Alkali Solubility of Carboxylated Polymer Emulsions

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Synopsis

The solubility of carboxylated polymer emulsions in an aqueous alkaline solution was studied. The alkali solubility was shown to depend on the degree of carboxylation, the hydrophilic nature of the noncarboxylic main components, the degree of polymerization, the glass transition temperature, the chain configuration, and the dissolution temperature. Emulsions of the copolymer containing acrylic acid units showed considerably different dissolution behavior from those containing methacrylic acid units, possibly owing to the difference in the distribution state of carboxylic units inside the particle. It is deduced that methacrylic acid units are distributed more homogeneously inside the particle than acrylic acid units.

INTRODUCTION

Some factors governing the solubility of carboxylated polymer emulsions in an aqueous alkaline solution have already been dealt with previously in a series of studies on these emulsions.[1,2] They include the concentration and type of carboxylic units incorporated for the carboxylation, the hydrophilic nature of the noncarboxylic main component, which is predictable from the value of the cohesive energy density (C.E.D.) of its homopolymer, and the dissolution temperature. In addition, the alkali solubility is judged to be related also to the chain configuration of the polymer, from the fact that carboxylated poly(methyl methacrylate) emulsion shows far lower solubility even at elevated temperature than is predicted from its hydrophilic nature and dissolution temperature.[2] Furthermore, the degree of polymerization and the glass transition temperature (T_g) of an emulsion polymer may be regarded as additional factors.

These factors are related to the alkali solubility in so complicated a manner that no definite relationship among them has yet been established. For this reason, in the present work we made an effort to deal with effects of these factors on the alkali solubility quantitatively as far as possible to establish a clear relationship between the factors and the alkali solubility.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and ethyl methacrylate (EMA) were supplied by Mitsubishi Rayon Co., Ltd., ethyl acrylate (EA) by Toa

Chemical Industry Co., Ltd., and styrene (St) by Asahi-Dow Ltd.   Acrylic acid (AA) and methacrylic acid (MAA) were reagent grade materials.   All these monomeric materials were used after purification by usual methods. Newrex C-1 was a relatively salt-free sodium dodecylbenzene sulfonate, supplied as a 73% paste by Nippon Oil and Fats Co., Ltd. Levenol WZ was a sodium sulfate of an adduct of nonylphenol with 20 units of ethylene oxide, supplied as a 25% aqueous solution by Kao-Atlas Chemicals. Emulgen 913 and 920 were adducts of nonylphenol with 13 and 20 units of ethylene oxide, respectively, supplied as 100% solids by Kao-Atlas Chemicals.   These surfactants were used as received.   Reagent grade ammonium persulfate and dodecyl mercaptan were used as initiator and chain transfer agent.   The aqueous sodium hydroxide solution was analytical grade.

Preparation of Emulsions

All the carboxylated polymer emulsions used as samples were prepared in the same manner as mentioned in the previous paper[1] with the use of 100 parts of monomeric materials, four parts of surfactant mixture of Emulgen 913 and Levenol WZ (3.2:0.8) or Emulgen 920 and Newrex C-1 (2:2), 0.3 part of potassium persulfate, 0.2 part of dodecyl mercaptan and distilled water of a quantity sufficient to regulate the monomer concentration in a range of 10–20% (the monomer concentration depended upon stability of polymerization system).   The reactions were continued until total solids content agreed within 2% with the theoretical value for 100% conversion. Though some quantity of water-soluble polymer was formed in the course of the emulsion polymerization, the emulsions obtained were subjected to experiment without further treatment to remove the water-soluble polymer, because its quantity was negligibly small.[1]

Measurement of Alkali Solubility

The dissolution behavior of a carboxylated polymer emulsion in an aqueous alkaline solution was followed by the measurement of optical density.   Between the optical density D of a diluted emulsion and the volume of the polymer particle V in it, there is the relation given by eq. (1) which combines Rayleigh's law of scattering and Lambert's law, when the optical density was measured by a cell of 1 cm. optical path:

$$D = A_R[(n^2 - n_0^2)/(n^2 + 2n_0^2)]^2 N V^2 \qquad (1)$$

where

$$A_R = 24\pi^3 n_0^4/2.303\lambda^4$$

N is the number of particles in a unit volume of the emulsion, n and n_0 are the refractive indices of the polymer and dispersion medium, respectively, and λ is the wavelength of the incident light in vacuum (610 mμ in the present work).   This equation is valid only when no selective absorption of

light occurs and the particle diameter is well below 0.1 λ. Equation (1) is now employed conveniently and widely when the relative size of particles is the only question.[3]

