Separation of Water-Soluble Polymer from Emulsion by Gel Filtration

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Synopsis

The separation of poly(acrylic acid) from its mixtures with polystyrene emulsion by gel filtration, without destroying the state of dispersion, was undertaken. It was found that the poly(acrylic acid) not absorbed on the polymer surface is almost completely separated by gel filtration, if the ionic strength in this emulsion is not so high. Furthermore, the gel filtration study revealed that poly(acrylic acid) molecules are not adsorbed on the polymer surface saturated with surfactant molecules, whereas poly(acrylic acid) molecules, when already adsorbed on the polymer surface, are not easily desorbed by adding another surfactant.

INTRODUCTION

Emulsion polymers are often carboxylated (copolymerization of an unsaturated acid monomer) for a number of purposes, such as imparting mechanical and freeze-thaw stability[1-4] or reactivity.[5-7] In the course of emulsion copolymerization of an unsaturated acid monomer, a small quantity of water-soluble polymer is an inevitable by-product.[8] Consequently, the study of the carboxylated polymer emulsion requires an experimentally complicated procedure to eliminate possible influences of the water-soluble polymer formed in the system. For this reason, a method of separating the water-soluble polymer from the carboxylated polymer emulsion without destroying its dispersion state would contribute to rapid progress of study in this field. Therefore, the separation of water-soluble polymer contained in an emulsion by gel filtration was undertaken.

Inasmuch as any direct approach to the separation of the water-soluble polymer from the carboxylated polymer emulsion seems to be difficult, the present work deals with the separation of poly(acrylic acid) (PAA) from its mixture with polystyrene (PSt) emulsion. As gel filtration is based on the principle of the filtration effect, the separability is believed to depend to a large extent on the degree C_a to which the polymer surface is covered with the surfactant being used. From this standpoint, the separability was studied principally in its connection with the type of surfactant and the degree of surface coverage. Furthermore, based on

experimental results obtained, the state of PAA adsorption on the polymer surface and the desorption behavior due to adding a surfactant were discussed.

EXPERIMENTAL

Materials

Styrene monomer was supplied by Asahi-Dow, Ltd. Acrylic acid monomer was reagent grade material. Both monomers were subjected to the usual purification. Emulgen 915 is an ethoxylated nonylphenol with 15 units of ethylene oxide, supplied as a 100% solid by Kao-Atlas Chemicals, and used as received. Monogen LH is a sodium lauryl sulfate, supplied as a 60% paste by Dai-Ichi Kogyo Seiyaku Co., Ltd. and, before use, purified by extraction with methanol and evaporation of the extract to remove a small quantity of salt impurity. Potassium persulfate and dodecyl mercaptan both of reagent grade were used as initiator and transfer agent, respectively.

Polymerization

The PSt emulsions were prepared in the same manner as described in the previous paper,[8] 100 g. of styrene monomer, 4 g. of Monogen LH or 4 g. of Emulgen 915, 0.3 g. of potassium persulfate, and 417 g. of distilled water being used. The average particle diameter under an electron microscope was 0.05 μ for the anionic and 0.50 μ for the non-ionic emulsion particles. The emulsions obtained were dialyzed in a cellophane tube for as long as 1 week. Despite this dialysis treatment, however, traces of an acidic substance (approximately 10^{-3} g.-equiv. based on the polymer) remained. The concentration of the emulsions was controlled at 17% of the polymer solid. After these treatments, appropriate quantities of the respective surfactants used in the emulsion preparation were added to the emulsions so as to regulate the coverage degree (C_a) at various levels.

Solutions of PAA were prepared in an aqueous solution at pH 2 with the use of 100 g. of the acrylic acid monomer, and an amount of potassium persulfate (0.5 — 5.0 g.) and dodecyl mercaptan (0–1.0 g.) sufficient to regulate the molecular weight to a desired level, and 900 g. of distilled water. The polymerization was carried out at 80°C. for 7 hr. The aqueous PAA solutions obtained were dialyzed in the same manner as the PSt emulsions and then subjected to gel filtration to eliminate polymer fractions with extremely high molecular weights. When determined by the method described in the literature,[9] the average molecular weights of the purified PAA were found to be 4×10^4 for PAA-1, 1.2×10^5 for PAA-2, and 3.6×10^5 for PAA-3. Since the PAA solutions were to be diluted during the treatment, they were condensed in advance to 10% before use.

