WELL–CHARACTERIZED MONODISPERSE POLYSTYRENE LATEXES AS MODEL COLLOIDS

J. W. Vanderhoff

Emulsion Polymers Institute, Lehigh University, Bethlehem, Pennsylvania 18015

Abstract – Monodisperse polystyrene latexes prepared with persulfate initiator
furnish the basis for an ideal model colloid: the particles are stabilized
with a known number of chemically bound sulfate groups, which can be hydro-
lyzed to uncharged hydroxyl groups and oxidized to weak-acid carboxyl groups.

Introduction

    An ideal model colloid should comprise monodisperse spherical particles
stabilized with a known number of chemically bound surface groups. Mono-
disperse polystyrene latexes (1) are a good starting point for the prepara-
tion of such an ideal model colloid. Their particle size can be varied syste-
matically over a wide range, and their bound surface groups are the endgroups
of the polymer molecules, so that variation of polymer molecular weight and
latex particle size can give different surface charge densities. Moreover,
the preparation of these latexes using persulfate initiator gives sulfate
endgroups, which can be hydrolyzed to hydroxyl groups, which, in turn, can be
oxidized to carboxyl groups, to give particles stabilized with the same num-
ber of three different surface groups. The purpose of this paper is to de-
scribe the preparation and characterization of such model colloids, starting
with the emulsion polymerization of styrene using persulfate initiator.

    The preparation of a latex by emulsion polymerization comprises two
stages: (i) particle nucleation; (ii) particle growth. For the latex to
be monodisperse, the particle nucleation stage must be short relative to the
particle growth stage. Despite many investigations, there is disagreement as
to the locus of particle nucleation: (i) monomer-swollen emulsifier micelles;
(ii) adsorbed emulsifier layer; (iii) aqueous phase; (iv) monomer droplets.
Whatever the locus of particle nucleation, the decomposition of persulfate is
considered to produce sulfate ion-radicals in the aqueous phase. These ion-
radicals are repelled by the negatively charged surface of a monomer-swollen
emulsifier micelle, polymer particle or monomer droplet and therefore remain
in the aqueous phase and add hydrophobic monomer units to form an oligomeric
radical. When this oligomeric radical attains a critical chain length, it
becomes surface-active and adsorbs on the surface of a micelle, polymer par-
ticle, or monomer droplet. If it cannot adsorb on a suitable surface, it
continues to grow until it exceeds its solubility in water and therefore
precipitates to nucleate a latex particle. Initiation in micelles is signi-
ficant only in the beginning of the polymerization, and the monomer droplets
usually are not a significant locus of particle nucleation. Therefore, once
the particle nucleation stage is completed, the monomer-swollen polymer par-
ticles are the principal locus of polymerization. The adsorption of an oli-
gomeric sulfate radical to initiate a polymeric radical and the termination
of this polymeric radical by adsorption of another oligomeric sulfate radical
should give two surface sulfate groups for each polymer molecule formed
assuming that no transfer reactions occur to introduce a different endgroup,
that termination inside the particle occurs by combination rather than by
disproportionation, and that none of the sulfate endgroups become buried in-
side the particle.

    Polystyrene latexes have been prepared using persulfate initiator for
many years, but only recently have methods been developed to determine the
number and loci of the sulfate surface groups. To determine these surface
groups, the latex is cleaned to remove the adsorbed emulsifier and solute
electrolyte, then the surface sulfate groups in the H^+ form are titrated con-
ductometrically with base. The latexes can be cleaned effectively by ion ex-
change (2-5) or serum replacement (6); dialysis is not effective in removing
the adsorbed emulsifier and solute electrolyte (3,5,6).

In ion exchange, the aqueous phase ions are replaced with H^+ and OH^- ions. If the aqueous phase ions are in equilibrium with the adsorbed ions, their removal from the aqueous phase causes desorption of the adsorbed ions to maintain the equilibrium until all of the adsorbed ions have been removed. In practice, this removal is quantitative (2-5). Ion exchange is rapid and easily carried out; however, commercial ion exchange resins contain leachable polyelectrolytes which adsorb on latex particle surfaces; these polyelectrolytes can be removed only by an arduous purification process (2-5).

