Title	LONG BRANCHING IN POLY(VINYL ACETATE) AND POLY(VINYL ALCOHOL)
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Citation	大阪大学, 1972, 博士論文
Version Type	VoR
URL	https://hdl.handle.net/11094/2500
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LONG BRANCHING IN POLY(VINYL ACETATE) AND POLY(VINYL ALCOHOL)

June, 1972

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CONTENTS

Long Branching in Poly(vinyl acetate) and Poly(vinyl alcohol)

INTRODUCTION

Among the structual characteristics of poly(vinyl acetate)(PVAc) and poly(vinyl alcohol)(PVA) such as molecular weight, molecular weight distribution, head-to-tail structures, terminal groups, stereoregularity, and branching, only the quantitative estimation of branching has not yet been achieved. The methods for the quantitative determination of branching include, in general, the infrared spectroscopic analysis of the polymer chain structure, the measurement of molecular weights and solution properties, the observation of the physical behavior of polymers, and kinetic studies. Although a combination of these methods may provide a more powerful tool for the quantitative determination of branching, the detection as well as quantitative estimation of branching in PVA has not been successful.

Since the concept of self-branching during the radical polymerization of vinyl acetate was first comfirmed by Inoue and Sakurada,[1] a number of investigations have been reported extensively. From the facts that during the polymerization of vinyl acetate in bulk the degree of polymerization of PVAc increased with conversion whereas that of derived PVA was almost constant irrespective of conversion, and that the degree of polymerization of PVAc and PVA were almost identical at the initial stage of polymerization, the branching has been anticipated to occur at the acetoxy group of PVAc[1,2].

Nakajima et al.[3,4] and Matsumoto et al.[5] have pointed out the presence of branching on PVAc from the studies of intrinsic viscosity and Huggins parameter k' of the polymers prepared to various conversions under various conditions. Burnett and Melville[6] carried out a study along a similar line by measuring the number and weight average molecular weight and concluded that PVAc which was polymerized at the temperature below -30°C had almost no branching. On the other hand, Matsumoto and Imai[7] have shown that the k'—viscosity relationship of PVA was independent of the preparative conditions of the parent PVAc.

Imoto, Ukida, and Kominami[8] studied the polymerization of vinyl trimethylacetate in the presence of PVAc to elucidate the position of the branching point at PVAc. When the isolated graft polymers were hydrolyzed, only PVAc was converted to PVA because the rate of alkali-catalyzed saponification of poly(vinyl trimethylacetate) was remarkably slower than that of PVAc. After removal of the poly(vinyl trimethylacetate) fragment, which had been bonded to the acetoxy group, by extraction, the number of trimethylacetate units remaining in the PVA was determined by infrared analysis. The ratio of the numbers of main chain branch and those of the side chain branch was estimated to be 1:40 at 60—70°C. This result indicated that most of branching occurred at the acetyl group and only a very little at the secondary carbon atom in the main chain.

Thus, nowadays it has become a common view that branching on the main chain occurs much less frequently than on the acetoxy group in the polymerization of vinyl acetate, and that the amount of long branching in PVA must be very small, if any.

On the other hand it should be noted that some reports which suggest the possibility of the presence of branching in PVA have been published to date.

Wheeler et al.[9,10] studied the branching formation of PVAc by kinetic analysis. They estimated the ratio of the rate constants for abstraction of hydrogen atoms at the α-position of main chain and at the acetoxy methyl group to be 0.5 at 70°C. This ratio suggests the presence of considerable amount of main chain branches.

Roland and Richards[11] studied the polymerization of ethylene in the presence of PVAc, indicating that polyethylene branches became attached to the main chain of PVAc as well as to the acetyl group. Considering a similar reactivity of the polyethylene growing radical and the PVAc growing radical both of which are not resonance stabilized, the polymerization of vinyl acetate might presumably participate in frequent transfer reactions in a similar manner.

Variations in the number of branches will also influence the PVA properties. Nakajima and Sakurada[12] investigated the molecular weight distribution of PVA derived from PVAc polymerized under various conditions. They suggested the presence of branched structure in PVA. Ukida et al.[13] reported that PVA was less crystalline and more easily swollen by solvents when the parent polymer was prepared at higher polymerization temperatures, and discussed that branching might have increased with polymerization temperatures. Nagai and

Sagane[14] attempted to estimate the degree of branching in PVA by determining the amount of terminal primary alcohol by infrared analysis. With copolymers of vinyl alcohol and allyl alcohol as references, the primary alcohol content in PVA was estimated to be 2—4 mol%, suggesting a fairly large number of branching.

Stockmayer et al.[15] determined the chain-transfer constants in the free-radical polymerization of vinyl acetate for various substances. They reported that the chain-transfer constants for isopropyl and sec-butyl acetate at 60°C are both larger than that for vinyl acetate. This fact shows that abstraction of the tertiary hydrogen atom is one of the important transfer processes in these esters. Hence they supposed that a similar process is also involved in transfer to polymer.

Thus, the exact experimental evidence for the presence of branches in PVA has not been reported to date. This work was undertaken to estimate quantitatively the long branching in PVAc and PVA, and to elucidate the mechanism of the branch formation using a new experimental method and kinetic analysis.

Two types of chain-transfer reactions can be suggested as leading to the formation of branched chains in the polymerization of vinyl acetate, i.e., the transfer to monomer and the transfer to polymer. In the first case, the growing chain radical transfers its activity to a monomer unit by abstracting there from a hydrogen atom. In this way a polymer chain having a terminal double bond is formed and the double bond is attacked by the growing radicals, thus leading to branched chains. In the second case, the growing chain radical transfers to a polymer molecule by abstracting a hydrogen atom, thus permitting the polymer chain to grow a branch. When a hydrogen atom is abstracted from the acetyl group of polymer or monomer, only a hydrolyzable branching will be resulted by either mechanism, while abstraction from the α-position of polymer or monomer will result in a nonhydrolyzable branching which will bring about the branching in the derived PVA.

In order to investigate the chain transfer to polymer, it is desirable to employ the experimental technique of the polymerization of a monomer in the presence of its polymer which is prepared and characterized precedingly. However it is not generally possible to do this, because it will be practically difficult to separate and to discriminate the initially added polymer and the newly formed polymer due to the similar solubility and the same chemical structure. When a cross-linked polymer is used as an initial polymer, the separation will become possible. Moreover, if the cross-linkage can be cleaved quantitatively afterwards without any change of chemical structures of the polymer, the characterization of the resulting branched polymer such as viscosity, molecular weight, and molecular weight distribution measurement in the solution state will also become possible.

Chapter I describes the preparation of a cross-linked PVAc gel in which the cross-linking is able to be quantitatively cleaved to revert to a polymer of the same molecular weight as original. The effective cross-linking was formed by the reaction of PVAc which was partially saponified to the extent of a few mol% and toluylene diisocyanate. The cross-linked PVA was derived by treating the cross-linked PVAc with a catalytic amount of sodium hydroxide in methanol without any change of the cross-linking urethane bonds. The cross-linkage was quantitatively cleaved by treatment with such an inorganic acid as hydrobromic acid releasing polymers of the same molecular weight as original.

In Chapter II, the polymerization of radioactive vinyl acetate in the presence of the cross-linked PVAc was investigated. This system made it possible to separate as well as to discriminate between the "graft polymer" and the newly polymerized "homo polymer". Furthermore, the degree of grafting onto the acetoxy methyl group and onto the main chain were both possible to be estimated. Consequently it turned out that the chain transfer to the polymer main chain takes place about 2.4 times as readily as that to the acetoxy methyl group at 60°C and about 4.8 times at 0°C.

Chapter III describes the kinetic analysis of the branching reaction on the basis of the results mentioned in Chapter II, the results of viscosity measurement of PVAc, and the quantitative determination of the carboxyl end group in the derived PVA. The chain-transfer constants to the α-positions and the acetyl groups on both the polymer and monomer were all determined, and copolymerization reactivity parameters of the terminal double bond were also estimated. After all it has become clear that the formation of nonhydrolyzable branching by terminal double bond copolymerization can be almost neglected, and that consequently all of the long branching in PVA are formed solely by the polymer-transfer mechanism. On the other hand, a large number of hydrolyzable branching in PVAc are prepared by the polymerization of the terminal double bond rather than by the polymer transfer.

In Chapter IV, to clarify the grafting behavior of vinyl trimethylacetate onto PVAc, the polymerization of radioactive vinyl trimethylacetate in the presence of a cross-linked PVAc gel is described. Contrary to the result reported by Imoto, Ukida, and Kominami[8], it became clear that the grafting onto the main chain of PVAc takes place about 2.8 times as readily as that onto the acetyl side group of PVAc. Considering the similar reactivities of both monomers, it should be reasonable to assume that vinyl trimethylacetate behaves like vinyl acetate in the chain-transfer reaction to PVAc.

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Chapter I

Cross-linking and Decross-linking of Poly(vinyl acetate)

ABSTRACT

An effective cross-linking was formed by the reaction of poly (vinyl acetate) which was partially saponified to the extent of a few mol% and toluylene diisocyanate in benzene. The yield of gel was markedly depended on the degree of saponification and the concentrations of polymer and diisocyanate. The cross-linked poly(vinyl alcohol) was derived by treating the corresponding poly(vinyl acetate) with a catalytic amount of sodium hydroxide in methanol without any change of the urethane cross-linking bonds. The cross-linking based on the urethane linkage was quantitatively cleaved by acids, especially by hydrobromic acid, releasing polymers of the same molecular weight as original.

INTRODUCTION

In the studies of graft copolymerization where a monomer is polymerized in the presence of a polymer, the mixture of resulting polymers can generally be separated into the individual components by solvent extraction due to the different solubilities of the homo polymer and the graft copolymer. However, a clean separation and purification of the graft copolymer is not always possible. In order to study the self-branching by the chain transfer to polymer during polymerization, it is desirable to employ the experimental procedure of polymerizing a monomer in the presence of previously prepared and characterized polymer. However it is not generally possible to do this because it will be difficult, in this case, not only to separate but also to discriminate the initially added polymer and the newly formed polymer from the system due to the same solubility and the same chemical structure.