When the pH of a carboxylated polymer emulsion was kept on the alkaline side, the polymer particles were dissolved from the surface layer to smaller ones, as previously reported.[1] Assuming that V_{org} and V_{alk} designate the original volume of a polymer particle and the volume of the one partially dissolved in alkali, respectively, and D_{org} and D_{alk} the respective optical densities of the emulsions containing the corresponding particles, then per cent alkali solubility χ is obtained as follows:

$$\chi(\%) = 100[1 - (V_{alk}/V_{org})] = 100[1 - (D_{alk}/D_{org})^{1/2}] \qquad (2)$$

The undissolved cores of the particles appeared to swell appreciably in alkali.[1] In eq. (2), however, the effect of swelling on optical density is ignored. Thus, we examined the effect of swelling on optical density, assuming that each particle swells homogeneously and its refractive index decreases in proportion to the volume fraction of water absorbed; it was found that the swelling of the particle has little effect on the optical density: the term of V^2 increases rapidly but the term $[(n^2 - n_0^2)/(n^2 + 2n_0^2)]^2$ decreases sharply with increasing quantity of water absorbed, and consequently the product of the two terms shows substantially no change. This result is supported also by the examination of Debye's equation.[4] Furthermore, the change in value of n_0 due to the addition of aqueous alkaline solution (aqueous NaOH in the present work) is negligible because the change of concentration is very small. These considerations justify us in concluding that eq. (2) gives a value fairly close to the true one.

The changes in optical density of an emulsion due to changes in pH were determined as follows. An emulsion was diluted with distilled water to 0.1% solids content, and 1000 ml. of the diluted emulsion was placed in a 2000-ml. flask provided with a stirrer, glass electrodes connected to an HM-5A type pH meter made by Toa Dempa Kogyo Co., Ltd., a thermometer, and a buret. The diluted emulsion was heated to 20°C. ± 0.5°C. on a water bath. Aqueous 0.1N NaOH was added dropwise from the buret at a rate of 1 ml. every 2 min. into the emulsion, which was stirred at 250 rpm. One minute after each addition of the aqueous NaOH, a part of the emulsion was removed into a quartz cell, 10 mm. square, and immediately the optical density was measured by using a photometric colorimeter (Shimazu Seisakusho, Model 5D). The emulsion sample was again returned to the flask after the measurement. In this measurement, each emulsion sample was diluted during addition of the aqueous NaOH, and hence the values of optical density obtained were corrected by employing Beer's law. The optical density behavior against pH was more or less affected by the rate of addition of aqueous NaOH. As long as the measurement was conducted under the same conditions, however, the reproducibility of the behavior was excellent. The full measurement of the optical density behavior took approximately 50 min.

When only the alkali solubility was to be obtained, the measurement of optical density of emulsion was conducted by the same procedure as already mentioned, except that aqueous NaOH was added dropwise, with stirring, in advance in a quantity sufficient to bring the emulsion to pH 11 at 20°C. In all the samples, the optical density leveled off well before the pH had reached a value appreciably lower than this value.

The alkali solubility was affected by the stirring condition and the length of time the added aqueous NaOH was allowed to stand and not by the manner of its addition. Some of the samples, after addition, with stirring, of sufficient aqueous NaOH to bring them to pH 11 at 20°C., were allowed to stand without further stirring to determine the relationship between solubility and time. The results are shown in Figure 1. The alkali solubility increases for 3–6 hr. and then reaches saturation. The difference between the alkali solubility obtained 50 min. after addition of aqueous NaOH and that obtained upon saturation varies to a large extent, depending upon the solubility of the samples. The samples with medium solubility show the largest time dependence. In all the samples, when they were left to stand with stirring, the solubility was lower by approximately 5% at elevated temperature 80°C. than without stirring. On the other hand, it was preliminarily confirmed that poly(ethyl acrylate) emulsion particles were hydrolyzed by 5.30 mole-% with stirring at 80°C. for 24 hr. and by 1.67 mole-% without stirring, and poly(methyl methacrylate) emulsion particles by 0.63 and 0.52 mole-%, respectively. Stirring appears to affect both the hydrolysis and coagulation of the emulsion system. With these conditions taken into consideration, the alkali solubility was determined after allowing each emulsion, subsequent to dropwise addition of aqueous NaOH with stirring, to stand at rest for 24 hr. without being stirred and to reach equilibrium solubility. It must be noted, however, that the real degree of carboxylation of the emulsion polymer differs to some extent from the calculated one when the solubility is determined at elevated temperature.
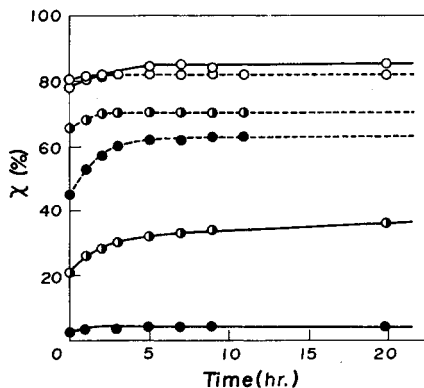

Fig. 1. Time dependence of alkali solubility: (O) EA/AA, 90/10; (◑) MMA/EA/AA, 54/36/10; (●) MMA/EA/AA, 81/9/10; (———) at 20°C.; (- -) at 80°C.