In serum replacement (6), the latex is confined in a cell with a semi-permeable membrane, e.g., Nuclepore filtration membrane, and water is pumped through the latex to literally replace the serum. The removal of adsorbed ions is quantitative provided the adsorption-desorption equilibrium is maintained. The Na^+ and K^+ ions are replaced by H^+ ions by pumping dilute hydrochloric acid through the latex followed by water to remove the excess acid. Serum replacement takes longer than ion exchange, but avoids the arduous resin purification step; moreover, the serum is recovered quantitatively in a form suitable for analysis.

In dialysis, the latex is confined with a semi-permeable membrane (e.g., in a dialysis bag), and the aqueous phase ions are removed by diffusion across this semi-permeable membrane. The rate of this diffusion can be increased by changing the water outside the bag more often or by using dialysis membranes of greater surface area (e.g., hollow fiber dialysis). In principle, the adsorbed ions should be removed quantitatively provided the adsorption-desorption equilibrium is maintained. In practice, however, the removal of adsorbed ions as well as the replacement of Na^+ and K^+ ions by H^+ ions is incomplete (2,3,6). The dialysis membrane must be considered a third phase in this process; moreover, the rate of dialysis decreases drastically with decreasing concentration gradient across the membrane (7).

The cleaned latex in the H^+ form is titrated conductometrically or potentiometrically with base to determine the surface charge (2,5,8). Conductometric titration is the more sensitive method when the overall conductance is very low as in a sample cleaned by ion exchange or serum replacement; potentiometric titration is the more sensitive when the conductance is relatively high. Figure 1 shows a typical conductometric titration curve (8). The solid line shows the experimental curve and the dashed line the theoretical curve. The theoretical curve lies slightly above the experimental curve; moreover, the slope of its descending leg is much greater. The difference in the descending slopes results from the distribution of the H^+ counterions in the double layer; some are held close to the particle surface and therefore do not contribute much to the overall conductance. The lower the electrolyte concentration and thus the greater the expansion of the electric double layer, the smaller the slope of the descending leg. The higher position of the theoretical curve results because the conductometric titration involves ion exchange as well as neutralization, which decreases the overall conductance.

Characterization by Ion Exchange and Conductometric Titration

Earlier work (2,3,5,9) described the characterization of monodisperse polystyrene latexes of 25-447nm particle diameter prepared using persulfate initiator, bicarbonate buffer, and four different emulsifiers. The latexes were ion exchanged using rigorously purified Dowex(H^+)-Dowex 1(OH^-) mixed resins and titrated conductometrically; this process was repeated until the surface charge was constant. These surface charges shown in Table I (3,5,9) correspond to 1.0-1.3 sulfate endgroups per polystyrene molecule (molecular weight determined by osmometry). To determine if any sulfate groups were buried inside the particle, the polymer was recovered from the ion-exchanged latex, dissolved in dioxane-water mixture, ion exchanged again, and titrated

TABLE I

Monodisperse Polystyrene Latexes

Surface Charge and Number of Sulfate Endgroups/Polymer Molecule (3,5,9)

Latex	Particle Diameter, nm	Surface Charge, $\mu C/cm^2$	Sulfate Endgroups/Molecule Surface	Total
A-1	25	0.5	12.4*	13.0*
A-2	88	3.3	0.98	1.57
A-3	234	2.0	0.87	1.59
B-1	158	4.2	1.26	1.21
B-2	248	5.7	1.02	1.23
C-1	254	5.4	0.95	0.94
D-1	109	1.6	0.95	----
D-2	187	1.8	0.90	----
D-3	285	4.9	1.03	1.63
D-4	447	8.1	0.93	2.07

A = Aerosol MA (bis-1,3-dimethylbutyl sodium sulfosuccinate)
B = Sipon WD (sodium lauryl sulfate)
C = Aerosol OT (di-2-ethylhexyl sodium sulfosuccinate)
D = potassium oleate
* μeq/gm polymer

