Study on Physical Properties of Poly(Vinyl Acetate) Emulsion Films Obtained in Batchwise and in Semicontinuous Systems

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SYNOPSIS

Emulsion polymerization of vinyl acetate was carried out batchwisely or semicontinuously in the presence of a nonionic surfactant or poly(vinyl alcohol) (PVA). From the investigation of degrees of polymerization of poly(vinyl acetate) (PVAc) during the course of polymerization and those of corresponding hydrolyzed PVA, it was clarified that the degrees of polymerization of the batchwise system are much larger than those of the semicontinuous system, and long branches and shorter branches are formed in the batchwise and the semicontinuous systems, respectively. The emulsion films obtained batchwisely had properties with better tensile strengths by two to four times (nonionic system) and 1.5 times (PVA system) than those obtained semicontinuously. The former films revealed a better water-resistant nature compared with the latter films. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl acetate) (PVAc) emulsion has been used in large quantities in several application fields, especially in adhesives of papers and woods. There have been many articles on PVAc emulsions,[1] most of which relate to the mechanism of the emulsion polymerization of vinyl acetate (VAc) with respect to the desorption of radicals out of particles, the grafting behavior of VAc onto poly(vinyl alcohol) (PVA) utilized as a protective colloid, and continuous polymerization from an academic point of view. Recently, two articles reported on the emulsion properties of PVAc obtained in the presence of PVA, wherein molecular weights with respect to the polymerization method were discussed.

The growing chain radical of PVAc is so reactive that chain-transfer reactions take place remarkably. The degree of polymerization is accordingly determined by the chain-transfer reactions at the usual polymerization temperature. At low conversion, only the chain transfer to the monomer should be taken into account. At high conversion, however, the chain-transfer reaction to the polymer takes place simultaneously, yielding branched polymers. In the semicontinuous emulsion polymerization of VAc, which is the common method to produce the emulsion industrially, the polymerization is carried out at high conversion. PVAc molecules in this case appear to be not linear but branched, so that the physical properties of the emulsion films thus obtained may be affected by the nonlinear PVAc molecules.

There have been several papers predicting the position of a hydrogen abstraction with the chain-transfer reaction to PVAc. Although Nozakura et al.[4] proposed the position at α-hydrogen in the main chains through a study of polymerizing VAc in the presence of gelled PVAc followed by hydrolysis and extraction, the abstraction of a hydrogen at methyl side groups,[5-7] which was proved to be more than 40 times easier compared with the α-hydrogen abstraction in the main chains,[5] seems to be more reasonable. In the latter case, the branched position can be cut off in the hydrolysis with alkaline methanol, which is usually applied to produce PVA.

This paper deals with some properties of the films of the PVAc emulsions that were polymerized batchwisely and semicontinuously in the presence of either a nonionic surfactant or PVA, in relation to degree of polymerization and branching of resulting PVAc.

EXPERIMENTAL

Reagents

VAc (produced by Kuraray Co.) was polymerized to approximately 10% conversion at 60°C in nitrogen atmosphere by adding 0.005 wt % 2,2-azobisisobutyronitrile (AIBN) and then distilled under reduced pressure.

Nonylphenyl ether of polyoxyethylene (n = 40) (a product of Sanyo Chemicals Co., Nonipol 400, N-400) was used as received. PVA (products of Kuraray Co.) was used after extracting sodium acetate in a Soxhlet apparatus with methanol. Degrees of polymerization and degrees of hydrolysis of PVA are as follows: PVA 205 (550/88%) and PVA 217 (1750/88%).

Initiators and calcium carbonate of reagent grades were used as received. Water was used after deionization. Dibutyl phthalate (DBP) was used as received.

Polymerization Procedure

A 500 mL Pyrex glass reactor equipped with a stirrer, a reflux condenser, a thermometer, a mess-burette sealed with nitrogen gas, and a three-way cock was degassed with repeated evacuation and nitrogen gas introduction, and prescribed amounts of water, VAc, and other additives were poured. After the mixture reached the prescribed temperature, an aqueous solution of initiator was poured. By withdrawing small amounts of emulsion at appropriate time intervals, conversions and degrees of polymerization were determined.

