Water-Dispersible Graft Copolymer Mixtures Prepared by Electron Irradiation. II. Dispersion Behavior

SHIGENORI EGUSA, TAKASHI SASAKI, and MIYUKI HAGIWARA, *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma 370-12, Japan*

Synopsis

Highly viscous systems made up of 70 wt% epoxy resin dissolved in 30 wt% monomer mixture of styrene and acrylic monomers were irradiated with 1.5 MeV electrons to initiate graft copolymerization. The obtained product of graft copolymer mixture was fed into a mixed solvent of n-butanol and cyclohexanone, and was heated 2 h at 70°C to form a predispersion. Then aqueous solution of 2-dimethylaminoethanol or ethanol was added to the predispersion, thus giving a stable dispersion in water or in ethanol. The particle diameter of the aqueous and ethanol dispersions is practically the same, thus suggesting that polymer particles are virtually generated during the predispersing procedure, and at this step the size of the particles is actually determined. The particle diameter increases inversely proportional to the polymer concentration in the predispersion. Furthermore, the particle diameter shows a tendency to decrease with an increase in the hydrophilicity of monomers used in the graft copolymerization. The stopped-flow measurement, on the other hand, reveals a characteristic pH dependence of the dispersion stability to the addition of NaCl. This result is interpreted based on a particle model consisting of a particle core of epoxy resin and its surrounding layer of acrylic copolymer.

INTRODUCTION

In a previous article of this series,[1] we reported a work on the electron-beam-initiated graft copolymerization of highly viscous systems composed of 70 wt% epoxy resin dissolved in 30 wt% monomer mixtures of acrylic acid and styrene. The work has shown that the polymerization reaction takes place both during and after the electron-beam exposure of about 5 sec duration, and lasts as long as 50 sec when the beam current is low. It was also shown that a certain amount of epoxy-acrylic graft copolymer is present in the obtained products, together with ungrafted epoxy resin and ungrafted acrylic copolymer of acrylic acid and styrene. Although not strictly quantitative, the content of such a graft copolymer was shown to have a tendency to increase with an increase in the electron-beam current.

In the present work, the graft copolymerization of highly viscous systems of epoxy resin dissolved in monomers was carried out for monomer mixtures consisting of methacrylic acid (MAAc), acrylic acid (AAc), styrene (St), ethyl acrylate (EA), methyl methacrylate (MMA), and 2-hydroxyethyl methacrylate (HEMA). The obtained products of graft copolymer mixtures were characterized with regard to the molecular weight distribution of ungrafted acrylic copolymer and the content of epoxy-acrylic graft copolymer. Then, the

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TABLE I
Monomer Composition, Molecular Weights of Acrylic Copolymer (M_n^2, M_w^2),
and Fraction of Grafted Epoxy (f)

Monomer composition[a] (wt%)	Electron-beam current (mA)	Number of exposures	Monomer conversion[b] (%)	Acrylic copolymer		
				M_n^2	M_w^2	f(%)
A: MAAc(12)/St(18)	0.6	12	97.2	2.2×10^4	3.0×10^5	3.4
	2.0	6	100.0	2.5×10^4	1.6×10^5	5.6
	6.0	3	99.2	1.7×10^4	7.4×10^4	8.1
	18.0	2	98.1	1.1×10^4	4.7×10^4	10.5
B: MAAc(12)/St(9)/MMA(9)	0.6	8	99.5	2.2×10^4	2.9×10^5	3.9
	2.0	4	93.9	1.6×10^4	2.8×10^5	3.6
	6.0	2	100.0	2.1×10^4	1.1×10^5	5.4
	12.0	1	99.6	2.0×10^4	8.9×10^4	7.9
	18.0	1	100.0	1.2×10^4	4.4×10^4	9.5
C: MAAc(12)/St(9)/EA(9)	0.6	8	98.7	2.1×10^4	2.5×10^5	3.2
	2.0	6	99.0	1.3×10^4	1.1×10^5	4.7
	18.0	2	98.3	7.9×10^3	3.6×10^4	13.9
D: MAAc(12)/St(9)/HEMA(9)	0.6	8	98.4	—	—	—
	2.0	4	100.0	2.1×10^4	2.9×10^5	5.5
	6.0	2	100.0	1.4×10^4	1.5×10^5	6.2
	18.0	1	100.0	1.9×10^4	7.1×10^4	9.7
E: AAc(12)/St(18)	0.6	8	93.7	1.3×10^4	3.6×10^5	4.7
	2.0	4	98.6	1.9×10^4	2.7×10^5	4.9
	6.0	2	99.8	1.7×10^4	1.3×10^5	6.5
	18.0	1	93.7	1.6×10^4	1.2×10^5	8.2