TABLE I
Compositions of 8-g. Samples for Separation Study

Sample no.	PSt emulsion				PAA		Distilled water, mg.	Stability
	Type	C_a, %	Amount of polymer, mg.	Amount of surfactant, mg.	Type	Amount of PAA, mg.		
I[a]	Anionic	41	994.2	39.8	PAA-1	31.0	6935.0	Poor
II		52	944.2	39.8		31.0	6935.0	Poor
III		80	994.2	61.7		31.0	6913.1	Good
IV		100	994.2	77.1		31.0	6897.7	Good
V		150	994.2	115.7		31.0	6859.1	Good
VI		52	994.2	39.8		62.0	6904.0	Good
VII		52	994.2	39.8		93.0	6873.0	Good
VIII[a]		41	994.2	39.8	PAA-2	31.0	6877.7	Good
IX[a]		41	994.2	39.8	PAA-3	31.0	6846.7	Phase separation
X	Non-ionic	Unsaturated	994.2	39.8	PAA-1	31.0	6935.0	Good
XI		Saturated	994.2	115.7		31.0	6859.1	Good

[a] Polymer emulsion is different from that in the other samples in preparation batch.

Preparation of Samples for Separation Study

A PSt emulsion and an aqueous PAA solution were mixed in the desired proportion and left to stand at room temperature for more than 48 hr. The compositions of the samples (each of 8 g. in size) are summarized in Table I. Samples I and II containing particles with very low C_a values were so unstable as to coagulate in a few days after the preparation. Sample IX, containing high molecular PAA-3, underwent phase separation on standing. The same samples were prepared again, and gave the same results.

Determination of Degree of Coverage of Polymer Surface

The C_a values of surfactants were determined by the soap titration method.[10]   In the calculation of C_a, the free surfactant in an aqueous phase at the critical micelle concentration (CMC) was corrected by using the literature value,[11] on assumption that electrolytes had already been removed completely from the system.

A distinct inflection point appeared at the CMC, on titration curves of the anionic emulsions with an aqueous Monogen LH solution, while it was very slight on the curves for the non-ionic emulsions with an aqueous Emulgen 915 solution.   Consequently, no C_a values could be obtained for the non-ionic emulsions, but their coverage states were designated as unsaturated or saturated.

Gel Filtration Method

The gel filtration was conducted by using a column made of Pyrex glass, measuring 25 mm. in inner diameter and 400 mm. in length and filled with swollen spherical gels to a height of 350 mm.   The bed volume was approximately 177 ml.   The column and the Sephadex G-200 gel were obtained from Pharmacia Fine Chemicals.   The treatment and use of Sephadex were in accordance with the directions given by the supplier.   The exclusion limit of Sephadex G-200 was 2×10^5 in molecular weight.

Each 8 g. sample was eluted descendingly with distilled water at room temperature, and the effluent was divided into 10 g. portions and dispensed into a fraction collector.   Approximately 180 ml. of the eluant was required for an 8 g. sample.   The elution rate, though it depended considerably upon the nature of the samples, was in the range of 10–20 ml./hr.   In general the elution rate was higher for the non-ionic emulsions than for the anionic ones.   The rate fell appreciably when the band of the emulsion reached the bottom of the column.   During the treatment no change was observed in dispersion state of the emulsion.

The solid matter in each fraction was determined gravimetrically and the PAA was determined conductometrically.   Filtration and the determination were carried out in duplicate on some samples, and good reproducibility was confirmed.

RESULTS AND DISCUSSION

Influence of Type and Concentration of Surfactant on Separability

Samples I–V were subjected to gel filtration. In all the samples, the emulsion was completely eluted out to the seventh fraction. Both recoveries of the total solids determined gravimetrically and the PAA determined conductometrically agreed with the theoretical values. The elution curves obtained are given in Figuré 1, in which the elution curve of sample I is omitted because of its closé resemblance to that of sample II. The shapes of the elution curves were preliminarily determined not to be affected by standing of the samples.

