Preparation and Characterization of Carboxylated Isoprene/Styrene Copolymer Latexes

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Synopsis

Carboxylated isoprene/styrene copolymer latexes were prepared, and the concentration of surface carboxyl groups and the freeze–thaw stability of these latexes were measured. It is clarified that the introduction method of the carboxylic monomer governs the distribution of carboxyl groups in latex particles. Introduction of the carboxylic monomer prior to the initiation of polymerization localizes only 12–13% of total carboxyl groups on the surface of particles, whereas introduction of the carboxylic monomer at the last stage of polymerization localizes more than 60% of total carboxyl groups on the surface of particles, though the percentage is strongly dependent on the conversion when the monomers are shot. These latexes show a remarkable increase in the freeze–thaw stability with the increase in the degree of neutralization of carboxyl groups in a fairly narrow range. There exists a linear relationship between the surface area occupied by a surface carboxyl group and the degree of neutralization of surface carboxyl groups at which the remarkable increase in the freeze–thaw stability is observed. The result suggests that the freeze–thaw stability is substantially determined by the density of carboxylate ion on the surface of particles.

INTRODUCTION

Carboxylated latexes stabilized with chemically bound carboxyl groups are excellent in mechanical stability,[1] freeze–thaw stability,[2] and compatibility with pigments[3] compared with latexes stabilized only with physically adsorbed soaps. Consequently, carboxylated latexes have become much important in industrial use. In general, carboxylated latexes are prepared by copolymerizing carboxylic monomers,[4] and the properties of these latexes are greatly dependent on the method of introduction of the carboxylic monomer,[3,5] which indicates that the method of introduction of the carboxylic monomer has a great effect on its polymerization behavior. Although some investigators have studied the polymerization behavior of carboxylic monomers with styrene[6] or ethyl acrylate,[7] the effect of the method of introduction of the carboxylic monomer on its polymerization behavior has scarcely been investigated.

In this paper, the authors prepared carboxylated isoprene/styrene copolymer latexes by two different methods of introduction of the carboxylic monomer, that is, the introduction prior to the initiation of polymerization (initial charge process) and the introduction at the last stage of polymerization (shot process), and measured the concentration of carboxyl groups chemically

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bound to the surface of particles and freeze–thaw stability of these latexes. Further, the authors attempted to elucidate the polymerization behavior of the carboxylic monomer.

EXPERIMENTAL

Materials

Polymer-grade isoprene (IP) (Kuraray Co., Ltd.) was used without further purification. Chemically pure-grade styrene (St), acrylic acid (AA), and methacrylic acid (MAA) were used after distillation under reduced pressure. Deionized water was used. Sodium dodecylbenzene sulfonate (SDBS) (Tokyo Chemical Industry Co., Ltd.) and sodium polyoxyethylene nonylphenyl sulfate (POE(10)) (Matsumoto Yushi Seiyaku Co., Ltd.) were used without further purification. Chemically pure-grade tert-dodecyl mercaptan (t-DDM) and extrapure-grade potassium persulfate (KPS), potassium chloride (KCl), and sodium hydroxide (NaOH) were used without further purification.

As ion exchange resins, quaternary ammonium resin (IRA-402) (Rohm & Haas Co., Ltd.) and sulfonic acid resin (IR-120B) (Rohm and Haas Co., Ltd.) were used after purification by the method described by Vanderhoff et al.[8] After the purification, the exchange capacities of these resins were 0.85 meq/g (wet) and 1.85 meq/g (wet) for IRA-402 and IR-120B, respectively.

Poly(acrylic acid) (PAA) was prepared by the polymerization of 5 g AA in toluene solution initiated by 0.084 g benzoyl peroxide at 80°C and purified by dissolving in ethyl alcohol and reprecipitating with diethyl ether.

Preparation of Latexes

Latexes were prepared in a conventional manner in a 500-ml glass vessel equipped with a stirrer. The initial-charge process latexes were prepared by the following procedure. The prescribed amounts of water, soap, initiator, and electrolyte were placed in the vessel. After the completion of dissolution, the prescribed amounts of monomers and modifier were emulsified, and the emulsion was heated to and kept at 70°C or 90°C until the polymerization was substantially completed.