Measurement of Degree of Polymerization

The degrees of polymerization of emulsion polymers were determined as the occasion demanded. A polymer emulsion was dried for approximately 24 hr. on a level glass plate and then for about 24 hr. in a vacuum oven at 50°C. The polymer film thus obtained was dissolved in acetone. The intrinsic viscosity was determined with an Ostwald viscometer. The degree of polymerization P was determined by the equation:[5]

$$[\eta] = 4.19 \times 10^{-3}\bar{P}^{0.66} \tag{3}$$

RESULTS

Effect of Glass Transition Temperature and Hydrophilic Nature of Carboxylated Polymer and Dissolution Temperature

Effects of T_g and the hydrophilic nature of the carboxylated emulsion polymers as well as dissolution temperature on the alkali solubility were quantitatively studied. For this purpose, different series of copolymer emulsions with compositions such as MMA–EA–AA, MMA–EA–MAA, EMA–EA–AA and St–EA–AA, were chosen as samples, in which the ratios of the noncarboxylic units were varied and the carboxylic units were kept at a constant level (10 mole-%). They were prepared with the surfactant mixture of Emulgen 913 and Levenol WZ. Of the above series, the MMA–EA–AA and MMA–EA–MAA series should show little change in hydrophilic nature even if the ratio of MMA and EA units was changed, because
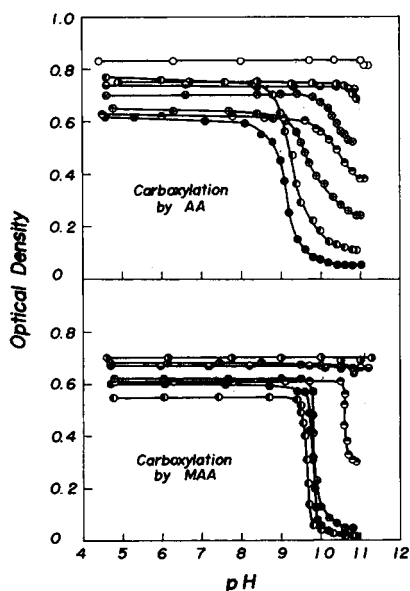

Fig. 2. Optical density vs. pH of carboxylated (10 mole-%) MMA–EA copolymer emulsions (at 20°C.): (O) MMA/EA = 100/0; (◖) 90/10; (◗) 80/20; (⊗) 70/30; (◉) 60/40; (⊕) 40/60; (◐) 20/80; (●) 0/100.

homopolymers of these units have strikingly similar C.E.D. values (88.4 cal./cc. for PEA and 89.3 cal./cc. for PMMA). The EMA–EA–AA series was chosen for the reason that the EMA unit has a chemical structure similar to that of the MMA unit but its homopolymer has a quite different C.E.D. value (80.1 cal./cc. for PEMA). The St–EA–AA series was chosen because of the markedly different chemical structure of St units from other monomeric units.

Carboxylated polymer emulsions, even at a constant carboxylation degree, show different dissolution behaviors, depending on the type of carboxylic units incorporated, as shown in Figure 2. The optical density variation with pH given in Figure 2 was measured at 20°C. for the MMA–EA–AA and MMA–EA–MAA copolymer emulsion series. Although the optical densities given in Figure 2 do not represent values in equilibrium, one may not make any serious mistake in discussing the dissolution behavior of the carboxylated polymer emulsion based on the optical density behavior with pH, even if the time dependence of solubility previously described is taken into account. The emulsions of the copolymer containing MAA units dissolve more sharply at higher pH than those containing AA units. In both series, the solubility increases rapidly with increasing content of EA units.