However, if a cross-linked polymer is used initially in the system, the separation will become possible, since cross-linked polymer is insoluble in all solvents. If the cross-linkage can be cleaved perfectly after polymerization and separation procedures without any change of chemical structures, the characterization of the graft polymer in solution will also become possible. Hence, the success in the preparation of the cross-linked gel polymer, which can be easily decross-linked afterwards to give a linear polymer of the same molecular weight as original, will open a new path in the study of chain transfer to polymer and graft copolymerization.

For the purpose of the investigation of self-branching of poly (vinyl acetate)(PVAc) and poly(vinyl alcohol)(PVA) an experimental technique for the cross-linking and decross-linking reaction of PVAc is described in this paper. Possible methods for the preparation of the cross-linking PVAc which is expected to be able to be decross-linked afterwards may be (i) treating PVA with dialdehyds and subsequent acetylation to give an acetal bond cross-linking, (ii) the reaction of partially saponified PVAc with dicarboxylic anhydrides to give an ester bond cross-linking, (iii) the reaction of partially saponified PVAc with diisocyanates to give an urethane bond cross-linking. It is desirable for the purpose of this study that the chemical structure of PVAc does not change except for the cross-linkages. In order for the cross-linking reagents to be effective, the cross-linking reaction should be as quantitative as possible under mild conditions. Futhermore, it is necessary for the cross-linking bond to remain intact under the deacetylation conditions of PVAc. In addition to these the most difficult problem is that the cross-linking bond can be quantitatively cleaved without any affection on the other structures to give polymers of the same molecular weight as original.

It is well known that the reactivity between the alcoholic hydroxyl group and isocyanate is considerably high, and that the urethane group undergoes acid- or alkali-catalyzed hydrolysis. Cross-linking of this type is considered to be most promising as compared to other methods.

This paper will be concerned with the cross-linking of partially saponified PVAc with toluylene diisocyanate and its decross-linking.

EXPERIMENTAL

Materials

Commercial toluylene diisocyanate (TDI)(2,4-/2,6- : 80/20) was distilled twice with a Vigreux column under reduced pressure: mp 11—13°C ; bp 120°C/10 mmHg.

Benzene was shaken three times with conc. H_2SO_4, washed several times with water, dried over $CaCl_2$ over night, refluxed with metallic sodium and then distilled with a Vigreux column.

Other solvents were purified in the usual way.

Preparation of PVAc

PVAc obtained commercially(Sekisui Chemical Co., Esnyl P-18) was hydrolyzed by the ordinary method[1], reacetylated according to McDowell's method[2] and then purified by reprecipitation into water from an acetone solution.

Fractionation of PVAc

PVAc was fractionated by the partial precipitation method using the solvent—nonsolvent system of acetone—water at 30°C. The polymer concentration was 2%(w/v). Water was added dropwise to a well stirred solution of the polymer in acetone until the mixture became cloudy. The precipitate was first dissolved by raising the temperature of the bath and then allowed to reprecipitate by lowering the bath temperature slowly to 30°C. The mixture was allowed to settle over night, a precipitate in a gel form was isolated, dissolved in benzene and recovered by freeze drying. The procedure was repeated for the isolation of the remaining fractions.

Partial Saponification of PVAc

For the purpose of introducing pendant hydroxy groups along the main chain which is available for the cross-linking reaction with diisocyanate, PVAc was partially saponified by NaOH in an acetone—water system. About 0.86 g of PVAc was dissolved in 43 ml of a mixtures of acetone and water (75/25, v/v). An appropriate amount of 0.3-N NaOH aqueous solution was added to the polymer solution and the reaction was carried out under stirring for 16 hr at 40°C. The partially saponified PVAc was separated by pouring the reaction mixture into a large amount of water. The product was washed with water, purified by reprecipitation into water from an acetone solution three times, dissolved in benzene and recovered by the freeze-drying technique.

Reaction of Partially Saponified PVAc with TDI

An ampoule containing partially saponified PVAc, benzene and TDI was degassed three times in a high vacuum system and then sealed. Reaction was carried out in a thermostat at 75°C for 9 hr. The reaction mixture was poured into a large excess of methanol and refluxed for several hours. The products of gel and soluble polymer were separated by extraction with methanol, acetone and benzene in this order. The soluble polymer and the gel polymer were dissolved and swollen respectively in benzene and were recovered by the freeze-drying technique.

Deacetylation of Cross-linked PVAc

One and a half grams of cross-linked PVAc which was obtained as mentioned above was swollen in 100 ml of methanol. One ml of 6-N NaOH aqueous solution was then added under stirring and the reaction vessel was kept at 40°C for 16 hr until the rigid precipitation of PVA was completed. The PVA was separated, washed with methanol, and dried under vacuo over night at 60°C.

Cleavage of Cross-link in PVAc

Hydrolysis by Acid. One part of the cross-linked PVA gel which was obtained by deacetylation of the PVAc gel and 40 parts of 3-N HCl or HBr aqueous solution were placed in an ampoule. After the atmosphere was replaced with nitrogen, the ampoule was sealed, shaken in a thermostat at 65°C for 17 hr and then at 95°C for 5 hr. The solid PVA began to swell at the initial stage of reaction, and within 30 minutes or less after the reaction temperature was elevated to 95°C, the swollen gel disappeared in the solution. When the reaction was carried out at the temperature of 95°C from the beginning, the product became colored. The regulation of the reaction conditions as above gave a white polymer as product. The decross-linked soluble PVA was separated by pouring the reaction mixture into a large excess of methanol, washed by methanol and dried in vacuo at 40°C. It was reacetylated as above.

Hydrolysis by Methanolic Alkali. One part of cross-linked PVAc, 100 parts of methanol and 50 parts of a 15-% NaOH solution in a mixture of methanol and water (75/25 : v/v) were placed in a flask equipped a reflux condenser, and the reaction was carried out for 24 hr under reflux.

Reaction with Phthalic Anhydride. An ampoule containing one part of the gel and 20 parts of phthalic anhydride was degassed in a vacuum system and then sealed. Reaction was performed by keeping the ampoule in a thermostat at 140°C for 5 hr. Polymer was separated by sublimation of phthalic anhydride under reduced pressure, washed by ether, and vacuum dried.

Swelling Ratio of Gel

The dried gel was weighed and immersed in acetone maintained at 30°C for 24 hr. At the end of the time the swollen gel was weighed. Swelling ratio was calculated as follows:

$$\text{swelling ratio} = \frac{\text{weight of swollen gel} - \text{weight of dried gel}}{\text{weight of dried gel}}$$

Infrared Spectra

The infrared spectra of insoluble polymers were taken by the KBr-tablet method and those of soluble polymers were measured with films which were prepared on rock salt plates by using a Hitachi EPI-G3 spectrometer.

Viscosity

Intrinsic viscosities of the acetone solution of polymer were measured at 30°C in a modified Ubbelohde type viscometer having a solvent flow time of 147 sec. The reduced specific viscosities were determined at five concentrations and intrinsic viscosities were determined by double plots of η_{sp}/C vs. $(\ln\eta_{rel})/C$ vs. C.

Osmotic Pressure

Osmotic pressures of the methyl ethyl ketone solutions of the samples were measured at several polymer concentrations using a Hewlett-Packard-502 High Speed Membrane Osmometer (Membrane : Aller feinst). The measurement temperature was 37°C.

Gel-Permeation Chromatography(GPC)

Molecular weight distribution was estimated by GPC of dimethyl formamide solutions of polymers using a Shimazu GPC-1A type under the condition: polymer concentration, 0.5—0.6 wt%; injection time, 100 sec; flow rate, 1 ml/min; temperature, 30°C.

RESULTS AND DISCUSSION

Fractionation of PVAc

When the acetyl side groups of PVAc are removed by hydrolysis, and are subsequently restored by acetylation, the processed polymer usually has a lower molecular weight than the original. This phenomenon is due to the hydrolytic cleavage of branches attached to the acetoxy groups on the polymer. For the purpose of the present study, it is necessary for the acetoxy branches of the starting PVAc to be removed by treatment in the hydrolytic condition before use, because such molecular weight degradation of PVAc will be caused in the procedure of hydrolytic cleavage of the urethan cross-linkage.

Nakajima[3] investigated the molecular weight changes of PVAc induced by repetition of hydrolysis and reacetylation, concluding that molecular weight change was observed only at the first hydrolysis. In our study, PVAc prepared by deacetylation and subsequent reacetylation of a commercial PVAc was used for the fractionation. Intrinsic viscosity of the sample was 0.61 whereas the value of the initial PVAc was 0.77, and this value did not change with further de- and reacetylation (0.61). Figure 1 shows this procedure and subsequent fractionation procedures in a block diagram. Since the molecular weight of the decross-linked polymer is to be observed as a measure of decross-linking comparing with the initial value as described later, and since the estimation of the degree of cross-linking is to be made by solubility characteristic of polymer, the molecular weight distribution of PVAc is desirable to be narrow. PVAc fractions used for the cross-