[a] Polymerization formula: 70 wt% epoxy resin and 30 wt% monomer mixture. Electron energy: 1.5 MeV. Duration of each exposure: ca. 3 sec.
[b] Determined from a powder of the obtained solid product.

graft copolymer mixtures were dispersed in water by the procedure involving the neutralization with 2-dimethylaminoethanol. The present paper mainly describes the dispersion procedure of graft copolymer mixtures, the particle size of obtained dispersions, and the stability of dispersions to the addition of electrolytes. The dispersion mechanism is discussed based on the data of the particle size of dispersions.

EXPERIMENTAL

The chemicals used here, the polymerization procedures with 1.5 MeV electrons, and the characterization techniques of obtained products are described in the previous paper of this series.[1] Five kinds of monomer compositions shown in Table I were studied for the polymerization formula of 70 wt% epoxy resin (Epikoto 1009) and 30 wt% monomer mixture.

The particle size of obtained dispersions was determined by the stopped-flow method. In this method, the number of particles in a dispersion is first evaluated from the kinetic behavior of rapid coagulation, and then the particle size is calculated by dividing the solid content in the dispersion by the number of particles. The particle diameter determined by this method is

known empirically to be near the weight-average diameter when the particles are polydispersed. The details are described elsewhere.[2]

The stability of aqueous dispersions was evaluated from the coagulation behavior in the presence of 1.5 mol/L NaCl at various pH. The NaCl solution was buffered at a desired pH by using a mixture of citric acid, potassium phosphate (monobasic), boric acid, barbital, and sodium hydroxide. The stopped-flow apparatus and experimental procedures for the stability measurement were essentially the same as described previously,[3] except the present measurement was made at a wavelength of 752 nm.

RESULTS AND DISCUSSION

Characterization of Graft Copolymer Mixtures

The electron-beam irradiation of polymerization systems shown in Table I was carried out in exactly the same way as described in the previous paper of this series.[1] The obtained solid product was grounded to a powder by using a sample mill, and was dried under vacuum at room temperature so that unreacted monomers could be removed from the product. Then the conversion of monomers was determined from the powder, with the recognition that the conversion thus determined could be somewhat higher than the true conversion to be determined from the original solid product. The conversion determined from the powder is shown in Table I together with the number of repeated exposures.

The gel-permeation chromatography (GPC) measurement was performed according to the procedure described previously.[1] The obtained GPC data were analyzed in exactly the same way as described in the previous paper,[1] thus giving the number- and weight-average molecular weights of ungrafted acrylic copolymer, M_n^2 and M_w^2, and a rough estimate of the fraction of epoxy resin having a grafted branch. The results are shown in Table I. The log-log plot of the molecular weight vs. the electron-beam current reveals that the decrease in M_w^2 with increasing beam current is strikingly greater than that in M_n^2, thus implying that the molecular weight distribution of acrylic copolymer becomes less broad at a higher beam current. This is the case for all the polymerization formulas in Table I, including formula E which has been described in the previous paper of this series.[1] The fraction of epoxy resin having a grafted branch, on the other hand, is seen to have a tendency to increase with increasing beam current for all the formulas in Table I, including formula E. The beam current dependence of M_n^2, M_w^2, and the fraction of grafted epoxy, therefore, will be interpreted in a similar manner as discussed for the formula E in the previous paper.[1]