Two peaks are observed on the elution curves of the solid matter as well as on those of the acid value. In the case of emulsions with the unsaturated particles, the two types of peaks are satisfactorily in agreement. In the emulsions with the saturated particles, however, these
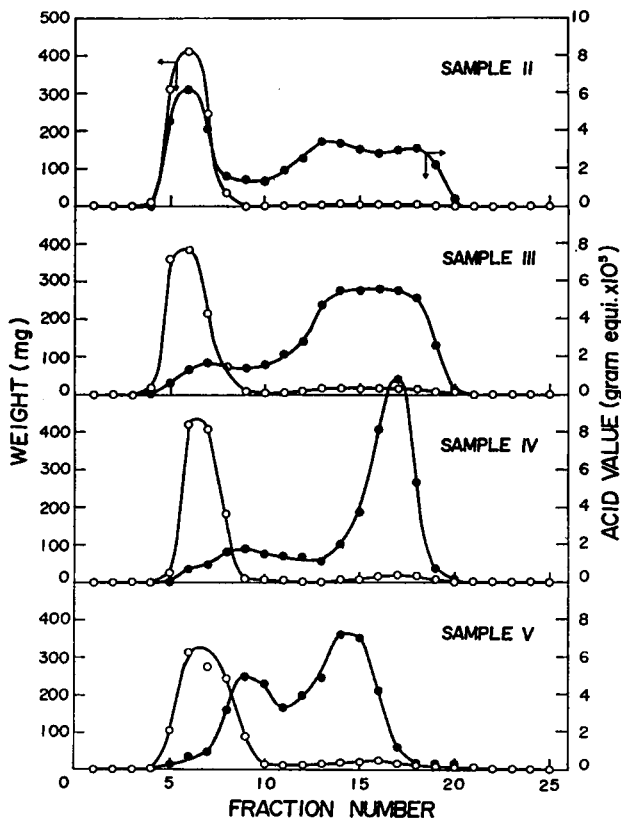

Fig. 1.   Elution curves of mixtures of PAA-1 with PSt emulsions covered with anionic surfactant at various levels: sample II, 52%; sample III, 80%; sample IV, 100%; sample V, 150%.

peaks did not agree in position. The positions of the first peak of the solid matter and the second peak of the acid value are affected little by the variables of the emulsion for all the samples except for sample V. The former position is characteristic for the polymer particles and the latter for PAA-1.

The appearance of the first peak in the acid value is concluded to have been caused by the adsorption of PAA molecules on the polymer surface; the area under the first peak (substantially corresponding to the quantity of PAA eluted together with the emulsion) decreases gradually with increasing C_a value of the emulsion up to saturation, beyond which it increases.
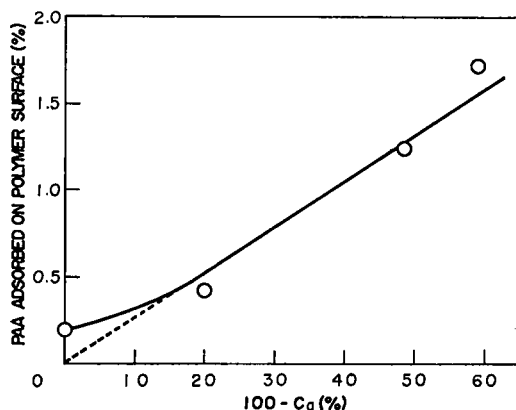

Fig. 2. Quantity of PAA adsorbed on polymer surface vs. unoccupied surface area.

The discrepancy in position between the two types of first peaks becomes gradually more notable with increasing concentration of the anionic surfactant, probably owing to an increase in ionic strength of the emulsions. This is supported by the fact that, as mentioned below, the position of the acid value is not changed by an increase in the concentration of the non-ionic surfactant for the non-ionic emulsions (Fig. 3). The position of the second peak of the acid value for sample V is shifted to smaller fraction number compared to those for the other samples, also owing to the increase in ionic strength

For Samples I–IV, the positions of the two types of second peaks and the ratios of the area under the respective second peaks are in fairly good agreement, but this is not so for sample V. This may be attributed to formation of micelles.