Subsequently, the χ value was determined at different dissolution temperatures and plotted against the ratio of MMA and EA units, as shown in Figure 3. The diagram shows that the alkali solubility increases rapidly with an increase in the ratio of EA units beyond a certain value. This
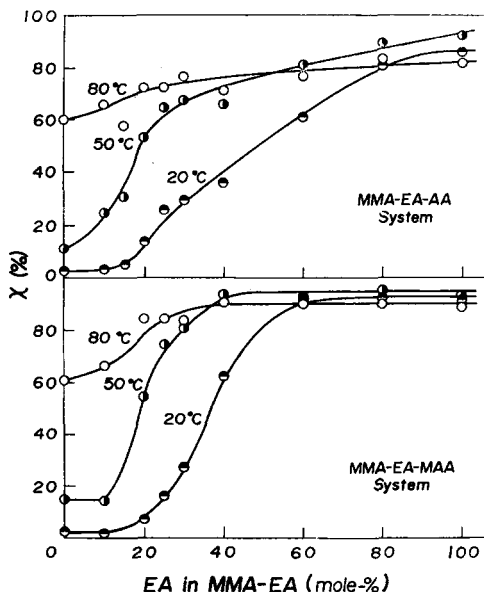

Fig. 3. Alkali solubility vs. MMA/EA ratio of carboxylated MMA–EA copolymer emulsions (10 mole-% carboxylation).

inflection in the ratio of EA units is sharper and higher in the carboxylated polymer emulsion with MAA units than that with AA units at the same dissolution temperature. This inflection shifts to a lower value as the dissolution temperature is elevated. In both series, the emulsions of copolymers rich in EA units, i.e., relatively soft copolymer emulsions, behave somewhat irregularly at 80°C. This tendency is not restricted only to these copolymer emulsion series, but observed generally in other copolymer emulsion series as will be described later. This phenomenon might be explained by inferring that the emulsion particles coagulated on standing at 80°C. for as long as 24 hr. Since poly(ethyl acrylate) emulsion retained its optical density substantially unchanged after standing under the same conditions, however, no clear reason can be given for this phenomenon.

The values of χ were plotted as the function of $\Delta T_{d,g}(T_d - T_g)$ in Figure 4, where T_d denotes dissolution temperature. The values of T_g were determined by calculation.[7,8] The diagram shows that the χ value is expressed only as a function of $\Delta T_{d,g}$, nearly regardless of the copolymerization compositions. Below T_g, especially, the χ value increases virtually in proportion to $\Delta T_{d,g}$.

Figure 5 shows the relationship of the χ value to the ratio of EMA and EA units as observed in the EMA–EA–AA copolymer emulsion series. The curves in the diagram have approximately the same shapes as those for MMA–EA–AA series, but the inflection beyond which the alkali solubility increases rapidly is more obscure for the EMA–EA–AA series.
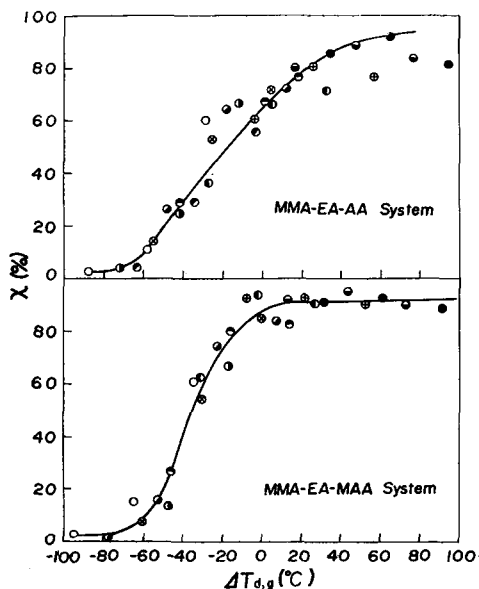

Fig. 4. Alkali solubility vs. $\Delta T_{d,g}$ of carboxylated (10 mole-%) MMA–EA copolymer emulsions: (O) MMA/EA = 100/0; (◐) 90/10; (◕) 85/15; (⊗) 80/20; (◑) 75/25; (◓) 70/30; (◖) 60/40; (⊕) 40/60; (◒) 20/80; (●) 0/100.
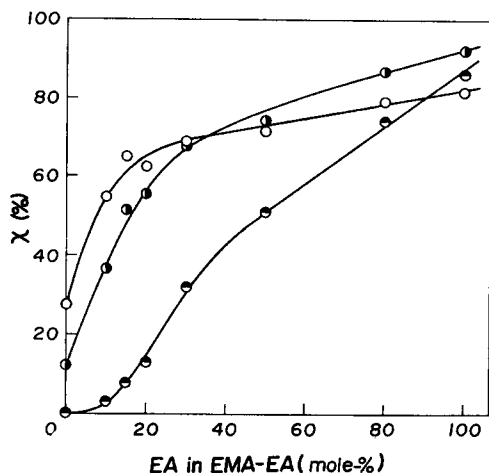
Fig. 5. Alkali solubility vs. EMA/EA ratio in EMA–EA–AA system (10 mole-% AA).

