

# Preparation and Structure of Poly(vinyl Alcohol)-Poly(vinyl Acetate) Composite Porous Membrane

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## Synopsis

The preparation of poly(vinyl alcohol) (PVA)-poly(vinyl acetate) (PVAc) composite porous membrane was investigated by extracting PVAc with solvent from films of PVAc lattices which were obtained by the emulsion polymerization of vinyl acetate (VAc) in the presence of PVA. The formation of the porous membrane depended upon whether or not PVAc in the latex film was easily extracted with solvent. In the case of using hydrogen peroxide (HPO)-tartaric acid (TA) as an initiator, in the film of the latex which was produced from the batch method in which all ingredients of the batch were put into the reaction vessel before starting polymerization, PVAc could be extracted over 90% of total PVAc with common organic solvents. In the film of the latex which was produced from the dropwise addition method of VAc and initiator, the PVAc extraction was about 20-30%. On the other hand, in the case of using ammonium persulfate as an initiator, the desired porous membrane was not obtained. The structure of the porous membrane obtained from the latex of the batch method by using HPO-TA consisted of spherical cells which were made up of PVA and grafted PVAc or insoluble PVAc like microgels, which were not extracted with organic solvent and were connected by small pores. The PVA-PVAc composite porous membrane is permeated by *n*-hexane with  $5.58 \times 10^{-2}$  mL/cm<sup>2</sup>-s at 0.5 kg/cm<sup>2</sup>, by benzene with only  $1.33 \times 10^{-3}$  mL/cm<sup>2</sup>-s even at 60 kg/cm<sup>2</sup>.

## INTRODUCTION

The PVAc lattices polymerized in the presence of PVA generally contain graft copolymers of PVA and PVAc.<sup>1-4</sup> These graft copolymers are either water-soluble, benzene-soluble, or insoluble in water and benzene,<sup>3,4</sup> and, because of the graft copolymers, the dried-down PVAc latex films are not easily dissolved in solvents.<sup>3</sup> On the other hand, Traaen has indicated that in the PVAc lattices the insoluble polymers are not graft copolymers, but are mainly microgels based on a consequence of the chain transfer reaction between growing radicals and PVAc molecules in polymer particles.<sup>5</sup> Schmit et al. have recently reported by means of quasielastic light scattering that in the emulsion polymerization of VAc the microgels are formed very easily, and possess some rigidity.<sup>6</sup> A thorough mixture of two polymers, of which one is soluble and the other is insoluble in the extraction solvent, is incompletely separated after an extraction time of 24 h in most cases.<sup>7</sup>

It is possible to prepare the porous PVA membrane by solvent extraction of PVAc from the film of the PVAc latex polymerized in the presence of PVA.<sup>8</sup> PVAc in all the PVAc latex films which contained PVA is not always effectively extracted with solvents for PVAc. A suitable selection of polymerization conditions leads to a good chance of a high rate extraction of PVAc from the PVAc latex film with common organic solvents, such as acetone, methanol, and benzene. In this work the preparation and structure of the porous membrane from the

emulsion polymerization of VAc in the presence of PVA will be further investigated.

## EXPERIMENTAL

### Materials

VAc of commercial grade was distilled before use. PVA (Kuraray PVA-117) with the average degree of polymerization ( $\overline{DP}$ ) of about 1700 and with the degree of saponification of  $98.8 \pm 0.2$  mol % was obtained from Kuraray Co., Ltd., and used without further treatment. Ammonium persulfate (APS), hydrogen peroxide (HPO), and tartaric acid (TA), to be used as initiator, were extra-pure-grade chemicals from Wako Pure Chemical Industries, Ltd., and were used without purification.

### Preparation of PVAc Lattices

The recipe and the various addition methods for VAc and initiator are shown in Figure 1. The polymerization methods [I], [II], and [III] indicate the dropwise addition of VAc and initiator, the dropwise addition of VAc and the stepwise addition of initiator, and the batch method in which all ingredients of the batch (water, VAc, PVA, and initiator) were put into the reaction vessel before starting polymerization, respectively. Polymerizations were performed in a 1-L five-necked separable flask equipped with a thermometer, a reflux cooler, a VAc dropping funnel, an initiator dropping funnel, and a stirrer. The flask was first charged with 250 g of aqueous solution containing 25 g of PVA and 20 g of water (in the case of the HPO—TA system, 20 g of aqueous solution containing 0.5 g

