The Mechanism of Extender Action by Potassium Persulfate in the Suspension Polymerization of Styrene

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Synopsis

The contribution by potassium persulfate to suspension stability in the bead polymerization of styrene which is stabilized by hydroxyl apatite (tricalcium phosphate) powders has been studied. Potassium persulfate, when used in lieu of an anionic surfactant as the extender, causes the formation of polystyrene sulfate in the aqueous phase. This anion-active polymer adsorbs on the surface of the hydroxyl apatite crystals and thus alters their wetting characteristics, causing them to become more effective suspension stabilizers. Polystyrene sulfates of molecular weights ranging from 2000 to 100,000 have been synthesized, characterized, and shown to be effective hydroxyl apatite extenders. The capability of polystyrene sulfate to adsorb onto hydroxyl apatite crystals is not strongly dependent upon the molecular weight of the polymeric ester. The tolerance of the system to high molecular weight polystyrene sulfate is relatively high since excess extender is taken up by dissolving in the monomer phase. The tolerance for water-soluble polystyrene sulfate, on the other hand, is low because excess extender of this type engages in double-layer adsorption on hydroxyl apatite, which renders the latter too hydrophilic to permit effective suspension stabilization. Use of a water-soluble polymerization inhibitor in the suspension polymerization system has no effect on suspension stability when sodium dodecylbenzene sulfonate or preformed polystyrene sulfate is used as the extender; however, suspension stability is destroyed when the inhibitor is used with persulfate, because it prevents the formation of polystyrene sulfate. Potassium persulfate is therefore more accurately described as a precursor of the active extender, which is the mono- or disulfate ester of polystyrene.

INTRODUCTION

The polymerization of styrene and other ethylenic monomers may be carried out in mass, solution, emulsion, or suspension media. Barring the special case wherein the solvent may participate in a chain transfer reaction with the growing chains, polymerizations in mass and in solution are equivalent since the solvent serves mainly as an inert diluent. Suspension polymerization, moreover, is a special case of mass polymerization wherein the reaction takes place inside the monomer–polymer globules (or beads) which are dispersed in water. The latter serves mainly as a heat-exchange medium. Emulsion polymerization proceeds by a completely different mechanism.

Under sufficiently strong agitation forces and with adequately small bead–water ratios, styrene can be induced to polymerize in suspension

without the aid of suspension stabilizers. Reliable and economic commercial processes utilize added suspension stabilizers which may or may not be soluble in the aqueous dispersion medium.

Water-soluble suspension stabilizers include the hydrocolloids, which may be of natural or synthetic origin. Poly(vinyl alcohol), hydroxyethyl cellulose, gelatin, alginate, and poly(methacrylic acid) are typical examples. This type of suspending agent has limited utility in the commercial production of crystal polystyrene because a portion of the suspending agent cannot economically be removed from the polymer. These inclusions cause turbidity and discoloration in the product.

Water-insoluble suspension stabilizers are finely divided solids such as talc, barium sulfate, aluminum hydroxide, and phosphates of calcium and magnesium. Commercially, the most significant of these is hydroxyl apatite, commonly referred to as tricalcium phosphate (TCP). The suitability of hydroxyl apatite is based on the facts that it is obtainable commercially at low cost as a powder of submicronic (i.e., less than 1 micron) particle size and that it can easily be removed from the finished polymer by treatment with dilute mineral acid.

Ramsden in 1903 was the first to report the emulsification of liquids by means of fine insoluble powders.[1] Because of the extensive early work of Pickering, emulsions of this type have frequently borne his name.[2] In 1923, Finkle and co-workers stated that the powder must collect at the interface in order to be effective.[3] They postulated that this would occur only when the solid is wet by both liquids with a finite angle of contact of the interface with the solid. The external phase will be the one which more readily wets the powdered solid.

In 1927, Scarlett and co-workers published results of a morphological study of Pickering emulsions.[4] Their photomicrographs clearly showed the presence of the finely divided solid on the surface of the emulsified droplets.

Röhm and Trommsdorff first used powdered solids (barium sulfate, talc, and aluminum hydroxide) in the suspension polymerization of hydrocarbons.[5] Hohenstein is credited with the development of the first polystyrene process utilizing tricalcium phosphate.[6] This made it possible in principle to prepare clear and colorless crystal polystyrene by a suspension process. Commercial feasibility was limited by the preferred low bead-to-water ratio (1:10).

Grim was the first to use tricalcium phosphate modified by a surface-active extender, i.e., an anionic amphipathic compound.[7] Grim's invention made commercial manufacture of crystal polystyrene by suspension polymerization a reliable, economic, and practical process.

THEORY OF EXTENDER ACTION

Tricalcium phosphate (TCP) is precipitated as acicular crystals of submicronic dimensions ($0.10 \times 0.05 \times 0.015$ μ).[8] Its hydration shell may range in thickness from 3 to 95 Å, dependent upon the method of measurement, and the weight of bound water correspondingly varies from about

20 to 800 mg/g. Since precipitated hydroxyl apatite crystals are uniquely small, the interfacial area (specific surface 50–100 m²/g) is uniquely important in determining the chemical properties of this mineral.

In many cases, the surface of precipitated hydroxyl apatite crystals contains adsorbed phosphate ions, the presence of which can be detected by comparison of x-ray diffraction patterns before and after ignition.[9] Whether or not adsorbed phosphate ion is present, the surface of the hydroxyl apatite crystal is predominantly electropositive. As a result, anionic surfactants are readily adsorbed by the hydroxyl apatite particles in a "head on" orientation. The shielding of the hydrophilic, electropositive surface by adsorbed long-chain hydrocarbons has the following simultaneous effects: (1) reduced agglomeration of hydroxyl apatite particles[7]; (2) reduced electropositive character of the surface; and (3) alteration of the contact angles at the liquid—solid interface.[10,11] As a result, there is increased attraction of the hydroxyl apatite particles to the oil–water interface.