TABLE II

Monodisperse Polystyrene Latex A-2

Oxidation of Sulfate and Hydroxyl Endgroups
(10^{-5}N silver nitrate; 6 hours at 90°)

Potassium Persulfate, %*	Number of Endgroups, μeq/gm Sulfate	Carboxyl	Hydroxyl
None (original)	22.5	none	----
10	11.7	22.0	11.2
15	8.0	24.7	10.2
30	6.4	26.3	10.2

* based on polymer

	Endgroups/Polymer Molecule
surface sulfate	0.98
total sulfate	1.57
sulfate + hydroxyl	2.06

conductometrically. The total number of sulfate endgroups was in the range
1.0-1.6 per polystyrene molecule (except for one latex which had a value of
2.07), suggesting that there are other endgroups besides sulfates.

One possibility is hydroxyl endgroups, which may be formed by a side
reaction of sulfate ion-radicals to form hydroxyl radicals (9) or hydrolysis
of the surface sulfate groups. To determine if hydroxyl groups were present,
the ion-exchanged latexes were oxidized by heating with persulfate and 10^{-5}
silver ion at 90°, then ion exchanged and titrated conductometrically to de-
termine the carboxyl groups. Table II (9) shows that some sulfate groups
were hydrolyzed and oxidized to carboxyl groups during this process, but the
carboxyl titration values corrected for this hydrolysis accounted satisfac-
torily for the requisite two endgroups per polystyrene molecule.

The extent of the side reaction of sulfate ion-radicals with water to
produce hydroxyl radicals was postulated to increase with decreasing pH.
Therefore, polymerizations were carried out using persulfate initiator but
with the pH of the polymerization adjusted to values in the range of pH
range 2-8(9). Table III (9) shows that, at the lowest pH, the endgroups
were about 90% hydroxyls and 10% sulfates; at pH 7-8, they were all sulfates.

These results showed that monodisperse polystyrene particles prepared
using persulfate initiator and bicarbonate buffer contain both sulfate and
hydroxyl surface groups. Some sulfate groups are on the particle surface,
while others are buried inside the particle. All of the hydroxyl groups are
on the particle surface. These results also showed that careful control of
the pH during polymerization can produce latex particles stabilized with only
surface sulfate groups.

Characterization by Serum Replacement and Conductometric Titration

For serum replacement (6), the latex is confined in a cell with a uni-
form-pore-size Nuclepore filtration membrane. Distilled, deionized water is
pumped through the latex until the conductance of the effluent stream is about
the same as that of the distilled, deionized water. This serum replacement
removes the adsorbed emulsifier and solute electrolyte quantitatively and
allows recovery of the serum in a form suitable for further analysis; however,
it does not replace the Na^{+} and K^{+} counterions of the surface groups with H^{+}
ions. To do this, dilute hydrochloric acid (ca. $10^{-4}N$) is pumped through the
latex, followed by distilled, deionized water to remove the excess acid. The
latex is then titrated conductometrically to determine the surface charge.

The pore size of the Nuclepore filtration membranes used is 0.50-0.75
times the particle diameter of the latex to be cleaned. The latex in the cell
is agitated close to the membrane to prevent clogging by deposited particles.
Even so, clogging is observed at higher pumping pressures and latex solids
contents, e.g., for 10-15% solids latex at 5 psi pressure, while 5-10% solids
latex at 2 psi gives no clogging. Suction filtration can also be used to in-
crease the rate of serum replacement.