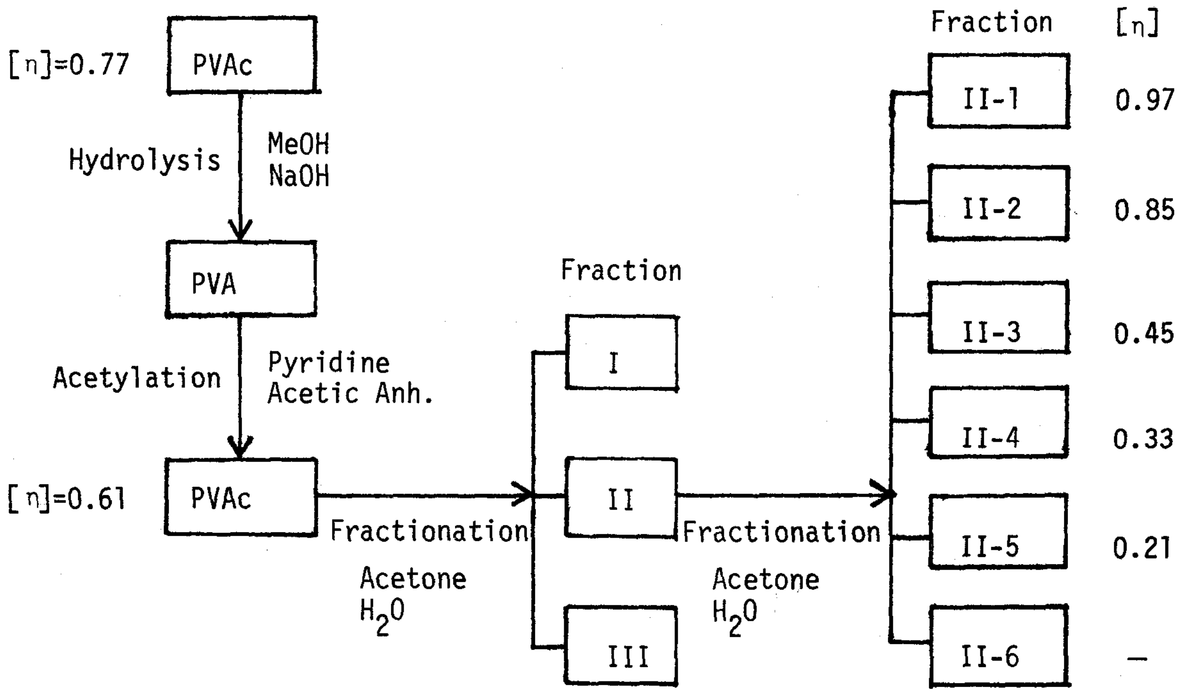


Figure 1. Hydrolysis, reacetylation, and subsequent fractionation procedures of PVAc.

linking reaction are listed in Table I.

The relation of viscosity and molecular weight of PVAc has been studied by many investigators. Nakajima[4] proposed a relationship between intrinsic viscosity in acetone and number-average molecular weight for the fractionated samples, and Wagner[5] proposed another relationship by using strictly fractionated samples. The relationship between intrinsic viscosity and number-average molecular weight of II-2, II-3, and II-4 fractions in Table I lies between those of Nakajima and Wagner. The values of $\bar{M}w/\bar{M}n$ which are determined by GPC as a measure of molecular weight distribution, as shown in Table I, are near to unity. From these facts, it will be clear that all the fractions have considerably narrow distributions of molecular weight.

Partial Saponification of PVAc

The results of partial saponification of fractionated PVAc are shown in Table II. After the reaction it was tried to determine the amount of residual NaOH in the reaction mixture by titration with hydrochloric acid using a pH meter or phenolphthalin as an indicator, but it was not detected in all cases. It is well known that the deacetylation reaction of PVAc in the system of NaOH and acetone containing water proceeds by the direct saponification of acetate groups which is different from the ester interchange in the system of NaOH and methanol.

Consequently, it can be considered that the procedure results in the quantitative saponification corresponding to the amount of NaOH

Table I. Intrinsic viscosities and number average molecular weight of the fractionated PVAc

Fraction	$[\eta]^{a)}$	$\overline{M}n^{b)}$	$\overline{M}w/\overline{M}n^{c)}$
II-2	0.85	175,000	1.5
II-3	0.54	118,000	1.3
II-4	0.33	62,200	1.4

a) in acetone, at 30°C, 100 ml/g.

b) osmotic pressure, MEK, 37°C.

c) GPC.

Table II. Partial saponification of fractionated PVAc[a)]

Fractionated PVAc		Acetone+H_2O[b)]	0.3N-NaOH	Degree of saponification
Fraction No.	wt.(g)	(ml)	(ml)	(mol%)
II-2	0.816	43	0.48	1.43
II-2	0.816	43	0.67	2.0
II-2	6.89	344	8.88	3.33
II-2	0.816	43	1.67	5.0
II-3	0.816	43	1.11	3.33
II-4	0.861	43	1.11	3.33

a) Reaction condition; at 40°C, for 16 hr.

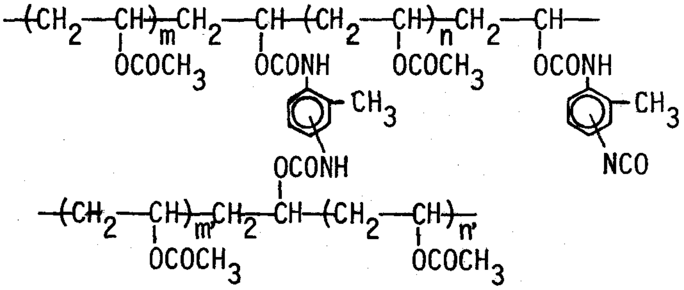
b) Acetone/H_2O; 75/25(v/v).

added initially in the system.

Cross-linking Reaction

The reactions of partially saponified PVAc and TDI were carried out under various conditions. The results are summerized in Table III. The reaction system was homogeneous at the start of the reaction, gelation took place in a few hours, and all the polymers set to gel completely under the appropriate reaction condition. In some cases, PVAc remained soluble at the end of the reaction depending on the reaction condition. It was recognized, however, that those soluble polymer had higher molecular weight than the original due to the intermolecular cross-linking.

Cross-linking does not necessarily result from such reactions. If polymer chains are not connected through urethane linkages, pendant isocyanate groups will result. The structure of the cross-linked PVAc may be illustrated as follows:



A cross-linked gel polymer which was purified by washing with benzene and a cross-linked soluble polymer which was purified by reprecipitation into n-hexane from a benzene solution indicated an absorption

Table III. Cross-linking reaction of partially saponified PVAc with TDI[a)]

Expt. No.	PVAc			Degree of Saponification mol%	Polymer conc. % (W/V)	TDI conc. % (W/V)	Gel Fraction		Sol Fraction		
	Fraction	[η]	$\overline{M}n$				%	Swelling Ratio	%	[η]	$\overline{M}n$
A-1	II-2	0.85	175,000	1.4_3	7	0.151	6.4	—	93.6	1.20	—
A-2	II-2	0.85	175,000	2.0	7	0.211	21.8	22.1	78.2	1.99	—
A-3	II-2	0.85	175,000	3.3_3	7	0.353	93.2	17.2	6.8	—	—
A-4	II-2	0.85	175,000	5.0	7	0.529	100	11.4	0	—	—
A-5	II-2	0.85	175,000	3.3_3	4.5	0.227	12.4	—	97.6	1.79	—
A-6	II-2	0.85	175,000	3.3_3	9	0.456	100	10.9	0	—	—
A-7	II-2	0.85	175,000	3.3_3	15	0.757	100	8.3	0	—	—
A-8	II-2	0.85	175,000	3.3_3	7	0.117	31.7	20.5	68.3	1.83	747,000
A-9	II-2	0.85	175,000	3.3_3	7	1.175	100	15.0	0	—	—
A-11	II-3	0.54	118,000	3.3_3	7	0.353	100	14.5	0	—	—
A-12	II-4	0.33	62,200	3.3_3	7	0.353	100	16.8	0	—	—
A-13	II-3	0.54	118,000	3.3_3	4.5	0.113	0	—	100	0.82	152,000

a) Reaction condition; solvent, benzene; temperature, 75°C; time, 9hr.

band at 2300 cm^{-1} in their IR spectra, as shown in Figure 2. The band may be due to the isocyanate group and it disappeared on treating the polymers with methanol probably because the pendant isocyanate groups were converted into carbamate groups. The cross-linked soluble polymer purified as above became insoluble after being kept dry for about a week, suggesting that further cross-linkings would be formed by the reaction between pendant isocyanate groups and unreacted hydroxy groups. In the case of the polymer once treated with methanol, such a solubility change was not observed at all. The infrared spectra of cross-linked PVAc treated with methanol are superimposable to that of original PVAc except for the small bands at about 1600 and 1520 cm^{-1} which may be assigned to the substituted benzene ring.

The cross-linking reaction is strongly influenced by the degree of partial saponification of the starting PVAc, the concentrations of polymer and TDI in the reaction system as listed in Table III.

Figure 3 shows the influence of the degree of saponification of PVAc on the yield and the swelling ratio of gel. The yield of gel increased remarkably and the swelling ratio of gel decreased with the increase of the degree of saponification of PVAc. The decrease of the swelling ratio means the increase of cross-linking density. It should be noted that the cross-linking proceeds even after the conversion into gel goes up to 100%.