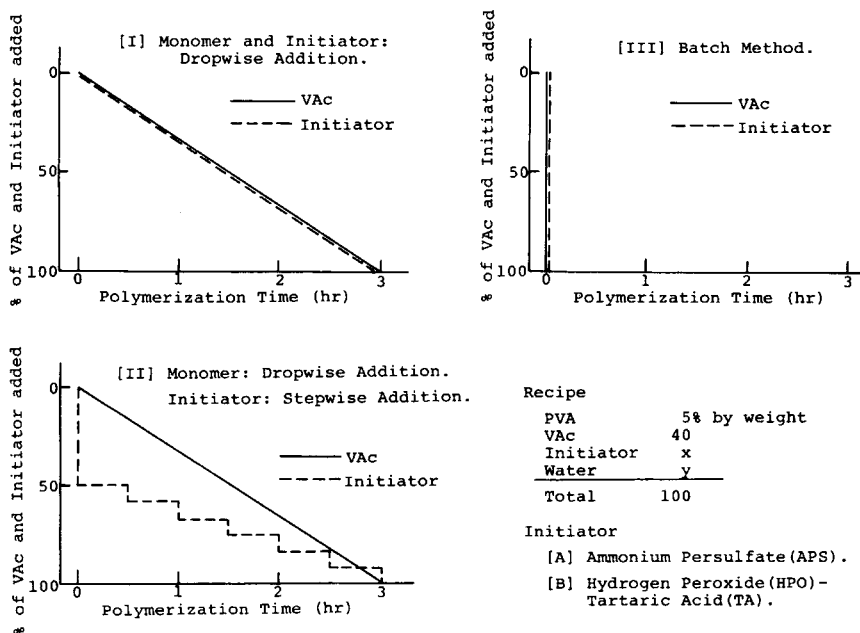


Fig. 1. Polymerization methods and recipe.

of TA as an activator), and immersed in the water bath thermostated at 85°C. The stirring speed was maintained at 150 rpm by Chemi Stirrer B-100 of Tokyo Rikakikai Co., Ltd.

In the method [I], when the temperature of the PVA aqueous solution attained 70°C, dropwise additions of 30 g of aqueous solution containing initiator and of 200 g of VAc were started. After the dropwise additions of initiator and VAc, about 3 h, the reaction mixture was allowed to stand for 30 min with 150 rpm stirring in the water bath at 85°C.

In method [II], the process was similar to the method [I], except that initiator was stepwise added as described (Fig. 1). When the temperature of the contents in the flask was raised to 70°C, 24 g of aqueous solution containing half the prescribed amount of initiator was first added, and then 1 g of aqueous solution containing one-sixth of the residual initiator was added at intervals of 30 min.

In method [III], when the temperature of an aqueous solution in the flask reached 70°C, 200 g of VAc and 30 g of aqueous solution containing initiator were added. Thereafter, the temperature of the water bath was adjusted to 70–75°C to prevent bumping during polymerization. If the temperature of the content in the flask went above 70°C, the temperature of the water bath was instantly raised to 85°C. After monomer refluxing was over, the reaction mixture was permitted to stand in the water bath at 85°C for 15 min. The obtained latex was cooled below 35°C, and conversions were determined gravimetrically.

### Measurement of PVAc Lattices

The PVAc latex viscosity was measured at 30°C by a Type BH Brookfield viscometer of Tokyo Keiki Co., Ltd., after keeping the PVAc latex in a water bath at 30°C for 1 h.

The solubility of the PVAc latex in a methanol–water mixture solvent was evaluated from the turbidity at 400 nm wavelength at 30°C by using water as the reference. After the PVAc latex was diluted with water until the solid content was at 10%, 2 mL of this solution was pipetted into another flask, followed by water of  $x$  mL and methanol of  $y$  mL in that order, where  $x$  and  $y$  were 58 mL. A Shimadzu spectrometer, Model Spectronic 20, was used for absorbance measurements.

The dispersion quantity was determined from the ratio of  $D_{400}$  to  $D_{600}$  at 30°C, where the value of  $D_{400}$  was fixed within 0.40–0.45.

### IR Spectra and Paper Chromatography of Polymers

The measurement of IR spectra of polymers was performed on films. The spectrometer used was Type IRA-1 of Japan Spectroscopic Co., Ltd.

Paper chromatography was conducted on Tokyo Roshi No. 50 filter paper. Acetone was used as developing solvent. After developing and drying, the paper was sprayed with either an aqueous iodine–iodide solution or an aqueous iodine–iodide solution containing boric acid.

