Synthesis of Starch-*graft*-Polyacrylonitrile Hydrolyzate and Its Characterization

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ABSTRACT: The graft copolymerization of three vinyl monomer species, acrylonitrile (AN), acrylamide (AAm), and acrylic acid (AA), onto starch was carried out with ceric salt (Ce salt) as an initiator. With 3 mmol/L Ce salt, the monomer activity onto starch decreased in the following order: AN > AAm > AA. Grafting efficiency with AN as the grafting monomer was greater than 90%, but with AA and AAm, it was less than 50%. Starch-*graft*-polyacrylonitrile was hydrolyzed to introduce amide and carboxyl groups into starch. The hydrolyzates were analyzed with infrared spectroscopy. The hydrolysis reaction was accelerated with increasing alkali concentration, reaction temperature, and time. The water absorbancy of the hydrolyzate increased with an increasing carboxyl molar fraction in the polymer, and it dissolved in water above a 0.6 molar fraction. The absorbancy of water was 2 times higher than that of a NaCl aqueous solution. The copper-ion-exchange capacity of the sample was greater in graft copolymers with higher carboxyl group contents. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1437–1443, 2001

Key words: starch-*graft*-polyacrylonitrile; alkali hydrolysis; infrared analysis; water absorbancy; copper-ion adsorption; FTIR; graft polymers; ion exchanges

INTRODUCTION

Starch (Sr) is an abundant natural polysaccharide and a low-cost material. Many chemical modifications of Sr have been carried out for its use. Graft copolymerization is one attractive method. We studied the graft copolymerization of various vinyl monomers onto cellulose,[1] chitin,[2] and chitosan.[3] The U.S. Department of Agriculture showed that starch-*graft*-polyacrylonitrile (Sr-*g*-pAN) hydrolyzate exhibits super absorbing properties.[4] Since then, the graft copolymerization of Sr has been studied by many workers.[5–31]

When nitrile (CN) groups of pAN are hydrolyzed, they become amide ($CONH_2$) and carboxyl (COOH) groups. However, the relationship between the hydrolysis conditions and the variation of the functional groups formed has not been discussed precisely. In this study, the functional groups of Sr-*g*-pAN hydrolyzate were analyzed conveniently with infrared (IR) spectrometric methods. The water absorbancy and metal-ion adsorption by the Sr-*g*-pAN hydrolyzate were also investigated.

EXPERIMENTAL

Materials

The Sr sample was provided by Matsutani Chemical Industry, Ltd. It contained amylose (30%) and amylopectin (70%).

Acrylonitrile (AN) was distilled under normal pressure, and acrylic acid (AA) was distilled under reduced pressure under nitrogen with a Widmer distillation apparatus. Acrylamide (AAm) was dissolved in 30 parts of hot benzene and recrystallized.

The initiator, a ceric salt solution (Ce salt), was prepared by the dissolution of cerium(IV) diammonium nitrate (0.1 mol) in nitric acid (1 mol) and used with a fixed quantity.

Graft Copolymerization

Sr (0.3 g) was weighed into a polymerization tube (15 mm in diameter and 110 mm long). To this was added water, and it was heated at 95°C for 30 min according to an already described method.[32] Then, the tube was cooled to the reaction temperature, and the monomer and initiator were introduced (total volume = 12 mL). The tube was sealed after a flush with nitrogen gas. The grafting reaction proceeded for the desired time at a constant temperature. Adding a few drops of a saturated aqueous hydroquinone solution terminated the reaction. The polymerization mixture was poured into a large amount of methanol for poly(acrylonitrile) (pAN) and poly(acrylamide) (pAAm) and acetone for poly(acrylic acid) (pAA). Homopolymers were extracted thoroughly in a hot dimethylformamide/acetone solution for pAN and in hot water for pAAm and pAA. For pAAm and pAA, as the samples swelled, they were extracted with mixing solutions of acetone (precipitant) and water (extractant), their ratio thereby being changed. The remaining product was considered a graft copolymer. The polymer yield was calculated with the following equations:[33]

Total conversion (%) =

(weight of polymer formed/

weight of monomer charged) × 100

Grafting (%) = (weight of polymer grafted/

weight of Sr charged) × 100

Grafting efficiency (%) =

(weight of polymer grafted/

weight of polymer formed) × 100

Hydrolysis of Graft Copolymer

Sr-*g*-pAN was hydrolyzed with a sodium hydroxide aqueous solution through changes in its concentration, reaction temperature, and reaction time (bath ratio = 1:100).