Seven polystyrene latexes prepared with persulfate initiator and bicar-
bonate buffer were characterizaed to demonstrate the efficacy of this method
(6). Three were monodisperse latexes prepared using conventional emulsifiers;
four were prepared using sodium styrene sulfonate or sodium vinyltoluene sul-
fonate as comonomeric emulsifiers. Each latex was subjected to serum re-
placement with water and then titrated conductometrically. Then, this sample
was ion exchanged to remove material not removed by serum replacement and ti-
trated again. Then, the sample was subjected to serum replacement with di-
lute hydrochloric acid to replace the Na^{+} and K^{+} counterions with H^{+} ions and
titrated. This sample was also ion exchanged and titrated again. These re-
sults were compared with those determined by ion exchange alone. Also, for

TABLE III

Monodisperse Polystyrene Latexes

Effect of pH of the Polymerization Medium (9)

pH	Particle Diameter, nm	Endgroups/Polymer Molecule		
		Surface Sulfate	Total Sulfate	Sulfate + Hydroxyl
1.9	143	0.19	0.20	1.84
3.3	132	0.55	1.00	1.75
4.4	133	0.62	1.05	2.00
5.0	128	0.71	1.10	2.00
6.4	130	0.46	0.55	2.01
7.8	129	1.40	2.07	2.07
11.6	162	0.62	1.00	1.42

TABLE IV

Surface Characterization of Polystyrene Latexes (6)

Treatment	Surface Charge Density						
	LS-1102-A	LS-1047-E	LS-1134-B	S-10	S-13	V-4	V-6
H_2O	0.55	1.42	0.74	2.09	1.30	0.62	0
H_2O + I.E.	1.20	2.31	2.23	10.9	18.5	4.98	50.3
H_2O + HCl + H_2O	1.13	2.32	2.34	11.0	18.2	4.95	50.7
H_2O + HCl + H_2O + I.E.	1.19	2.32	2.34	10.9	18.2	4.96	50.9
I.E.	1.35	2.56	2.34	11.4	20.3	5.29	52.4
Dialyzed	1.01	1.48	1.43	4.04	5.08	1.66	14.7
Dialyzed + I.E.	1.35	2.06	2.20	9.81	18.3	5.12	51.3

comparison, latex samples were dialyzed for one month and then titrated. These samples were then ion exchanged and titrated again.

Table IV shows the results of these experiments. Serum replacement with water gave low values for the surface charge because of incomplete replacement of the Na^+ and K^+ ions by H^+ ions. However, serum replacement with water, hydrochloric acid, and water gave values equal to, or slightly less than, those obtained by ion exchange, demonstrating the efficacy of this new cleaning method. The values for the dialyzed samples were also significantly lower than those obtained by ion exchange.

Dialysis

Table IV shows that dialysis is ineffective in cleaning the latexes for characterization. Earlier work (3,5) also showed that dialysis is ineffective in removing the adsorbed emulsifier and replacing the Na^+ and K^+ counterions with H^+ ions. Others have also found that dialysis does not remove emulsifier completely. Brodnyan and Kelley (10) found that aqueous solutions of C14-tagged sodium lauryl sulfate equilibrated upon dialysis, but only 9.5% and 22% of the emulsifier was removed from latexes dialyzed under the same conditions. Matijevic et al. (11) dialyzed a butadiene-styrene copolymer latex prepared using rosin acid soap for 160 days and removed only about 50% of the emulsifier. As mentioned above, Edelhauser (7) showed that the concentration gradient across the dialysis membrane must exceed a critical value to make the dialysis proceed at a practical rate. In contrast, Ottewill and Shaw (12) found from electrophoretic mobility measurements and desorption of radioactive emulsifier that all of the emulsifier was removed by dialysis or at least that a constant surface charge was obtained.

Endgroups Produced by Persulfate Initiator

The foregoing latexes prepared using persulfate initiator and bicarbonate buffer contained surface sulfate groups and, in some cases, surface hydroxyl groups. None of these latexes contained carboxyl groups. These latexes had final pH values of 7-8. If the bicarbonate buffer was omitted, the final pH of the latex was 2-3 because of the bisulfate ion generated by the persulfate decomposition.