It is, of course, possible that second-layer adsorption of anionic surfactant can occur after monolayer adsorption is complete. Surface-active anions in the second layers attach themselves in the reverse orientation; the hydrocarbon chains penetrate the palisade layer of the monofilm and present their ionic heads to the external aqueous phase. At this point, the adsorption-modified particles of hydroxyl apatite become increasingly hydrophilic once more and their affinity for an oil–water interface diminishes. In principle, the course of this adsorptive modification of the crystal surface can be followed by contact angle measurements. Hildebrand and co-workers are credited with first making the observation that contact angle measurements should enable one "to predict whether or not a given solid powder can stabilize an emulsion and also which liquid will become the dispersed phase."[3] Schulman and Leja later showed the correlation between the contact angles developed on the solid surface of barium sulfate crystals at the solid–water–oil interface as a result of surfactant adsorption and the stability and phase continuity of insoluble powder-stabilized oil–water emulsions.[10]

Wenning later extended this concept to the study of styrene–water emulsions and to styrene suspension polymerization.[11–13] He called these disperse systems which are stabilized by "solid emulsifiers" three-phase emulsions, to distinguish them from the ordinary two-phase emulsions, which are stabilized by soluble hydrocolloids.[14] It is the modification of the powder surface by adsorption of surface-active anions which was termed "extension" by Grim in his description of the first practical application of extender action to the suspension polymerization of ethylenic monomers.[7]

The work of Schulman and Wenning makes it understandable why Grim's concentration ranges on the anionic extender are small, finite, and all-important. Grim's preferred usage of hydroxyl apatite powders of submicronic particle size is a verification of the fact that the greater the interfacial coverage achieved by a given amount of powder, the smaller

is its average particle size.[15]   His extender principle states that greatest
suspension stability results from the use of submicronic powders which,
by virtue of surface modification, are deflocculated and driven to the oil-
water interface.[7]

The theory of extender action by anionic surfactants is considered to be
well established.   Initially surprising and thus not immediately explainable
was the discovery of Hohenstein that potassium persulfate in small amounts
(<100 ppm) was effective as a replacement for anionic surfactant as an
extender for hydroxyl apatite in the suspension polymerization of styrene.[16]
It is toward the elucidation of the mechanism of persulfate extender action
that this investigation is addressed.   Much of what follows is based upon
two well-established principles: (1) Styrene polymerization by free-radical
mechanisms terminates predominantly by combination, giving unbranched
chains.[17−24]   (2) Initiation of styrene polymerization by potassium per-
sulfate results in the placement of sulfate groups at the ends of the poly-
styrene chains.[25−31]

EXPERIMENTAL

Styrene was Sinclair-Koppers Company commercial grade containing
10–15 ppm *tert*-butylcatechol as inhibitor.   Monomer was not further
refined before use.   Potassium persulfate, benzoyl peroxide, and *tert*-
butyl perbenzoate were commercial materials used as received.   Dithio-
diglycol (DTDG) was purchased from Thiokol Chemical Company on
special order.

Tricalcium phosphate (TCP) was a commercial grade purchased from
the Monsanto Company.   Figure 1 reveals the asymmetry of the par-
ticles.   The specific surface, by BET technique, was 80 m^2/g.   X-Ray
diffraction analysis gave crystalline reflections characteristic of the com-
pound hydroxyl apatite.   Only trace amounts of adsorbed phosphate
ions were detected.   The ratio (calcium equivalents per phosphate group)
for a typical sample was found to be 3.28 by x-ray fluorescence and 3.30
by chemical analysis.   Water loss on ignition at 900°C was 6.59%.

The polystyrene bead preparations were made in 12-oz citrate bottles
which were agitated end over end about a transverse axis through their
centers in a heated oil bath.   In most cases, the following standard recipe
was employed: styrene, 100 ml.; water, 100 ml; TCP, 1.0 g; benzoyl
peroxide, 0.20 g; *tert*-butyl perbenzoate, 0.05 g; extender, variable;
time/temperature cycle, 7 hr at 90°C; 3 hr at 115°C.

Surface and interfacial tensions were measured with a duNuoy tensiom-
eter using standard techniques.   No ring corrections were applied.

RESULTS

Preparation of Sulfated Polystyrene

A number of experiments were conducted to demonstrate qualitatively
that persulfate initiation of styrene polymerization in the aqueous phase
results in sulfation of the resulting polymer.   In one instance, 200 ml water

Fig. 1. Electron photomicrograph of tricalcium phosphate.

containing varying amounts of dissolved persulfate ranging from 1.0 to 0.01 g was placed in bottles and 10 ml styrene was carefully layered on top.   Following a nitrogen purge, the capped bottles were placed in a 60°C oven without agitation.   Within 2 hr, a turbidity in the water phase was observed for the more concentrated persulfate systems.   All samples developed turbidity within 24 hr.   The presence of organic sulfate was confirmed by a qualitative methylene blue test.[32]   The aqueous surface tension was depressed in the more concentrated persulfate cases by as much as 20–30 dynes/cm.   When a water-soluble polymerization inhibitor, dithiodiglycol, was present at 0.5% aqueous concentration with persulfate,

or when persulfate was omitted, no turbidity developed and the methylene blue test was negative.

Similar experiments were performed in which the reactants were agitated for 5 hr at 90°C. Readily observable and analytically detectable amounts of polymer were produced in the water phase at aqueous persulfate concentrations as low as 0.005%. At higher persulfate concentrations (0.25% and 0.50%), the sytrene conversions to polymer were quantitative. At 5 and 0.05 ppm persulfate, no polymer solids could be seen or detected by determination of nonvolatile content. Polystyrene was positively identified in the aqueous phase in these cases by infrared techniques. Organic sulfur could not be confirmed because of interference from reaction by-products. At persulfate levels of 0.5% to 0.005%, polymer spheres of colloidal size (1000–6000 Å) were identified by electron microscopy. The anionic character of these polymer particles was confirmed by electrodeposition.

Polymers produced thermally and by persulfate initiation have been clearly distinguished from each other by other means. Thermal polymer produced in the monomer layer in the absence of persulfate dries to a clear glassy film, whereas colloidal polymer produced by persulfate initiation in the aqueous phase dries to a white, opaque crazed film owing to limited coalescence of the hard particles. Thermal polymer tests negatively with methylene blue because of the absence of ionic species.