The variations of CN, $CONH_2$, and COOH group contents were measured with a Fourier transform infrared spectrophotometer (PerkinElmer model 1600).

Water Absorbancy and Metal Adsorption

The sample (60-mesh pass) was immersed in water and a 0.85% NaCl aqueous solution at 25°C for 24 h. Then, the absorbed amount of water in the sample was measured and calculated with the following equation:

Water Absorbancy = (wet weight of sample

− dry weight of sample)/dry weight of sample

The sample (60-mesh pass) was treated with 1*N* hydrochloric acid into an acid-type sample. After treatment, copper-ion adsorption was measured with an atomic absorption spectrophotometer (Hitachi model 170-50A).

RESULTS AND DISCUSSION

Graft Copolymerization

Ce Salt Concentration

Sr was grafted with three vinyl monomers (AN, AAm, and AA) through changes in its Ce salt concentration.

AN was grafted onto Sr at 25°C for 20 min.

As shown in Figure 1, the polymerization did not occur without Ce salt. However, the total conversion and grafting increased with increasing Ce salt concentration and were constant around 3 mmol/L. The grafting efficiency decreased slightly with an increase in the Ce salt concentration, but they were all above 90%. From these results, the products were almost graft copolymers, and homopolymer was scarcely formed.

The results with AAm and AA as the grafting monomers are shown in Figures 2 and 3, respectively. The total conversion and grafting increased with an increase in the Ce salt concentration and attained a maximum around 1 (AAm) and 3 mmol/L (AA). The grafting efficiencies of both monomers were very low, below 50%. Concerning these graft polymerization results, it is thought that the propagation reaction and termination reaction occur at the same time and above
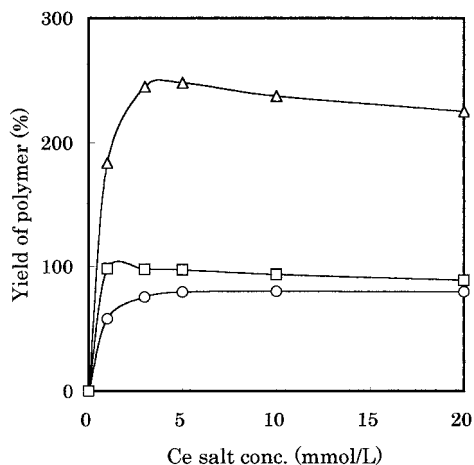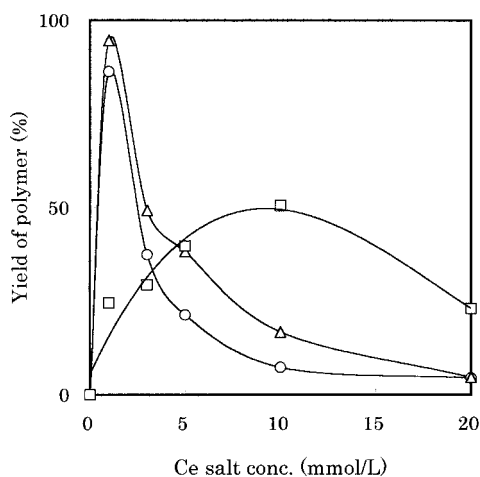
Figure 1 Effect of the Ce salt concentration on the polymer yield [Sr, 0.3 g; AN, 1.57 mol/L; H_2O, 12 mL (monomer + Ce salt); 25°C; 20 min]: (○) total conversion, (△) grafting, and (□) grafting efficiency.
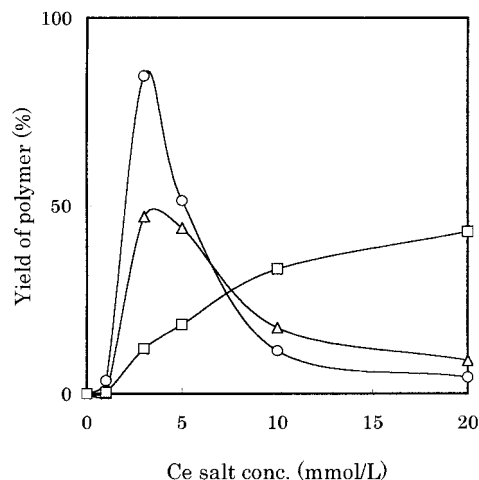
a certain Ce salt concentration; the termination reaction between growing polymer radicals and Sr radicals preferentially occurs. We used the samples obtained for IR analysis to make the calibration line.

