of both a conductivity cell and a UV absorption cell analyzing at a wavelength of 254 nm. The ITP conditions used are outlined in Table II with a 0.15% solution of hydroxyethylcellulose (HEC) as the supporting medium for the leading electrolyte. This increases the solution viscosity and allows the movement of ions without inducing hydrodynamic flow. Propionic acid (a small percentage is converted to the propionate ion at the pH used) was used as a tailing ion to ensure that a wide range of mobilities were covered. The analysis was also checked with acetic acid (acetate) as the tailing ion. This has a higher mobility than propionic acid, thereby reducing the range of mobilities available; consistency was confirmed by the observation that the number of products remained constant. It is reasonable to assume that the only products observable by ITP were those seen in this analysis and that any species of very low electrophoretic mobility were not excluded.

In each polymerization latex particles were formed. These were separated from the aqueous phase by ultrafiltration over an anisotropic, hydrophilic Amicon “YMT” membrane on polycarbonate. The species present were found not to adsorb onto the surface of the membrane. This was verified in two ways. Samples prepared by ultracentrifugation

<table>
<thead>
<tr>
<th>Table I. The Recipes Used in the Different Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
</tr>
<tr>
<td>$\text{[S}_2\text{O}_5^-\text{]}$</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
</tr>
<tr>
<td>Styrene</td>
</tr>
<tr>
<td>H$_2$O</td>
</tr>
</tbody>
</table>
Table II. Conditions Used for ITP Analysis

<table>
<thead>
<tr>
<th>ITP Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leading electrolyte</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Terminating ion</td>
</tr>
<tr>
<td>Counter ion</td>
</tr>
<tr>
<td>Current</td>
</tr>
</tbody>
</table>

showed the same concentration of products as that by filtration. Quantitative measurements of the filtered products as a function of subsequent filtrations showed no significant adsorption.

Varying ITP conditions were used to check that no micelles or mixed zones were present. This involved varying the operating current from 60 to 20 mA, changing the injection volume and decreasing the concentration by dilution (1 : 3, sample : water). This had no effect on the observed isotachopherograms. In addition the leading ion concentration was increased to 0.01 from 0.005 M. This has the effect of increasing the zone concentrations, possibly above the critical micelle concentration for any of the species within the zone. The relative zone length would change significantly if micelles formed. As no effect was observed this provided reliable evidence that the ITP analysis was of charged oligomers and not micelles of the products.

Model Compounds

**Synthesis of 2-Phenylethylsulfate (PES), Sodium Salt\(^9\)**

Diethyl ether (10 mL) was cooled to \(-5^\circ C\). Four milliliters of chlorosulfonic acid was added very slowly with stirring followed by phenyl ethanol (6.4 mL) over 20 min. After standing for 30 min at \(-5^\circ C\) very concentrated sodium hydroxide was added dropwise until the pH was approximately 7. A white precipitate formed immediately and it was necessary to add an additional 20 mL of diethyl ether. The solid was allowed to stand for 30 min before filtering. The solid was recrystallized from ethanol/water mixture (9 : 1) with hot filtering and cooling to \(-10^\circ C\) to enable the final solid to be isolated. The yield was approximately 21%. \(^1\)H-NMR and mass spectrometry analysis showed the compound to be pure PES, sodium salt.

**Synthesis of 2,4-Diphenylpentan-1-ol Hydrogen Sulfate (DPPS), Sodium Salt**

This was prepared by the Institute of Drug Technology, Aust. Ltd. The synthesis was designed for preparation from the starting material, 1,3-diphenylbutanone, which was the closest analogue to a di-styrene compound available. The first step in the synthesis was to substitute the ketone functionality with a \(CH_2\) group, in order to increase the stability of the final sulfated compound by not attaching it to the \(\alpha\) carbon atom. This was achieved by the use of a Wittig reagent, triphenylphosphinium bromide. The alkene was subsequently converted to the alcohol via the anti-Markovnikov addition at the double bond\(^10\) using 9-borobicyclononanone. This was followed by sulfation with chlorosulfonic acid as described above.\(^9\)

2-(\(\text{-Phenylsulfonyl}\))ethylsulfate (PSES) was synthesized by C J Pijls and used as received. The general procedure for the synthesis was as follows. Diethyl ether (40.0 g) was added to 0.3 M chlorosulfonic acid (10 mL) with stirring, at 2–3°C, under a nitrogen atmosphere. Slow addition of 0.1 M 2-phenyl ethanol (10 mL) was followed by reaction over 30 min. The mixture was then poured over 60 g of crushed ice in order to remove the remaining chlorosulfonic acid. The mixture was neutralized with bicarbonate, then washed twice with 30 g diethyl ether to remove unsulfonated material. The remaining water was removed by film evaporation and the products dried in a vacuum oven.