## Preparation and Measurement of Membrane

The latex film from the PVAc latex was formed by casting 1.8 mm in thickness on a poly(ethylene) plate at room temperature (about 26°C). The latex film was dried further in a vacuum desiccator for 24 h, and extracted in a Soxhlet extractor with acetone for 20 h. After extraction, the obtained white membrane was immersed in *n*-hexane to exchange acetone, and was quickly dried with blowing air which had been passed through calcium chloride. The membrane was further dried *in vacuo* for 10 h.

The permeability of the membrane to *n*-hexane, cyclohexane, and benzene was investigated at room temperature under various pressures with a Type RO-filter of Bio Engineering Co., Ltd.

## Electron Micrographing

The samples were treated with gold under a vacuum below  $10^{-5}$  Torr with an Akashi Type VDE vacuum evaporator equipped with an electron-motive gimbal. Electron micrographs of the samples were obtained with a Hitachi-Akashi Type MSM-2 scanning electron microscope.

## RESULTS AND DISCUSSION

### PVAc Lattices

In the methods [I] and [III] using APS, the PVAc lattices coagulated during polymerization or cooling. In the HPO—TA system, stable PVAc lattices were formed in every polymerization method. The results of the polymerization and the properties of the PVAc lattices obtained are summarized in Table I.

Conversions of all polymerizations were nearly 100%. In the dropwise addition of VAc the viscosity of the PVAc latex is greatly influenced by the polymerization condition, especially by an amount of initiator added before the starting of polymerization (Table I). High viscosity PVAc latex was very convenient for casting and forming the latex film. The PVAc particle size, which was evaluated from the dispersion quantity (Table I), was in the order of [I] > [II] > [III] in the method using HPO—TA. The PVAc particle size in method [II] using APS was larger than that in any method using HPO—TA. In general, the viscosity of a latex is dependent upon the particle size. In the PVAc latex in the presence of PVA, the viscosity of the latex will also be greatly affected by the interaction of PVA and the particles, the content of the PVA—PVAc graft copolymer, and the molecular weight of PVA etc., except the particle size. This explains why the viscosity of the PVAc latex is independent of the particle size.

Figure 2 depicts some solubility results of the PVAc latex in a mixture of methanol and water. The absorbances at 400 nm wavelength, which were adopted for convenience as a measure of the solubility, showed the minimum at 5.0/1.0 ratio (by vol) of methanol/water in every case. The minimum turbidities in the solubility measurement of the PVAc lattices formed by method [II] using APS and by method [I] using HPO—TA were higher than others. The PVAc lattices formed by method [III] using HPO—TA dissolved in the methanol/water (5.0/1.0–4.0/2.0) mixtures. The PVA and the solution-polymerized PVAc ( $\overline{DP} \doteq 500$ ), initiated by benzoyl peroxide in methanol, resulted in a

TABLE I  
Results of Polymerizations and Properties of PVAc Lattices

	[A] Ammonium persulfate		Polymerization methods <sup>a</sup>					
	[II]	[I]	[I]	[I]	[II]	[II]	[III]	[III]
Initiator (wt %)	0.20	0.40	0.06	0.12	0.06	0.12	0.06	0.12
Activator, TA (wt %)	—	—	0.10	0.10	0.10	0.10	0.10	0.10
Conversion (%)	99.6	99.3	99.4	99.2	99.4	99.9	98.4	98.3
Viscosity of latex (CP at 10 rpm)	7,560	134,000	13,400	30,400	15,800	61,500	5,100	3,700
Dispersion quantity ( $D_{400}/D_{600}$ )	1.08	1.19	1.26	1.22	1.39	1.31	1.53	1.54
Extraction from latex film with acetone (%) <sup>b</sup>	28.4 (32.0)	35.5 (40.0)	21.5 (23.6)	25.7 (29.9)	62.4 (70.2)	71.7 (80.7)	83.0 (93.5)	85.6 (96.5)
Relative viscosity of polymer extracted with acetone <sup>c</sup>	1.15	1.13	1.24	1.17	1.11	1.09	1.59	1.30
Swelling of latex film in acetone <sup>d</sup>	Very large	Very large	Very large	Very large	Large	Large	Small	Small

<sup>a</sup> See Figure 1.

<sup>b</sup> Values in brackets indicate percentage of polymers extracted with acetone to total PVAc.

<sup>c</sup> Acetone was used as solvent. Determination of viscosity was carried out at 30°C.

<sup>d</sup> Very large, large, and small imply increases of 70–90%, 20–30%, and 2–3% in area, respectively.