Reaction Time

We carried out the graft copolymerization of AN onto Sr, varying the reaction time, with a 3 mmol/L Ce salt concentration to obtain various grafting samples for hydrolysis (Fig. 4). In this reaction, no induction period was observed. The

Figure 3 Effect of the Ce salt concentration on the polymer yield [Sr, 0.3 g; AA, 1.57 mol/L; H_2O, 12 mL (monomer + Ce salt); 40°C; 1.5 h]: (○) total conversion, (△) grafting, and (□) grafting efficiency.

conversion increased rapidly until 20 min and then was constant. In this case, the grafting efficiency was also high, greater than 90%.

IR Analysis of Graft Copolymer

IR Spectra of Sr-g-pAN and Its Hydrolyzate

IR spectra of Sr-*g*-pAN before and after hydrolysis are shown in Figure 5. Figure 5(A) is the spectrum of the original Sr-*g*-pAN. A sharp absorption attributed to CN groups is shown at 2250 cm^{-1}. If Sr-*g*-pAN was hydrolyzed, the absorp-

Figure 2 Effect of the Ce salt concentration on the polymer yield [Sr, 0.3 g; AAm, 1.57 mol/L; H_2O, 12 mL (monomer + Ce salt; 40°C; 1.5 h]: (○) total conversion, (△) grafting, and (□) grafting efficiency.
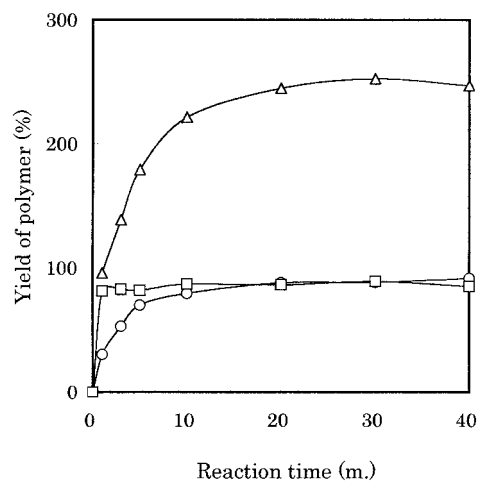
Figure 4 Effect of the reaction time on the polymer yield [Sr, 0.3 g; Ce salt, 3 mmol/L; H_2O, 12 mL (monomer + Ce salt); 25°C]: (○) total conversion, (△) grafting, and (□) grafting efficiency.
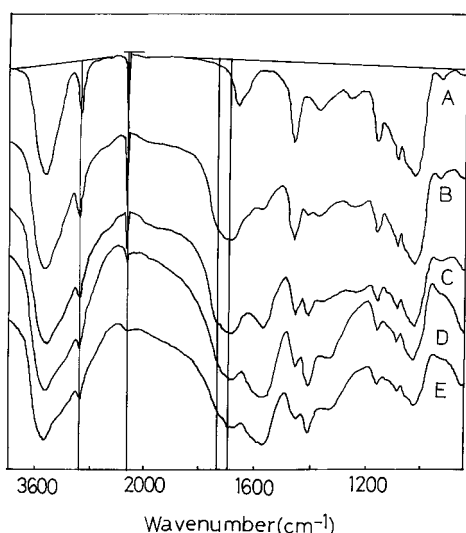
tions attributed to COOH and CONH$_2$ groups appeared at 1720 and 1690 cm^{-1}, respectively. As an increase in the alkali concentration, that is, a hydrolysis reaction, proceeded, the absorption of CN groups decreased and the absorptions of COOH and CONH$_2$ groups increased.