Bench-scale quantities of sulfated polystyrene were prepared by agitating 1600 g of 10% aqueous potassium persulfate solution with 160 ml styrene at reflux temperature at 1 hr. After 15 min, turbidity developed in the water phase. Turbidity increased with time, and after 30–45 min the product precipitated completely. Absence of monomer odor indicated a high degree of monomer conversion.

The number-average molecular weight (by osmotic pressure determination) of the reprecipitated polymer was 2200, and the sulfate content was 0.1360%.[32] Based upon these data, it was calculated that 3% of the polymer chains were sulfated on one end.

The mother liquor from this experiment was acidic (pH 1) and surface active (surface tension 37.5 dynes/cm). Infrared spectra of the precipitated water-soluble solids revealed the presence of polystyrene, but organic sulfate could not be confirmed due to the presence of inorganic sulfur compounds. Methylene blue tests gave positive results on mother liquor and on solids recovered therefrom. Surface activity of the mother liquor was also indicated by its ability to solubilize in water an oil-soluble dye.

The experiment was repeated, and, because of the acidity and the proneness of sulfate esters to hydrolyze, samples of the reaction mixture were withdrawn at several intervals during the run. As the results in Table I indicate, there was a buildup of organic sulfate content to a maximum, followed by a decay. Undoubtedly, acid-catalyzed hydrolysis was occurring throughout the heating period because the maximum sulfation calculated was only 10%. Additional experiments of this type confirmed

TABLE I
Preparation of Sulfated Polystyrene[a]

Sample no.	Sampling time, min	Polymer characteristics		
		M_n	Sulfate content, ppm	Chains sulfate, %
Unbuffered				
34a	10	4200	800	3.5
34b	20	—	1200	5.3[b]
34c	30	2700	2500	7.0
34d	40	2500	4000	10.4
34e	60	4000	1100	4.6
Alkaline medium				
59–1	30	6370	1500	10.0
59–2	40	5800	1750	10.6
59–3	50	6220	1730	11.2
59–4	60	6390	1630	10.8

[a] Recipe: water, 1600 ml; styrene, 160 ml; $K_2S_2O_8$, 160 g. The mixture was heated for 1 hr at reflux.
[b] Assumed M_n 4200.

these results. Polymers with M_n ranging from 2100 to 5000 were obtained for which degrees of sulfation ranging from 1% to 10% were calculated. Maximum sulfation always occurred after about 40 min of reaction time. Acid-catalyzed hydrolysis was further confirmed by conducting the experiment at pH > 7.0 with ammonia additions. The results are also shown in Table I.

More dilute persulfate solutions produced higher molecular weight polymers. Some of these results are summarized in Table II. Samples 6-1 and 6-2 were prepared by techniques which closely follow those of Matsumoto and Ochi[31] (see ref. 31, Table 5, example 14), except that their reaction time was 28.5 hr. Their molecular weight (derived from viscosity measurements) was about 300,000. They calculated a degree of sulfation which is about ten times our value. Calculation of intrinsic viscosity for Matsumoto's and Ochi's polymer, using their data and their viscosity/molecular weight function, gives the value 0.92 dl/g, just twice the value we measure on our polymers. Reasons for these discordant results are not apparent. In any case, it is clear from Table II that hydrolytic loss of organic sulfate groups persists in the more dilute persulfate systems.

Sulfated polystyrene was prepared at still greater persulfate dilutions (100 ppm on the water phase) by heating the aqueous solution at reflux for 4 hr with $1/_{50}$ its weight of styrene. The system pH was maintained above 7.0 with ammonia. The final aqueous solids content indicated a styrene conversion of 91%. The stable colloidal dispersion was agglomerated by freezing, after which the solid product was separated by filtration and dried. The serum contained water-soluble polymer, as was indicated by the solids content (0.019%) and by a determination of organic sulfate (1.9 ppm).

TABLE II
Preparation of Sulfated Polystyrene

Sample no.	Recipe			Reaction temp., °C	Reaction time, hr	Product characteristics			
	Water	Styrene	$K_2S_2O_8$			Intrinsic viscosity, dl/g	M_n	Sulfate content, ppm	Chains sulfated, %
6-1	180 g	20 g	1 g	70	2	0.45	42,500	167	7.4
6-2	180 g	20 g	1 g	70	19	0.46	45,100	48	2.3
55-4	100 ml	10 ml	0.5 g	90	5	0.16	<16,000	194	<3.2
55-8	100 ml	10 ml	0.25 g	90	5	0.30	28,000	108	3.2

The characteristics of the solid product are summarized in Table III. Some variation in molecular weight is indicated; however, the calculated chain sulfation is constant at about 200%. This result is interpreted to mean that, on the average, each polystyrene chain is terminated on each end by a sulfate group. One experiment at lesser persulfate dilution (50 ppm) produced about the same molecular weight product, but the sulfation was reduced to 1.3 per chain.

TABLE III
Characteristics of Polystyrene Sulfates
Prepared in Very Dilute (100 ppm) Persulfate Solution

Sample	$[\eta]^a$, dl/g	M_n	SO$_4$ content, ppm	Chains sulfated, %
58	0.48	77,500	2600	210
70	0.68	109,700	1800	206
71	0.58	95,500	2200	219
81[b]	—	96,300	1300	131

[a] Toluene solvent at 30°C.
[b] Persulfate concentration 50 ppm.

Evaluation of Sulfated Polystyrenes as TCP Extenders

Centrifugal separation of solids from the dilute persulfate-initiated latices (200 ml water, 20 ml styrene, 0.5 g potassium persulfate reacted for 5 hr at 90°C) permitted independent evaluation of polymer solids and serum as TCP extenders in the standard bead recipe. When used in approximately equal amounts with TCP, whole latex and latex solids each were active TCP extenders, as evidenced by the formation of polymer beads. Gross coagulation of the polymer phase resulted when either latex serum or no anionic additive was introduced. The centrifuged polymer used in these tests contained 108 ppm sulfur and had a number-average molecular weight of 28,000 and a toluene intrinsic viscosity of 0.30 dl/g.