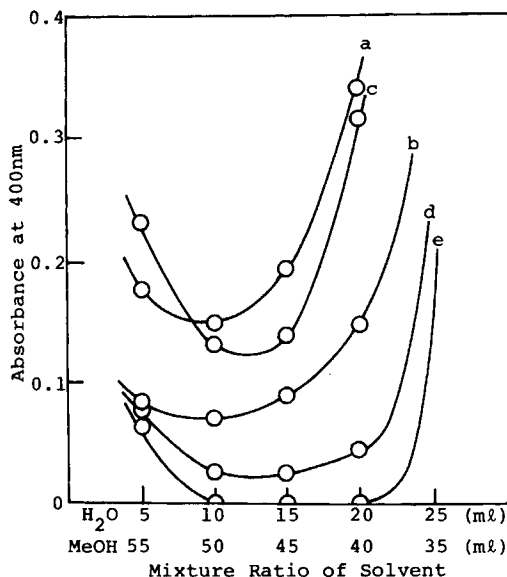


Fig. 2. Solubility of PVAc latex in methanol-water mixtures: (a) [II], APS (0.20%); (b) [III], APS (0.40%); (c) [I], HPO (0.06%)—TA (0.10%); (d) [II], HPO (0.06%)—TA (0.10%); (e) [III], HPO (0.12%)—TA (0.10%).

transparent solution at the same mixture ratio of methanol and water. Consequently, the turbidity in methanol/water (5.0/1.0–4.0/2.0) suggests the existence of insoluble materials in the PVAc lattices, such as PVAc with higher branched or higher molecular structures formed during the polymerization.

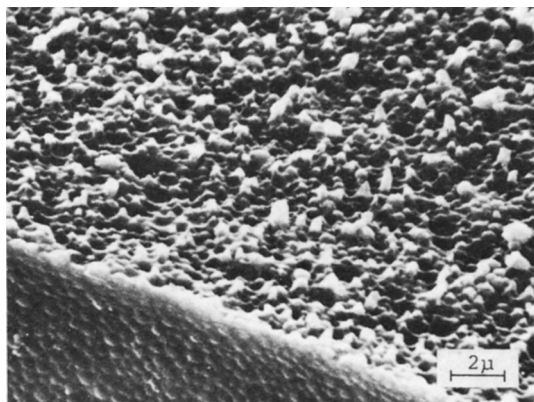
### Extraction with Acetone

The transmittance of the PVAc latex films, which were formed above the minimum film-forming temperature, varied from a high value for methods [II] and [III] using HPO—TA to a low value for method [II] using APS and method [I] using HPO—TA. The difference in these values depends upon the PVAc particle size in the PVAc latex.

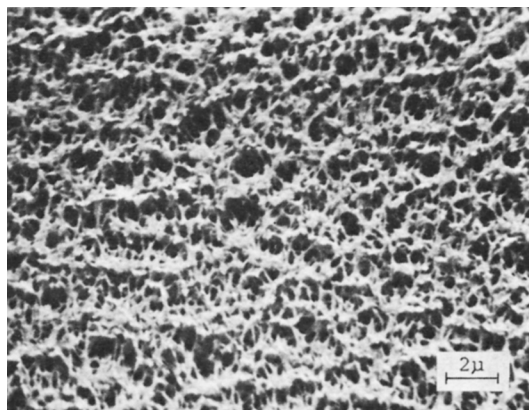
When the latex films were extracted by acetone, they changed from semi-transparent to white. The extraction percentage with acetone for the latex film is represented in Table I. These values were independent of solvents for PVAc, such as methanol and benzene. The swelling of the latex film in acetone showed the opposite relation, compared to the extraction percentage (Table I). In the latex films of the HPO—TA system, the extracted polymer to total PVAc was about 25% in method [I], 70–80% in method [II], and over 90% in method [III]. This tendency is closely associated with the solubility of the PVAc latex in methanol/water (5.0/1.0) (Fig. 2). Comparing the latex films prepared by method [II], the amount of the polymer extracted with acetone was greater in the HPO—TA system than in the APS system. In the polymerization systems using the same initiator, even if the same amount of initiator is taken, the amount of the extracting polymer is dependent on the polymerization method. In the polymerization systems using different initiators, even if the same polymerization method is adopted, the amount of the extracting polymer relates to the nature of initiators.

In the emulsion polymerization of VAc, microgels are formed in the PVAc particles.<sup>5,6,9</sup> According to the data reported by Traaen,<sup>5</sup> the formation of the microgels is most probably a consequence of chain transfer reaction onto PVAc particles; and the number of the chain transfer reactions increases as the pH value of the latex decreases. Actually the pH value of the PVAc latex was 2.4–2.6 in the APS system and 3.4–3.6 in the HPO—TA system. If APS is used as an initiator, because of sulfuric acid produced by the side reaction of APS, the latex will be acidic, as compared with latex from the HPO—TA system. The polymers formed in the APS system did not dissolve in a methanol/water mixture.