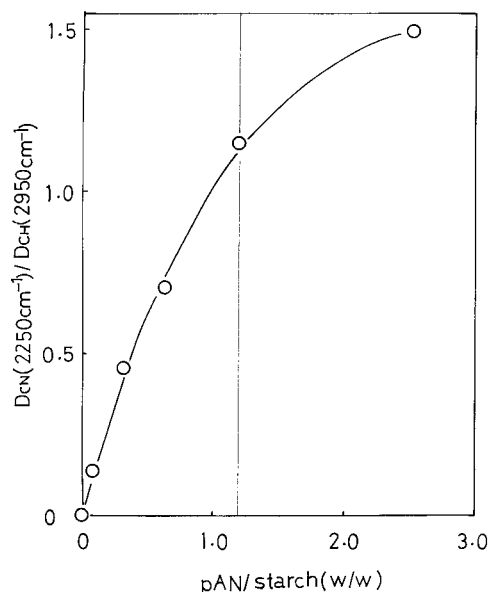### IR Spectra of the Mixture of Sr and pAN

To determine the grafting with IR spectroscopy, we mixed the Sr and pAN homopolymer, changing their mixing ratio. We performed IR measurement of the mixtures to obtain their IR spectra. Although the figure is not shown, the spectra were like those in Figure 5. As shown in Figure 5, the baseline was drawn, and the absorption ratio was calculated. Each absorption was divided by the CH absorbance (2950 cm^{-1}), which was attributed to Sr to correct the sample concentration.

Figure 6 shows the relationship between the absorption ratio of CN groups and the amount of pAN in the mixture. The absorption ratio of CN groups increased almost linearly around 1.2 pAN/Sr (w/w) and then deviated, increasing the pAN concentration.

Sr-g-pAN with 252.2% grafting was measured with IR spectroscopy. The absorption ratio of CN groups divided by CH$_2$ groups was 1.49. The amount of pAN was calculated to be 2.55 with the calibration line shown in Figure 6. This value was

Figure 6   Relationship between the absorbance ratios (D_{CN}/D_{CH}) and mixing weight ratio of pAN and Sr (KBr method; sample:KBr = 1:150).

almost equal to the result obtained from gravimetric measurements. Because a percentage error might have existed, this line could be used as the calibration line. Fortunately, as the hydrolysis progressed, the pAN/Sr absorption ratio decreased and shifted to the linear part of the calibration line.

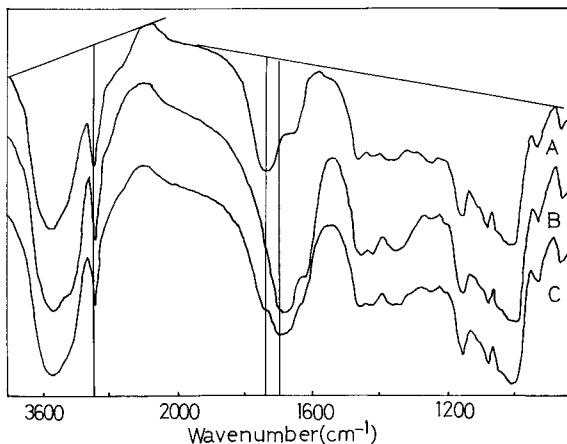We confirmed that the value of grafting could be obtained conveniently with IR spectroscopy.

IR Spectra of the Mixture of Sr-g-pAA and Sr-g-pAAm

IR spectra of Sr-g-pAA, Sr-g-pAAm, and their mixtures are shown in Figure 7.