The preparation of the shot process latexes was carried out as follows. The emulsion composed of the prescribed amount of ingredients was prepared as described above and heated to and kept at 76°C (step 1). At 60–70% conversion, the prescribed amounts of soaps dissolved in water were introduced (step 2). Then the prescribed amounts of monomers and initiator dissolved in water were introduced at conversion higher than 80% (step 3). Step 3 was continued until the polymerization was substantially completed.

Conversions were determined gravimetrically with both processes.

Characterization of Latexes

The particle diameter of the latexes was determined as number average by electron microscopy, after hardening the particles with osmium tetraoxide.

The purification of the latexes was carried out as reported by Vanderhoff et al.[8] The latex diluted to solids content of 2–5% (wt) was mixed with an ex-

cess amount of ion exchange resins and stirred till constant pH and conductance were observed. After completion of the ion exchange, the latex was filtered through filter paper (No. 1 filter paper obtained from Toyo Roshi Co., Ltd.) placed on a filter funnel to remove the ion exchange resins. The solids content of the separated latex was determined gravimetrically.

Potentiometric and conductometric titration of the ion exchanged latexes was performed at room temperature by monitoring pH and conductance. Conductance determination was carried out using a Yokogawa-Hewlett-Packard, Ltd. 4255A universal bridge equipped with a dip-type conductance cell. A $N/100$ aqueous solution of sodium hydroxide was used as titrant. The concentration of surface carboxyl groups was expressed in terms of milliequivalent of surface carboxyl groups found per 1 g of polymer. The surface area occupied by a surface carboxyl group was calculated by the following procedure and expressed in terms of square angstroms. First, the total surface area of particles per 1 g of polymer was calculated regarding the density of polymer as 1 g/cm^3. Next, the number of surface carboxyl groups per 1 g of polymer was calculated from the concentration of surface carboxyl groups described above. Then the surface area occupied by a surface carboxyl group was calculated dividing the former by the latter.

The separation of the serum from the particles was achieved by the freeze–thaw coagulation of particles and filtration. The filtration was carried out by the method described above for the removal of the ion exchange resins from the latex. The solids content of the separated serum was determined gravimetrically.

The freeze–thaw stability of the latexes was judged by the change in appearance as follows. After the latex, neutralized with the 5N aqueous solution of sodium hydroxide, if necessary, was frozen at −18°C for 6 hr, the frozen latex was kept at room temperature until it thawed.

RESULTS AND DISCUSSION

Preparation of Latexes

The polymerization recipe and results of the initial charge process are shown in Tables I and II, respectively. In both runs in Table II, the stability of the latexes during the polymerization was fairly good with substantially no coagulation.

TABLE I
Polymerization Recipe of the Initial Charge Process

Ingredient	Amount, g
Water	110
IP	45
St	50
MAA	5
POE(10)	7
KPS	0.5
KCl	0.5
t-DDM	0.09

TABLE II
Polymerization Results of the Initial Charge Process

Run no.	Polymerization temperature, °C	Polymerization time, hr	Conversion, %
S-1061	70	7	95.5
S-1068	90	5½	93.9

In Table III, the standard polymerization recipe of the shot process is shown. This process is composed of three steps. In step 1 IP and St are co-polymerized to a conversion of 60–70%; in step 2, the latex is stabilized with an additional amount of soaps; and in step 3, the mixture of the carboxylic monomer and St is introduced (shot) along with additional initiator at various conversions higher than 80% and the polymerization is substantially completed. The polymerization recipe and results are shown in Table IV. In all runs in Table IV, the stability of the latexes during the polymerization was sufficient, despite the difference in the polymerization recipe and shot conversion.

Problems on the Determination of Surface Carboxyl Groups

The determination of surface carboxyl groups, that is, carboxyl groups chemically bound to the surface of particles, has been studied by some investigators,[9,10] and the method for the determination has already been established. Recently, however, some problems on the determination of surface carboxyl groups such as the effect of water-soluble polymers containing carboxyl groups[11,12] and the fractionation of particles with ion exchange[13] have been reported. From this point of view, some problems on the determination of surface carboxyl groups were investigated in detail.

Effect of the Ion Exchange of Latexes

A typical ion exchange behavior is shown in Figure 1. It is clear that the ion exchange is completed within 40 min in the fifth step, where the total amount of ion exchange resins reaches approximately five times that of solids in the latex.