Measurement

Degrees of polymerization of PVAc (P_{Ac}) were calculated from intrinsic viscosities measured in acetone at 30°C using the following equation[8]:

$$[\eta] = 7.94 \times 10^{-3} \times P_{Ac}^{0.62}$$

To determine degrees of polymerization of PVA (P_A), PVAc was hydrolyzed with the usual alkaline methanolysis and intrinsic viscosities of the resulting PVA were measured in water at 30°C. The degrees of polymerization were calculated by using the following equation[9]:

$$[\eta] = 7.50 \times 10^{-3} \times P_A^{0.64}$$

Mechanical properties of PVAc films with DBP were measured by using Shimadzu Autograph M-100 at 20°C. Degrees of swelling and degrees of solubility of PVAc films with DBP in water were measured as follows: The films of 500 μ in thickness were immersed in water at 30°C and weighed after wiping off the water on the surfaces at the prescribed time.

RESULTS

PVAc Emulsion Obtained Using a Nonionic Surfactant

VAc was polymerized batchwisely or semicontinuously using a nonionic surfactant. In Table I are listed the emulsion recipe, the method, and the results. In the batchwise polymerization, an experi-

Table I Emulsion Polymerization Method, Recipe, and Results Using Nonionic Surfactant

No.	Method	Recipe (Wt) VAc	Recipe (Wt) H₂O	Recipe (Wt) N-400	Recipe (Wt) KPS[h]	Recipe (Wt) CaCO₃	Polymerization Temp. (°C)	Polymerization Time (h)	Conversion (%) Stage 1	Conversion (%) Stage 2	Conversion (%) Final
BN-1	Batchwise	100	200	3.0	0.05	0.12	60	4.75	—	—	99.2
BN-2	Batchwise	100	200	3.0	0.05	0.12	60	1.50	—	—	55.7
SN-1	Semicontinuous	10 + 90[a]	200	3.0 + 2.4[b]	0.20	0.50	60	1 + 9[c]	84.8[d]	86.5,[e] 89.1[f]	97.9
SN-2	Semicontinuous	10 + 90[a]	200	3.0 + 2.4[b]	0.80	1.98	70	1 + 11[c]	92.8[d]	90.5,[g] 92.8[f]	97.5

[a] 10 was added initially and 90 was added incrementally.
[b] 3.0 was added initially and 2.4 was added incrementally.
[c] Stage 1 (batchwise) was 1 h and stage 2 (continuous) was 9 or 11 h. VAc was added during 6 h in stage 2.
[d] Conversion just before incremental addition.
[e] At 3.5 h in stage 2.
[f] At 6.8 h in stage 2.
[g] At 5 h in stage 2.
[h] Potassium persulfate.

Table II   Degrees of Polymerization of PVAc and PVA Obtained in Table I

| No. | Method | Before Continuous Addition | | After Polymerization | | |
		Conversion (%)	P_{Ac}	Conversion (%)	P_{Ac}	P_A
BN-1	Batchwise	—	—	99.2	13420	2520
BN-2	Batchwise	—	—	55.7	6680	3280
SN-1	Semicontinuous	84.8	1940	97.9	1570	575
SN-2	Semicontinuous	92.8	1470	97.5	845	329

ment (BN-1) was completed to almost 100% conversion and the other one (BN-2) was stopped intentionally at about one-half the polymerization to clarify the effect of conversion. In the semicontinuous polymerization, 10% of the total amount of the monomer was fed initially and polymerized to 85% (SN-1) and 93% (SN-2) conversion, and then the residual 90% of the monomer were added incrementally while keeping the conversions at 85–90% (SN-1) and 90–95% (SN-2).

In Table II are listed the degrees of polymerization of PVAc thus obtained and of the hydrolyzed PVA. In the batchwise system, the degrees of polymerization of PVAc were very high (more than 6000), although those of PVA were in the range of 3000. On the other hand, those of PVAc obtained in the semicontinuous system were lower than 1600, and those of PVA were only 575 (SN-1) and 329 (SN-2).

Figure 1 shows the degrees of polymerization of PVAc during the course of emulsion polymerization along with those of PVA derived from the corresponding PVAc. In the batchwise polymerization (BN-1), the degrees of polymerization of PVAc increased markedly with increasing the conversion, contrary to those of PVA, which were lower than those of the corresponding PVAc, which decreased moderately. The degree of polymerization of PVAc obtained in BN-2 (P_{Ac} = 6680) is in good agreement with that of BN-1 at a conversion of 56% in Figure 1. In the semicontinuous polymerization (SN-1), the degrees of polymerization of PVAc and PVA were almost kept constant, and the former were three times higher than the latter.