In Figure 7(A,B), the absorptions attributed to COOH and CONH$_2$ groups are shown at 1720 and 1690 cm^{-1}, respectively.

In Figure 7(C), the absorption of both is shown.

As shown in Figure 7, the baseline was drawn, and the absorption ratio was calculated. Figure 8 shows the relationship between D_{COOH}/D_{CONH2} and the molar ratio of pAA and pAAm. The absorption attributed to COOH groups increased with an increase in the molar ratio of pAA. The variation of functional group contents of the hydrolyzate was calculated with the calibration lines of Figures 6 and 8.

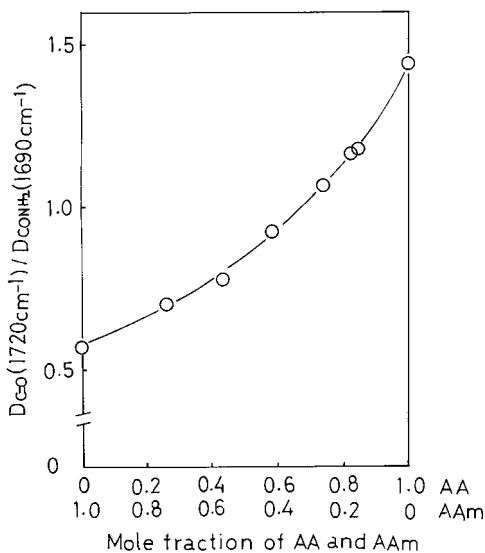**Figure 5**   IR spectra (KBr method; sample:KBr = 1:150) of Sr-g-pAN before and after hydrolysis: (A) original sample (grafting = 252.3%), (B) sample with 0.5N NaOH, (C) sample with 1N NaOH, (D) sample with 2N NaOH, and (E) sample with 3N NaOH.

Figure 7 IR spectra (KBr method; sample:KBr = 1: 150) of (A) Sr-*g*-pAA (G25.9%), (B) Sr-*g*-pAAm (G29.2%), and (C) a mixture of Sr-*g*-pAA (G25.9%) and Sr-*g*-pAAm (G29.2%).
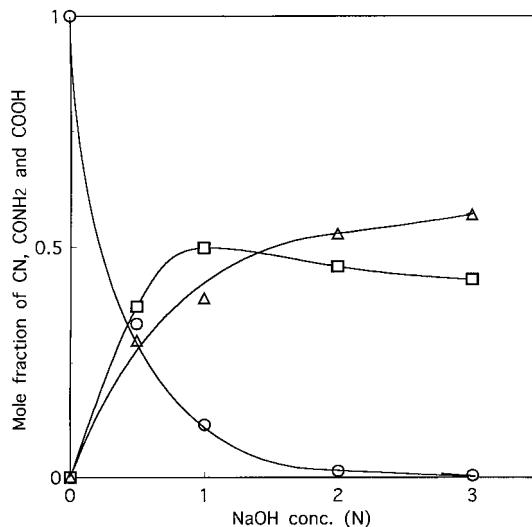
Hydrolysis of Sr-*g*-pAN

Alkali Concentration

The effect of the alkali concentration on hydrolysis is shown in Figure 9. Hydrolysis was carried out at 50°C for 5 h.

CN groups decreased rapidly, increasing the alkali concentration, and became almost 0 above $2N$. However, $CONH_2$ and COOH groups in-
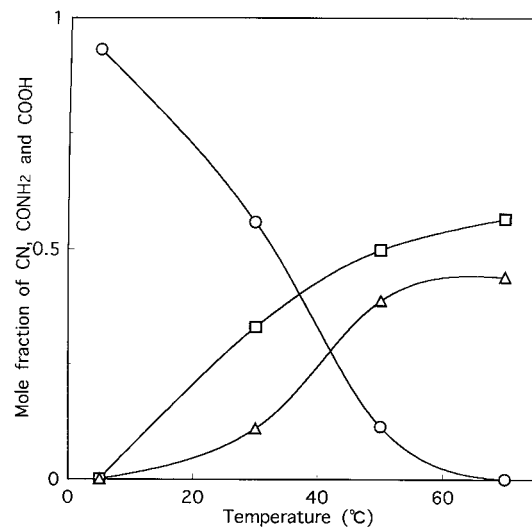