Highly sulfated polystyrene (sample 58, Table III) was tested as a TCP extender over a range of concentrations. At a level of 0.001 g in the standard bead recipe, the suspension failed. At levels ranging from 0.005 to 2.0 g, stable bead systems resulted. Although this work revealed no upper limit of operability using PSS-58, the trend of the bead size distributions in Table IV may be an indication that somewhat higher levels of extender would cause suspension failure. Comparison of these data with results derived from the use of more conventional extenders reveals a comparable degree of bead size control.

Many sulfated polystyrenes were so tested. Without exception, all had extender activity at levels which were dependent upon the molecular weight of the extender polymer and its sulfate content. Even the water-soluble species recovered from the sera of the preparative experiments exhibited activity as TCP extenders, indicating that extender activity is independent of molecular weight over a broad range.

TABLE IV

The Use of High Molecular Weight Polystyrene Sulfate as a TCP Extender.   Screen Analyses of Products[a]

Screen size	PSS-58 used in standard recipe						Conventional extenders used in standard recipe[b]					
	0.005 g	0.010 g	0.050 g	0.10 g	1.0 g	2.0 g	A	B	C	D	E	F
+10	94	0.1	—	—	—	—	32.0	—	3.0	1.0	—	—
+20	6	74.3	2.0	9.0	3.6	4.3	66.3	1.0	58.0	6.8	7.5	—
+30	—	22.0	6.0	1.9	4.3	10.4	1.9	1.0	23.0	23.3	20.5	4.4
+40	—	34.3	65.4	12.7	15.0	33.0	—	23.5	14.0	46.6	37.0	57.8
+50	—	0.2	20.0	42.7	21.0	18.7	—	24.5	1.0	13.6	14.5	15.3
+60	—	0.1	5.1	22.3	27.0	18.0	—	19.6	0.5	5.8	10.0	8.7
−60	—	—	1.7	11.5	28.6	15.0	—	30.4	0.5	2.9	11.0	14.0

[a] Values in columns given in wt-%.

[b] A = 0.016 g Calcium oleate; B = 0.032 g calcium oleate; C = 0.024 g sodium oleate (120/80 styrene/water); D = 0.032 g sodium oleate (120/80 styrene/water); E = 0.005 g sodium dodecylbenzene sulfonate; F = 0.005 g potassium persulfate.

This point was further verified by separating one polystyrene sulfate (PSS) sample (M_n 4700; sulfate content 1230 ppm; sulfation 6%) into nine molecular weight fractions. The sulfate content of the fractions varied from 79 ppm for the highest molecular weight fraction to >12,000 ppm for the lowest. All produced stable bead suspensions in the standard recipe at the 0.05-g level. The water-soluble anionic polymer from the serum of this same preparation was separated by precipitation methods into six fractions. Each of these, at 0.05 g, produced beads in the standard recipe.

Sulfated polystyrenes prepared in concentrated persulfate systems contained 10% or less sulfated species. These, too, at appropriate levels were suitable extenders. The operable limits for extender activity were not accurately defined in any of these cases, yet extender activity was observed over several decades of PSS concentration (e.g., <0.05 g to >5.0 g). Assuming that unsulfated species are inactive as TCP extenders, this means that the anionic species are active at very low levels (e.g., <0.0005 g in some cases).

The activity as an extender of unsulfated polystyrene was verified by testing a low molecular weight (thermal) polystyrene (M_n 2100) and a high molecular weight polystyrene from a conventional bead process (M_n ca. 120,000). When tested at varying levels up to amounts equal to the TCP level employed in the standard recipe, neither species produced stable bead suspensions.

Adsorption of Sulfated Polystyrene by TCP

Water (1000 ml), TCP (10 g), styrene (10 ml) and potassium persulfate (0.10 g) were agitated at 94°C for 3 hr. The treated TCP was removed by filtration and dried at 100°C to constant weight along with an untreated TCP sample. The dried samples were then ignited to constant weight at 500°C. The loss in weight of the treated sample, after applying the blank correction, indicated that 22.6% of polymer solids had adsorbed on the TCP surface.

Many experiments of this type were performed. Variations included (a) persulfate concentration and (b) sorption of preformed PSS by TCP. The results, always positive and always carrying a blank correction, varied from 1% to 25%, depending upon the experimental conditions.

Each of the surface-modified TCP samples was subsequently tested in the bead recipe and found to produce stable suspensions without the use of additional extender.

As a further demonstration that TCP treated with in situ or externally synthesized PSS presents a modified surface to its environment, 1-g quantities were agitated in a blender with 100 g each of water and styrene. The resulting emulsions were immediately poured into a graduate and allowed to equilibrate at room temperature. Results varied somewhat, depending on the treatment; typical data are presented in Table V.

TABLE V
Emulsification by Surface-Treated TCP

Phase volume, ml			
Settled TCP	Water	Emulsion	Styrene
Untreated TCP			
12	88	14	86
12	76	14	96
6	90	10	94
9	89	8	94
6	89	13	92
Treated TCP			
0	6	105	89
0	74	112	14
0	0	113	87
0	60	130	10
0	60	108	32

TCP was preconditioned by heating 100 ml water, 1 g styrene, and 1 g TCP with 0.005–0.02 g potassium persulfate in bottles at 90°C for 4 hr, after which the remaining ingredients of the standard recipe were introduced and the usual heating cycle applied. Under these conditions, stable bead slurries were produced. When styrene was omitted during the preconditioning period, the suspensions failed.