Figure 2 gives the relationship between the area of the polymer surface not covered by the anionic surfactant and the quantity of PAA eluted together with the emulsion. All the PAA eluted with the emulsion cannot be attributed to adsorption of the PAA molecules on the polymer surface, because, if one plots the percentages of the PAA in the solid matter against the fraction numbers, the values are not constant but

rise with the increasing fraction number. However, for the samples having C_a values below 100%, the rates of increase in the percentage of the PAA are so small that one may not be greatly mistaken in concluding that substantially all the PAA eluted together with the emulsion has resulted from the adsorption on the polymer surface. On the other hand, inasmuch as the samples are diluted during the gel filtration, the C_a may naturally be reduced. With the principle of gel filtration in mind, however, one may readily conclude that substantially no free PAA will be adsorbed, through dilution, on the polymer surface, of which coverage is impaired by the action of the surfactant.
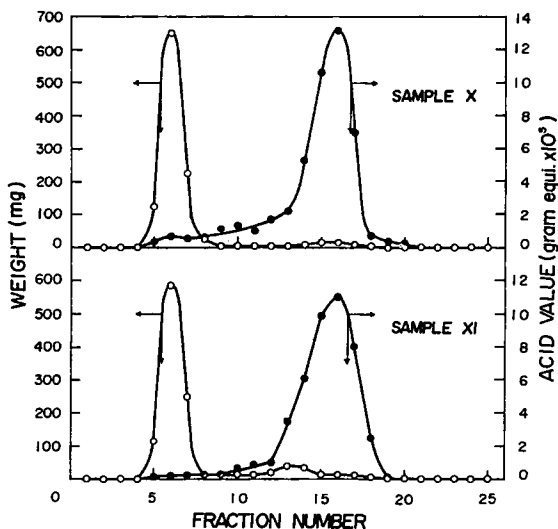

Fig. 3. Elution curves of mixtures of PAA-1 with PSt emulsions covered with non-ionic surfactant at various levels: sample X, unsaturated; sample XI, saturated.

Plots of the unsaturated emulsions are substantially on a straight line passing through the origin, whereas that of the saturated emulsion deviates considerably from it. This fact suggests that increasing ionic strength will cause the separability to decrease. The area occupied by a carboxyl group is calculated from the slope of the line in Figure 2 to be 33 A.², the value of which closely approximates that of a soap of a straight-chain molecule. On the other hand, it is known[12] that a unit of acrylic acid has a cross-sectional area of 28 A.². These facts suggest that PAA molecules are adsorbed on the polymer surface in a stretched configration.

Figure 3 shows the elution curves of the non-ionic emulsion. The shapes of the peaks are considerably sharper than those of the anionic emulsions. All the peaks except for the second peak of the solid matter of sample XI are seen approximately at the same positions as on the curves in Figure 1. Beyond the saturation, the second peak of the solid matter shifted to smaller fraction number. This fact suggests that a

non-ionic surfactant forms larger micelles than an anionic one. Also
in this case, the complete separation of the PAA is impossible even beyond
the saturation, a very small amount of PAA being eluted together with
the emulsion.

As already shown in Figures 1 and 3, the majority of the emulsion
is contained in two or three fractions. Therefore, by cutting the frac-
tions containing less emulsion polymer before and after the peak, one can
get much better separation. In sample XI, for example, when only
the sixth and seventh fractions were picked up, one could get an emulsion
of 4.2% solid matter, which contains $4.2 \times 10^{-5}\%$ PAA based on the
polymer. The recovery of the emulsion polymer is approximately 84%
in this case. Furthermore, when this separated emulsion was again
subjected to gel filtration and the fractions before and after the peak were
cut as well, there was obtained an emulsion of 1.3% solid matter which
contained a trace of PAA (ca. $8.5 \times 10^{-6}\%$). The recovery was approx-
imately 61% with respect to the original sample.