Since PVAc emulsion cannot form films at room temperature, a plastisizing agent, DBP, was added to the emulsion (10 parts per hundred polymer) and films were formed. To equalize the quantities of the nonionic surfactant in the films, corresponding

amounts of N-400 were added to BN-1. Table III reveals the properties of PVAc films thus obtained.

Large differences were observed between the films from the batchwise polymerization and those from the semicontinuous one. First, tensile strengths of the former were much larger than those of the latter by two to four times, and, second, water absorption by the former were markedly smaller than those by the latter while the degrees of solubility in water
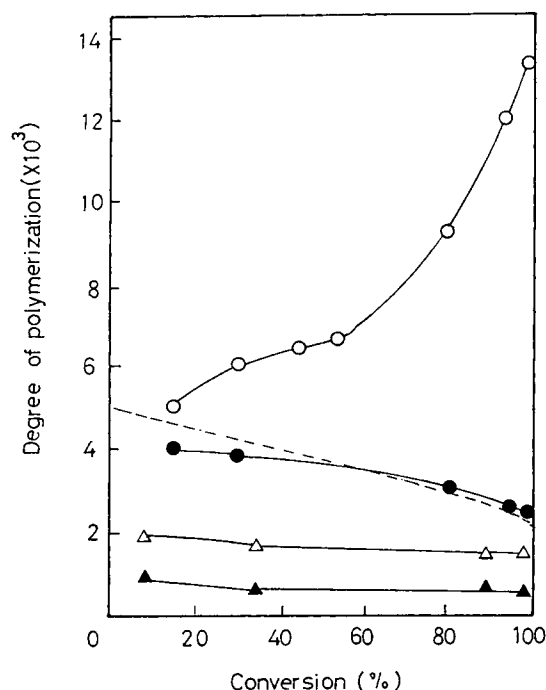

Figure 1   Change in degrees of polymerization of PVAc and hydrolyzed PVA during the course of polymerization: (○) P_{Ac} of a batchwise system (BN-1); (●) P_A of hydrolyzed PVAc of BN-1; (△) P_{Ac} of a semicontinuous system (BS-1); (▲) P_A of hydrolyzed PVAc of BS-1. Dotted line: Theoretical curve calculated from eq. (6).

Table III   Properties of PVAc Films Polymerized in the Presence of a Nonionic Surfactant

| No. | Mechanical Properties | | Resistance to Water | | | Solubility in Acetone (%) |
	Tensile Strength (kg/cm^2)	Elongation (%)	Degree of Swelling[a] (%)	Degree of Solubility[a] (%)	Spot Test (min)	
BN-1	124	998	52	4.3	> 30[b]	100.0
BN-2	133	1005	72			100.0
SN-1	71	728	224	3.5	> 30[c]	100.0
SN-2	34	669	606	2.4	12	96.6

[a] At 30°C for 7 days in water; degree of swelling = water absorbed × 100/weight of PVAc; degree of solubility = soluble solid × 100/weight of PVAc.
[b] Clear.
[c] Slightly turbid.

were at the same level. To make clear the difference of water absorption by the PVAc films, the degrees of swelling were plotted against the square root of the immersion time in Figure 2. There was also a difference in turbidity by a water spot (the spot test), i.e., whereas the former did not become turbid after 30 min, the latter became turbid in 30 min (SN-2) and in less than 12 min (SN-3) (No. 5

printed letters under the films could not be read after 12 min due to whitening of the film.)

PVAc Emulsion Obtained Using PVA as a Protective Colloid

The same kind of experiments as for the nonionic surfactant system were carried out using PVA as a protective colloid and are listed in Table IV. The PVAc polymerized with the recipe listed in Table IV were not soluble in acetone due to the well-known formation of the grafting of PVAc onto PVA, so that the polymers were solubilized in dimethyl sulfoxide, a common solvent to PVAc and PVA, precipitated in water to separate nongrafted PVA, and extracted with acetone to obtain nongrafted PVAc. Degrees of polymerization of PVAc thus obtained were measured and are listed in Table V. The degrees of polymerization of PVAc polymerized in the batchwise system were also extremely high compared with those polymerized in the semicontinuous one.