Further model compounds such as \(p\)-styrenesulfonate (SS), sodium dodecyl sulfate (SDS), octyl sulfonate, etc., were analytical grade and used as received.

Surface Activity

A series of experiments was carried out to test the propensity of both model compounds and reaction products to adsorb on the surface of latex particles. These experiments were performed by mixing a solution of known concentration of the molecule under investigation with seed latex that had been made using styrene sulfonate as a comonomer. The seed latex had been subsequently cleaned by extensive rinsing over ion exchange resin. There was no observable ITP trace from the separated aqueous phase (sensitivity of approximately \(4.8 \times 10^{-6} M\)) and thus the latex should have been stabilized primarily by bound species. After mixing with the compounds of interest, the seed latex was separated using the filtration method described above and analysis was performed using isotachophoresis. Concentration measurements in the aqueous phase were made using hydrogen octyl sulfonate (\(C_8H_{17}SO_3^-\)) as an internal standard, with filtration and seed addition effects being evaluated.
RESULTS AND DISCUSSION

First, a kinetic scheme covering the known reactions in the aqueous phase is presented:

\[ \text{Initiator decomposition:} \]
\[ \text{SO}_2\text{O}^- \rightarrow 2\text{SO}^- \]  

\[ \text{Initial propagation step:} \]
\[ \text{SO}_2^- + M \leftrightarrow M_2\text{SO}_2^- \]  

\[ \text{Subsequent propagation:} \]
\[ M_i\text{SO}_2^- + M \rightarrow M_{i+1}\text{SO}_2^- \]

\[ \text{Bimolecular termination:} \]

an example is presented showing termination by combination (I) and disproportionation (II) between two \( M_i\text{SO}_2^- \) species to illustrate the different chemical structure of the two products:

Here \( M \) represents a monomer unit, \( M_i\text{SO}_2^- \) represents a monomeric radical with a sulfate end group, \( M_{i+1}\text{SO}_2^- \) an oligomeric radical composed of \( i \) monomer units and a sulfate end group, \( z \) is the number of monomer units a primary free radical must add on before it enters a latex particle (i.e., becomes at least surface active), and \( M_{i+1}\text{SO}_2^- \) is thus the entering group. The thermal decomposition rate coefficient for initiator is \( k_d \), the propagation rate coefficient of the sulfate anion radical is \( k_{pi} \), the propagation rate coefficient of the oligomeric radicals is \( k_p \), the rate coefficient for termination between two aqueous phase radicals is \( k_t \), and the pseudo first-order entry rate coefficient per latex particle of aqueous phase radicals is \( p \). Note that the two products of the disproportionation in eq. (4) will differ in molecular weight, because one of the species is unsaturated. The two products will also give different UV absorptions.

It is impossible to use ITP analysis to detect the (too) low concentration of oligomeric radicals in the aqueous phase (ca. \( 10^{-8} M \) based on calculations by Maxwell et al.\(^1\)). However, it is possible to detect termination products, since these products may build up over the course of the reaction to concentrations detectable by ITP. It must be noted, however, that the limiting concentrations detectable under the ITP conditions used here are quite high. Initiator concentrations of \( 10^{-2} M \) gave undetectable quantities of termination products, that is, less than approximately \( 10^{-4} M \).\(^4\)

Four model compounds were analyzed by ITP: \( p \)-styrenesulfonate (SS), phenylethylsulfate (PES), 2-(\( p \)-phenylsulfonate)ethylsulfate (PSES), and 2,4-diphenylpentan-1-ol hydrogensulfate (DPPS). There structures are shown below. These represent, respectively, an unsaturated styrene monomer unit with one sulfate group \( \text{[MSO}_2^- \text{(unsat)}] \), a styrene unit with one sulfate group \( \text{[MSO}_2^- \text{]} \), a styrene unit with two sulfate groups \( \text{[M(SO}_2^-]_2 \) \), and two monomer units with one sulfate group \( \text{[M}_2\text{SO}_2^- \) \). These are generally four of the most likely termination products resulting from the chemistry of \( \text{S}_2\text{O}_5^- \) and styrene in water. It should be noted that the actual products of termination in the aqueous phase may have different isomeric structures than the model compounds that are supposed to represent them. However, the differences in the electrophoretic mobility of the model compounds and the true termination products are probably small compared to the difference in the mobility of, say, a distyrene sulfate and a monostyrene sulfate.