Dispersion Procedure and Particle Size

A powder of obtained solid product (usually 6 g) was fed into a mixed solvent (usually 6 mL) of n-butanol and cyclohexanone (usually 5 : 1 by volume), and was heated 2 h at 70°C to form a predispersion. To this predispersion, 1 N aqueous solution of 2-dimethylaminoethanol was added gradually with stirring up to 30% neutralization of carboxylic acid monomers used in the graft copolymerization. Deionized water (usually 94 mL) was then

added gradually with stirring, thus obtaining polymer particles dispersed in water.

An example of polymer particles thus obtained is shown by a scanning electron micrograph in Figure 1. This example is for a dispersion formed from the reaction product of the formula A exposed at a beam current of 18.0 mA. The polymer particles are seen to range in diameter from ca. 0.2 to ca. 0.5 μm. The particle size determination by the stopped-flow method gave the average diameter of 0.32 μm for this dispersion, thus showing the effectiveness of the stopped-flow method for the present work.

The influence of the mixed solvent composition of n-butanol and cyclohexanone on the particle size of the resulting dispersion was studied by using the reaction product of formula C exposed at a beam current of 18.0 mA. A predispersion containing 6 g of the reaction product in 6 mL of the mixed solvent of various compositions was formed according to the procedure described above. Then 94 mL of ethanol instead of the 2-dimethylaminoethanol aqueous solution was added gradually with stirring, thus obtaining polymer particles dispersed in ethanol. The particle diameter of the dispersion is plotted in Figure 2 as a function of the volume fraction of cyclohexanone in the mixed solvent. The particle size is seen to have a minimum at the volume fraction of 1/6. Based on this finding, subsequent operations of the predispersing procedure were performed by using the mixed solvent of n-butanol and cyclohexanone in the volume ratio of 5 : 1.

The influence of the polymer concentration in a predispersion on the particle size of the resulting dispersion was studied by using the reaction
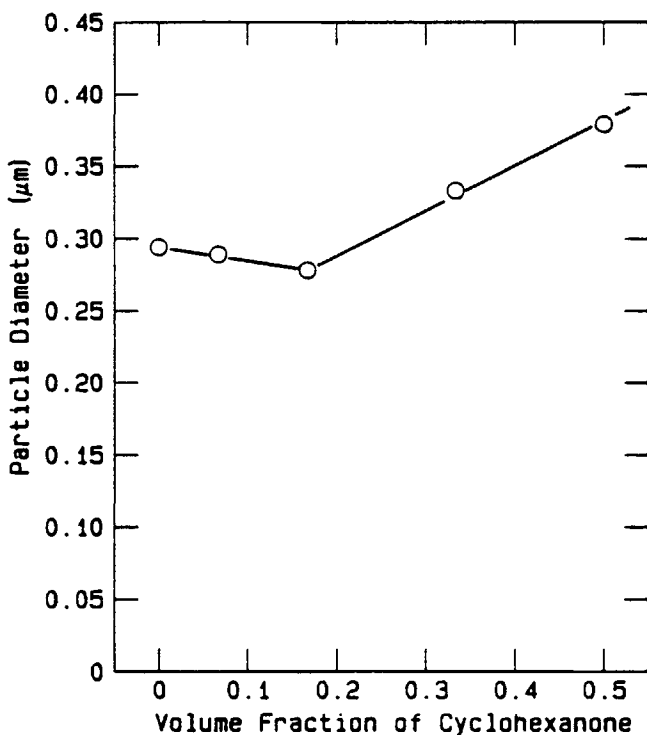
Fig. 2. Particle diameter of the dispersion in ethanol as a function of the volume fraction of cyclohexanone in a mixed solvent of n-butanol and cyclohexanone. This result is for the reaction product of formula C exposed at a beam current of 18.0 mA, and dispersed in ethanol.