TABLE III
Standard Polymerization Recipe of the Shot Process

Ingredient	Amount, g		
	Step 1	Step 2	Step 3
Water	120	20	10
IP	48	—	—
St	62.4	—	7.2
AA or MAA	—	—	variable
POE(10)	1.7	0.57	—
SDBS	2.4	0.8	—
KPS	0.6	—	0.6
NaOH	0.2	—	—
t-DDM	0.3	—	—

TABLE IV
Polymerization Recipe and Results of the Shot Process

	Polymerization recipe		Polymerization result		
Run no.	Steps 1 and 2[a]	Step 3, g	Shot conversion, %	Polymerization time, hr	Conversion, %
S-1101	A	AA 1.2	95.0	$19^1/_3$	91.7
S-1106	A	AA 2.4	82.2	$21^1/_6$	94.2
S-1113	A	AA 2.4	91—92	23	about 100
S-1258	A	AA 2.4	90—95	12	about 100
S-1095	A	AA 2.4	98.4	$21^1/_6$	92.9
S-1112	A	AA 2.4	97—98	22	about 100
S-1107	B	AA 2.4	93—94	25	93.5
S-1100	A	AA 3.6	94.0	$19^1/_3$	98.2
S-1102	A	MAA 2.8	94.0	$22^1/_3$	96.4

[a] A = Standard polymerization recipe in Table III; B = amount of soaps was reduced to ¾ relative to that of the standard polymerization recipe in Table III.

Although it is well known that inorganic electrolytes are easily removed by ion exchange, it is not always the case for soaps, unpolymerized carboxylic monomers, and water-soluble polymers containing carboxyl groups, which might affect the determination of surface carboxyl groups. This was confirmed with some model compounds. The aqueous solutions of SDBS, POE(10), and AA, the concentrations of which are 19.1 mmole/l., 4.3 mmole/ l., and 27.8 mmole/l., respectively, were ion exchanged with an excessive amount of ion exchange resins and filtered. The filtrates exhibited the same pH and conductance as pure water, and no acidic species was found by conductometric titration with the aqueous solution of sodium hydroxide. The aqueous solution containing 1 g/l. PAA was ion exchanged with a large amount of IRA-402, that is, 114 times that of PAA, filtered, and titrated conductometrically with an aqueous solution of sodium hydroxide. The amount of PAA removed by ion exchange was not more than 13% (wt) of the total
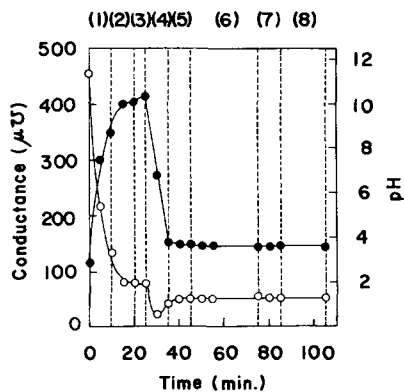

Fig. 1. Ion exchange behavior of shot process latex S-1113: (O) conductance; (●) pH. The amount of solids in the latex is 4.97 g, and the amount of ion exchange resins added is as follows: (1) IRA-402, 5.2 g; (2) IRA-402, 5.1 g; (3) IRA-402, 5.0 g; (4) IR-120B, 4.4 g; (5) IR-120B, 4.6 g; (6) IR-120B, 4.5 g; (7) IRA-402, 4.7 g; (8) IR-120B, 3.9 g.
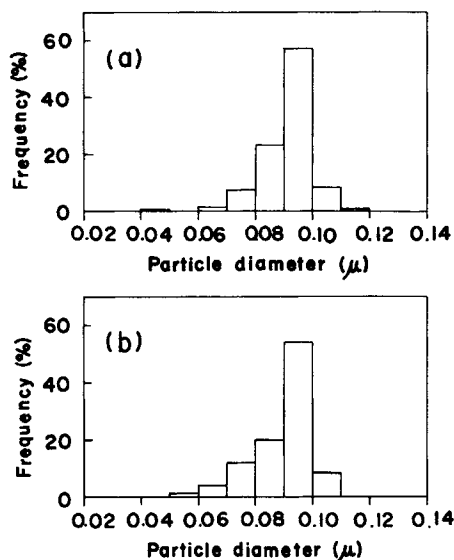
Fig. 2. Change in particle diameter distribution and number-average particle diameter of shot process latex S-1113 with ion exchange: (a) original, number-average particle diameter 0.090 μ; (b) ion exchanged, number-average particle diameter 0.092 μ.

amount. These experimental results indicate that soaps and carboxylic monomers are completely removed by ion exchange, but water-soluble polymers containing carboxyl groups cannot easily be removed.