Emulsion polymerization proceeds mainly in particles.<sup>10</sup> In methods [I] and [II] of VAc since the composition of the particles is predicted to be PVAc-rich, and since refluxing of VAc during polymerization is slight the particles are similar to high conversion in mass polymerization.<sup>11</sup> Moreover, if APS of a thermal decomposition initiator with a high activation energy is used, or if HPO—TA redox initiator is added dropwise, the system will be kept in a low radical concentration from the early stage of polymerization. Accordingly, in the emulsion polymerization, the formation of the polymers with high branched and high

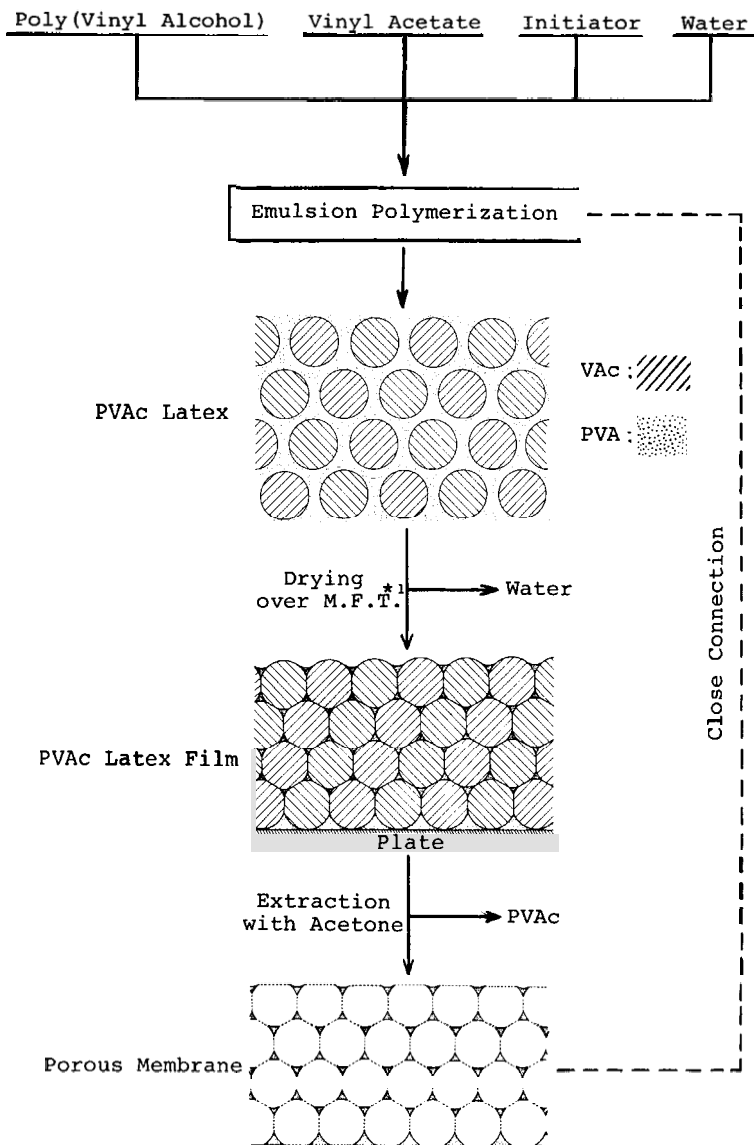


(a) Crack surface view of PVAc latex film.



(b) Cross-section view of porous membrane.

Fig. 3. Electron micrographs of PVAc latex film and porous membrane from method [III], using HPO (0.12%)—TA (0.10%).



\*1: M.F.T. = Minimum film-forming temperature.

Fig. 4. Flow sheet for preparation of porous membrane.

molecular structures is a natural result. This fact may also have bearing on the lower extraction percentage with acetone from the PVAc latex films.

The relative viscosities of the polymers extracted with acetone are shown in Table I. The extracted polymers are not limited only to low molecular weight. The extraction percentage with acetone was independent of the viscosity of the PVAc latex (Table I), suggesting that the PVAc particle size is not directly relevant to the extraction percentage.