In Table VI are listed the properties of films with DBP from the PVAc emulsion polymerized in the presence of PVA. Whereas mechanical properties of the films from the batchwise system were almost the same level as those obtained in the presence of a nonionic surfactant listed in Table III, those obtained in the semicontinuous system in the presence of PVA showed much improvement compared with those obtained in the semicontinuous system in the presence of a nonionic surfactant (cf. tensile strengths of SN-1 [71 kg/cm^2] and SN-2 [34 kg/cm^2] in Table III vs. those of SP-1 [99 kg/cm^2] and SP-2 [88 kg/cm^2] in Table VI), although they were still lower than those obtained in the batchwise system.
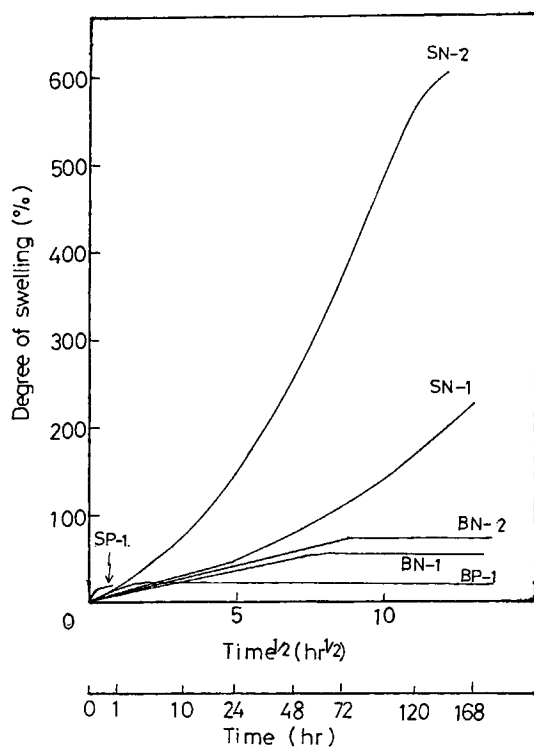

Figure 2   Relation between degrees of swelling of PVAc films immersed in water and immersion time.

Table IV   Emulsion Polymerization Method, Recipe, and Results Using PVA as a Protective Colloid

| | | Recipe (Wt) | | | | | Polymerization | | Conversion (%) | |
| | | VAc | H$_2$O | PVA | KPS | CaCO$_3$ | Temp (°C) | Time (h) | Stage 1 | Final |
No.	Method									
BP-1	Batchwise	100	200	8^a	0.050	0.12	60	5.5	—	99.0
BP-2	Batchwise	100	113	9^b	0.030/0.030^c	0.00	70	2.5	—	97.5
SP-1	Semicontinuous	10 + 90^d	200	8^a	0.80	0.59	70	1 + 11^e	94.1	100.0
SP-2	Semicontinuous	10 + 90^d	113	9^b	0.13	0.00	70	0.5 + 2^e	93.2^f	98.2

^{a} PVA 205.
^{b} PVA 217.
^{c} H$_2$O$_2$/tartaric acid, instead of KPS.
^{d} 10 was added initially and 90 was added incrementally.
^{e} Stage 1 and stage 2.
^{f} Conversion just before incremental addition.

There were differences in water absorption between the films from the PVA system and those from the nonionic one mentioned previously. The films from the batchwise PVA system absorbed only 17.8% of water; on the other hand, those from the semicontinuous system were almost broken into pieces due to their weak resistance to water. The water absorption procedure is shown in Figure 2. The latter films were whitened within 2 min, indicating also the weak resistance to water, whereas the former showed stronger resistance, although they were weaker compared with those obtained in the batchwise nonionic system.