The isotachopherogram of SS is shown in Figures 2(a) and (b). It can be seen that a single zone corresponds to SS. The UV absorption [Fig. 2(b)] is off scale on the equipment used. The isotachopherogram of PES is illustrated in Figures 3(a) and (b). This is seen to be pure within the detection limits discussed previously and to have a zone height similar to SS. The isotachopherogram of PSES is shown in Figures 4(a) and (b). The component with the lower zone height was assumed to be PSES, while the upper zone, with the same zone height as PES,
was assumed to be PES impurity. Here the UV signal is useful in establishing identity as PSES and PES exhibit the same absorption [Fig. 4 (b)] at 254 nm and both can be postulated to have single phenyl groups. This impurity may have been a by-product formed during the production of PSES through incomplete reaction of the phenyl ethanol starting product. The impurity could also be a hydrolysis product of PSES formed at the low pH conditions of the ITP analysis or simply arising from the inherent thermal instability of the compound. Figures 5 (a) and (b) show the isotachopherogram of DPPS. This has an impurity, also identified by $^1$H-NMR, of ethyl sulfate formed during the synthesis procedure. It is in the ratio of approximately 1 : 1 (as determined by $^1$H-NMR) with the DPPS and does not interfere with the identification of the $M_2$SO$_4$ analogue. Its presence does, however, make it impossible to use this as a standard compound for relating zone length to concentration.

**Figure 2.** Isotachopherogram of p-styrene sulfonate (SS) with both UV absorption and characteristic zone resistance. The standard compound is octyl sulfonate. The time axis for both responses are different because of the linear separation of the two detectors.

**Figure 3.** Isotachopherogram of phenylethylsulfate (PES) with both UV absorption and characteristic zone resistance. The standard compound was octyl sulfonate.

**Identification of Termination Products**

Figures 6 and 7 show typical isotachopherograms for the reactions performed. The zone heights are consistent throughout all the analyses, although the zone lengths or product concentrations vary significantly with reaction time. By comparing relative heights of the model compounds, assignments of the products can be made. The zones that are important are labelled and compared to model compounds in Table III.

Although the zone heights of the model compounds in Table III are not in complete agreement with the zones observed, it must be remembered that the compounds formed are not necessarily identical to the model compounds. The model compounds are more an indication of the electrophoretic mobilities of the termination products. For example, the di styrene sulfate [$M_3$ (SO$_4$)] termination product (zone f), if based on the addition of two styrene monomers to a sulfate group has a molecular weight of 305 amu, whereas the model compound (DPPS), which
Figure 4. Isotachopherogram of 2-(p-phenylsulfonate)ethylsulfate (PSES) with both UV absorption and characteristic zone resistance. The standard compound was octyl sulfonate. The major impurity was identified as PES.

Figure 5. Isotachopherogram of 2,4-diphenylpentan-1-ol hydrogensulfate (DPPS) with both UV transmission and characteristic zone resistance. The standard compound was octyl sulfonate. The major impurity was identified as ethyl sulfate.
The compound with the highest degree of polymerization observed in the isotachopherograms and the species with the smallest electrophoretic mobility was the distyrene sulfate (M$_2$SO$_4$). This is an important observation as it allows testing of the reaction mechanism presented above [eqs. (3)–(7)]. The validity of any conclusions are weakened somewhat by not having the capacity to conduct the ITP analysis at the reaction temperature of 50°C. Increased solubility at this temperature may have enabled observable (higher) concentrations of oligomers with higher degrees of polymerization, (e.g., sulfate initiator fragments with three styrene monomer units attached [M$_3$SO$_4$]), to be seen if they were part of the reaction scheme. However, if there were high concentrations of the M$_2$SO$_4$ radicals in solution then it would be assumed that there would exist termination products from them.

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Table III. Results of Isotachopherograms for Surfactant-Free Emulsion Polymerization for All Compounds Observed in Experiments S10, 11, 13: Relative Heights and UV Absorptions Were Averaged Over All Measurements Obtained

<table>
<thead>
<tr>
<th>Zone Label</th>
<th>Resistance</th>
<th>UV Absorption</th>
<th>Analogue Compound</th>
<th>Resistance</th>
<th>UV Absorption</th>
<th>Assignment of Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.28</td>
<td>0.5</td>
<td>0.31 (PSES)</td>
<td>0.6</td>
<td>M(SO$_2$I)$_2$</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>0.49</td>
<td>1.0</td>
<td></td>
<td></td>
<td>M$_3$(SO$_3$)$_2$</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>0.68</td>
<td>high</td>
<td>0.69 (SS)</td>
<td>high</td>
<td>MSO$_4$ (unsat)</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>0.88</td>
<td>0.6</td>
<td>0.80 (PES)</td>
<td>0.6</td>
<td>MSO$_4^-$</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>1.26</td>
<td>high</td>
<td></td>
<td></td>
<td>M$_2$SO$_4$ (unsat)</td>
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<tr>
<td>f</td>
<td>1.37</td>
<td>1.2</td>
<td>1.33 (DPPS)</td>
<td>1.2</td>
<td>Cl$^-$</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>C$<em>6$H$</em>{17}$SO$_3$</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>1.0</td>
<td>0</td>
<td></td>
<td></td>
<td>CH$_3$CH$_2$COO$^-$</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>3.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A product such as tristyrene disulfate [M$_3$(SO$_2$I)$_2$] resulting from termination by combination between MSO$_4$ and M$_2$SO$_4$ [eq. (8)] should have a high probability of occurring.