In contrast, others have found carboxyl groups in polystyrene latexes prepared using persulfate initiator. Ottewill and Shaw (12) cleaned latexes prepared with various emulsifiers by dialysis and found carboxyl groups by variation of electrophortic mobility with pH, infrared spectra of the dried polymer, and potentiometric titration of dried polymer redispersed in water. Later, Ottewill et al. (13) reported carboxyl groups in polystyrene latexes prepared with hydrogen peroxide initiator and sodium laurate emulsifier as well as in emulsifier-free latexes prepared using persulfate; in addition, Krieger et al., Fitch et al., Homola et al., and Gultepe and Everett (13) reported carboxyl groups in latexes prepared using different methods. In some cases, the latexes were cleaned by dialysis and, in other cases, by ion exchange, but some of the ion exchange resins were not purified.

These results are in disagreement with the foregoing findings that only sulfate and hydroxyl groups are produced by persulfate initiator, particularly with bicarbonate buffer. There are several possible sources of the carboxyl groups found by others: (i) hydrolysis of sulfate groups followed by oxidation; (ii) dissolution of carbon dioxide in the latex; (iii) oxidation of surface sulfate groups, particularly in the presence of small concentrations of heavy metal ions; (iv) hydrolysis of ester groups for copolymers containing methacrylate and acrylate esters; (v) side reactions of initiating species. Another possibility is the contamination of the latex by oxidation products of the dialysis membranes (14).

TABLE V

Effect of Polymerization Recipe on Surface Groups (15.16)

Latex	Emulsifier	Initiator	Buffer	Surface Charge $\mu eq/gm$		pH
				Sulfate	Carboxyl	
41	Aerosol MA	$K_2S_2O_8$	$NaHCO_3$	6.99	none	7.0
W23	Aerosol MA	$K_2S_2O_8$	$NaHCO_3$	7.71	none	8.3
520	none	$K_2S_2O_8$	none	9.34	1.45	2.0
520'	none	$K_2S_2O_8$	none	6.45	3.07	2.6
520"	none	$K_2S_2O_8$	$NaHCO_3$	9.10	none	8.0
42	Aerosol MA	$K_2S_2O_8$	$NaHCO_3$, KH_2PO_4	6.95	1.41	7.0
43	Aerosol MA	$K_2S_2O_8$	$NaHCO_3$, $Na_2B_4O_7$	6.80	4.60	8.7
43'	Aerosol MA	$K_2S_2O_8$	$NaHCO_3$, $Na_2B_4O_7$	6.79	3.48	8.0
43"	none	$K_2S_2O_8$	$NaHCO_3$, $Na_2B_4O_7$	9.87	3.43	8.7
W1	Aerosol MA	$K_2S_2O_8$	NaOH, KH_2PO_4	4.01	9.70	7.0
W2	Aerosol MA	$K_2S_2O_8$	$NaHCO_3$, NaOH,KH_2PO_4	3.12	3.57	8.7
44	Aerosol MA	$K_2S_2O_8$	$NaHCO_3$, $AgNO_3$	5.63	3.15	8.5
44'	Aerosol MA	$K_2S_2O_8$	$NaHCO_3$, $AgNO_3$	3.50	1.21	8.0
44"	none	$K_2S_2O_8$	$NaHCO_3$ $AgNO_3$	8.42	2.90	8.0
W21	Aerosol MA	$(NH_4)_2S_2O_8$	NH_4OH	7.28	none	2.7
W22	Aerosol MA	$(NH_4)_2S_2O_8$	NH_4OH	7.89	none	2.3
716D	Aerosol MA	$(NH_4)_2S_2O_8$	none	5.01	2.36	2.2

TABLE VI

Effect of Ageing on Ion Exchanged (H^+ Form) Latex 41

| | Surface Charge, μeq/gm | | |
Ageing Time, days	Sulfate	Carboxyl	Total
0	7.02	3.06	10.88
1	7.79	2.92	10.71
4	6.86	4.04	10.90
8	6.97	4.73	11.70
11	6.26	5.22	11.48
15	4.39	6.88	11.27
22	1.08	7.13	8.21
32	none	9.73	9.73
---	none	10.83	10.83

TABLE VII

Effect of Ageing on Ion Exchanged (H^+ Form) Latex W21

| | Surface Charge, μeq/gm | | |
Ageing Time, days	Sulfate	Carboxyl	Total
0	6.47	3.64	10.11
1	6.63	3.82	10.47
4	5.30	6.14	11.44
8	5.54	4.34	9.78
11	4.84	5.69	10.31
15	3.45	5.14	8.59
22	1.27	6.33	7.60
32	none	9.01	9.01
---	none	9.29	9.29