It may be predicted that, when two types of noncarboxylic units whose homopolymers have different C.E.D. values are combined, the χ value will not be expressed as a simple function of $\Delta T_{d,g}$ as in the case of carboxylated MMA–EA copolymer emulsions. Figure 6 verifies this assumption. The value of χ at a given $\Delta T_{d,g}$ increases with increasing ratio of the units whose homopolymer has a higher C.E.D. value, such as EA units in the emulsion copolymer. This shows that a rise in the hydrophilic nature of an emulsion polymer results in an increase in the alkali solubility. Also in this case the χ values at the dissolution temperature of 80°C. are lower than those at 50°C. for the emulsions of copolymer rich in the EA units.
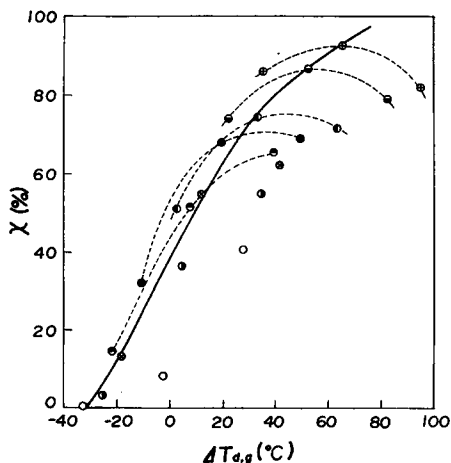

Fig. 6. Alkali solubility vs. $\Delta T_{d,g}$ of EMA–EA–AA system (10 mole-% AA); (O) EMA/EA = 100/0; (◑) 90/10; (◓) 85/15; (⊗) 80/20; (●) 70/30; (◐) 50/50; (◒) 20/80; (⊕) 0/100.
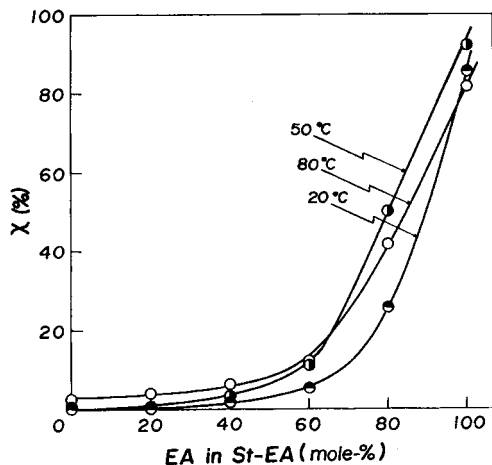
Fig. 7. Alkali solubility vs. St/EA ratio in St–EA–AA system (10 mole-% AA).

Carboxylated St–EA copolymer emulsions showed the lowest alkali solubility of the four series, as shown in Figure 7. However, the hydrophilic nature of this series of emulsion copolymers predictable from the C.E.D. value (82.8 cal./cc. for PSt) was appreciably higher than that of EMA–EA–AA copolymers for the same level of EA and AA units. This result indicates that alkali solubility can not be predicted only from the C.E.D. value of the homopolymers as determined for the respective monomeric units in the copolymers, if their chemical structures are markedly different. The shape of the curves in Figure 7 is much different from that for the methacrylate series. The value of χ against $\Delta T_{d,g}$ is given in Figure 8.
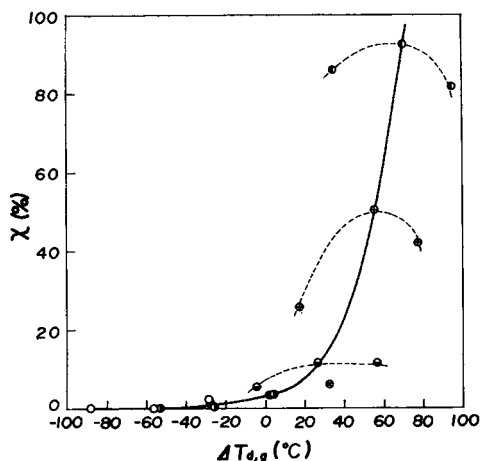

Fig. 8. Alkali solubility vs. $\Delta T_{d,g}$ of St–EA–AA system (10 mole-% AA): (O) St/EA = 100/0; (◑) 80/20; (⊗) 60/40; (◒) 40/60; (◐) 20/80; (◉) 0/100.
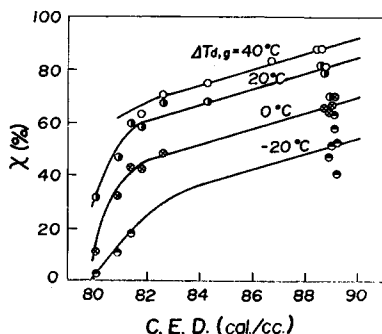
Fig. 9. Relationship between alkali solubility of carboxylated polymer emulsion and value of C.E.D. of polymers from their noncarboxylic units in the MMA–EA–AA and EMA–AA–AA systems (10 mole-% AA).