Influence of Concentration and Molecular Weight of Poly(acrylic Acid)

Samples VI and VII were subjected to gel filtration, and the quantity
of PAA adsorbed on the polymer surface (PAA eluted together with
emulsion) was plotted against PAA added to the polymer. The result
is shown in Figure 4. The quantity of PAA adsorbed is found to increase
slightly in proportion to the quantity added. This fact shows that the
respective quantities of two types of adsorptive substances (PAA and
surfactant) adsorbed on a polymer surface may have some bearing upon
their concentrations present freely in an aqueous phase.

Subsequently, an experiment was carried out to determine the possible
effect of molecular weight of PAA on the quantity to be adsorbed on the
polymer surface; it was found that the molecular weight has no influence
whatever on the separability. The quantity of the PAA adsorbed on the
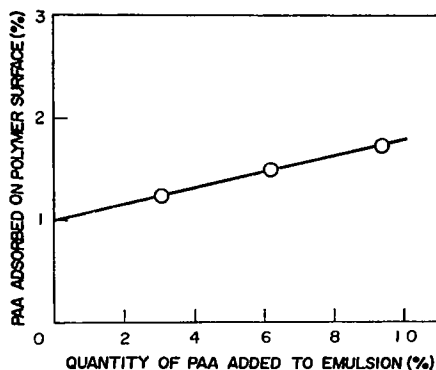

Fig. 4. Quantity of PAA adsorbed on polymer surface vs. its concentration in emulsion.

polymer surface was 1.72% based on the polymer in sample VIII (the average molecular weight of PAA-2 is 1.2×10^5) while that for sample I was 1.73% (the molecular weight of PAA-1 is 4×10^4). Though the effect of the molecular weight beyond the exclusion limit was a matter of interest, it could not be clarified because of the phase separation of sample IX as already mentioned.

The difference between the elution curves of sample I and sample VIII was that the second peak of the acid value for the latter shifted to smaller fraction number. Obviously, this was in correspondence to difference in molecular weight of PAA for the two runs.

Desorption of Poly(acrylic Acid) by Surfactant

In the course of emulsion copolymerization of an unsaturated acid monomer, water-soluble polymer is formed outside the polymer particles, which are partially covered with the surfactant, and it is adsorbed on the unoccupied polymer surface. For this reason, it may be impossible to accomplish the separation of water-soluble polymer from a carboxylated polymer emulsion in the same manner as described so far.
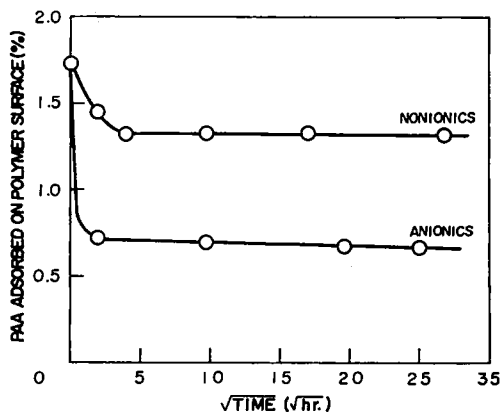

Fig. 5. Desorption behavior of PAA adsorbed on polymer surface on adding another surfactant.

To determine this, Monogen LH and Emulgen 915, each as 10% aqueous solution, were added to sample I in quantities sufficient to saturate the polymer surface in place of the PAA, and changes in the quantity of the PAA adsorbed on the polymer surface were determined at appropriate intervals. The quantity of the PAA adsorbed began to decrease rapidly within 4 hr. but the rate of decrease slowed down shortly thereafter, as shown in Figure 5. With respect to the desorption of PAA, the anionic surfactant and the non-ionic one were similar in tendency but different greatly in degree of desorption.