Inhibition of the Aqueous Phase Reaction

After having determined that 0.5% aqueous dithiodiglycol contentration is sufficient to prevent styrene polymerization in the aqueous phase when 0.005 to 0.05 g potassium persulfate is present, the standard bead recipe was run with the variations and results shown in Table VI. It will be observed that when either sodium dodecylbenzene sulfonate (SDBS) or

TABLE VI
Bead Tests in the Presence of Water-Soluble Inhibitor
(Standard Bead Recipe)

Sample no.	Extender		Amt. DTDG,[a] g	Result
	Type	Amt. g		
46-A	SDBS[b]	0.005	none	beads
46-B	$K_2S_2O_8$	0.005	none	beads
46-D	SDBS	0.005	1.0	beads
46-E	$K_2S_2O_8$	0.005	1.0	lump
37-J	PSS[c]	0.02	1.0	beads
37-K	PSS	0.05	1.0	beads
42-1	PSS	0.05	none	beads
54-11	PSS	0.10	1.0	beads
54-9	PSS	0.10	none	beads

[a] DTDG = Dithiodigycol.
[b] SDBS = Sodium dodecylbenzene sulfonate.
[c] PSS = Polystyrene sulfate.

polystyrene sulfate is charged to the standard recipe in the presence of the water-soluble polymerization inhibitor, dithiodiglycol, a stable bead dispersion results. Only when potassium persulfate is used with DTDG does coagulation follow.

Surface-Active Properties of Sulfated Polystyrene

Water-soluble species of sulfated polystyrene exhibit typical properties of a water-soluble surfactant. Reference has already been made to the lowering of aqueous surface tension which was observed for the aqueous filtrate that was recovered from a bench-scale preparation of PSS. Organic sulfate and polymeric styrene were detected in these filtrates by methylene blue tests and infrared scans, respectively. Surface tension depressions varying from 4 to 28 dynes/cm were measured on the aqueous subnatant layer resulting from quiescent heating of styrene layered over persulfate solutions. As Figure 2 shows, the surface tension depression increases with the concentration of persulfate initiator, presumably because of an increase in the amount of sulfated polystyrene present.

Dilute polystyrene sulfate latices were prepared by heating a 0.5% solution of potassium persulfate with $1/_{10}$ its volume of styrene at 90°C for 5 hr. The surface tension of the filtered aqueous phase was 45.5 dynes/cm. This liquid readily foamed when sparged with nitrogen. The collapsed foam exhibited about the same surface tension as the initial fluid.

As mentioned previously, water-soluble PSS solubilizes an oil-soluble dye in water, indicating again its surface activity.

High molecular weight PSS $(M_n$ 77,500), when dissolved in styrene, (0.02 wt-%) depresses the styrene–water interfacial tension 10 dynes/cm. For comparison, a 0.005 wt-% aqueous solution of SDBS, when layered
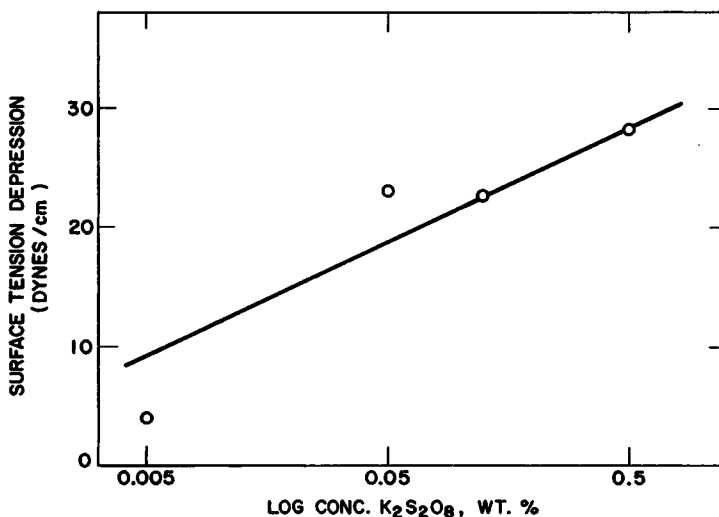

Fig. 2. Surface tension depression by sulfated polystyrene.

under an equal volume of styrene, depressed the interfacial tension 24 dynes/cm.

No attempt was made to determine the molecular weight range in which polystyrene sulfate solubility becomes greater in styrene than in water. This would probably be around M_n 2000 for a doubly sulfated polystyrene chain.

Operable $K_2S_2O_8$/TCP Ratios

While no attempt was made to determine the exact stoichiometry involved in achieving stable bead suspensions using persulfate as the TCP extender, some useful inferences can be gained from the following experiment. Using the standard bead recipe, containing in this case 1.25 g TCP, amounts of persulfate equal to 0.0001 and 0.0005 g were insufficient to produce stable polystyrene suspensions while ten times these amounts produced beads. In the same recipe using 0.21 g TCP, 0.0001 and 0.0005 g $K_2S_2O_8$ produced a stable suspension.

Mixed Extender Systems

Many types of anionic surfactants may be employed as extenders in the TCP stabilized suspension polymerization of styrene.[7] In order to gain further insights on the mechanism of persulfate extension, a series of suspension polymerizations was conducted in which anionic surfactant and potassium persulfate were used simultaneously in varying amounts. The

TABLE VII
Mixed Extender Systems (Standard Bead Recipe)

| | Extender, g | | |
Sample no.	SDBS g	$K_2S_2O_8$ g	Result
97–6	0.00010	—	lump
97–4	0.00025	—	lump
97–3	0.00050	—	beads
97–2	0.0010	—	beads
97–1	0.0050	—	beads
4–16	—	0.000005	lump
4–12	—	0.000010	lump
4–5	—	0.000025	beads
4–1	—	0.000050	beads
81–7	—	0.00050	beads
4–17	0.00010	0.000005	lump
4–19	0.00025	0.000005	lump
4–13	0.00010	0.000010	lump
4–14	0.00020	0.000010	beads
4–15	0.00025	0.000010	beads
4–7	0.00010	0.000025	beads
4–8	0.00015	0.000025	beads
4–9	0.00020	0.000025	beads
4–10	0.00025	0.000025	beads
4–2	0.00010	0.000050	beads
4–3	0.00020	0.000050	beads

results, summarized in Table VII, indicate that persulfate and anionic surfactant can be used in combination with favorable results. A more detailed study involving bead size distributions would be required to determine if the effects are additive or synergistic. It appears from this survey that no synergism is involved; stable suspensions are achieved when adequate amounts of adsorbable anionic species are available, irrespective of type. This same conclusion follows from a similar study in which two types of conventional anionic extender were charged simultaneously in varying amounts.