\[ \text{\begin{align*} &\text{\Hochschild} + \text{\Hochschild} \xrightarrow{k} 2\text{\Hochschild} \quad \text{eq. (8)} \\
&\text{\Hochschild} + \text{\Hochschild} + \text{\Hochschild} \quad \text{eq. (8)} \end{align*}} \]

This would have a zone height relative to C$_6$H$_{17}$SO$_3$ of about 0.7 to 0.8, as there is normally, for a given charge, a linear response between molecular weight and electrophoretic mobility,$^4$ and a UV absorption of about 1.6–1.8 relative to other absorptions. As there was no distinct zone of this description we can conclude that there was not a large amount of this product created. The zone (c in Figs. 6 and 7) in this region, however, can at times appear as a mixed zone with high UV absorption; it is therefore possible that some of this species was produced in addition to the unsaturated MSO$_4$ product. If it were at small concentrations it would not appear as a separate zone and its characteristic UV absorption would be swamped by the SS-like molecule.

Concentration of Termination Products

Figures 8–11 show the variation of product concentrations with reaction time for three of the four experiments performed. Unfortunately, these data cannot be used to make unambiguous conclusions as to the correctness of the reactions (3)–(7) or their attendant rate coefficients. This is apparent from Figure 12 as there is continuing product evolution past 100% monomer conversion, indicating that subsequent reactions such as hydrolysis contribute to the accumulated products. The experiment S112 did not have any termination products that could be observed quantitatively. Exploratory experiments with initiator concentrations lower than $10^{-2}M$ also showed this effect. Therefore, a minimum initiator concentration of approximately $5 \times 10^{-2}M$ was needed to obtain enough product to be observable. In theory, this lower limit could be

Figure 8. Concentration of aqueous phase components as a function of time for experiment S110. The compounds shown are: (○) styrene disulfate [M$_1$(SO$_2$I)$_2$], (△) distyrene disulfate [M$_3$(SO$_2$I)$_2$], (△) unsaturated styrene sulfonate [M$_x$SO$_4$(unsat)], (X) styrene sulfonate (M$_3$SO$_4$), (□) unsaturated di styrene sulfonate [M$_2$SO$_4$(unsat)], and (■) di styrene sulfonate (M$_2$SO$_4$). The lines joining the points are for visualization purposes only.
Figure 9. Concentration of aqueous phase components as a function of time for experiment SI11. The compounds shown are: (○) styrene disulfate \([\text{M}_1(\text{SO}_4)_2]\), (△) distyrene disulfate \([\text{M}_2(\text{SO}_4)_2]\), (△) unsaturated styrene sulfate \([\text{M}_1\text{SO}_4(\text{unsat})]\), (×) styrene sulfate \([\text{M}_1\text{SO}_4]\), (□) unsaturated distyrene sulfate \([\text{M}_2\text{SO}_4(\text{unsat})]\), and (■) distyrene sulfate \([\text{M}_2\text{SO}_4]\). The lines joining the points are for visualization purposes only.

Figure 10. Concentration of aqueous phase components as a function of time for experiment SI13. The compounds shown are: (○) styrene disulfate \([\text{M}_1(\text{SO}_4)_2]\), (△) distyrene disulfate \([\text{M}_2(\text{SO}_4)_2]\), (△) unsaturated styrene sulfate \([\text{M}_1\text{SO}_4(\text{unsat})]\), (×) styrene sulfate \([\text{M}_1\text{SO}_4]\), (□) unsaturated distyrene sulfate \([\text{M}_2\text{SO}_4(\text{unsat})]\), and (■) distyrene sulfate \([\text{M}_2\text{SO}_4]\). The lines joining the points are for visual representation only.

Figure 11. Concentration of aqueous phase components as a function of time for experiment SI13, showing the range from 0 to 400 min. The compounds shown are: (○) styrene disulfate \([\text{M}_1(\text{SO}_4)_2]\), (△) distyrene disulfate \([\text{M}_2(\text{SO}_4)_2]\), (△) unsaturated styrene sulfate \([\text{M}_1\text{SO}_4(\text{unsat})]\), (×) styrene sulfate \([\text{M}_1\text{SO}_4]\), (□) unsaturated distyrene sulfate \([\text{M}_2\text{SO}_4(\text{unsat})]\), and (■) distyrene sulfate \([\text{M}_2\text{SO}_4]\). The lines joining the points are for visual representation only.

changed by using a lower leading ion concentration. If it is too low, however, the voltage needed to generate the desired current is above the capability of the instrument.