TABLE VIII

Effect of Ageing Conditions on Ion Exchanged (H^+ Form) Latex 43' (16)

| | | Surface Charge, μeq/gm | | |
Treatment	pH	Sulfate	Carboxyl	Total
initial	8.0	---	---	---
ion exchanged	3.5	6.79	3.48	10.27
ion exchanged; 14 days at ca. 25°	---	none	10.47	10.47
pH adjusted to 3.35 with 0.1N HCl; 142 days at ca. 25	3.35	6.78	3.64	10.42

TABLE IX

Effect of Ageing Conditions on Ion Exchanged (H$^+$ Form) Latex 520" (16)

Ageing Temp.,°C	Time,days	Surface Charge, μeq/gm		
		Sulfate	Carboxyl	Total
---	none	8.57	none	8.57
ca. 25	30	5.35	2.73	8.08
ca. 25	44	none	8.22	8.22
90	4.0	none	none	0.00*
90	8.8	none	none	0.00*

*latex stable; conductance (0.2 gm polymer/100 ml) about same as distilled deionized water; slight negative charge by electrophoresis; equivalent to one group/33000 Å^2
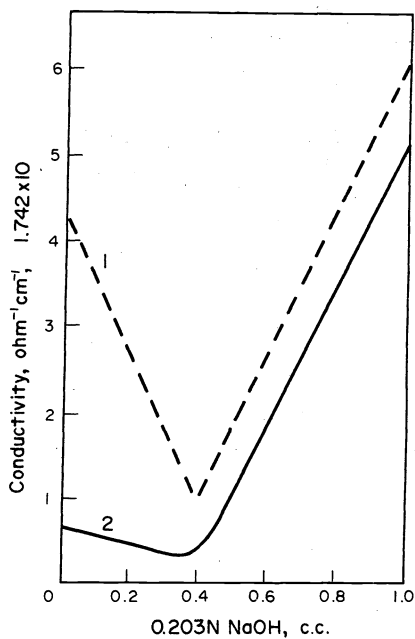

Figure 1.   Conductometric titration of ion-exchanged 234nm-diameter monodisperse polystyrene latex: 1. theoretical curve calculated assuming 100% dissociation; 2. experimental curve.

To determine the effect of different polymerization conditions on the polymer endgroups produced, polymerizations were carried out using the standard bicarbonate buffer as well as other variations. Table V (15,16) shows that the use of the persulfate-bicarbonate combination with and without emulsifier gave latexes of final pH 7-8 with only sulfate groups. The addition of 10^{-5} silver ion gave a latex of pH 8.5, but with weak-acid groups, presumably because of oxidation of the sulfate groups. The omission of the bicarbonate buffer gave latexes of lower pH with weak-acid groups. The formation of weak-acid groups in these latexes is not merely an effect of pH during the polymerization: potassium dihydrogenphosphate, sodium borate, and sodium hydroxide, even in combination with sodium bicarbonate, gave both strong-acid and weak-acid groups, and pH values of 7-9. Also, the ammonium persulfate-ammonium hydroxide system gave latexes with pH values of 2-3, but only strong-acid groups. The omission of the ammonium hydroxide did not change the pH, but gave weak-acid groups.

Preparation of Model Colloids

It has been shown (9) that polystyrene particles with only sulfate surface groups can be prepared at pH 7-8 using persulfate initiator and bicarbonate buffer. Two monodisperse polystyrene latexes prepared in this way lost their strong-acid surface groups during storage over a period of a few years. These latexes showed no surface charge by conductometric titration or microcapillary electrophoresis. Nevertheless, they were stable despite their zero surface charge, and oxidation followed by conductometric titration gave carboxyl groups, indicating that somehow the surface sulfate groups had hydrolyzed to hydroxyl groups.