Judging from the extraction percentage of polymer and from the swelling of the latex film in acetone (Table I), it is concluded that method [III] using HPO—TA is most suitable for making the porous membrane. The selection



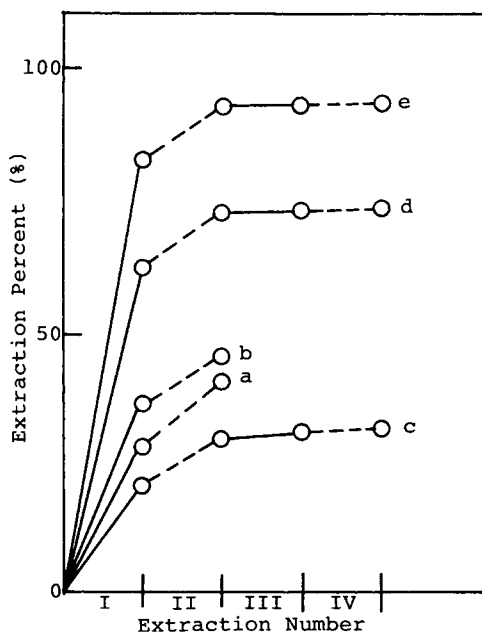


Fig. 5. Alternative extraction results of PVAc latex films with acetone and boiling water: (a) [II], APS (0.20%); (b) [II], APS (0.40%); (c) [I], HPO (0.06%)—TA (0.10%); (d) [II], HPO (0.06%)—TA (0.10%); (e) [III], HPO (0.06%)—TA (0.10%); (—) extraction with acetone; (---) extraction with boiling water.

of an initiator and its concentration and of the monomer concentration in the first stage of polymerization are of importance for preparing the porous membrane.

Figure 3 indicates the electron micrographs of the crack surface view of the latex film and the cross-section view of the porous membrane obtained from method [III] using HPO (0.12%)—TA (0.10%). In conclusion, assuming that the PVAc particles are all the same size, the flow sheet for the preparation of the porous membrane can be roughly illustrated (Fig. 4).

### Structure of Porous Membrane

It follows from the electron micrographs (Fig. 3) that the structure of the porous membrane obtained from method [III] using HPO (0.12%)—TA (0.10%) consisted of spherical cells which were made up of polymers and were connected by small pores. The porosity of the porous membrane was over 87%. Since the extraction percentage with acetone was independent of the film thickness, the pores, which were formed by extracting a part of PVAc from the latex film, passed through the porous membrane.

In order to check the presence of graft copolymers, the alternative extraction of the latex films with acetone and boiling water was repeated twice (Fig. 5). The extraction percentage of the polymer (extraction no. II) extracted with boiling water corresponded closely to the value of charged PVA in every case, and the extraction percentages of the polymers (extraction nos. III and IV) were very small. The latex film of method [III] using HPO (0.12%)—TA (0.10%) lost the

film form in boiling water after extraction with acetone, while the latex film of method [II] using APS went partially to pieces during the treatment of extraction no. III with acetone. IR spectra of some extracted polymers are given in Figure 6. The polymers of extraction no. II extracted with boiling water were almost PVA, regardless of the kind of initiators. Consequently, even if the residual polymers which were not extracted with acetone and boiling water were obtained, it is dubious whether the polymers were graft copolymers.