The concentrations of termination products shown are derived from relative zone lengths. Only two of the model compounds used were pure and the difference in zone heights for these compounds was small, making it difficult to use these to quantify the various zone concentrations. Calibration was performed through the use of a series of alkyl sulfonates of carbon chain lengths 4, 8, and 12. These gave a graph of zone height (or mobility) versus the number of moles that pass the detector per second (Fig. 13). This could be extrapolated over the range of zone heights (mobilities) required. The total concentration in the sample can then be calculated from the total zone length in seconds and the injection volume. The linear extrapolation over the range of mobilities considered may be subject to some error (ca. ±20% maximum).

There are several interesting features to the change in the product concentrations with time. The following discussion will focus on: (1) how the identified products change with time and relative to one another, (2) the mechanism of termination in the
aqueous phase, and (3) the implications of these results for the model of Maxwell et al.1

1. The concentrations of aqueous phase termination products all increase with time until high conversion is reached (Fig. 12). Once the monomer concentration in the polymerizing system is reduced significantly, then subsequent reactions of the water soluble products give rise to changes in the concentration of some species. These reactions could also be the adsorption onto existing particles by any surface active species (examined more fully in a later section). Most notable are the variations in concentration of the distyrene sulfate and disulfate compounds. The $M_2S$O$_4^-$ concentration increases in all experiments late in the polymerization, while the $M_2(SO_4)_2^-$, which is initially high, falls in concentration. This would indicate that the products that occur at the end of the polymerization are the result of hydrolysis, or similar reactions, leading to the removal of sulfate groups as is in eq. (9):

$$\text{-S}_2\text{C=O + H}_2\text{O} \rightarrow \text{S}-\text{S} + \text{H}_2\text{O} \quad (9)$$

In addition, the higher initiator concentration of experiment SI13 shows a slightly different trend with the unsaturated $M_2SO_4^-$ increasing with time, possibly at the expense of the saturated $M_2SO_4^-$ which actually decreases over this region (1000–2000 min) despite increasing steadily over the 0–1000 min time region. Therefore it could be postulated that there is hydrogen abstraction from the termination products by the sulfate radicals, e.g.:

Figure 12. Conversion (measured by gravimetry) as a function of time for experiments SI10, SI11, and SI13.
of a carbonyl group. This could occur via the following mechanism utilizing, e.g., the product from reaction (9):

\[
\text{(12)}
\]

The above reaction is possible with any primary and secondary alcohols that may be formed during reaction.

Evidence for creation of both hydroxy and carbonyl groups is shown in Figures 14–16. Proton NMR analysis on a freeze-dried sample of the final product of SI13 in deuterated chloroform (Fig. 14) and in D₂O (Fig. 15) show both the presence of aromatic and aliphatic protons. In addition there is a very broad band at ca. 1.75 ppm that is present in the CC₁₃D spectra but is absent from the D₂O. This is strongly suggestive of a hydroxy group attached to the alkyl chains present in the molecules. This functional group can undergo exchange in the presence of D₂O and it is consequently absent from the spectra in D₂O. As the spectrum is on a sample containing many compounds it is difficult to give a complete identification of the products formed and establish where the OH groups are actually attached. The IR spectrum of the same product shown in Figure 16 also demonstrates the presence of hydroxy functionality with a very strong absorption at 3400 cm⁻¹. The existence of some carbonyl functionality is also evident as there is a small absorption at 1600–1700 cm⁻¹, characteristic of such a group.

The important consideration of these subsequent reactions is that it makes it very difficult to model the product formation over time. While monomer concentration in the aqueous phase is at its saturation value (4 × 10⁻³ M) the propagation reaction between monomer and sulfate radicals should be the dominant reaction as it has been shown to be in the diffusion limit, with a rate coefficient of 2 × 10⁹ dm³ mol⁻¹ s⁻¹. As the hydrolysis or hydrogen abstraction reactions are unlikely to be this fast, given the existence of high concentrations of sulfated products and the conclusions of Okuba and Mori, the reaction scheme as presented in eqs. (3)–(7) should be an accurate representation of the main reactions controlling entry. It is probably somewhat simplistic at later times when side reactions such as those discussed above may become more important. Without knowing greater isomeric information, perhaps from NMR data on well-separated product components, it is hard to evaluate the extent of these reactions throughout the course of the polymerization.