Figure 9 Effect of the NaOH concentration on the functional group content of Sr-*g*-pAN hydrolyzate [Sr-*g*-pAN (grafting = 252.3%), 1.0 g; NaOH solution, 100 mL; 50°C, 5 h]: (○) CN, (△) $CONH_2$, and (□) COOH.

creased with an increase in the alkali concentration, and the latter decreased slightly above $1N$.

Hydrolysis Temperature

Hydrolysis was carried out at various reaction temperatures with $1N$ NaOH for 5 h.

As shown in Figure 10, CN groups decreased

Figure 8 Relationship between the absorbance ratios ($D_{C=O}/D_{CONH2}$) and the molar fraction of AA and AAm (KBr method; sample:KBr = 1:150) in a mixture of Sr-*g*-pAA (G25.9%) and Sr-*g*-pAAm (G29.2%).

Figure 10 Effect of the reaction temperature on the functional group content of Sr-*g*-pAN hydrolyzate [Sr-*g*-pAN (grafting = 252.3%), 1.0 g; $1N$ NaOH solution, 100 mL; 5 h]: (○) CN, (△) $CONH_2$, and (□) COOH.
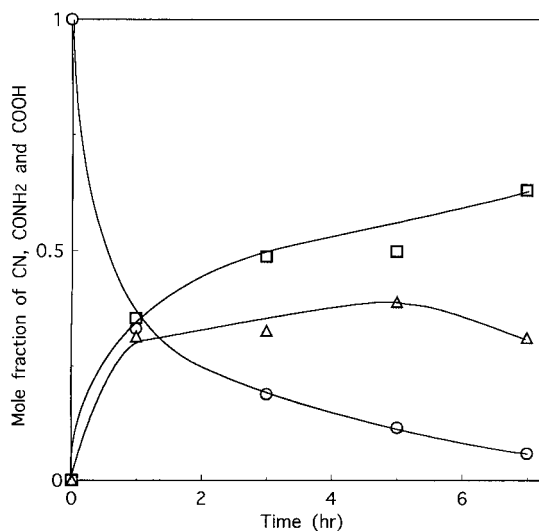
Figure 11 Effect of the reaction time on the functional group content of Sr-*g*-pAN hydrolyzate [Sr-*g*-pAN (grafting = 252.3%), 1.0 g; 1*N* NaOH solution, 100 mL; 50°C]: (○) CN, (△) CONH$_2$, and (□) COOH.

rapidly, and so CONH$_2$ and COOH groups increased with increasing reaction temperature.

CN groups hardly hydrolyzed at 5°C but hydrolyzed completely at 70°C. The hydrolysis reaction was affected largely by temperature.

Hydrolysis Time

The effect of the reaction time on hydrolysis was investigated with 1*N* NaOH at 50°C. As shown in Figure 11, CN group contents decreased rapidly for 1 h and slowly afterward. However, after 7 h, CN groups did not hydrolyze completely at this reaction temperature. Therefore, CONH$_2$ and COOH groups increased, and the former decreased slightly after 1 h. This indicates that CONH$_2$ groups hydrolyzed further to COOH groups.

Characterization of the Hydrolyzate

Absorption of the Hydrolyzate

The relationship of pure water, a NaCl aqueous solution, and the molar fraction of COOH, CONH$_2$ is shown in Figure 12.

The absorption was very low until a 0.3 molar fraction of COOH and increased until a molar ratio of 0.6. However, the hydrolyzate sample was soluble in water above 0.6. The dissolved graftmer could be used as a coagulant. The absorption was largely dependent on the amount of COOH

groups in the sample. A sample with a molar fraction of 0.55 absorbed 400 times more water than the original Sr. This value is comparable to those of commercial absorbents. The absorption of the NaCl aqueous solution was very low. The absorption of the same sample with a molar fraction of 0.55 was only a quarter.