The cross-linking reaction is extremely dependent on the concentration of polymer solution as shown in Fegure 4. A considerably high concentration was required to obtain a quantitative yield of

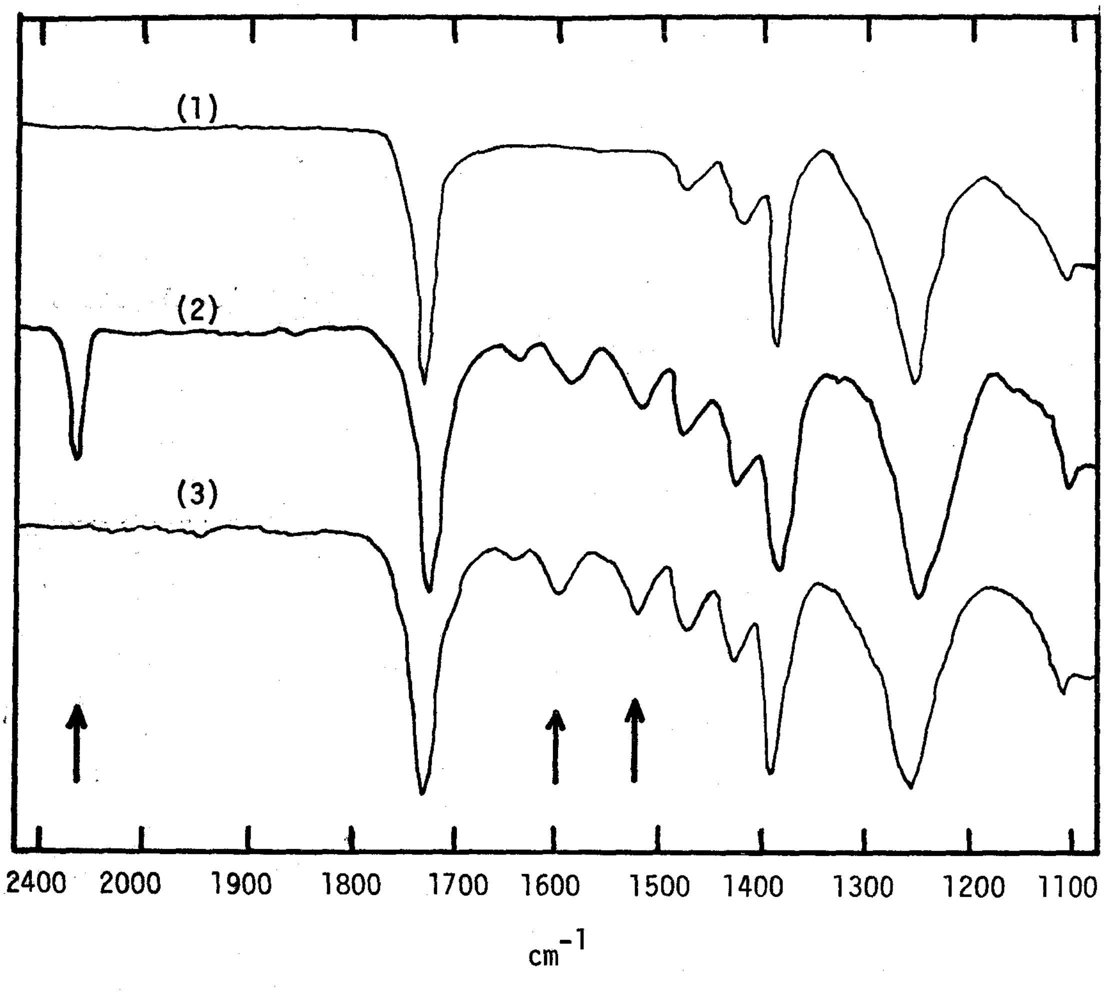


Figure 2. IR spectra of PVAc, cross-linked PVAc, and cross-linked PVAc after treating with methanol; (1), original PVAc; (2), cross-linked PVAc; (3), cross-linked PVAc after treating with methanol.

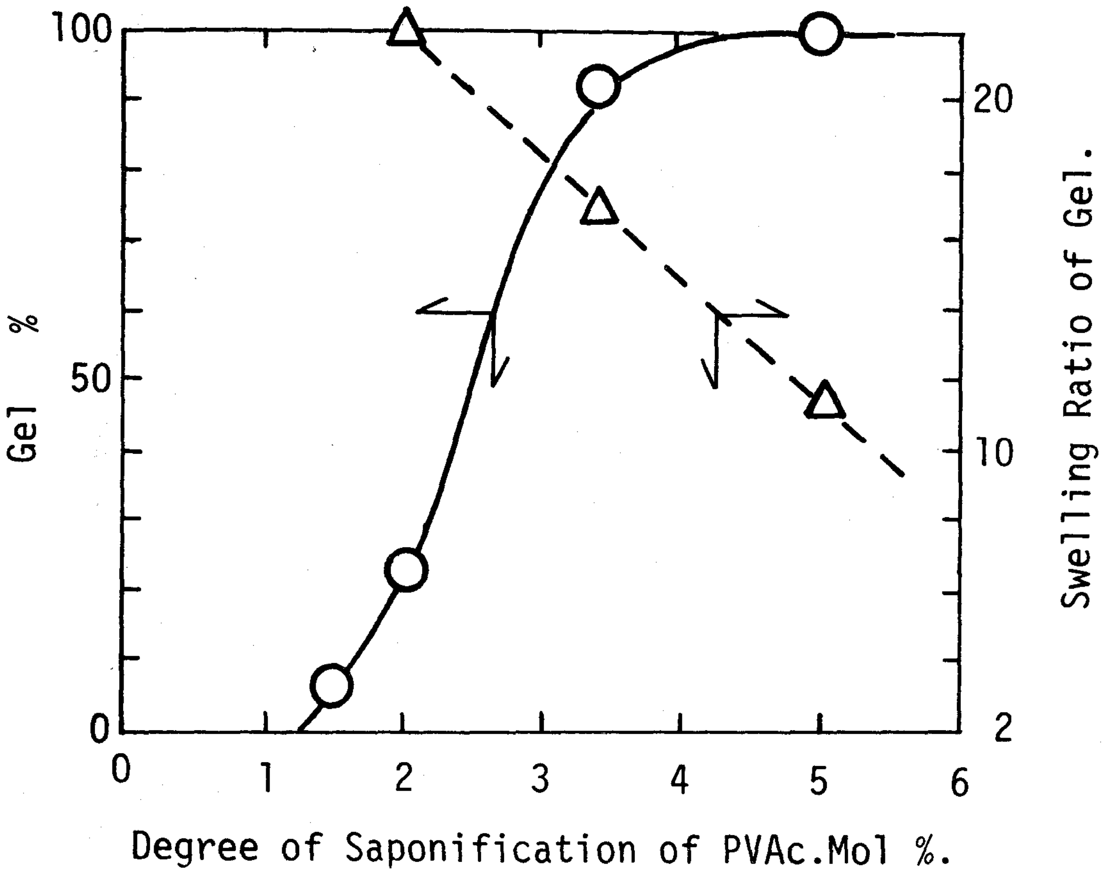


Figure 3. Effect of the degree of saponification of PVAc on the yield of gel and swelling ratio: polymer concentration, 7 %(w/v); TDI/-OH (mol ratio) = 1.5/1; reaction temperature, 75°C; reaction time, 9 hr.

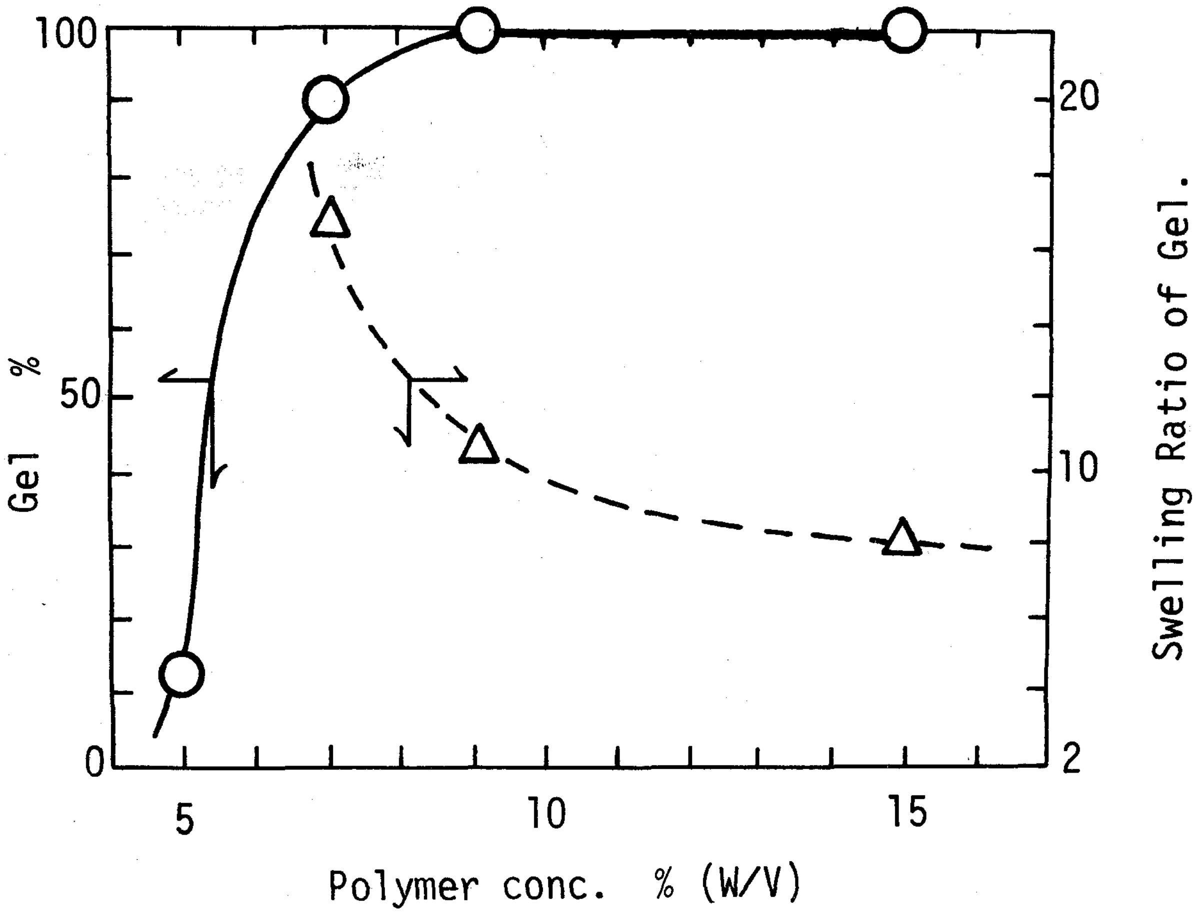


Figure 4. Efect of the polymer concentration on the yield of gel and swelling ratio: degree of saponification of PVAc, 3.33 mol%; TDI/-OH (mol ratio) = 1.5/1; reaction temperature, 75°C; reaction time. 9 hr.

gel, namely the concentration more than 9% gave a quantitative yield whereas less than about 5% hardly afforded gel product under the same reaction condition.