To establish a well-defined relationship between the hydrophilic nature of an emulsion polymer and alkali solubility, the χ values were plotted against C.E.D. values of the homopolymers and copolymers as determined from the noncarboxylic units in MMA–EA–AA and EMA–EA–AA systems, as shown in Figure 9. The values of C.E.D. for the copolymers were calculated simply from those for the homopolymers on the basis of additivity from the copolymerization composition. Inasmuch as the carboxylation degree is constant (10 mole-%) in this experiment, the variation in hydrophilic nature of the emulsion polymer should depend only on that of the noncarboxylic components.

In Figure 9, the χ value increases abruptly and then approximately linearly with the calculated C.E.D. value at a constant $\Delta T_{d,g}$, although some plotted points deviate appreciably from the lines.

Effect of Degree of Carboxylation

Inasmuch as the rise in carboxylation degree improves the hydrophilic nature of emulsion polymer but simultaneously elevates its T_g value,[8] it was considered of interest to study how the alkali solubility would be affected by a change in copolymerization compositions of MMA–AA and MMA–MAA copolymer emulsions prepared with a Emulgen 920–Newrex C-1 surfactant mixture. Figure 10 shows the dissolution behavior at 20°C.

The dissolution behavior varies in some different ways with the increasing degree of carboxylation in the MMA–AA and MMA–MAA series. In the former series, the dissolution tendency on the acidic side and the dissolution degree on the alkaline side become more marked and the pH value at which the carboxylated polymer emulsion dissolves sharply falls gradually with increasing degree of carboxylation, while in the latter series, little change occurs on the acidic side, and the degree of pH shift is much smaller. However, no marked difference was noted between the two series as regards the tendency of alkali solubility being improved with the increasing carboxylation degree.
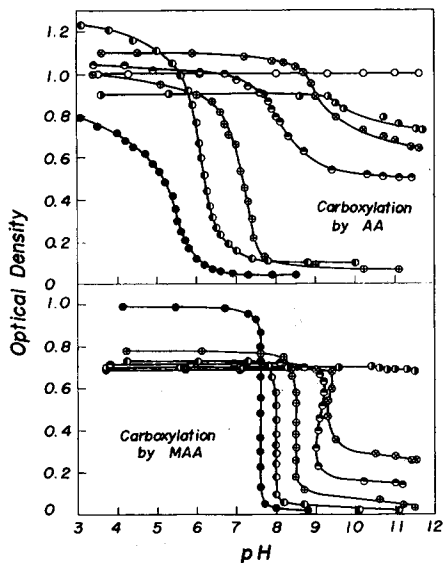
Fig. 10. Optical density vs. pH of carboxylated MMA polymer emulsion at different degrees of carboxylation (20°C.): (O) 10 mole-%; (◑) 15 mole-%; (⊗) 20 mole-%; (◐) 25 mole-%; (⊕) 30 mole-%; (◖) 40 mole-%; (●) 50 mole-%.

The values of χ are plotted against the concentration of the carboxylic units in Figure 11. No change is seen in the alkali solubility below 10 mole-% carboxylation in either the MMA–AA or MMA–MAA copolymer emulsion series. Beyond these carboxylation degrees, the solubility rises almost linearly with the increasing degree of carboxylation, but the rate of rise eases off gradually beyond approximately 30 mole-%. At low degrees of carboxylation, AA units contribute more effectively to the alkali solubility than the MAA units, but beyond 15 mole-%, this relation is reversed. A small difference between the χ values of the carboxylated (at 10 mole-%) MMA copolymer emulsions in Figure 11 and those in Figure 3 reveals that the surfactant used for the preparation of carboxylated polymer emulsion may have some effect on the alkali solubility.

Figure 12 shows the χ value against the degree of carboxylation for the EA–AA and EA–MAA copolymer emulsion series. Unlike the MMA copolymer emulsion series, the solubility of EA copolymer emulsion series increases rapidly from the start, with increasing degree of carboxylation. Also in this case, AA units are more effective in enhancing alkali solubility to an emulsion than MAA units.

On the other hand, copolymerization of St units with the carboxylic units failed to give sufficiently high conversion; hence no accurate data on the alkali solubility were obtained. The study of these emulsions, however, showed that carboxylated PSt emulsions showed an extremely low solubility compared to the other copolymer emulsions. For example, only 3–4% St–AA (50:50 in monomer mixture) copolymer emulsion converted to approximately 90% could be dissolved, even at 80°C.
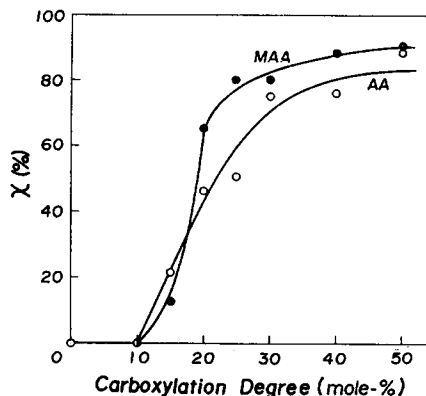
Fig. 11. Relationship between alkali solubility and degree of carboxylation of carboxylated MMA polymer emulsions (20°C.).