2. Initially, the product of highest concentration is that of the distyrene disulfate \([M_2(SO_4)_2]\) (Fig. 11). This would be expected from the reaction

Figure 14. ¹H-NMR spectrum for the freeze dried product of experiment SI11 in CDCl₃.
scheme presented in eqs. (3)–(7). As the rate of propagation between the sulfate radical and styrene has been measured at the diffusion limited value, as discussed above, the radical of highest aqueous-phase concentration in the polymerization system is the MSO₄⁻. This means that termination between two of these species should produce the dominant products as outlined in eq. (6). This is obviously the case. In addition, as M₄(SO₄)₂ is the dominant product species, the mechanism by which the termination occurs could be concluded to be primarily by combination at early times [eq. (6)]. However, there is also the formation of relatively high concentrations of M₅SO₆⁻, so that disproportionation cannot be ruled out as a termination mechanism. If disproportionation were to occur it would be expected that there would be similar concentrations of the unsaturated M₅SO₆⁻ also present [eq. (6)]. As this is not the case there are four possible routes leading to the formation of the observed products:

a. Disproportionation is unfavorable in comparison to combination and the M₅SO₆⁻ species observed are the result of hydrolysis of

Figure 15. ¹H-NMR spectrum for the freeze dried product of experiment SI11 in D₂O.

Figure 16. IR spectrum for the freeze-dried product of experiment SI11.
the M\(_1\)(SO\(_4\))\(_2\) formed from termination by combination between sulfate radicals and styrene sulfate radicals. The existence of hydroxyl functionality, which results from such a reaction, was discussed above. This postulate also has some supporting evidence from the ITP results as the M\(_1\)SO\(_4\) from the reaction mixture had a lower mobility (higher resistance) than the analog compound used. This may indicate the presence of an OH group which would act to decrease mobility. In the presence of buffer, and therefore higher pH conditions (final pH = 6), the change in experimental products at the end of polymerization is reduced (Fig. 8). This is consistent with hydrolysis being favored at low pH conditions as shown by experiments SI11 and SI13 (Figs. 9 and 10), where the change in product concentrations is greater. The final pH in both these cases was of order 2–3. The buffer seemed to have little other effect.

The small concentration of unsaturated M\(_2\)SO\(_4\) formed in the above scenario could simply be from hydrogen abstraction of the M\(_1\)SO\(_4\) product by sulfate radicals as shown in eqs. (10) – (11) and termination by the disproportionation route could be postulated to be very unfavorable. The unsaturated M\(_2\)SO\(_4\), for which styrene sulfonate is an analog, that results from disproportionation, propagates in competition with styrene monomer in the aqueous phase. The rate coefficient for the propagation of a monomer such as styrene sulfonate is unknown but may be similar to styrene. This would deplete the concentration of this product in the aqueous phase and means that disproportionation may be a competing termination mechanism with combination, with the saturated M\(_1\)SO\(_4\) the only observable remnant.

c. Transfer to monomer or other compounds in the aqueous phase results in the formation of M\(_1\)SO\(_4\) product, which is observed in this system. Thus, disproportionation would not need to be part of the reaction scheme. The rate of transfer compared with propagation would preclude this possibility, although the measurements are for nonpolar media. Water may influence the ratio of propagation to transfer and there may also be an effect of chain size on this ratio. Clearly, such reactions in the aqueous phase merit further study to elucidate the rate coefficients in this important regime.

d. The concentrations of all species are strongly influenced by their adsorption isotherms which could be dependent on particle size. As will be shown later in this article, only the M\(_3\)SO\(_4\) species can adsorb at the particle surface and for the M\(_2\)(SO\(_4\))\(_2\), M\(_1\)SO\(_4\) (saturated and unsaturated) species under discussion, such a route is unavailable.

As points c and d must be considered unlikely, it is possible that some disproportionation termination is occurring in the aqueous phase. Energetically the combination reaction must be considered more favorable as it is a barrierless (radical–radical recombination) reaction. The disproportionation reaction involves hydrogen abstraction (bond breaking) and would be expected to have a significant enthalpic barrier. As the species reacting are charged and the free radical sites are likely to be sterically hindered, this may contribute to the disproportionation reaction over the combination mechanism. These results show unambiguously that combination is the most favorable reaction while there are a number of reasonable reaction pathways that could lead to the formation of the products that could also arise from disproportionation. Thus, it is not possible to rule out disproportionation entirely but it is unlikely to be as important as the combination reaction.