The fractionation of particles with ion exchange was examined. The ion exchange of the shot process latex S-1113 containing 2.36 g solids was performed using 6.12 g IRA-402 and 5.97 g IR-120B. In Figure 2 are shown the particle diameter distribution and number-average particle diameter of the latex before and after the ion exchange. It is clear from Figure 2 that ion exchange causes little fractionation of particles and does not affect the determination of surface carboxyl groups.

Effect of Water-Soluble Polymers

As described above, water-soluble polymers containing carboxyl groups which may affect the determination of surface carboxyl groups cannot easily be removed by ion exchange. Therefore, it is necessary to confirm the existance of such polymers. From the 410 g shot process latex S-1112, 111 g serum containing 0.88% (wt) solids was obtained by freeze–thaw coagulation. It was confirmed by ultramicroscopy that the serum does not contain any particles. The serum was ion exchanged with an excess of ion exchange resins and filtered. The filtrate exhibited the same pH and conductance as pure water, and no acidic species was found by conductometric titration with an aqueous solution of sodium hydroxide. This indicates that the solids in the serum are composed of soaps and inorganic electrolytes. Consequently, it may be concluded that the shot process does not give any water-soluble polymers containing carboxyl groups. Taking into account the method of introduction of carboxylic monomers, this may also be the case for the initial charge process.
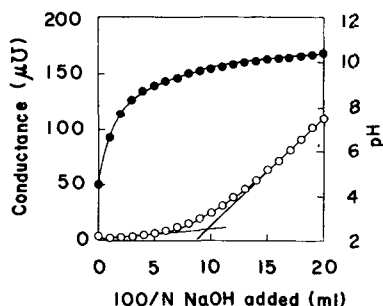
Fig. 3. Potentiometric and conductometric titration curves of ion exchanged shot process latex S-1113: (O) conductance; (●) pH.

Reproducibility of the Determination of Surface Carboxyl Groups

Typical potentiometric and conductometric titration curves of an ion exchanged latex are shown in Figure 3. No substantial difference was observed between the titration curves of the initial-charge process latexes and those of the shot process latexes. As shown in Figure 3, the rise of pH is monotonous, which only suggests the presence of poly(carboxylic acid)[14] and does not give any quantitative information. The conductometric titration curve shows two linear parts with different slopes, and the concentration of surface carboxyl groups can be determined as the point of intersection. Recently, some investigators[10,15] have demonstrated that surface sulfate groups resulting from the fragments of the initiator, that is, sulfate groups chemically bound to the surface of particles, can also be determined by potentiometric or conductometric titration with aqueous solution of a base. Although the latexes in Table II and IV may also have sufficient concentration of surface sulfate groups, Figure 3 does not clearly show the initial sharp decrease and successive sharp increase in conductance and the sharp increase in pH at the equivalence point which are characteristic of the titration of surface sulfate groups with a strong base.[16] This indicates that the concentration of surface sulfate groups is much smaller than that of surface carboxyl groups, and the former can reasonably be neglected in the determination of the latter. In Table V is shown the reproducibility of the determination of surface carboxyl groups based on the above-described procedure. From Table V, it is clear that the concentra-

TABLE V
Reproducibility of Determination of Surface Carboxyl Groups

Latex	Run no.	Concentration of surface carboxyl groups, meq/g[a]	
		Original data	Mean value
S-1061	CT-6	0.187	
	CT-7	0.195	0.196
	CT-8	0.205	
S-1113	CT-9	0.0759	
	CT-11	0.0763	0.0742
	CT-490	0.0704	

[a] Milliequivalents of surface carboxyl groups found per 1 g polymers.