Effect of Degree of Polymerization

The work carried out so far ignored the effect of the degree of polymerization of the emulsion polymer. However, inasmuch as all the polymer emulsions were prepared by the same polymerization recipe (except for surfactants) and procedure, one may be justified in regarding their polymerization degrees to be nearly equal.

It seems reasonable for one to conclude that the polymerization degree naturally has some effect on the alkali solubility, if one remembers that solubility of a polymer is generally improved gradually with the decreasing polymerization degree. The alkali solubility of the two series of EA–AA (95:5) and EA–AA (90:10) copolymer emulsions with different degrees of polymerization, prepared with the surfactant mixture of Emulgen 913 and Levenol WZ, was therefore measured at 20°C. The degree of
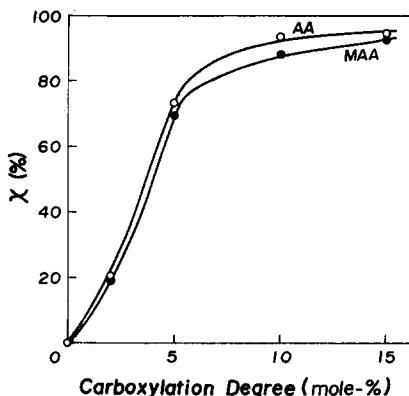

Fig. 12. Relationship between alkali solubility and degree of carboxylation of carboxylated EA polymer emulsions (20°C.).
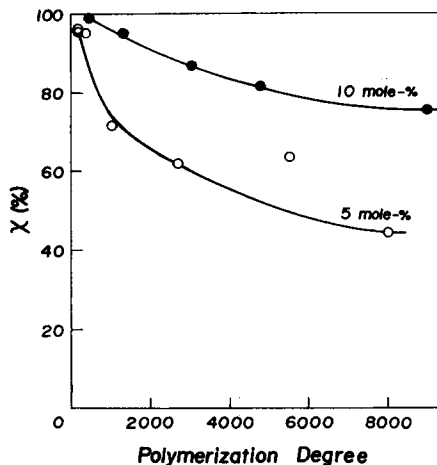
Fig. 13. Relationship between alkali solubility and degree of polymerization of EA–AA copolymer emulsions (20°C.).

polymerization was controlled by varying the amount of dodecyl mercaptan in the polymerization recipe.

Figure 13 shows that the alkali solubility decreases gradually with increasing degree of polymerization. The effect of the degree of polymerization is far more marked for the emulsions of copolymers with lower degrees of carboxylation.

DISCUSSION

The results obtained in the present work pose several problems requiring special discussion here: the one is the distribution of carboxyl groups within the emulsion particle and its influence on the alkali solubility, and the other is the meaning of the inflection beyond which the alkali solubility increases rapidly and which is characteristic for the alkali-solubility curves, especially for methacrylate copolymer emulsions.

As previously reported, unsaturated carboxylic units appear to be concentrated in the surface layers of emulsion particles during the emulsion polymerization process, the thickness of these layers depending upon the type and quantity of carboxylic units taking part in the carboxylation. The most plausible picture of such concentration phenomenon is one in which, as can be expected from the chemical structure similar to that of a surfactant of carboxylic units, carboxylic units are solubilized in palisade layers of surfactant micelles in the same way as an alcohol[10] at the initial stage of polymerization and, at a later stage (after disappearance of micelles), they are supplied to the polymer particles formed in such a way that they are co-adsorbed with surfactant molecules on the polymer particles. Decreasing the hydrophilic nature of carboxylic units may allow them to diffuse more deeply into the interior of the particle and consequently the

surface layer in which they are concentrated will increase in thickness. Observation of this phenomenon has also been reported by other investigators.[11,12]   MAA units are less hydrophilic than AA, as is predictable from their chemical structure, and hence the former units may form rather a thick surface layer in which the units are distributed relatively homogeneously, whereas the latter units form a surface layer in which their concentration decreases sharply from the surface inwardly.

Owing to such difference in the tendency of concentration in the surface layers between AA and MAA units, the carboxylated polymer emulsions with MAA units might show a different dissolution behavior from those with AA units.   As shown in Figures 2 and 9, the former emulsions are less soluble in acid and more easily soluble in alkali than the latter, and they show lower solubility at low degrees of carboxylation, as shown in Figure 11.