product of the formula C exposed at a beam current of 18.0 mA. Predispersions containing 1–6 g of the reaction product in 6 mL of the n-butanol/cyclohexanone mixed solvent were formed in the same way as above. The predispersions were then treated either with ethanol or with 2-dimethylaminoethanol aqueous solution, thus obtaining polymer particles dispersed in ethanol or in water. The particle diameter is plotted in Figure 3 as a function of the reciprocal of the polymer concentration in the predispersion. It is seen that the particle diameter of the ethanol dispersion (○) increases inversely proportional to the polymer concentration. In addition, the particle diameter of the aqueous dispersion (●) is practically the same as that of the ethanol dispersion, especially for the polymer concentrations above 1/2 g/mL.

The identical particle diameter of the ethanol and aqueous dispersions strongly suggests that polymer particles are generated during the predispersing procedure, and at this step the size or the total number of the particles is actually determined. In fact, such particles are known to be generated in polymeric oil-in-oil emulsions (POO emulsions).[4] According to a mechanism proposed by Molau,[4] POO emulsions are formed as a result of phase separation of incompatible polymers dissolved in a common (mutual) solvent, and are stabilized by the emulsifying effect of graft or block copolymers made up of the incompatible polymers. For the predispersions
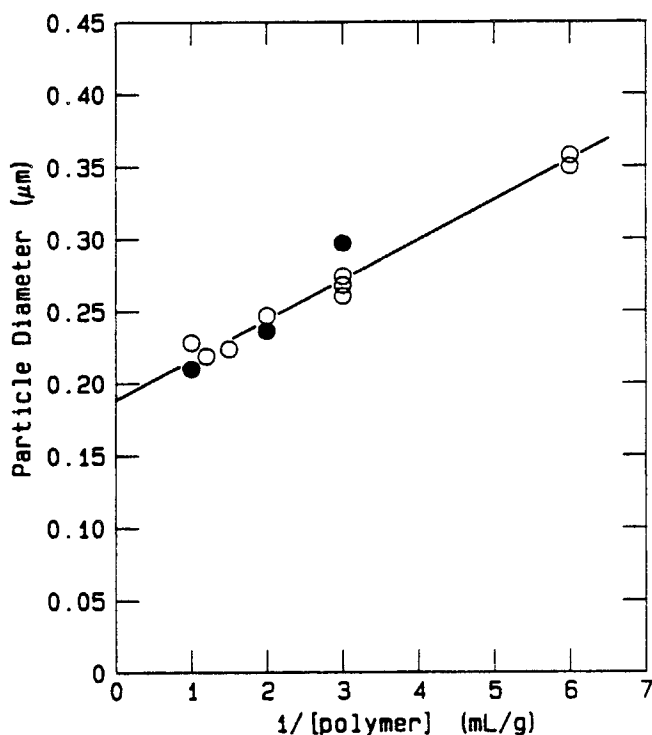
Fig. 3. Particle diameter of the dispersion in ethanol (○) or in water (●) as a function of the reciprocal of the polymer concentration in the predispersion. The graft copolymer mixture used here is the same as that in Figure 2.

prepared here, it is assumed that ungrafted epoxy resin and ungrafted acrylic copolymer form the disperse and continuous phases, respectively, with epoxy-acrylic graft copolymer accumulated at the boundary between the two phases. This assumption is based on the fact that the n-butanol/cyclohexanone mixture used here as a common solvent is a poor solvent for epoxy resin, and that a certain amount of epoxy-acrylic graft copolymer is present in the graft copolymer mixture obtained here (see Table I). When ethanol or aqueous alkali of 2-dimethylaminoethanol is added to these predispersions, the disperse phase of epoxy resin is expected to separate from one another without coagulation. This will be the case particularly for the addition of aqueous alkali, because the electrostatic repulsion arising from the dissociated carboxyl groups of epoxy-acrylic graft copolymer will aid the disperse phase to separate from one another. In fact, no aqueous dispersion is obtained when pure water in place of aqueous alkali is added to the predispersion.