TABLE VI
Results of Determination of Particle Diameter and Surface Carboxyl Groups

‾Latex	Particle diameter, μ	Concentration of surface carboxyl groups, meq/g		Distribution of carboxyl groups (surface/total)	Surface area occupied by a surface carboxyl group, $Å^2$
		Surface[a]	Total[b]		
S-1061	0.102	0.0763	0.581	0.131	128
S-1068	0.092	0.0710	0.581	0.122	153
S-1101	0.086	0.110	0.140	0.786	105
S-1106	0.102	0.169	0.278	0.608	57.8
S-1113	0.090	0.205	0.278	0.737	54.1
S-1258	0.091	0.217	0.278	0.781	50.6
S-1095	0.110	0.224	0.278	0.805	40.4
S-1107	0.098	0.205	0.278	0.736	49.7
S-1100	0.099	0.315	0.412	0.765	31.9
S-1102	0.100	0.193	0.277	0.698	51.7

[a] Milliequivalents of surface carboxyl groups found per 1 g polymers.
[b] Milliequivalents of carboxylic monomer added per 1 g polymers.

tion of surface carboxyl groups of both types of latex can be determined within an error of ±5%.

Determination of Particle Diameter and Surface Carboxyl Groups

The particle diameter and the concentration of surface carboxyl groups of the latexes prepared by the initial charge process or by the shot process were measured, and the results are shown in Table VI. The particle diameter of all latexes in Table VI is about 0.1 μ.

It is apparent from Table VI that the initial charge process localizes only 12–13% of total carboxyl groups on the surface of particles, irrespective of the polymerization temperature. On the other hand, the shot process localizes more than 60% of total carboxyl groups on the surface of particles, irrespective of the amount and species of the carboxylic monomer and the amount of soaps. In this case, however, the shot conversion largely affects the distribution of carboxyl groups as follows: with increasing the shot conversion from less than 90% via 90–95% to higher than 95%, the localized carboxyl groups on the surface of particles increases from less than 70% via 70–80% to higher than 80%, respectively. These results indicate that the method of introduction of the carboxylic monomer strongly affects the polymerization behavior of the carboxylic monomer which will govern the distribution of carboxyl groups.

The surface area occupied by a surface carboxyl group was calculated. The results have already been shown in Table VI. The surface areas of the initial-charge process latexes are fairly large in comparison with the molecular area of the usual anionic soap.[16] On the other hand, the surface areas of the shot process latexes are in the range of 40–60 $Å^2$, which is close to the molecular area of the usual anionic soap,[16] except for two runs where the amount of the carboxylic monomer was reduced to ½ or increased to ³⁄₂ relative to that of the standard polymerization recipe. Consequently, we may conclude that the shot process latexes are stabilized mainly with surface carboxyl groups,

TABLE VII
Relationship between Degree of Neutralization of Surface Carboxyl Groups and
Freeze—Thaw Stability

Latex		Change in FTS[a] with DN[b]				
S-1068	DN	0.00	2.47	2.71	2.96	3.21
	FTS	C	C	A	A	A
S-1101	DN	0.38	1.05	1.56	1.73	1.89
	FTS	C	C	C	B	A
S-1106	DN	0.25	0.47	0.69	0.91	1.13
	FTS	C	C	C	A	A
S-1113	DN	0.20	0.38	0.57	0.75	0.93
	FTS	C	C	C	B	A
S-1258	DN	0.19	0.36	0.53	0.70	0.88
	FTS	C	C	B	A	A
S-1095	DN	0.19	0.35	0.52	0.68	0.85
	FTS	C	C	A	A	A
S-1107	DN	0.20	0.39	0.57	0.75	0.93
	FTS	C	C	C	A	A
S-1100	DN	0.13	0.37	0.60	0.84	1.08
	FTS	C	A	A	A	A
S-1102	DN	0.22	0.41	0.60	0.79	0.99
	FTS	C	C	C	A	A

[a] Freeze—thaw stability: A = no change; B = partially coagulated; C = coagulated.
[b] Degree of neutralization of surface carboxyl groups.

whereas the initial-charge process latexes are stabilized with both surface carboxyl groups and physically adsorbed soaps.

The number of the surface carboxyl groups chemically bound to a particle is in the range of 10^4–10^5 for all latexes in Table VI. Because of the uncertainty of the calculation, however, a detailed discussion is difficult.

Freeze–Thaw Stability of Latexes

On the basis of the fact that both type of latexes have approximately the same particle diameter and total solids content, whereas surface areas occupied by a surface carboxyl group differ from each other severalfold, these latexes may be interesting samples to study the effect of surface carboxyl groups on freeze–thaw stability.