These two types of the emulsions, prepared by adding Monogen LH and Emulgen 915 to Sample I corresponded in composition to samples

IV and XI, respectively, but the quantities of the PAA adsorbed were quite different. From the fact that the adsorbed PAA is desorbed on addition of another surfactant, it is obvious that a surfactant is adsorbed more strongly on the polymer surface than PAA. However, the exchange of adsorbed PAA with surfactant occurred with marked difficulty compared to the exchange of an adsorbed surfactant with another one.[13,14] This may be attributed to the fact that PAA has high molecularity and consequently more adsorptive points and, at the same time, smaller diffusion rate than a non-ionic surfactant.

On the basis of the results obtained here, it may be concluded that PAA already adsorbed on the polymer surface is not desorbed completely by addition of a surfactant and that, as a result, it is impossible to accomplish a complete separation of PAA by gel filtration. In the case of the emulsion prepared with a non-ionic surfactant, however, the emulsion particles formed are generally much larger, and therefore are covered far more satisfactorily with the surfactant than those prepared with an anionic surfactant. For this reason, one can expect much better separation for a carboxylated polymer emulsion prepared with a non-ionic surfactant.

CONCLUSION

PAA contained in PSt emulsion, if it is free in the aqueous phase without being adsorbed on the polymer surface, is capable of being almost completely separated by gel filtration without destroying the dispersion state of the emulsion. When the polymer surface is not covered completely with surfactant molecules, PAA is eluted together with the emulsion adsorbed on the polymer particles. PAA molecules may be adsorbed in a rather stretched configuration on the polymer surface not covered with surfactant molecules. The quantity of PAA adsorbed on the polymer surface depends on the concentration of the surfactant, which is proportional to the C_a value, as well as that of PAA. Inasmuch as the adsorptive tendency of PAA is lower than that of a surfactant, the PAA adsorbed on the polymer surface is desorbed when another surfactant is added. In this case, however, even if a surfactant is added in a quantity sufficient to cover the polymer surface in place of PAA, a considerable quantity of PAA will remain adsorbed after having been allowed to stand at rest for a very long time. An anionic surfactant desorbs a larger quantity of PAA than a non-ionic one.

In a case where a water-soluble polymer is to be separated from carboxylated polymer emulsion, one obtains easier separation from a non-ionic emulsion than from an anionic one, since the particles of the former are covered with the surfactant more densely and, moreover, the increase in the quantity of the surfactant to be added has no effect on the separability of the gels.

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Résumé

On tentait de séparer par la gel-filtration l'acide polyacrylique de la mélange d'acide polyacrylique et d'émulsion polystyrolénique sans ruiner l'état de dispersion. On trouvait, ensuite, que l'acide polyacrylique qui n'était pas adsorbé à la surface de polymère peut être séparé presque entièrement au moyen de la gel-filtration pourvu que l'intensité d'ion se trouve pas si très haute. Par ailleurs, l'expérimentation sur cette gel-filtration a démontré que la molécule d'acide acrylique n'est pas adsorbée à la surface du polymère saturé des molécules de l'agent tensioactif, tandis que l'acide polyacrylique adsorbé à la surface polymérique n'est pas facilement désorbé par l'addition des molécules de l'agent tensioactif.

Zusammenfassung

Die Absonderung der Polyakrylsäure von deren Gemischen mit Polystyrolemulsion mittels der Gel-Filtrierung wurde vorgenommen, ohne dabei den Dispersionszustand zu zerstören. Es wurde festgestellt, dass die Polyakrylsäure, die auf der Polymeroberfläche nicht adsorbiert ist, durch die Gel-Filtrierung beinahe völlig absonderbar ist, vorausgesetzt, dass die Ionentiter (Ionenstärke) der Emulsion nicht so hoch ist. Ferner lief die Gel-Filtrierungsuntersuchung darauf hinaus, dass während die Polyakrylsäurenmoleküle auf der mit den Molekülen von kapillaraktiven Mitteln gesättigten Polymeroberfläche nicht mehr adsorbiert wurden, wogegen die Polyakrylsäurenmoleküle, die schon einmal auf der Polymeroberfläche adsorbiert waren, nicht mehr desorbiert werden konnten, auch wenn zu dieser Oberfläche hinterher die Moleküle von kapillaraktiven Mitteln hinzugefügt wurden.