3. The model proposed by Maxwell et al. for the entry of radicals from the aqueous phase into latex particles postulated that the distyrene sulfate radicals were responsible for the entry process. This was deduced as a result of extensive modeling of experimental kinetic data and thermodynamic considerations of surface active species. The data presented here are of direct relevance to the validity of this model as the assumptions made in developing it were twofold: (1) radicals entered particles from the aqueous phase very quickly once they grew to become surface active, and (2) growth of the oligomer to become surface active was the rate-determining step. Analysis of the termination products helps establish what radical species remain in the aqueous phase and which may have been adsorbed at particle interfaces.

Several complicating factors make the interpretation of results difficult. The temperature of the ITP analysis is not the reaction temperature. In addition, the formation of particles throughout the course of polymerization with the attendant coagulation and growth reactions makes the system quite complex. This will impinge on the ability to understand effectively the entry process as the
adsorption step will be influenced by the particle population changing during the course of the polymerization. To overcome this problem seeded experiments need to be carried out. Under the ionic strength conditions created by the high initiator concentration this is difficult because of inherent instability of the latex to coagulation. Seeded experiments also introduce surfactants that can interfere with the interpretation of the isotachopherograms and may also become involved in some of the reactions.  

The ITP results show that there is a large aqueous phase concentration of the M_2SO_4_\textsuperscript{2-} molecules. The reaction scheme outlined above assumed that the propagation steps, subsequent to the addition of the first monomer unit to the sulfate radical, had the long chain rate rate coefficient (258 dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1} at 50°C),\textsuperscript{20} whereas the first step [eq. (4)] is many orders of magnitude faster. There exists some evidence\textsuperscript{8} for this assumption although it has not been measured directly. Thus, the population of M_2SO_4_\textsuperscript{2-} radicals is likely to be somewhat less than that of the M_1SO_\textsuperscript{2-} radicals. As the entry theory only considers the population of radicals of entering length, their concentration must be inferred from the reaction products present. The termination products possible from the reaction of the M_2SO_\textsuperscript{2-} with other likely species are: M_2(SO_4)_\textsuperscript{2-}, M_3(SO_\textsuperscript{2-})_\textsuperscript{2}, and M_4(SO_\textsuperscript{2-})_\textsuperscript{2} for termination by combination with SO_\textsuperscript{2-}, M_3SO_\textsuperscript{2-}, and M_4SO_\textsuperscript{2-}, respectively; M_2SO_\textsuperscript{2-} (saturated and unsaturated), M_1SO_\textsuperscript{2-} (saturated and unsaturated) for termination by disproportionation with SO_\textsuperscript{2-}, M_3SO_\textsuperscript{2-}, and M_4SO_\textsuperscript{2-}. There can also be termination between radicals of higher degrees of polymerization if they exist. As already stated, the radical of highest concentration is the M_1SO_\textsuperscript{2-} and should therefore be the most likely termination partner of any M_2SO_\textsuperscript{2-}. Since combination was shown to be the dominant termination mechanism when considering the M_1SO_\textsuperscript{2-}, it would be likely that the termination product of highest concentration would be the M_3(SO_\textsuperscript{2-})_\textsuperscript{2}. As previously pointed out, there is no evidence that this zone is present, although the result is somewhat ambiguous because of the presence of species of similar electrophoretic mobility. The M_4(SO_\textsuperscript{2-})_\textsuperscript{2} product should in principle be observable at a relative zone height of approximately 0.9–1.0. There is no zone observed at this height, although the concentration could be too low to be seen. As the M_3(SO_\textsuperscript{2-})_\textsuperscript{2} compound has been shown to decrease in concentration at the end of polymerization it is possible that these products are also unstable. It is unlikely, however, that larger disulfates would be any more unstable than the M_4(SO_\textsuperscript{2-})_\textsuperscript{2} because of the greater separation of charge, and it can be concluded that their concentration never reaches detectable levels.

Disproportionation could give high concentrations of M_2SO_\textsuperscript{2-} in the aqueous phase as observed. Products for this reaction [eq. (13)], however, should include higher concentrations of the unsaturated compound than is observed:

\[
\ce{\text{M}_2\text{SO}_4^- + \text{M}_2\text{SO}_4^- \rightarrow \text{M}_3\text{SO}_4^- + \text{SO}_4^{2-}}
\]

Again, it is possible that the unsaturated compounds could react further with free radical attack on the double bond as outlined in the previous section. The concentration of unsaturated M_2SO_\textsuperscript{2-} increases at the end of the reaction in the experiment with 1 × 10\textsuperscript{-1}M persulfate concentration (SI13), while the saturated M_2SO_\textsuperscript{2-} increases in the experiments SI11 and SI12. Concurrent with the increase in the concentration of the unsaturated M_2SO_\textsuperscript{2-} in experiment SI13 which has a high initiator concentration, is a decrease in the concentration of saturated compound so that the total distyrene sulfate concentration shows similar trends to the experiments at lower initiator concentrations. This would indicate that hydrogen abstraction [e.g., eqs. (10)–(11)] is occurring when there are more sulfate radicals produced than can react with monomer. Abstraction may be occurring throughout the reaction and could possibly be the mechanism whereby formation of the unsaturated compounds occurs. If, as suggested, disproportionation is not the major termination mechanism, then the only way the M_2SO_\textsuperscript{2-} product can be formed is through the hydrolysis of the M_2(SO_\textsuperscript{2-})_\textsuperscript{2}. Evidence for this last (and favored) suggestion was discussed above.