The change of the freeze–thaw stability of these latexes with neutralization of surface carboxyl groups was examined. The results are shown in Table VII, where the degree of neutralization of surface carboxyl groups was calculated on the assumption that sodium hydroxide is not occluded in the interior of particles. It is apparent from Tables VI and VII that shot process latexes with the surface area occupied by a surface carboxyl group ranging from 30 to 60 $Å^2$ show a remarkable increase in the freeze–thaw stability with increase in the degree of neutralization of surface carboxyl groups in a fairly narrow range. In this transition range, an almost linear relationship between the degree of neutralization of surface carboxyl groups and the surface area occupied by a surface carboxyl group is observed, as shown in Figure 4. In general, since poly(carboxylic acid) has a rather small dissociation constant,[14] its degree of dissociation will approximately be identical with the degree of neutralization,[17] and this may also be the case with surface carboxyl groups. Consequently, the almost linear relationship in Figure 4 suggests that the
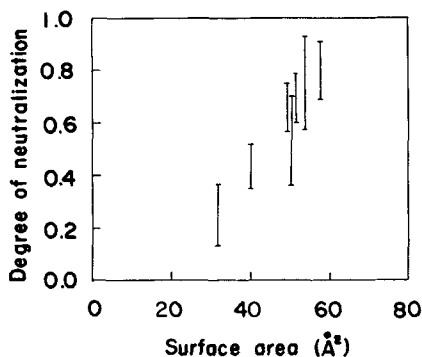
Fig. 4. Relationship between degree of neutralization of surface carboxyl groups and surface area occupied by a surface carboxyl group in the transition range of the freeze–thaw stability.

freeze–thaw stability is substantially determined by the density of carboxylate ion on the surface of particles. On the other hand, latexes S-1101 and S-1068, with the surface area occupied by a surface carboxyl group broader than 100 Å^2, show an increase in the freeze–thaw stability at a degree of neutralization of higher than 1. This may be attributed, as reported by Muroi et al.,[9] to the swelling of surface layer of particles composed of carboxylated polymers which will increase the density of surface carboxylate ion. Further, the shot process latexes S-1113 and S-1107, which were prepared with different amounts of soaps and have a nearly identical surface area occupied by a surface carboxyl group, show substantially the same relationship between degree of neutralization of surface carboxyl groups and freeze–thaw stability. This suggests that physically adsorbed soaps do not appreciably contribute to freeze–thaw stability.

References

1. S. Muroi, *Kogyo Kagaku Zasshi*, **68**, 1796 (1965).
2. S. Muroi and J. Nomura, *Kogyo Kagaku Zasshi*, **68**, 1800 (1965).
3. G. L. Meier (to Dow Chemical Co.), U.S. Pat., 3,575,913 (1971).
4. D. C. Blackley, *High Polymer Latices*, Maclaren, London, 1966, pp. 294–295.
5. H. Hoechst, Japan. Kokai, 71-5,641 (1971).
6. T. Matsumoto and M. Shimada, *Kobunshi Kagaku*, **22**, 172 (1965).
7. S. Muroi and K. Hosoi, *Kobunshi Kagaku*, **26**, 424 (1969).
8. H. J. van den Hul and J. W. Vanderhoff, *J. Colloid Interfac. Sci.*, **28**, 336 (1968).
9. S. Muroi, *J. Appl. Polym. Sci.*, **10**, 713 (1966).
10. H. J. van den Hul and J. W. Vanderhoff, *Brit. Polym. J.*, **2**, 121 (1970).
11. B. W. Greene, *J. Colloid Interfac. Sci.*, **43**, 449 (1973).
12. J. Hen, *J. Colloid Interfac. Sci.*, **49**, 425 (1974).
13. G. D. McCann, E. B. Bradford, H. J. van den Hul, and J. W. Vanderhoff, *J. Colloid Interfac. Sci.*, **36**, 159 (1971).
14. H. Morawetz, *Macromolecules in Solution*, Interscience, New York, 1965, pp. 348–356.
15. K. Furusawa, W. Norde, and J. Lyklema, *Kolloid-Z. Z. Polym.*, **250**, 908 (1972).
16. J. W. Vanderhoff and H. J. van den Hul, *J. Macromol. Sci. Chem.*, **7**, 677 (1973).
17. H. Freiser and Q. Fernando, *Ionic Equilibria in Analytical Chemistry*, Wiley, New York, 1963.