Detection of Sulfated Organic Species in Persulfate-Extended Polystyrene Bead Slurries

Polystyrene beads were recovered from suspension polymerization systems in which potassium persulfate (or SDBS) was used as the TCP extender. These bead slurries were acidified to pH 1.8 with hydrochloric acid to dissolve the TCP, after which the beads were filtered off and washed ten times with distilled water to remove chlorides and phosphates. Small quantities of the dried beads were dissolved in chloroform and tested with methylene blue. Positive tests were obtained in each case.

The presence of organic sulfate in the aqueous phase was demonstrated by heating 1000 ml of 0.01% potassium persulfate solution with 10 ml styrene and 10 g TCP at 94°C for 3 hr. The clear serum was isolated by filtration and concentrated to 10 ml. One milliliter of the concentrate produced a stable suspension when used as the extender in the standard bead recipe. The presence of organic sulfate was also confirmed by a methylene blue test.

In another experiment, 1 ml concentrated aqueous serum from the standard recipe containing persulfate as extender, but no soil-soluble initiators, was used as the extender in a subsequent bead test based on the standard recipe. Good-quality polystyrene beads were produced.

It was also demonstrated that TCP from a persulfate-extended suspension polymerization of styrene could be recovered and reused in a subsequent suspension polymerization without added extender. Raw bead slurry was recovered from a large-scale reactor run which had been conducted by the persulfate process.[16] The slurry was filtered through cheese cloth to isolate the polymer beads. The filtrate was filtered through a fine screen to separate the TCP which was mixed with polymer fines. No additional water was introduced in order to avoid desorption of the extender from the TCP powder. The filtrate was refiltered several times, however, to achieve maximum retention of solids.

To determine the amount of TCP contained in the filter cake, a portion was dried at 100°C, then treated with hydrochloric acid to dissolve the TCP. This residue was then washed and dried, and the amount of TCP it initially contained was calculated by difference. As a check, a portion of the original TCP filter cake was extracted with methyl ethyl ketone, a solvent for polystyrene. Good checks on the composition of the recovered

powder were obtained by the two methods. The results were: TCP, 13%; water, 40%; polymer fines, 47%.
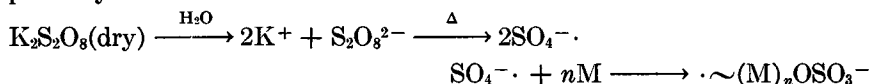
Two grams of the damp filter cake (containing but 0.26 g TCP, dry basis) was charged to the standard bead recipe without additional TCP or extender. Duplicate runs each produced beads, whereas control runs containing up to 2 g (dry basis) untreated TCP without added extender resulted in coagulation of the suspension. These results were independently confirmed several times.

Similarly, a bead slurry from a suspension polymerization extended by SDBS was so treated to recover the TCP for reuse. Again, beads were produced when the recovered TCP was used in the suspension polymerization of styrene. In this case, however, it was necessary to use sufficient wet filter cake to provide at least 1 g TCP (dry basis) in order to preserve suspension stability when using recovered suspending agent.

It was also proved that polymer fines are not themselves either primary stabilizers for styrene bead polymerization or TCP extenders. Only coagulated suspensions were produced when fines were used with or without TCP even in amounts substantially greater than those resulting from the use of the recovered TCP-fines mixtures as described above.

DISCUSSION

The initiating action of potassium persulfate in free-radical polymerization is viewed as deriving from the attack on monomer (M) in the aqueous phase by sulfate ion radicals:

$$K_2S_2O_8(\text{dry}) \xrightarrow{\ H_2O\ } 2K^+ + S_2O_8{}^{2-} \xrightarrow{\ \Delta\ } 2SO_4{}^-\cdot$$

$$SO_4{}^-\cdot + nM \longrightarrow \cdot{\sim}(M)_n OSO_3{}^-$$

The growing chain thus contains a sulfate ester ion as a terminal group. Termination of the growing chain by another active chain or by a sulfate ion radical produces a dead polymer chain that contains terminal sulfate groups on each end.

Hydroxyl-terminated polystyrene can occur in this system by (a) hydrolysis of the sulfate ester or by (b) initiation and/or termination of styrene polymerization by hydroxyl free radicals generated by the hydrolysis of sulfate ion radicals. According to Bartlett, there is no direct reaction between hydroxyl radicals and sulfate ion radicals.[33]

Early efforts to prepare PSS by reacting styrene with 10% aqueous persulfate solutions resulted in low degrees of sulfation. The decline in organic sulfate content with extended reaction time in the unbuffered case (see Table I) is attributed to hydrolysis of the polymeric sulfate ester. When pH was maintained above 7, there was little dependence of polymer sulfate content upon reaction time, but the extent of sulfation still hovered about 10%. Evidently, a considerable amount of sulfate ion-radical hydrolysis persists under these conditions and produces hydroxyl free radicals

$$SO_4{}^-\cdot + H_2O \longrightarrow HSO_4{}^- + OH\cdot.$$
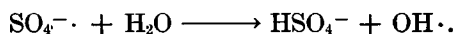
This is inferred by the fact that no other source of initiating free radicals is present, and the hydrolytic stability of PSS in neutral or alkaline media was demonstrated by extended heating of PSS solutions at temperatures as high as 150°C. Only at very high levels will hydroxyl-terminated polystyrene favorably influence polystyrene bead stability when used as a TCP extender. This has been proved using either hydrogen peroxide itself or a polystyrene made by hydrogen peroxide initiation as the sole extender additive to the standard bead recipe.

As expected, the molecular weight of the product PSS increases as the concentration of persulfate is reduced. Simultaneously, the degree of polymer sulfation increases because of reduced hydrolysis of the sulfate ion radicals and of polymeric sulfate ester. Quantitative sulfation in dilute (100 ppm) persulfate systems was achieved by maintaining pH > 7. In the TCP-stabilized suspension system, pH is maintained >6 by the buffering action of the sparingly soluble suspending agent.[7] This has been confirmed experimentally in this study.