Figure 5 shows the effect of TDI concentration on the yield of cross-linking. The yield of gel was quantitative above a certain concentration in the range of this experiment. At a high TDI concentration of 4.7% the increase of swelling ratio of gel was observed suggesting the decrease of cross-linking density presumably because of the increase of the pendant isocyanate groups. This facts indicate that it is not desirable for obtaining effective cross-linking to use a large excess of TDI.

Deacetylation of Cross-linked PVAc

PVA was obtained by treating the cross-linked PVAc with a catalytic amount of sodium hydroxide in methanol. In the infrared spectra of this PVA, as shown in Figure 6, an absorption at 1740 cm^{-1} associated with the ester group disappeared, although bands at 1600 and 1520 cm^{-1} remained unaltered and an absorption at 1700 cm^{-1} due to the carbonyl in the urethane group, which was a shoulder band in case of the cross-linked PVAc, appeared as a peak. Except for these peaks, the spectrum coincides well with that of normal PVA derived from uncross-linked original PVAc. PVA thus obtained from gel PVAc was entirely insoluble but swelled in water.

Table IV shows the intrinsic viscosities and the molecular weights of soluble cross-linked PVAc and those after deacetylation

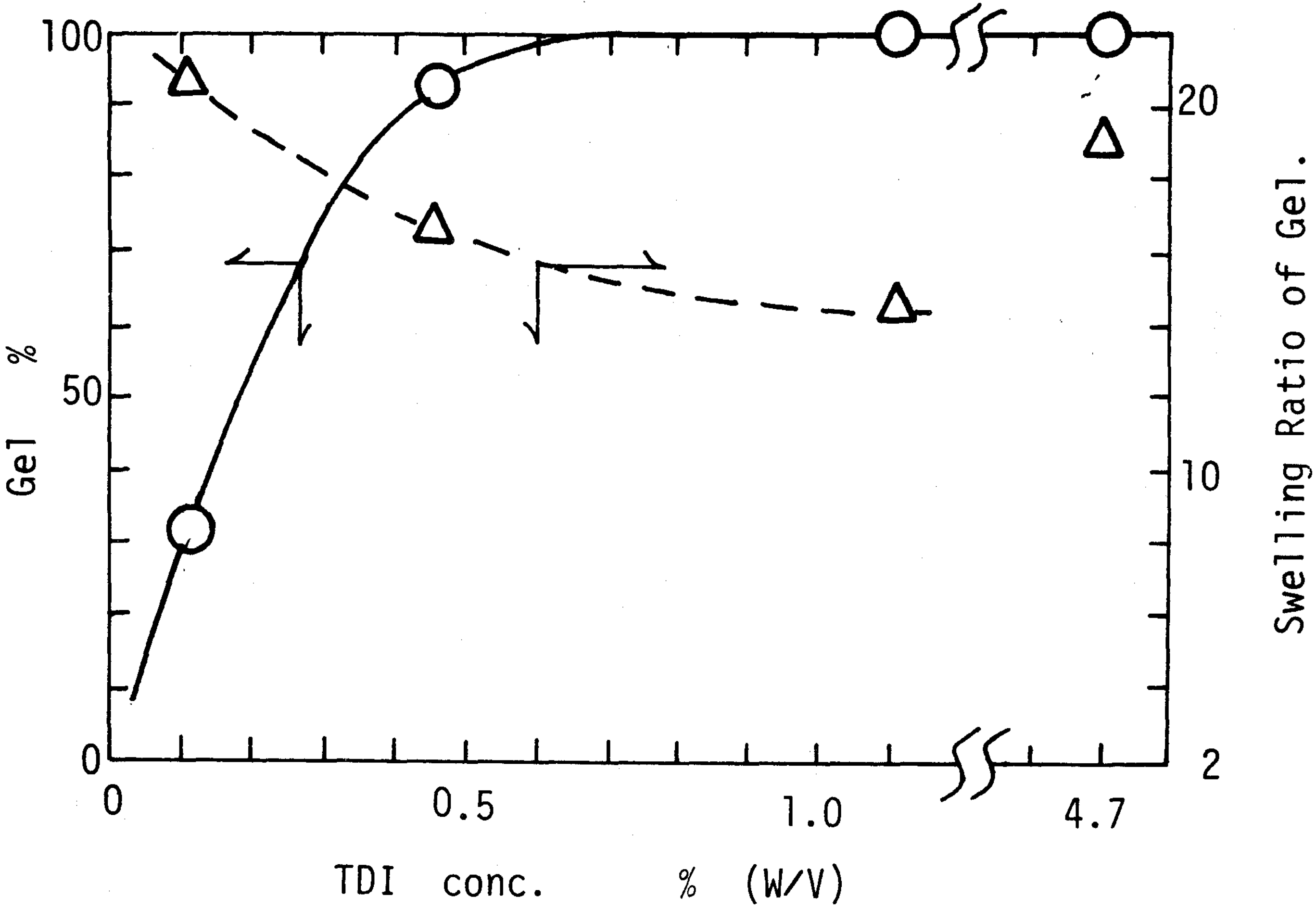


Figure 5. Effect of the TDI concentration on the yield of gel and swelling ratio: degree of saponification of PVAc, 3.33 mol%; polymer concentration, 7 %(w/v); reaction temperature, 75°C; reaction time, 9 hr.

Table IV. Intrinsic viscosities and number-average molecular weights of cross-linked PVAc (soluble) after deacetylation and reacetylation[a)]

Expt.	Initial PVAc		Cross-linked PVAc		After De- and Re-Acetylation	
No.	[η]	$\overline{M}n$	[η]	$\overline{M}n$	[η]	$\overline{M}n$
A-2-1	0.85	175,000	1.99	—	1.98	—
A-8-1	0.85	175,000	1.83	747,000	1.97	781,000
A-13-1	0.54	118,000	0.82	152,000	0.81	155,000

a) Deacetylation: MeOH-NaOH, at 40°C, for 16 hr.

and reacetylation, comparing with those of the original polymers. The molecular weight of the cross-linked PVAc, which was greater than that of the original owing to the intermolecular cross-linking, was held almost constant within the experimental error after deacetylation and subsequent acetylation. It is known that low molecular urethane compounds, in general, are hydrolyzed by acid or alkali[6-9]. In these cases, however, an excess of acid or alkali is usually used at elevated temperatures. On the other hand the deacetylation of PVAc in methanol proceeds by an ester interchange mechanism with a catalytic amount of alkali under a mild condition. Consequently, it is obvious that the urethane cross-linking between polymer chains was not affected at all under the reaction condition of deacetylation of PVAc.

Cleavage of Cross-linkage in PVAc

As the method of decomposition of urethane, hydrolysis by acid or alkali[6-9], reductive decomposition using phosphonium iodide[10], hydrogenation using Raney-Ni[11] or palladium[12], and Ing's method[13-14] using phthalic anhydride have been reported. The cleavage of cross-linkage (decross-linking) was tried in the present study in accordance with these methods.

Table V shows the intrinsic viscosities and number average molecular weights of PVAc after the hydrolytic cleavage of the urethane cross-linking of PVA by HBr and HCl. Intrinsic viscosities and molecular weights of decross-linked PVAc agreed very closely with those of the original, especially in the case of HBr. Figure 6 shows IR

Table V. Intrinsic viscosities and number-average molecular weights of PVAc after hydrolytic cleavage of urethane cross-linking bond[a)]

Initial PVAc			Cross-linked PVAc		Acid	De-cross-linked PVAc	
Fraction	$[\eta]$	$\overline{M}n$	$[\eta]$	$\overline{M}n$	(3N)	$[\eta]$	$\overline{M}n$
II-3	0.54	118,000	0.82	152,000	HBr	0.46	115,000
II-3	0.54	118,000	0.82	152,000	HCl	0.70	134,000
II-2	0.85	175,000	Gel		HBr	0.84	178,000
II-3	0.54	118,000	Gel		HBr	0.53	116,000
II-3	0.54	118,000	Gel		HCl	0.52	124,000
II-4	0.33	62,200	Gel		HBr	0.34	61,700

a) Reaction condition; 17hr(at 60°C) + 5hr(at 95°C).