As there are several alternative reactions which could lead to the observed products, without information regarding the individual rate coefficients it is hard to make strong conclusions concerning the behavior of radicals in the system. It would appear, however, that there is not strong evidence for M_2SO_\textsuperscript{2-} radicals undergoing termination reactions in the aqueous phase, particularly if combination is the more energetically favored mechanism.

**Surface Activity of the Reaction and Model Compounds**

Figures 17 and 18 show the adsorption characteristics of the model compounds and the reaction products (from SI11). For each compound ITP analysis was used to measure: the initial relative concentration, the subsequent concentration after
that solution had undergone filtration, and finally the aqueous phase concentration after mixing with seed latex and separation by filtration. These results show that the filtration step does not influence the aqueous phase concentrations (within experimental error) as the relative concentrations before and after are constant. After addition of seed particles the concentration of some compounds in the aqueous phase is reduced appreciably. As the concentration in the aqueous phase has decreased, the remainder must have adsorbed on the surface of the latex particles, that were present prior to filtration. The decrease in aqueous phase concentration that is seen by those compounds is compared to SDS (Fig. 17) which displays strong surface active behavior. The results show that the only product compounds to demonstrate appreciable adsorption onto latex particle surfaces are those with a minimum of two styrene units attached to the sulfate head group. This is in excellent agreement with the thermodynamic rationalizations set forth by Maxwell et al. for this process.

The above result also demonstrates why probable termination products for the M₂SO₄ moieties are not observed. It is highly likely that they will exist at the particle surface and undergo reactions there. Termination at the particle surface with radicals within the particles could also occur. This may lead to the formation of the M₂SO₄ product, of which there is a considerable concentration in the aqueous phase, from a reaction not in the aqueous phase. These experiments also demonstrate that the formation of large quantities of surface active material is possible in the emulsion polymerization of styrene and that it is not all bound to the particle surface. It is this that makes so-called surfactant free emulsion polymerization possible, although the term is something of a misnomer.

CONCLUSIONS

Three important conclusions can be drawn from the experimental results presented here. The first is that bimolecular termination of small charged oligomeric radicals in the aqueous phase appears to be predominantly via combination. While some disproportionation products are observed there is ambiguity surrounding this reaction as there are a number of pathways to these products. Second, the distyrene monosulfate compounds are demonstrated to be surface active while compounds with smaller hydro-
phobic tails are not. This supports the assumptions of the model for entry of free radicals into latex particles of Maxwell et al., that surface active free radicals "enter" latex particles by a two-step process: following its propagational growth in the aqueous phase a radical must adsorb onto a latex particle, and then it must propagate into the latex particle. Entry of radicals into latex particles before being surface active is unlikely, and the hydrophobic tail for sulfate radicals must be at least two styrene units long to achieve surface activity. The surface active species arising from termination, that are observed to achieve surface activity. The surface active species arising from termination, that are observed in this study, could not propagate into the latex particles. However, the combination products that would have resulted from termination with the di-tertiary butyl peroxide would enter latex particles by a two-step process: first, the species postulated to be responsible for entry, are not observed in the aqueous phase utilizing this technique. This provides support for the conclusions that species of this size and type are surface active and are more likely to adsorb at the latex particle surface. Third, the presence in the aqueous phase of termination products in styrene emulsion polymerizations dictates that initiator efficiencies must be less than 100%; an important result considering that 100% initiator efficiencies are often assumed for these systems.

Finally, analysis of aqueous phase termination products of emulsion polymerization by ITP has proved to be a useful technique because not only can the degree of polymerization of these species be determined but too can their charge. Future work should include more exhaustive qualitative and quantitative calibration of these products, perhaps at lower detection levels and at elevated temperatures in an attempt to probe more fully the aqueous free radical chemistry in emulsion polymerization. Other techniques, such as NMR, could also be brought to bear more fully on the problem. An examination of the possible side reactions such as hydrolysis would be important in resolving more fully the complete aqueous phase chemistry. Such knowledge is important in establishing the kinetics of both free radical entry and particle formation. The techniques developed here for styrene are also applicable to other monomer systems and could be used in elucidating mechanistic understanding of emulsion polymerization.

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REFERENCES AND NOTES


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