It is apparent that potassium persulfate readily effects the polymerization of styrene in the absence of added surfactant by attack of the small amount of styrene dissolved in the water phase (620 ppm at 80°C) by sulfate ion radicals. The chain propagates by adding more styrene units as dissolved monomer is encountered and attacked. When the chain grows to a size sufficient that water solubility is exceeded, the polymer curls up on itself so as to expose the minimum hydrocarbon surface to the surrounding aqueous medium. The polar sulfate ion on the initiating end of the chain orients toward the water phase, thus conferring a measure of colloidal stability to the "particle" by hydration and by coulombic repulsion of its neighbors. Particle stability is very low at this point because there are very few chains per particle. As a result, the particle grows by means of two simultaneously occurring processes: (a) continued addition of styrene units to the growing chain(s) and (b) agglomeration with other embryonic particles. Due to the plasticity conferred to the particles by the solubilized monomer within, interparticle collisions are irreversible and coalescence to spheres is rapid. The incipient particle thus behaves like a soap micelle initially in that it is the locus of particle initiation and it solubilizes monomer.

By the described growth mechanism, a particle adds stabilizing sulfate ions to its surface at a faster rate than that of surface increase. This self-regulating agglomeration and particle growth proceeds in an orderly fashion to produce a colloidally stable dispersion. Large particles are more stable than small particles because the sulfate ion population is limited by the number of attached chains per particle, and only the larger particles provide the opportunity to increase the surface density of stabilizing ionic groups. Stable, higher-solids emulsifier-free latices which are generated in this way are possible only with more water-soluble monomers like vinyl acetate and acrylonitrile[30] and by using higher persulfate concentrations.[34] High solubility of the monomer in water favors more prolific particle initia-

tion; high initiator levels favor lower polymer molecular weights and higher particle surface charge density.

Negatively charged polystyrene latex particles of the type described can adsorb onto TCP particles because of the electropositive nature of the latter. TCP particles so modified are attracted to the bulk styrene–water interface to an increased degree. As a result, polystyrene bead stability is enhanced. That most of the sulfate-terminated polystyrene is swept up into the latex particles is indicated by the fact that centrifuged latex serum was ineffective as a TCP extender, at least in the amounts used. That not all the PSS is incorporated in the latex particles is testified by the reduced surface tensions measured in many of these soap-free latices.

These antecedents make it possible to present the following rational explanation of the mechanism by which potassium persulfate provides extender action in a TCP-stabilized suspension polymerization of styrene. During initial heatup of the reactants to polymerization temperature, which usually requires 30–90 min, persulfate decomposition and aqueous-phase polymerization of styrene occur. Because of the presence of TCP in the system, PSS becomes adsorbed on the TCP surface very rapidly, and "latex particles" do not have the opportunity to form. Generation of PSS probably occurs as soon as the reaction temperature approximates 50°C, whereas styrene bead polymerization does not begin until higher temperatures are attained. Thus, adsorptive conditioning of the TCP is well underway, if not complete, by the time any significant amount of peroxide-initiated polymerization takes place within the monomer droplets of the suspension. While this sequence probably applies to large-scale reactor runs, it is not limiting because persulfate extension is equally successful in small bottle-scale experiments where temperature equilibrium is much more rapid. In any case, the persulfate-initiated reaction becomes quite rapid at 90°C, as indicated by the 43-min half-life of potassium persulfate, and is completed within 3–4 hr.[35]

A dependence of the susceptibility of TCP to surface modification by PSS on the molecular weight of PSS was not expected and, in fact, was not found. Both water-soluble PSS species (M_n <2000) and water-insoluble species (M_n 100,000) were found to be active TCP extenders. Adsorption of anionic materials on the TCP surface is depicted as occurring head-on, with the polar group next to the TCP surface.[10] It therefore seems possible and probable that PSS may adsorb even before the growing chain has been termined by reaction with another radical. Moreover, termination of the active PSS chain after adsorption is not precluded since free radicals exist in the water phase and oil phase as well. The type of terminating species will therefore be determined by the environment. Since adsorption of PSS by TCP renders that surface more lipophilic than before and thus modifies the wetting characteristics of the suspending agent sufficiently to increase its affinity for the styrene–water interface, PSS termination could occur after TCP has been adsorbed on the bead surface. If this should occur, TCP adsorption to the bead becomes even more tenacious by virtue of surface "grafting."

Low molecular weight PSS should pack more closely on the TCP surface as a result of reduced steric hindrance, as compared with longer-chain PSS. Thus, the limiting adsorption area for low molecular weight PSS may approach that of a conventional anionic surfactant. A given weight of short-chain PSS contains more molecules than does the same weight of long-chain species. On the other hand, long-chain PSS should be more effective as a surface modifier, chain for chain, since a lower adsorption density of long chains will create a lipophilic atmosphere around TCP particles which is probably just as effective for surface modification as a tighter packing of shorter chains. Adsorbed long chains on the water phase side of the TCP particle will curl up on the particle surface because of their water insolubility. This action results in the shielding of certain otherwise available adsorption sites. Long chains adsorbed on the oil phase side of the TCP crystal at the oil–water interface will be more extended and kinetically will occupy a greater volume element than will shorter chains. In any event, the results are exactly the same: longer chains find fewer TCP adsorption sites than short chains, but fewer are required in order to achieve a given degree of surface modification. Thus the system should be self-regulating with respect to the molecular weight of the adsorbate, and the experimental results bear this out.

The capacity of the suspension system to tolerate large amounts of PSS extender does appear to have a dependence upon molecular weight, however. Early experiments aimed at finding the upper limit of tolerance for PSS as an extender in the standard bead recipe revealed that suspension failure occurred when 5 g or more PSS was used per 1 g TCP. At 2 g PSS/g TCP, stable suspensions were produced. The PSS sample used in this series had the following characteristics: M_n 2200, 3.1% of the chains. sulfated. Final pH of the reaction medium in the case of the failures due to high PSS content was about 4. Since TCP-stabilized suspensions become unstable for other reasons below pH 5.5–6.0, failures in these cases were attributed to the low pH which, in turn, must have resulted from acidic components carried into the system by the high levels of PSS.