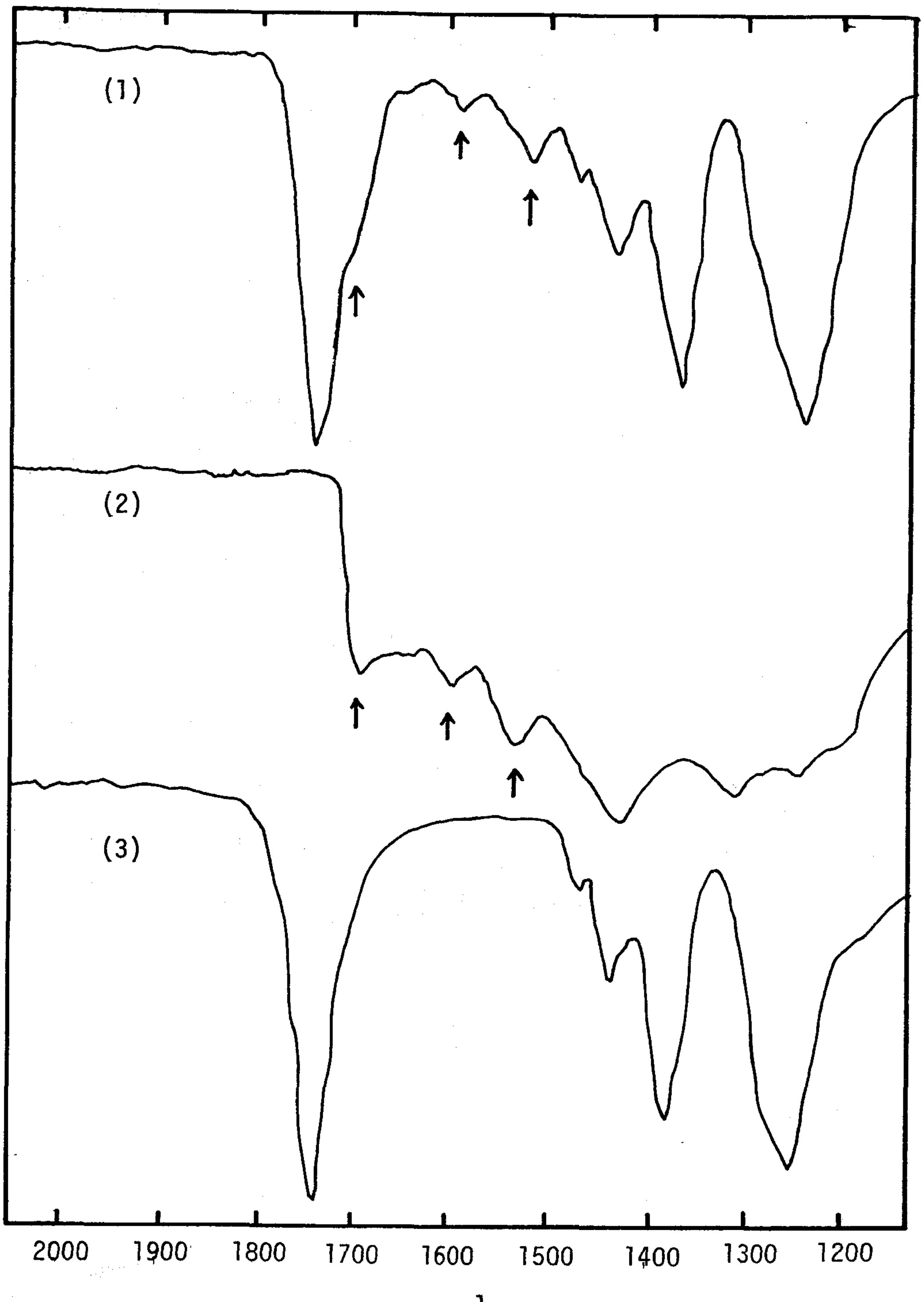


Figure 6. IR spectra of cross-linked PVAc, cross-linked PVA derived from it, and decross-linked PVAc; (1), cross-linked PVAc; (2), cross-linked PVA; (3), decross-linked PVAc.

spectra of decross-linked PVAc which was hydrolyzed with HBr. Absorption bands at 1600 and 1520 cm^{-1} disappeared perfectly to give the coincident spectra with those of the original PVAc. It is clear from these facts that the urethane cross-linking is cleaved quantitatively by the hydrolysis with HBr.

The hydrolytic decross-linking of gel PVA was tried using a 3-N NaOH aqueous solution under the same conditions as the cases of acids, however, the polymer was highly colored and remained insoluble. Using lower concentrations of alkali, e.q., a 1-N NaOH aqueous solution, the coloration of polymer could be avoided but the solubilization of gel did not take place and, in addition, the decrease in absorbances at 1600 and 1520 cm^{-1} was not observed in IR spectra.

The hydrolysis by alcoholic alkali was next tried in accordance with the method as described in experimental part. When the PVAc with lower degree of cross-linking ($\overline{Mn} = 1.52 \times 10^5$) was used, a PVAc with $\overline{Mn} = 1.20 \times 10^5$ was obtained by subsequent reacetylation, indicating a good agreement with the original molecular weight of $\overline{Mn} = 1.18 \times 10^5$, and the absorption bands at 1600 and 1520 cm^{-1} disappeared in the resulting polymer. In the case of gel PVAc with higher degree of cross-linking, only about 50% of the degree of solubilization was observed. Side reactions such as the reverse aldol reaction are generally attended by the treatment of PVA with alkali[15]. Therefore mild conditions should be employed to avoid these side reactions. However such mild conditions are not sufficient for the hydrolysis of the urethane cross-linking bond.

Decross-linking according to Ing's method[12-13] was examined by treating the cross-linked PVAc with phthalic anhydride. In the cases of soluble PVAc with lower cross-linking density, the intrinsic viscosities and IR absorbances with respect to the urethane cross-link of the resulting polymer both decreased but quantitative decross-linking did not occur. In addition, in the case of a gel PVAc with higher cross-linking density, the solubilization of gel was not entirely observed.

Cleavage of the urethane cross-linking bond by phosphonium iodide[10] was also tested in acetic acid at 50°C, however, a deep coloration developed and solubilization of gel was not entirely observed.

Consequently, it turned out that the acid-catalyzed hydrolysis was the best method for the cleavage of the urethane cross-linking bond in PVAc.

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Chapter II

Polymerization of Vinyl Acetate in the Presence of Cross-linked Poly(vinyl acetate)

ABSTRACT

Nowadays it is a common view that poly(vinyl acetate) has many branches at the acetyl side group, but that the corresponding poly(vinyl alcohol) has little branching. In order to study the branching in poly(vinyl acetate) and poly(vinyl alcohol) which is formed by the chain transfer to polymer, the polymerization of ^{14}C labeled vinyl acetate in the presence of cross-linked poly(vinyl acetate), which was able to be decross-linked to give soluble polymers, was investigated at 60°C and 0°C. This system made it possible to separate as well as to distinguish the "graft polymer" from the newly polymerized "homo polymer". Furthermore, the degree of grafting onto the acetoxy methyl group and onto the main chain were estimated. It became clear that, in the polymerization of vinyl acetate, the chain transfer to the polymer main chain takes place about 2.4 times as frequently as that to the acetoxy group at 60°C and about 4.8 times at 0°C.

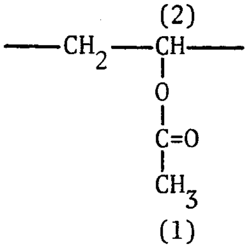
INTRODUCTION

Since the concept of self-branching during the polymerization of vinyl acetate was first comfirmed by Inoue and Sakurada[1], a number of investigations have been reported extensively. Osugi[2] proposed that the branching occurred at the acetyl group from the study of saponification. From the facts that the degree of polymerization of poly(vinyl acetate)(PVAc) increased with conversion during the bulk polymerization of vinyl acetate whereas that of the corresponding poly(vinyl alcohol)(PVA) remained unchanged irrespective of conversion, the branching has also been anticipated to occur exclusively at the acetoxy group of PVAc[1,2]. The idea was supported by the fact that the degree of polymerization of PVAc and PVA were almost identical at the initial stage of polymerization.

Nakajima et al.[3,4] and Matsumoto et al.[5] have pointed out the presence of branching in PVAc from the studies of intrinsic viscosity and Huggins parameter k' of the polymers prepared at various conversions under various conditions. Burnett and Melville[6] carried out a study along the similar line by measuring the number- and weight-average molecular weight, concluding that PVAc which was polymerized at the temperature below -30°C had almost no branching. In contrast, Matsumoto et al.[7] have examined Huggins parameter of PVA in detail and the results did not suggest the presence of branching in PVA. In order to study the branching in PVAc and PVA, Imoto, Ukida, and Kominami[8] polymerized vinyl trimethylacetate in the presence of PVAc. They saponified the graft copolymer and deduced that most of the branching occurred at the acetyl group and only a very little at the secondary carbon atom in the main chain.

Thus, it is nowadays a common view that PVAc has many branches at the acetoxy group whereas the presence of branching in the corresponding PVA is almost negligible.

It should be noted, on the other hand, that some reports suggested the possibility of the presence of branching in PVA. Wheeler et al.[9,10] studied the self-branching of PVAc kinetically. They pointed out that the branching occurred at 1- and 2-position, that about half of the branches were hydrolyzable, and that the branches occurred with greater frequency at higher conversions. The branching at 2-position has an important meaning with respect to the branching of PVA.



$-CH_2-CH(-O-C(=O)-CH_3)-$

Roland and Richards[11] carried out the polymerization of ethylene in the presence of PVAc and indicated that many polyethylene branches became attached to the main chains as well as to the acetoxy groups of the PVAc. The PVAc growing radical, not being resonance stabilized, is considered to have a similar reactivity to the polyethylene growing radical and should presumably participate in frequent transfer reactions in a similar manner to the polyethylene radical.

Nkajima and Sakurada[12] investigated the molecular weight distribution of PVA derived from PVAc obtained under various polymerization conditions, suggesting the presence of the branched structure in PVA. Ukida et al.[13] reported that PVA was less crystalline and more easily swollen by solvents when the parent polymer was prepared at higher polymerization temperatures, and discussed that the branching might have increased with the polymerization temperature.

Nagai and Sagane[14] analyzed the infrared spectra of PVA and noted the deformation of the shape of the 9.1 μ band. This deformation had been speculated to be caused by mixing of the secondary alcohol band into the primary alcohol band and was found to be larger than that expected from linear PVA. Hence they discussed the possibility of the branching structure.

Clarke, Howard, and Stockmayer[15] determined the chain-transfer constants in the free-radical polymerization of vinyl acetate for various substances. They found that the chain-transfer constants for isopropyl and sec-butyl acetate at 60°C are both larger than that for vinyl acetate. This fact shows that abstraction of the tertiary hydrogen atom is one of the important transfer processes in these esters. Hence they supposed that a similar process is involved in the transfer to polymer.

Experimental evidence for the presence of branches in PVA, however, apparently not been reported to date.

Long branching in PVAc during the polymerization might be formed by two mechanisms, one is the chain transfer to polymer in which hydrogen atom of the polymer is abstracted by free radicals to create a initiating site for a branch. The other is the copolymerization of the terminal double bond, which is formed by the abstraction of a hydrogen atom from the monomer, and the subsequent polymerization. Branching by the radical transfer either to a polymer or a monomer can occur in two ways. When a hydrogen atom is abstracted from the acetyl group of the polymer or the monomer, only a hydrolyzable branching will be resulted by either mechanism, while the abstraction from the α-position in the monomer or the polymer will result in the nonhydrolyzable branching which will bring about the branching in the corresponding PVA.