DISCUSSION

In the typical emulsion polymerization such as styrene, the degree of polymerization of the resulting

Table V   Solubility of PVAc in Acetone and Degrees of Polymerization of Soluble PVAc Obtained in Table IV

| | | After Polymerization | | |
No.	Solubility in Acetone (%)	Conv. (%)	P_{Ac}	P_A
BP-1	34.2	99.0	16890	2820
BP-2	53.7	97.5	10800	2490
SP-1	53.1	100.0	960	410
SP-2	26.3	97.5	1600	—

polymer is determined by the ratio of the rate of polymerization in a particle and that of radical entry into a particle. In the bulk polymerization of VAc at around 60°C, the degree of polymerization of PVAc is extremely small in comparison with the kinetic chain length, which is defined as numbers of monomer polymerized with an initiator radical. The chain-transfer reaction to the monomer should accordingly be taken into account to predict the degree of polymerization of PVAc polymerized in the batchwise emulsion polymerization. At high conversion, the chain-transfer reaction to the polymer should also be considered, but it is complicated to predict the degree of polymerization of PVAc associated with the chain transfer to the polymer, which results in the formation of branches. However, the branches in PVAc can be cut off at the branched portion in the alkaline hydrolysis, since the chain-transfer reaction to PVAc occurs at a hydrogen in acetyl side groups. Thus, the number-average degree of polymerization of PVA, $P_{n,A}$, instead of that of PVAc, can be expressed as follows:

$$\frac{1}{P_{n,A}} = C_m + C_p \frac{[P]}{[M]} + \frac{\rho}{N r_p} \qquad (1)$$

where C_m and C_p refer to the chain-transfer constants to the monomer and the polymer, respectively; $[M]$ and $[P]$ are the concentration of the monomer and of the polymer (expressed by monomer unit) at conversion x, respectively; N denotes number of particles, ρ is the rate of radical entry into a particle; and r_p is rate of polymerization in a particle.

Table VI   Properties of PVAc Films Polymerized in the Presence of PVA

| No. | Mechanical Properties | | Resistance to Water | | |
---	Tensile Strength (kg/cm^2)	Elongation (%)	Degree of Swelling[a] (%)	Degree of Solubility[a] (%)	Spot Test (min)
BP-1	146	773	17.8	5.3	> 30[b]
BP-2	114	880	27.7	7.0	2
SP-1	99	728	(Broken)	—	2
SP-2	88	630	—	—	—

[a] At 30°C for 7 days in water; degree of swelling = water absorbed × 100/weight of PVAc; degree of solubility = soluble solid × 100/weight of PVAc.
[b] Clear.

Considering C_m as being equal to C_p and neglecting the third term in the right-hand side compared with the other two terms, we obtain eq. (2):

$$\frac{1}{P_{n,A}} = \frac{1}{1-x} C_m \tag{2}$$

Since $P_{n,A}$ expresses the degree of polymerization of PVAc (based on PVA) formed immediately after conversion x and the degree of polymerization is determined by chain-transfer reactions, number-average, viscosity-average, and weight-average degrees of polymerization until conversion x can be calculated by the following equations,[10] where $P_{n,A} : P_{v,A} : P_{w,A}$ is expressed by $1 : \{(1 + \alpha)\Gamma(1 + \alpha)\}^{1/\alpha} : 2$ (α is in $[\eta] = KP_A$):

$$\bar{P}_n = \frac{\int_0^x dx}{\int_0^x \frac{1}{P_{n,A}} dx}$$

$$= \frac{1}{C_m} \times \frac{x}{-\ln(1-x)} \tag{3}$$

$$\bar{P}_v = \frac{1}{C_m} \{(1 + \alpha)\Gamma(1 + \alpha)\}^{1/\alpha}$$

$$\times \left\{ \frac{\int_0^x (1-x)^\alpha dx}{\int_0^x dx} \right\}^{1/\alpha}$$

$$= \frac{1}{C_m} \{(1 + \alpha)\Gamma(1 + \alpha)\}^{1/\alpha} \times \frac{1}{(1 + \alpha)^{1/\alpha}}$$

$$\times \left\{ \frac{1 - (1-x)^{1+\alpha}}{x} \right\}^{1/\alpha} \tag{4}$$

$$\bar{P}_w = \frac{2}{C_m} \int_0^x (1-x) dx$$

$$= \frac{2}{C_m} \left(1 - \frac{1}{2} x\right) \tag{5}$$

By substituting $\alpha = 0.64$, eq. (4) can be written as eq. (6):

$$\bar{P}_v = \frac{1}{C_m} \times 0.867 \times \left\{ \frac{1 - (1-x)^{1.64}}{x} \right\}^{1/0.64} \tag{6}$$

Among many C_m data reported, we regard it as 2.0×10^{-4}, which is based on the viscosity-average degree of polymerization. Since C_m is based on the number-average in the equations described above, 2.0×10^{-4} should be converted to 3.70×10^{-4} (i.e., $1.849 \times 2 \times 10^{-4}$). $\bar{P}_v$ calculated from eq. (6) is shown in Figure 1 as a dotted line. The experimental data of the degree of polymerization based on PVA are in fairly good agreement with the calculated values, although there are some discrepancies between both values at low conversions. This may be attributed to the formation of a lower degree of polymerization of PVAc during the particle-formation stage.