According to the above-mentioned mechanism of polymer particle formation, the particle size of the disperse phase in the predispersion will be actually determined by the number of graft copolymers accumulated at the boundary between the disperse and continuous phases. Then, the particle diameter which increases inversely proportional to the polymer concentration in the predispersion (Fig. 3) suggests that the number of graft copolymers

accumulated at the phase boundary decreases with a decrease in the polymer concentration. This means that the graft copolymer can distribute itself not only at the phase boundary but also in the disperse and/or continuous phases in the predispersion. It is therefore expected that the particle size of the resulting dispersions in ethanol or in water depends not only on the amount of graft copolymer in the graft copolymer mixture but also on the distribution characteristics of the graft copolymer in the predispersion.

The influence of the monomer composition on the particle size of the resulting dispersion was studied by using the reaction products of the formulas A to E (Table I) exposed at a beam current of 6.0 mA. The formation procedures of a predispersion and its final dispersion were exactly the same as described for Figure 3. The particle diameter of the dispersion in ethanol is plotted in Figure 4 as a function of the reciprocal of the polymer concentration in the predispersion. It is seen that the particle diameter increases inversely proportional to the polymer concentration for all the polymerization formulas studied here. It is also seen that at each polymer concentration the particle diameter decreases in the order of the formula A > B > C > D ≈ E, although at 1 g/mL the order is not definite for the formulas C, D, and E. This result indicates that the number of polymer particles or the total area of the phase boundary in the predispersion increases in the order of the formula
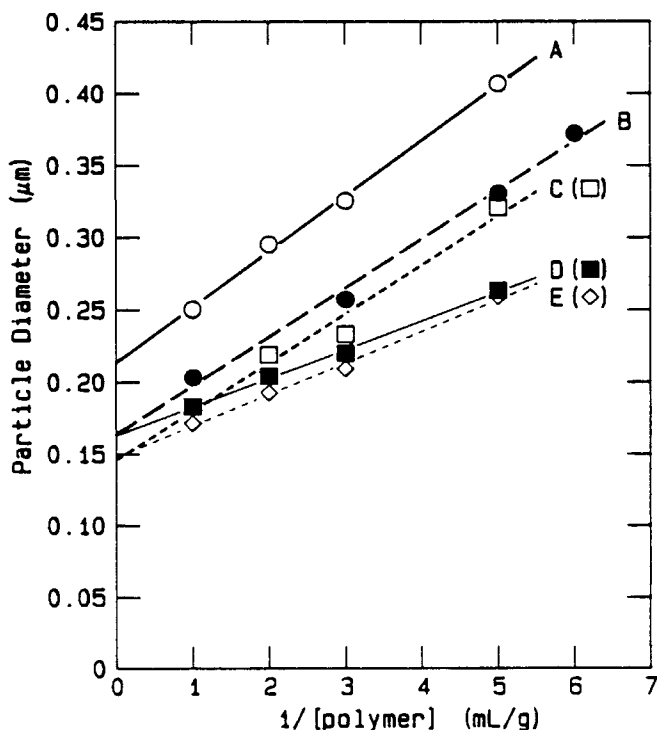

Fig. 4.   Particle diameter of the dispersion in ethanol as a function of the reciprocal of the polymer concentration in the predispersion. These results are for the reaction products of formulas A to E exposed at a beam current of 6.0 mA.

A < B < C < D ≈ E. This order appears to agree with that of hydrophilicity of monomers used in the present formulas (see Table I). An increase in the hydrophilicity of monomers will aid the resulting epoxy-acrylic graft copolymer to distribute itself at the phase boundary in the predispersion, thus leading to an increase in the number of polymer particles or to a decrease in the particle size. This effect due to the hydrophilicity of monomers seems to be mainly responsible for the observed dependence of the particle diameter on the monomer composition (Fig. 4). In fact, the amount of graft copolymer is only slightly dependent on the monomer composition, as is suggested from a comparison of the fraction of grafted epoxy for a beam current of 6.0 mA in Table I.