This work was undertaken to study the chain transfer to polymer with respect to branching in the free-radical polymerization of vinyl acetate.

In order to investigate the polymer transfer, it is desirable to employ the experimental technique in which a monomer polymerizes in the presence of the corresponding polymer. However it is not generally possible to employ such a technique, because it will be difficult to separate as well as to distinguish the initially added polymer and the newly formed polymer due to the same solubility and the same chemical stracture.

In a preceding paper[16], the preparation of cross-linked PVAc gel, which was able to be decross-linked by treating with inorganic acids to give soluble polymers with the same molecular weight as the original, was described. When vinyl acetate, in which the vinyl carbon is labeled with ^{14}C, is polymerized in the presence of such a cross-linked gel, the separation becomes possible owing to the difference in solubility and also the discrimination becomes possible by the radioactivity measurement. Moreover, the degree of branching on the acetoxy group and the main chain are possible to be estimated, since the cross-linkage is not affected at all by deacetylation with MeOH—NaOH system and since thus obtained PVA gel having radioactive branches on its main chain is able to be decross-linked to give a branched PVA without any impurity of homo polymer.

EXPERIMENTAL

Preparation of PVAc Gel

PVAc gels were prepared in accordance with the preceding paper[16]. A commercial PVAc (Sekisui Chemical Co., Esnyl P-18) was saponified, reacetylated, and then subjected to the fractionation by the partial precipitation method using the solvent—nonsolvent system of acetone—water. The fractions with sharp molecular weight distribution were partially saponified to the extent of 3.3 mol% and then treated with toluylene diisocyanate in benzene to yield 100% of gel. The reaction conditions were as follows: the polymer concentration, 9%(w/v); the TDI concentration, 0.456%(w/v); temperature, 75°C; time, 9 hr. The PVAc gels were washed successively with methanol, acetone, and benzene under reflux, and recovered by freeze-drying technique. The number-average molecular weight and intrinsic viscosity in acetone of the initial PVAc (before cross-linking) for the preparation of the gel used for expt No. 114—121 were 1.78×10^5 and 0.85 respectively, and those for expt No. 122—125 were 1.18×10^5 and 0.54 respectively.

Polymerization Procedure

An ampoule containing a PVAc gel, labeled vinyl acetate, and 2,2'-azobisisobutyronitrile(0.01 mol% of the monomer) was degassed seven times in a high vacuum system ($<10^{-3}$ mmHg) and then sealed. polymerizations were carried out in a thermostat at 60°C and 0°C. In the photo-sensitized polymerization at 0°C, an ampoule was irradiated with an ultraviolet lamp (Toshiba SHL 100-UV). The polymer was separated by pouring the reaction mixture into a large excess of n-hexane, washed by petroleum ether, added into benzene, and then freeze-dried.

The specific radioactivity of vinyl-1,2-^{14}C acetate used for this experiment was about 24.8 μCi/mol. This radioactive monomer obtained from England Nuclear Corp. was washed with a 5-% $NaHSO_3$ aqueous solution several times, washed with water, dried with $CaCl_2$ and then distilled through a Widmer column three times, bp 72—73°C.

Separation Procedure

The separation procedures for the polymerization products are shown schematically in Figure 1. Soluble radioactive PVAc, termed 1C fraction, which was formed in the polymerization of the monomer in the presence of PVAc gel was separated by extraction with acetone. This extraction was carried out in the following way. In a 1-l flask containing the polymer, equipped with a reflux condenser, 700-ml acetone was added and refluxed for about 8 hr. The flask was then allowed to stand overnight at room temperature to give a precipitate of gel. The supernant was sucked off by the use of a siphon and then fresh acetone was added to effect further extraction. These procedures were repeated for 10 days with a one-cycle-per-day period. By a repetition of this process, the mixture may be separated completely into its constituents. To determine the end point of the extraction, 50 ml sample of the every supernant solution was collected, 10 ml of toluene containing scintillators was added after the evaporation of acetone, and then radioactivity was measured. An example of the data is shown in Figure 2. The end point was reached in about five days. The residual gel onto which radioactive branches should have grafted was saponified by the MeOH—NaOH system and divided into two parts. One of these was allowed to decross-link by treating with 3-N HBr aqueous solution according to the preceding paper to give a soluble PVA, and then acetylated by the pyridine—acetic anhydride system giving 34C fraction in Figure 1. This fraction have radioactivity which is due to the grafting on both the acetoxy group and the main chain of PVAc. Another part was separated by extraction with water into a soluble and a gel PVA. The former was acetylated. The PVAc,

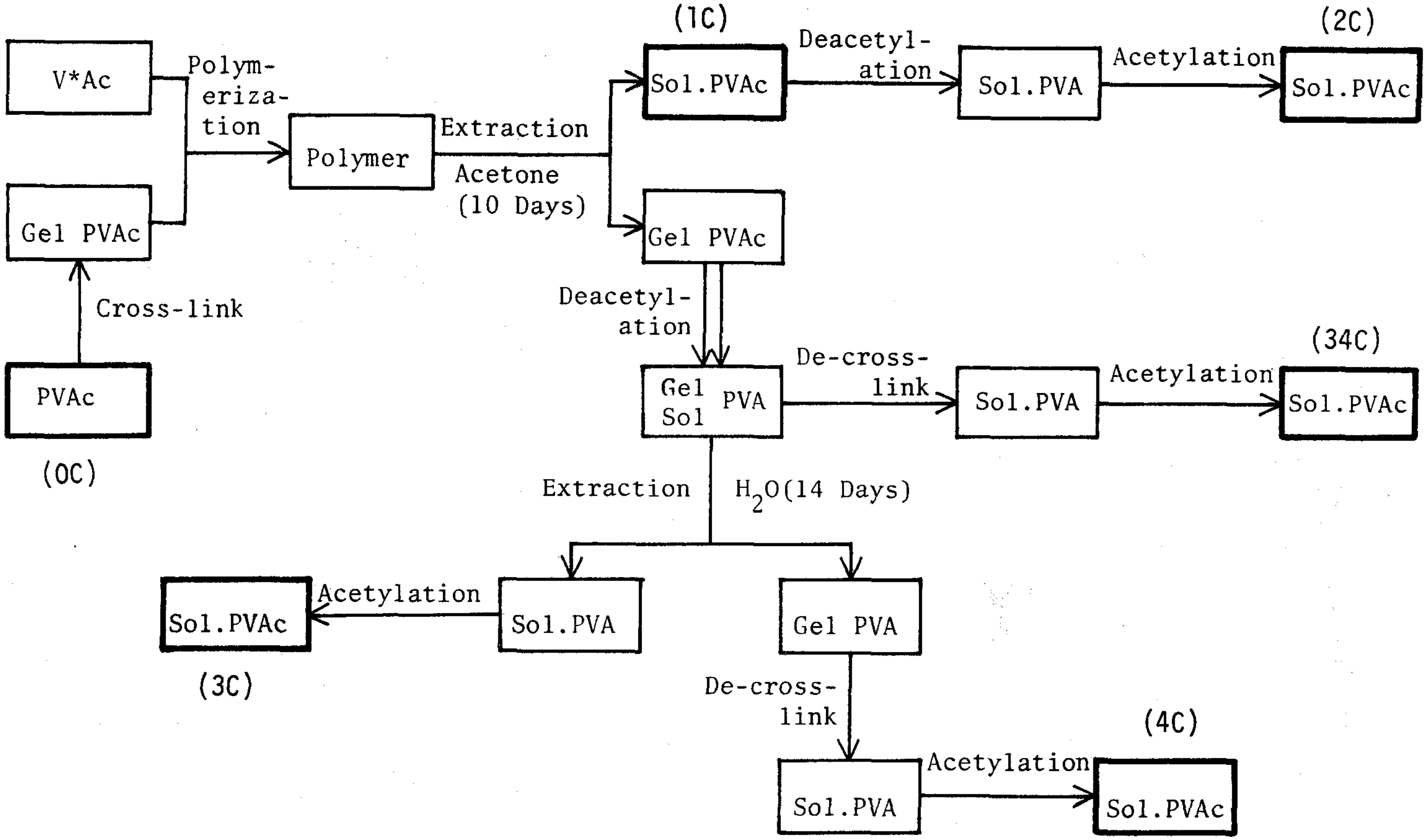


Figure 1. Block diagram of polymerization and separation procedures.