The observation that even highly carboxylated polymer particles were not dissolved perfectly in an aqueous alkaline solution suggests that their cores were left with an extremely low carboxylic unit concentration or in a state containing no carboxylic unit at all.   Furthermore, the following observation reported in a previous paper[13] lends some support to this concept.   When a film cast from the solution mixture of the carboxylated PEA prepared by emulsion polymerization with hexabis(methoxy methyl)-melamine was cured and extracted by ethyl acetate, a polymer containing no carboxyl groups was found in the extract.

No direct knowledge about the dependence of distribution state of carboxylic units inside particles on polymer composition has been acquired by the present work.   However, in view of the observation that the alkali solubility depended only on $\Delta T_{d,g}$ and had no bearing on the composition of both the series of MMA–EA–AA and MMA–EA–MAA copolymer emulsions (Fig. 3), it seems reasonable to conclude that the distribution state of the carboxylic units is not affected by the composition, at least in these cases.

The influence of degree of polymerization on the alkali solubility may be similarly explained by the heterogeneity of the distribution of carboxyl groups inside particles, i.e., a reduction in the degree of polymerization causes the carboxylated polymer to dissolve more easily in an aqueous alkaline solution.   Therefore, the lower the polymerization degree, the less will just soluble polymer molecules contain carboxyl groups and, consequently, the more deeply will the dissolution progress toward the center of the particles.   This concept is supported by the following observation on electron microscopy of an EA–AA (95:5) copolymer emulsion.   The lower the degree of polymerization, the more markedly the particles are swollen at alkaline pH and the smaller they become on reacidification. This tendency is nearly equivalent to that observed in the case of increasing degree of carboxylation, as already reported.[1]

The inflection seen on the curves in Figures 3 and 9 may be attributed to the destruction of the folding configuration of PMMA due to the incorpora-

tion of another type of monomeric unit. Tobolsky et al.[14] have pointed out, as a result of the measurement of folding energy ranging in value from −350 to −700 cal./mole, that almost all polymethacrylates are found to have folding configurations and that the folding energy of butyl methacrylate–butyl acrylate copolymer decreases to zero in a fairly narrow range of 10–30 mole-% of butyl acrylate units. Thus, the folding configuration changes to Gaussian distribution chains in this range. On the basis of this result, the rapid improvement in the alkali solubility of carboxylated MMA copolymer emulsions beyond the inflection can be easily interpreted by inferring that below the inflection, the alkali solubility may be obstructed considerably by fairly high folding energy. This concept is also supported by the results of the observation of x-ray diffraction fringes. Though the diffraction fringe of carboxylated (at 10 mole-%) PMMA has two halos corresponding to lattice constants of 4 and 8 A., respectively, the former halo disappears upon incorporation of 20–40 mole-% of EA units. A similar phenomenon should be observed in EMA copolymer emulsions, but no such distinct inflection as observed in MMA copolymer emulsions is seen, as evident from Figure 5. On the other hand, St copolymers are judged to behave in a completely different way from methacrylate copolymers, as they gave quite different curves of alkali solubility versus composition, as is apparent from Figures 3, 5, and 7.

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Résumé

La solubilité d'émulsions polymériques carboxylées dans une solution aqueuse alkaline a été étudiée. La solubilité en milieu alealin a été démontrée dépendre principalement du degré de carboxylation, de la nature hydrophile des composants principaux noncarboxylés, du degré de polymérisation, de la température de transition vitreuse, de la configuration de la chaîne, de la température de transition vitreuse, de la configuration de la chaîne, de la température de dissolution. Les émulsions de copolymères contenant des unités d'acide acrylique montraient des comportement de dissolution considérablement différents de ceux contenant des unités méthacryliques, peut-être par suite de différences de distribution d'état des unités carboxliques au sein de la particule. On en conclut que les unités d'acide méthacrylique sont réparties de fason plus homogène au sein des particules que les unités acryliques.

Zusammenfassung

Die Löslichkeit der carboxylierten Polymeremulsionen in einer wässrigen alkalischen Lösung wurde untersucht. Die Alkalilöslichkeit hängt hauptsächlich vom Carboxylierungsgrad, von der hydrophilen Natur der nicht-carboxylischen Hauptkomponenten, dem Polymerisationsgrad der Glasumwandlungstemperatur, der Kettenkonfiguration und der Lösungstemperatur ab. Die Emulsionen von Copolymeren mit Acrylsäurebausteinen zeigten ein von denjenigen mit Methacrylsäurebausteinen sehr verschiedenes Löslichkeitsverhalten, möglicherweise wegen des Unterschiedes im Verteilungszustand der Carbonsäurebausteine im Teilchen. Es wird daraus geschlossen, dass Methacrylsäurebausteine im Teilchen homogener verteilt sind als Acrylsäurebausteine.