The influence of the electron-beam current on the particle size of the resulting dispersion was studied by using the reaction products of the formula B exposed at the beam currents of 0.6, 2.0, 6.0, and 18.0 mA. A predispersion and its final dispersion in ethanol were prepared in exactly the same way as described for Figure 3. The obtained plot of the particle diameter vs. the reciprocal of the polymer concentration in the predispersion was scarcely dependent on the beam current, and was actually identical with that shown in Figure 4 for formula B exposed at 6.0 mA. This result and the fraction of grafted epoxy which increases with an increase in the beam current (Table I) suggest that the particle diameter is determined not only by the amount of graft copolymer and the monomer composition of grafted branches but also by other factors such as the molecular weight distribution of grafted branches. The weight-average molecular weight of acrylic copolymer (Table I), in fact, decreases with an increase in the beam current, thus suggesting that the molecular weight of grafted branches is dependent on the electron-beam current. At the present time, however, no clear explanation can be offered to the particle size independent of the beam current. Further studies are therefore required for a detailed discussion of this point.

Dispersion Stability

The stability measurement by the stopped-flow method was performed to characterize polymer particles from the viewpoint of colloid chemistry. This study was made by using the reaction product of the formula C exposed at a beam current of 6.0 mA. The predispersion and the final dispersion in water were formed in exactly the same way as described for a dispersion in Figure 1. The obtained dispersion was diluted with deionized water to the solid content of 2.0%, and was stored at room temperature. The particle diameter was 0.18 μm when measured 2 days after the dispersion formation, and was almost unchanged even after the 8-months storage.

Equal volumes of the dispersion and a 3 mol/L NaCl solution were mixed rapidly, and the coagulation behavior was followed at a wavelength of 752 nm. Then, the stability ratio was evaluated from the ratio of the rate constant for rapid coagulation to that for doublet formation from two primary particles.[3,5] The stability ratio is plotted in Figure 5 as a function of the pH after the mixing. It is seen that the stability ratio in the pH region below ca. 5 is quite low in both the measurements made 2 days (o) and 8 months (●) after the dispersion formation. The stability ratio begins to increase with increasing pH

In this connection, it is worth noting that such a decrease in the stability in the high pH region is not observed for polymer particles having chemically bound acid groups on the particle surface (see Fig. 8 in Ref. 3). If, therefore, acrylic copolymer is bonded chemically on the surface of a particle obtained here, the dispersion stability will be increased in the high pH region for lack of the desorption of the acrylic copolymer. It is quite possible that the carboxyl group of acrylic copolymer reacts with the epoxide group of epoxy resin during a long-term storage, thus chemically binding the acrylic copolymer on the particle surface. In fact, the titration of dispersions obtained here showed that the amount of epoxide groups decreases slowly with the storage time,[6] thus strongly supporting the above speculation on the carboxyl/epoxide reaction. It is reasonable to conclude, therefore, that the increased stability after the 8-month storage is due to the acrylic copolymer which has been chemically bound on the particle surface during the storage.

CONCLUSIONS

The electron-beam irradiation of highly viscous systems of epoxy resin dissolved in monomers was carried out for monomer mixtures consisting of MAAc, AAc, St, EA, MMA, and HEMA. It was shown that the obtained product of graft copolymer mixture is dispersed in water or in ethanol through a predispersion in a mixed solvent of n-butanol and cyclohexanone. The particle diameter of the dispersion was found to increase inversely proportional to the polymer concentration in the predispersion. In addition, the particle diameter showed a tendency to decrease with an increase in the hydrophilicity of monomers used in the graft copolymerization.