Copper-Ion Adsorption

The effect of the COOH molar fraction on the copper-ion adsorption and adsorption ratio was considered.

As shown in Figure 13, the copper-ion adsorption increased with an increase in the COOH molar fraction, that is, AA contents, and attained 2.2 mmol/g. The adsorption ratio also increased with increasing COOH group contents(ca. 60% at a molar fraction of 0.55).

CONCLUSION

Three vinyl monomer species, AN, AAm, and AA, were grafted onto Sr with Ce salt as an initiator. The vinyl monomer activity onto Sr was in the following order: AN > AA > AAm. Sr-*g*-pAN was hydrolyzed to introduce CONH$_2$ and COOH groups into Sr. The functional group contents of CN, CONH$_2$, and COOH in the hydrolyzate were analyzed with IR spectroscopy. Two calibration lines were made with the IR spectra of a pAN and Sr mixture and a Sr-*g*-pAAm and Sr-*g*-pAA mix-
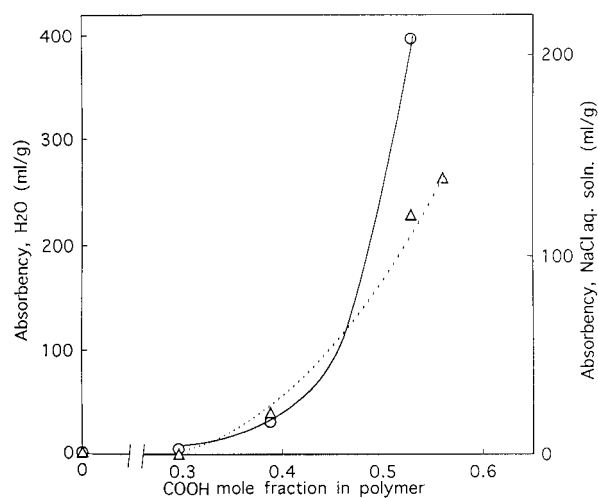
Figure 12 Effect of the COOH molar fraction in the polymer on the water and salt-solution absorbancy at 25°C for 24 h: (○) H$_2$O and (△) 0.8% NaCl aqueous solution.
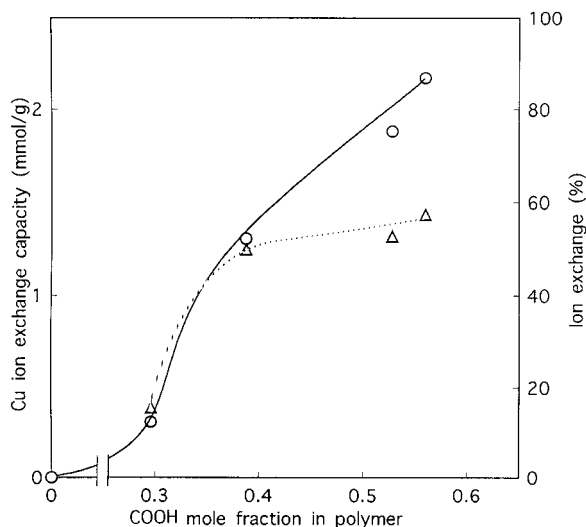
Figure 13 Effect of the COOH molar fraction in the polymer on (○) the copper-ion-exchange capacity and (△) the ion exchange (%; hydrolyzate sample, 0.1 g; 0.01*M* copper solution, 25 mL; 25°C; 24 h).

ture. The hydrolysis reaction was accelerated with the alkali concentration, reaction temperature, and time increasing. The obtained hydrolyzate exhibited a high water absorbancy and ion-exchange property. The water absorbancy of the hydrolyzate increased with an increasing COOH molar fraction in the polymer, and it dissolved in water above a 0.6 molar fraction. The absorbancy of water was 2 times higher than that of a NaCl aqueous solution. The copper-ion-exchange capacity of the sample was greater in graft copolymers with higher COOH group contents.

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