In the latex film of method [III] using HPO—TA, the residual polymers after

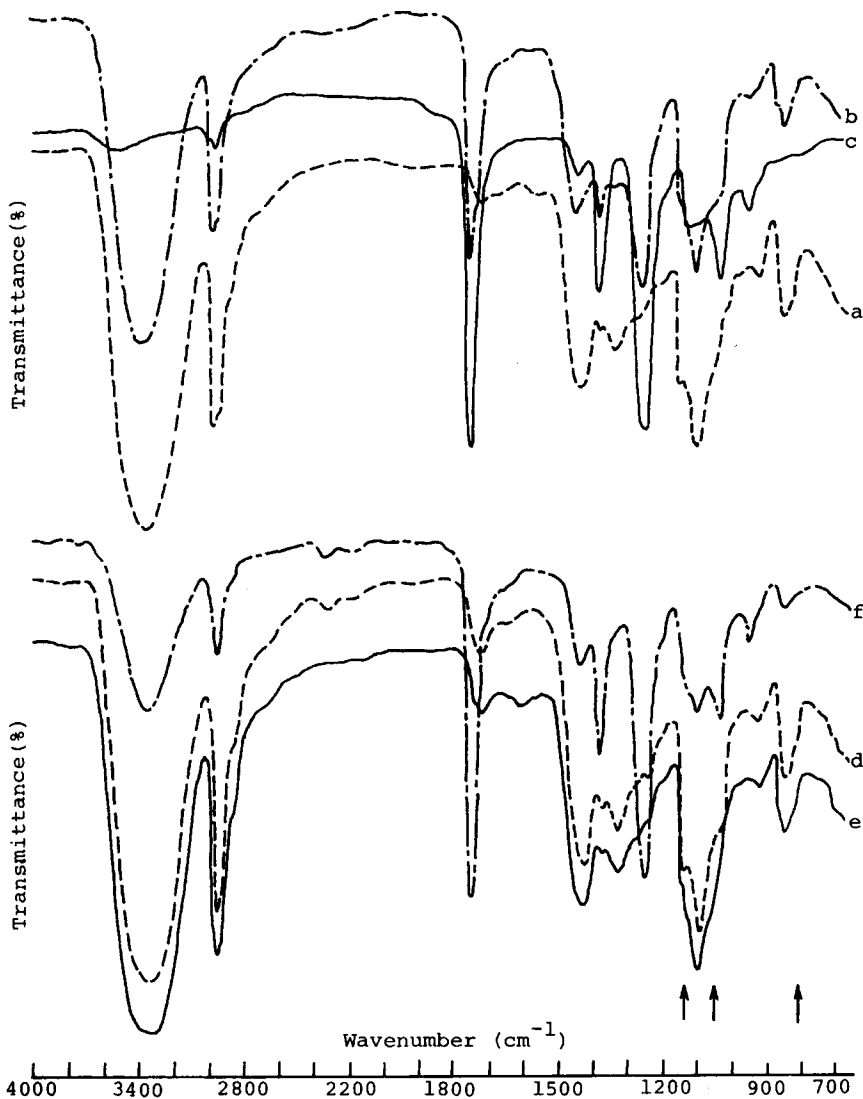


Fig. 6. IR spectra of polymers: (a) PVA, degree of saponification of  $98 \pm 0.2$  mol %, Kuraray PVA-117; (b) Partially saponified PVAc, degree of saponification of  $88 \pm 1.0$  mol %, Kuraray PVA-205; (c) PVAc, DP  $\approx$  500; (d) [II], APS (0.40%), extraction number II, (see Fig. 5); (e) [III], HPO (0.12%)—TA (0.10%), extraction number II; (f) [III], HPO (0.12%)—TA (0.10%), residual polymer. The arrows show the appearance of characteristic bands (8.8, 9.55, and 12.35  $\mu$ ) for the PVA—PVAc graft copolymers reported by Hartley<sup>3</sup> and Gavati et al.<sup>4</sup>

the alternative extractions did not dissolve in methanol or water, but dissolved in a methanol–water mixture. From the IR spectrum (Fig. 6), the content of PVAc in the residual polymer was higher than that in the polymer of extraction no. II extracted with boiling water. Hartley<sup>3</sup> and Gavatt et al.<sup>4</sup> have shown that the characteristic bands of IR spectra for the graft copolymers between PVA and PVAc were observed at 8.8, 9.55, and 12.35  $\mu$ . All absorption maxima in spectra of the polymers obtained in this study were present in those of either PVA and PVAc of partly saponified PVAc.

The paper chromatograms of the extracted and the residual polymers are shown in Figure 7, together with those of PVA and PVAc. PVA and PVAc are detected by the blue and red–violet color reactions with an iodine–iodide aqueous solution,<sup>12,13</sup> respectively. Since the color reactions are due to  $-(\text{CH}_2-\text{CHOH})_n-$  and  $-(\text{CH}_2-\text{CHOCOCH}_3)_n-$  groups in polymers,<sup>14,15</sup> the graft copolymers between PVA and PVAc are colored bluish-red or reddish-blue according to their contents. PVA used in our experiment did not develop a color reaction with a dilute iodine–iodide aqueous solution ( $2 \times 10^{-3}$  N). For the purpose of increasing the sensitivity of the PVA detection, an iodine–iodide aqueous solution contained boric acid was also used.<sup>16</sup> Boric acid was used as the concentration saturated in the iodine–iodide aqueous solution. PVAc was the polymer with  $\overline{DP} \approx 500$  prepared from the methanol solution polymerization with benzoyl peroxide. The polymer of extraction no. I extracted with acetone resulted in the same red-violet color as PVAc with the iodide–iodide aqueous solution, regardless of the existence of boric acid. The polymer of extraction no. I extracted with acetone was PVAc. This result was also supported by the IR spectrum. Comparing the results of paper chromatograms of the extracted polymers with those of PVA and PVAc, the largest part of the polymer of extraction no. II extracted with boiling water is the PVA homopolymer, in which only a very little polymer, like the PVA–PVAc graft copolymer seems to be included. The residual polymer after extractions is the PVA–PVAc graft copolymer. A reddish-blue color reaction corresponding to the graft copolymer was obtained by using an iodine–iodide aqueous solution saturated with boric acid. However, owing to a lack of direct proof about the graft copolymer, e.g.,