The stopped-flow measurement of the dispersion stability to the addition of NaCl revealed that although the stability ratio is quite low in the pH region below ca. 5, the ratio begins to increase with increasing pH at ca. 5 and then begins to decrease at the pH of ca. 7. It was also revealed that the stability ratio in the pH region above ca. 6 increases strikingly after the 8-month storage. These findings were interpreted based on a particle model consisting of a particle core of epoxy resin and its surrounding layer of acrylic copolymer.

References

1. S. Egusa, T. Sasaki, and M. Hagiwara, *J. Appl. Polym. Sci.*, **34**, 2163 (1987).

2. S. Egusa, *J. Colloid Interface Sci.*, **86**, 135 (1982).

3. S. Egusa and K. Makuuchi, *J. Colloid Interface Sci.*, **79**, 350 (1981).

4. G. E. Molau, *J. Polym. Sci.*, **A3**, 1267 (1965); **A3**, 4235 (1965).

5. E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948, p. 164.

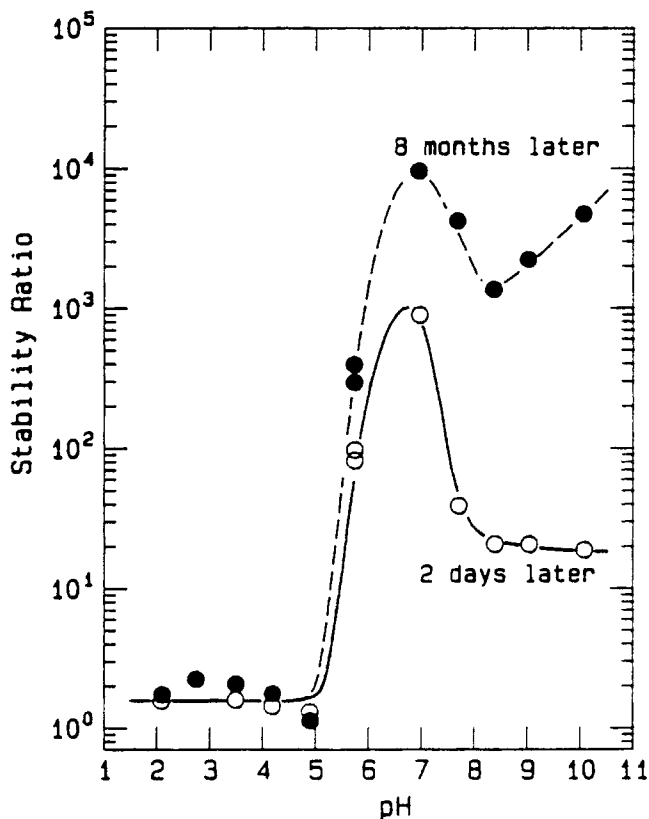6. F. Hosoi, Japan Atomic Energy Research Institute, private communication.

Fig. 5.   Stability ratio of the dispersion in water as a function of the pH after the addition of NaCl to a concentration of 1.5 mol/L: measured 2 days (○) and 8 months (●) after the dispersion formation. This result is for the reaction product of formula C exposed at a beam current of 6.0 mA.

at ca. 5, and then begins to decrease at the pH of ca. 7. It is also seen that the stability ratio measured after 8 months is strikingly higher than that measured after 2 days in the pH region above ca. 6.

These findings can be explained if we assume a particle model consisting of a particle core of epoxy resin and its surrounding layer of acrylic copolymer. According to this model, the improved stability in the pH region above ca. 5 is explained by the electrostatic repulsion[5] arising from the dissociated carboxyl groups of acrylic copolymer adsorbed on the particle surface. The stability maximum at the pH of ca. 7 and the decreasing stability with increasing pH, on the other hand, is explained by the competition between the dissociation of carboxyl groups and the desorption of acrylic copolymer from the particle surface into the water phase. The degree of dissociation of carboxyl groups increases with increasing pH, thus increasing the dispersion stability. At the same time, however, the electrostatic repulsion due to the dissociated groups and the increased solubility of acrylic copolymer at high pH will drive the acrylic copolymer into the water phase, thus decreasing the dispersion stability with increasing pH.