The first attempts to deliberately hydrolyze the sulfate groups to hydroxyls at acid pH values were unsuccessful; the latexes flocculated before all of the sulfate groups were hydrolyzed (17). However, it was found later (16) that allowing the latex in the H^{+} form to stand at ambient conditions resulted in the disapperance of the sulfate groups and the appearance of carboxyl groups. Tables VI and VII show the results for two such latexes. Table VIII shows that this oxidation of sulfate groups to carboxyl groups cannot be achieved by storage at pH 3.35. Moreover, it was found (16) that allowing the latexes in the H^{+} form to stand at 90° instead of room temperature resulted in the hydrolysis of the sulfate groups to hydroxyls. Table IX shows the results for one such latex.

Thus these results show that monodisperse polystyrene latexes prepared using persulfate initiator and bicarbonate buffer are a good starting point for the preparation of ideal model colloids. These latexes as prepared contain only sulfate groups. Storage of these latexes in the H^{+} form at 90° gives the all-hydroxyl form and storage at room temperature gives the all-carboxyl form. These latexes with the same number of three different surface groups ---- sulfate, carboxyl, hydroxyl ---- can be used as colloids for investigations of colloidal phenomena.

References

1. For a brief history of the early preparation of monodisperse polystyrene latexes, see J. W. Vanderhoff, Preprints, A.C.S. Division Org. Coatings Plastics Chem. 24, (2), 223 (1964).

2. H. J. van den Hul and J. W. Vanderhoff, J. Colloid Interface Sci. 28, 336 (1968).

3. J. W. Vanderhoff, H. J. van den Hul, R. J. M. Tausk, and J. Th. G.
    Overbeek, "Clean Surfaces: Their Preparation and Characterization for
    Interfacial Studies," G. Goldfinger, editor, Marcel Dekker, New York,
    1970, p. 15.

4. G. D. McCann, E. B. Bradford, H. J. van den Hul, and J. W. Vanderhoff,
    "Polymer Colloids," R. M. Fitch, Ed., Plenum Press, New York, (1971),
    p. 29.

5. H. J. van den Hul and J. W. Vanderhoff, J. Electroanal. Chem. $\underline{37}$, 161
    (1972).

6. S. Ahmed, M. S. El-Aasser, G. H. Pauli, G. W. Poehlein, and J. W.
    Vanderhoff, accepted for publication, J. Colloid Interface Sci.

7. H. Edelhauser, J. Polymer Sci. $\underline{C27}$, 291 (1969).

8. W. C. Wu, M. S. El-Aasser, and J. W. Vanderhoff, "Emulsions, Latices,
    and Dispersions," P. Becher and M N. Yudenfreund, editors, Marcel
    Dekker, New York, 1978, p.71.

9. H. J. van den Hul and J. W. Vanderhoff, Brit. Polymer J. $\underline{2}$, 121 (1970).

10. J. G. Brodnyan and E. L. Kelley, J. Colloid Sci. $\underline{20}$, 7 (1965).

11. C. G. Force, E. Matijevic, and J. P. Kratohvil, Kolloid Z. Z. Polymere
    $\underline{223}$, 31 (1968).

12. J. N. Shaw and R. H. Ottewill, Nature $\underline{208}$, 681 (1965); ibid. Kolloid
    Z. Z. Polymere 215, 161 (1967).

13. R. H. Ottewill et al., I. M. Krieger et al., R. M. Fitch et al., A.
    Homola et al., P. H. Everett and M. E. Gultepe, Discussions and Pre-
    prints NATO/ASI "Polymer Colloids," Trondheim, Norway, June 30 - July 11,
    1975.

14. D. E. Yates, R. H. Ottewill and J. W. Goodwin, J. Colloid Interface Sci.
    $\underline{62}$, 356 (1977).

15. W. C. Wu, Ph.D. thesis, Lehigh University, 1977.

16. A. Kamel, M. S. El-Aasser, and J. W. Vanderhoff, unpuslished research
    results, 1979.

17. S. M. Ahmed, M. S. Research Report, Lehigh University, 1976.