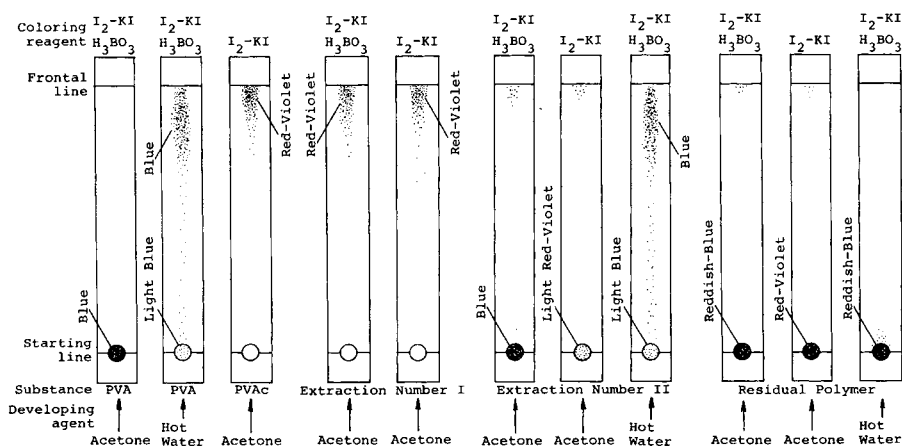


Fig. 7. Results of paper chromatography of PVA, PVA, extracted polymers, and residual polymer. PVAc latex; method [III], using HPO (0.12%)—TA (0.10%).

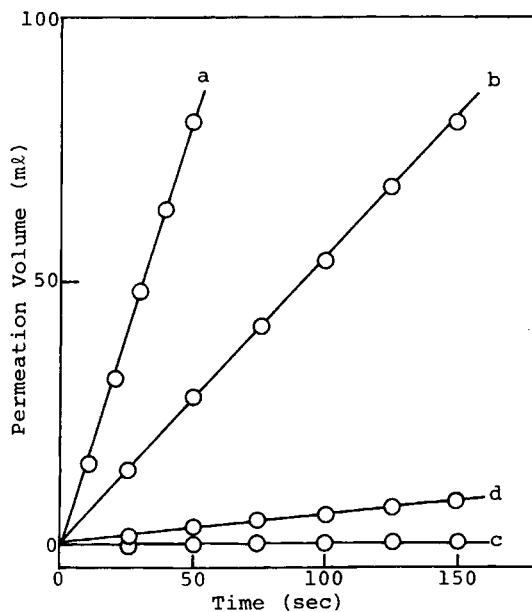


Fig. 8. Permeability of PVA—PVAc composite porous membrane from method [III] using HPO (0.12%)—TA (0.10%) to organic solvents. (a) *n*-Hexane at 0.5 kg/cm<sup>2</sup>; (b) cyclohexane at 0.5 kg/cm<sup>2</sup>; (c) benzene at 0.5 kg/cm<sup>2</sup>; (d) benzene at 60 kg/cm<sup>2</sup>.

the evidence for the bond structure between PVA and PVAc, confirmation of the graft copolymer about the residual polymer after extractions must be further investigated.

Figure 8 displays the permeability of the porous membrane from method [III] using HPO (0.12%)—TA (0.10%) to *n*-hexane, cyclohexane, and benzene. *n*-Hexane and cyclohexane were able to permeate through the porous membrane with  $5.58 \times 10^{-2}$ , and  $1.93 \times 10^{-2}$  mL/cm<sup>2</sup>·s at 0.5 kg/cm<sup>2</sup>, respectively, but benzene with only  $1.33 \times 10^{-3}$  mL/cm<sup>2</sup>·s at 60 kg/cm<sup>2</sup>. The different permeability between *n*-hexane and cyclohexane is explained by viscosity. A strange phenomenon for benzene is due to the grafted PVAc or the insoluble PVAc like microgels inside the cells of the porous membrane. As the PVAc swells in benzene and shrinks in *n*-hexane or cyclohexane, it acts by organic solvents as valves of small pores passed through between cells. If the porous membrane is dipped in benzene, the size is barely affected by the solvent, because the swelling of the PVAc occurs merely in cells. The membrane obtained by employing the emulsion polymerization of VAc in the presence of PVA is certainly the PVA—PVAc composite porous membrane.

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