Later attempts to find the limits of PSS tolerance employed a higher molecular weight extender (M_n 77,500, 210% of the chains sulfated). A minimum of 0.005 g PSS/g TCP was required to produce beads, while 2 g PSS/g TCP (the maximum level tested) did not destabilize the suspension. In the latter case, however, a reversal in the maximum bead size of the product toward larger beads possibly was an indication that an unstable condition was being approached (Table IV).

On the other hand, there were many instances in which suspension failures occurred when water-soluble PSS species were used in amounts much less than 1 g PSS/g TCP. (Actual PSS levels are not known in these cases, since the PSS was not isolated and characterized). The best example of this behavior occurred when the water-soluble residue from the precipitation fractionation of a PSS (M_n 4700, sulfation 6%) was used in varying amounts as extender. Stable suspensions were produced at 0.005 g

PSS/g TCP and up to 0.20 g PS/g TCP.   At 0.4 g PSS/g TCP and higher, suspension failure occurred.

Operable limits for potassium persulfate as extender (precursor) were defined for the standard bead recipe.   These were 0.01 g and 0.000025 g, respectively, per 1 g TCP.   The fact that 1.5–2.0 g $KHSO_4$ per 1 g TCP is required to destabilize an otherwise operable persulfate-extended recipe is an indication that failure of persulfate at high levels to stabilize the suspension was not due to a salt effect.   That failure in these cases is due to the generation of intolerable levels of very low molecular weight PSS seems to be more consistent with the experimental results.   Excess amounts of PSS of molecular weight great enough to have appreciable solubility in the monomer (>2000–3000) are probably taken up by the monomer phase after the adsorptive capacity of the TCP has been satisfied.   On the other hand, excess amounts of water-soluble PSS species have no refuge except to engage in double-layer adsorption on the TCP.   This phenomenon is known to cause destabilization of the polymer suspension because it renders the TCP too hydrophilic for adsorption at the styrene–water interface.

It is therefore concluded that, while TCP is nonselective in its ability to adsorb PSS of high and low molecular weights, the tolerance of the system for long-chain anionic extender is greater because excess extender is taken up by the oil phase.   This conclusion is supported by the fact that anion-active species have been detected in the final beads of polystyrene as well as in aqueous serum.   Experiments using conventional anionic surfactant (SDBS) in conjunction with potassium persulfate indicate additivity of effects.   Again, excess oil-soluble PSS which may be generated in situ is taken up by the monomer phase, while excess SDBS causes destabilization by double-layer adsorption.   Each species present competes equally for adsorption sites on the TCP surface, consistent with the relative diffusion rates of the various species.

Doubly sulfated polystyrene presents no rational difficulty in this theory because the flexibility of the polystyrene chains permits the molecule to double back on itself and to occupy two adsorption sites on the TCP surface which are not necessarily adjacent.   Polystyrene disulfate molecules therefore supply two adsorption equivalents of extender.

Recovery of PSS-extended TCP from a bead polymerization followed by its reuse in a subsequent suspension polymerization without added extender attests at once to the hydrolytic stability of PSS in the TCP-buffered system and to the strength of the adsorption bonds.   The latter is also indicated by the fact that high molecular weight PSS, after adsorption on TCP from benzene solution, was not removed by three thorough benzene washes on a filter.   Adsorbed PSS was proved by determining the amount of adsorption by weight difference after ignition and by the fact that the treated TCP stabilized a styrene suspension polymerization without added extender being present.

Finally, the destabilization of persulfate-extended suspension polymer-

izations by the water-soluble inhibitor dithiodiglycol, and the lack of effect on suspensions which are extended by preformed anionic species (SDBS or PSS), would appear to offer additional confirmation of the mechanistic concepts presented.

It was expected that tertiary butylcatechol (TBC) contained in the styrene monomer might reduce the molecular weight of the PSS formed in the bead systems. This expectation was based on the following reasons: (a) water solubility of TBC (0.2% at 80°C), (b) chain transfer activity of TBC (C_s = 0.36 with styrene at 60°C)[36]; and (c) effectiveness of TBC as a chain terminator. TBC in the water phase should therefore reduce PSS molecular weight by chain transfer or by radical capture, especially since its aqueous concentration is significant compared with that of styrene. Extensive efforts to identify TBC-terminated polystyrene in the water phase by thin-layer and ion-exchange chromatography were unsuccessful.

CONCLUSIONS

The use of potassium persulfate as a TCP adjuvant in lieu of the more conventional anionic surfactants depends upon the in situ formation of polystyrene sulfate, which is the active extender species. If the formation of PSS is prevented by the presence of a water-soluble polymerization inhibitor, potassium persulfate is ineffective as a TCP modifier. Water-soluble inhibitor has no effect on suspension stability when conventional surfactant or preformed PSS is used as the extender.

Because excess oil-soluble PSS is taken up by the monomer phase, suspension stability is not sensitive to the amount of high molecular weight PSS present. On the other hand, excess water-soluble PSS destroys the suspension because the low molecular weight extender engages in double-layer adsorption on TCP which adversely affects the affinity of the surface-modified TCP for the monomer–water interface. With this exception, the molecular weight of PSS has little influence on the stability of TCP-stabilized suspensions of polystyrene.

Mono- and disulfate esters of polystyrene ranging in molecular weight from 2000 to 100,000 have been prepared, characterized, and successfully employed as TCP extenders. While these materials readily undergo acid-catalyzed hydrolysis, giving hydroxyl-terminated polystyrenes which are ineffective as extenders, PSS is quite resistant to hydrolysis at neutral pH's and above. pH control in the bead system is not a major consideration, since the aqueous phase is adequately buffered by the sparingly soluble TCP crystals.

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