During the course of the batchwise emulsion polymerization using a nonionic surfactant, the degree of polymerization of PVAc increases with increasing conversion due to the chain-transfer reaction to the polymer that forms branched PVAc. The lengths of the branches appear to be high since the degree of polymerization of PVA in Figure 1 is more than 2000 even in higher conversions.

In the semicontinuous system using a nonionic surfactant, degrees of polymerizations of PVAc are less than 1600 during the course of polymerization. This comes from the fact that the degree of polymerization in the first stage where 10% of the total

amount of the monomer is fed, forming 5% on the basis of water, may be smaller due to the course of particle formation and that in the continuous stage the conversions are kept high at more than 90%, yielding branched polymers that have shorter and denser chain lengths. The higher the conversion at the incremental addition, the shorter and the denser the branches.

The polymer molecules obtained in the semicontinuous system are supposed to be not enough to entangle with each other due to the lower degrees of polymerization and also due to the shorter and denser branches, whereas in the batchwise polymerization, those are long enough to entangle with each other. This appears to be the reason for the fact that the PVAc emulsion films obtained from the semicontinuous system show the weaker mechanical properties and the weaker water resistance compared with those obtained from the batchwise one. (Tensile strength of the PVAc film of SN-2 obtained in the semicontinuous/nonionic system [34 kg/cm^2] is markedly lower than that of BN-1 obtained in batchwise/nonionic system [124 kg/cm^2] in Table III).

When PVA is used as a protective colloid, consideration on the chain lengths and branching of the resulting PVAc is difficult due to the grafting of PVAc onto PVA. Degrees of polymerization of PVAc obtained in this case were measured on the soluble parts of the solids. The same tendency as obtained in the nonionic system can be observed, i.e., the degrees of polymerization of PVAc from the batch system are considerably higher than those from the semicontinuous system. This also causes the difference in the mechanical properties.

It is worth noticing that in the same semicontinuous system the tensile strengths of the films from the PVA protective colloid recipe are twice as strong as those from the nonionic surfactant recipe, whereas there is almost no difference between those for PVA and noionic surfactant recipe in the batch system, as mentioned previously. This may be attributed to the strengthening effect of PVA network in the films, which will be discussed later along with the behavior in the water-immersion experiments. The effect may be enhanced when the tensile strengths are low.

As shown in Figure 2, water absorption to PVAc films are at first almost proportional to the square root of immersion time and seem to reach constant values. The initial slopes are related to diffusion constants of water molecules in PVAc films and increase in the order BN-1 < BN-2 < CN-1 < CN-2 = BP-1 < CP-2. In other words, resistance of the PVAc films to water becomes worse in that order.

This fact is thought to be related to two reasons: One comes from the easiness of the entanglement of PVAc molecules described above, and the other must be related to the morphology of the PVAc films containing nonionic surfactant or PVA. The nonionic surfactant is partly soluble in PVAc, so that the molecules are present in PVAc films as islands, whereas PVA molecules exist in PVAc films as a network structure. The structure is thought to be caused by the nonsolubility of PVA in PVAc, localization of PVA on particle surfaces by grafting with PVAc molecules, and strong intermolecular interaction of PVA molecules. This network structure of PVA molecules causes the increase in the mechanical properties of films mentioned previously.

CONCLUSION

In the batchwise emulsion polymerization of VAc at around 60°C, degrees of polymerization are high enough for the PVAc molecules to entangle with each other, although long branches are formed with increasing conversion. In the semicontinuous system, however, degrees of polymerization in terms of the linear portion are remarkably lower due to the chain-transfer reaction to the polymer because of high conversion. This means the frequent formation of short branches. In this case, the sufficient entanglement of PVAc molecules with each other may be difficult. This leads to weaker mechanical properties of the films as well as weaker resistance to water immersion.

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