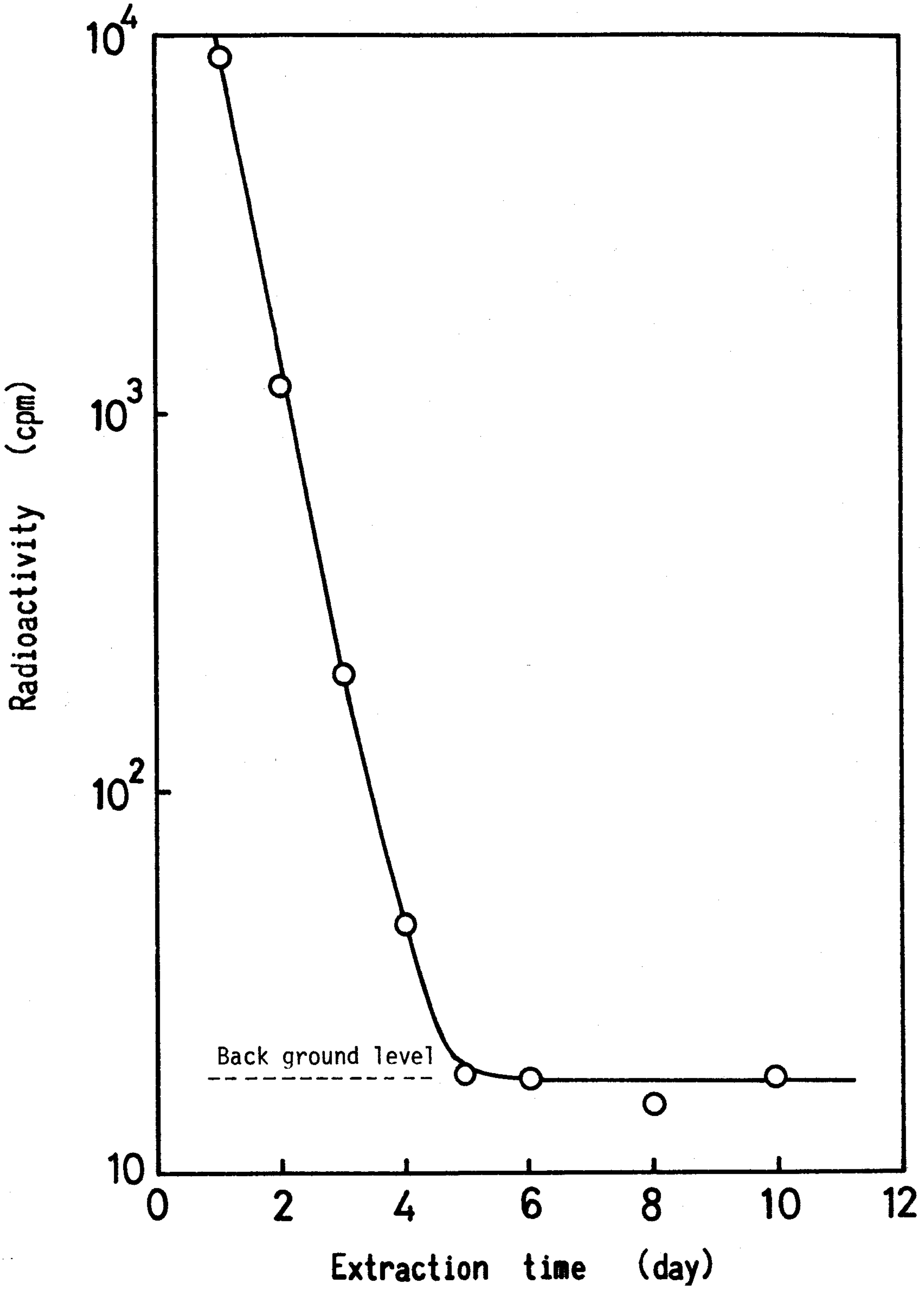


Figure 2. Relationship between extraction time and radioactivity of extract by acetone from the polymerization mixtures of exp No. 114. The extraction solvent was replaced every day.

3C fraction, thus obtained should be a branch itself attached to the acetoxy groups of PVAc gel, and the latter was decross-linked by 3-N HBr aqueous solution and acetylated to give PVAc of 4C fraction which should have radioactive branches attached to the main chain.

Radioactivity

About 0.1 g of PVAc was dissolved into 10 ml of toluene containing scintillators (5-g PPO and 0.3-g dimethyl POPOP in 1-l toluene). Radioactivity of the solution was measured by a Tri-Carb Scintillation Spectrometer Model 3002. Counting efficiency was about 78 %.

Viscosity

Intrinsic viscosities of acetone solutions of polymer were measured at 30°C in a modified Ubbelohde type viscometer having a solvent flow time of 147 sec. The reduced specific viscosities were determined by double plots of η_{sp}/C vs. C and $(\ln\eta_{rel})/C$ vs. C.

Osmotic Pressure

Osmotic pressures of the methyl ethyl ketone solutions of the samples were measured at several polymer concentrations using a Hewlett-Packard 502 High Speed Membrane Osmometer at 37°C.

Gel- Permeation Chromatography(GPC)

Molecular weight distribution was estimated by GPC of tetrahydrofuran solution of polymers using a Shimazu GPC-1A Type under the conditions as follows: polymer concetration, 0.5—0.6 wt%; injection time, 100 sec; flow rate, 1 ml/min; temperature, 30°C.

RESULTS AND DISCUSSION

The experimental results are summerized in Table I. The polymerizations of vinyl-1,2-^{14}C acetate in the presence of PVAc gel were all carried out in bulk using 2,2'-azobisisobutyronitrile (0.01 mol% of monomer) as an initiator. The weight ratio of the monomer to the PVAc used for the polymerization was a little greater than the swelling ratio of the gel to the monomer. From the radioactivities of 34C fraction and 4C fraction (Figure 1) the total degree of grafting (G_1) and the degree of grafting onto the main chain (G_2) of PVAc were calculated as listed in Table I. It should be noted that the grafting has occurred to a significant extent onto the main chain of PVAc. Figure 3 and 4 show the increase in the total degree of grafting and the degree of grafting onto the main chain with respect to the increase in conversion. Both the degree of grafting, G_1 and G_2, increased with conversion. In contrast to the common view, the degree of branching at the main chain of PVAc was greater than that at the acetoxy group. Further it became clear that the chain transfer to polymer, especially to main chain, occurred significantly even at the low temperature of 0°C.

The ratios of the degree of grafting onto the acetoxy group to

Table I. Total degree of grafting (G_1) and degree of grafting onto main chain (G_2) a)

Expt. No.	V*Ac/Gel (wt.)	Conv. (%)	Radioactivity (cpm/0.1g) (34C)	(4C)	Degree of grafting (%) G_1	G_2
at 60°C, AIBN 0.01 mol%/V*Ac, PV*Ac : 49229 cpm/0.1gr.						
115	21.4	1.6	1099	654	2.02	1.34
117	21.5	4.35	3395	2370	7.41	5.06
116	21.5	4.39	2967	2115	6.39	4.49
121	27.2	14.0	11470	8409	30.38	20.60
119	22.1	21.5	14802	10658	43.65	26.53
120	20.4	26.3	20168	13939	69.40	39.49
114	20.8	40.2	26930	17711	119.5	62.20
at 0°C, AIBN 0.01 mol% + UV, PV*Ac : 48138 cpm/0.1gr.						
122	15.5	5.70	8003	6191	19.94	14.60
123	15.5	6.62	8786	7320	22.33	17.91
124	15.5	15.4	16790	14180	53.56	41.76
125	15.5	20.8	20254	17340	72.64	56.30

a) Polymerization ; Bulk.

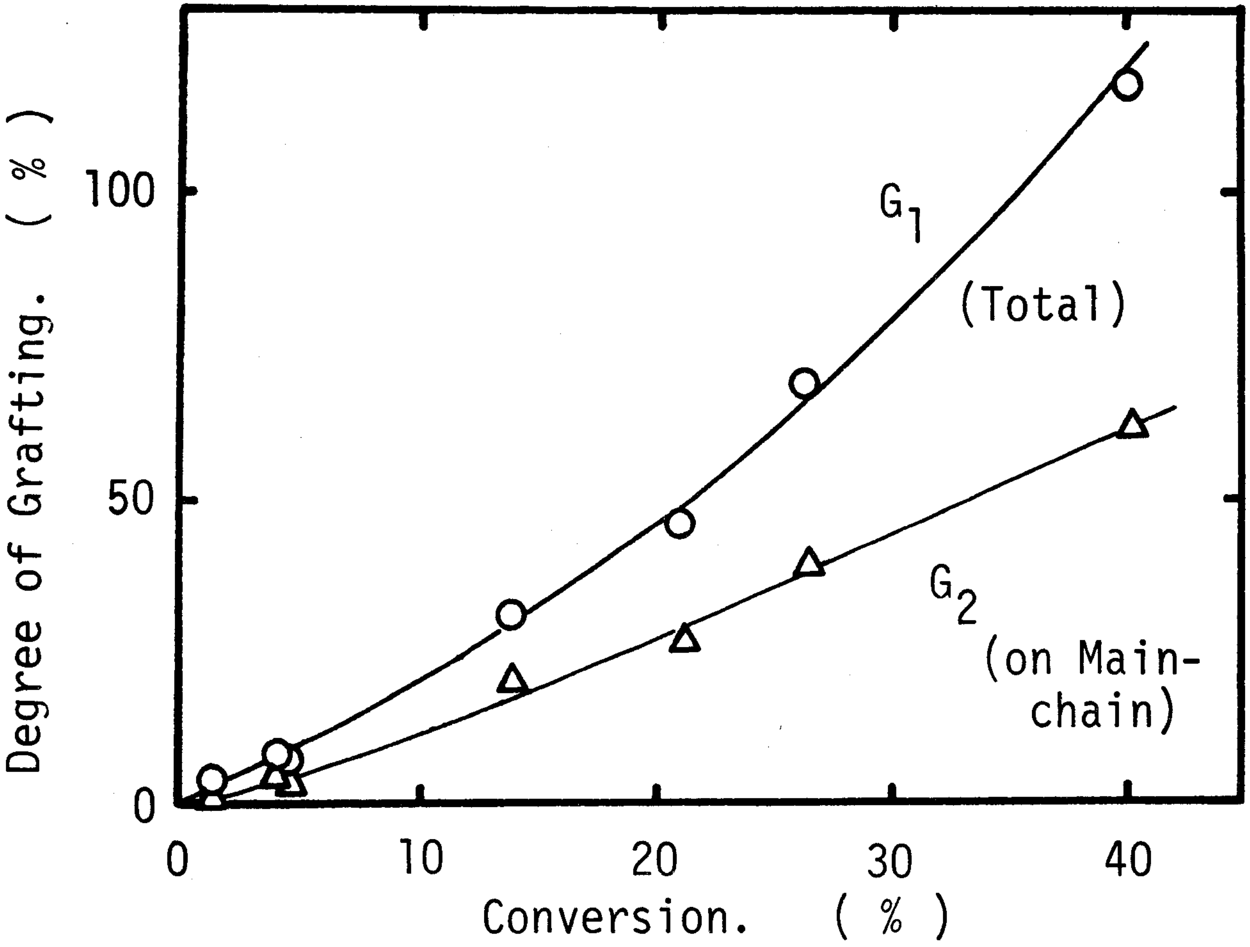


Figure 3. Relationship between degree of grafting and conversion: polymerization conditions; bulk, 60°C, AIBN 0.01 mol%/monomer.

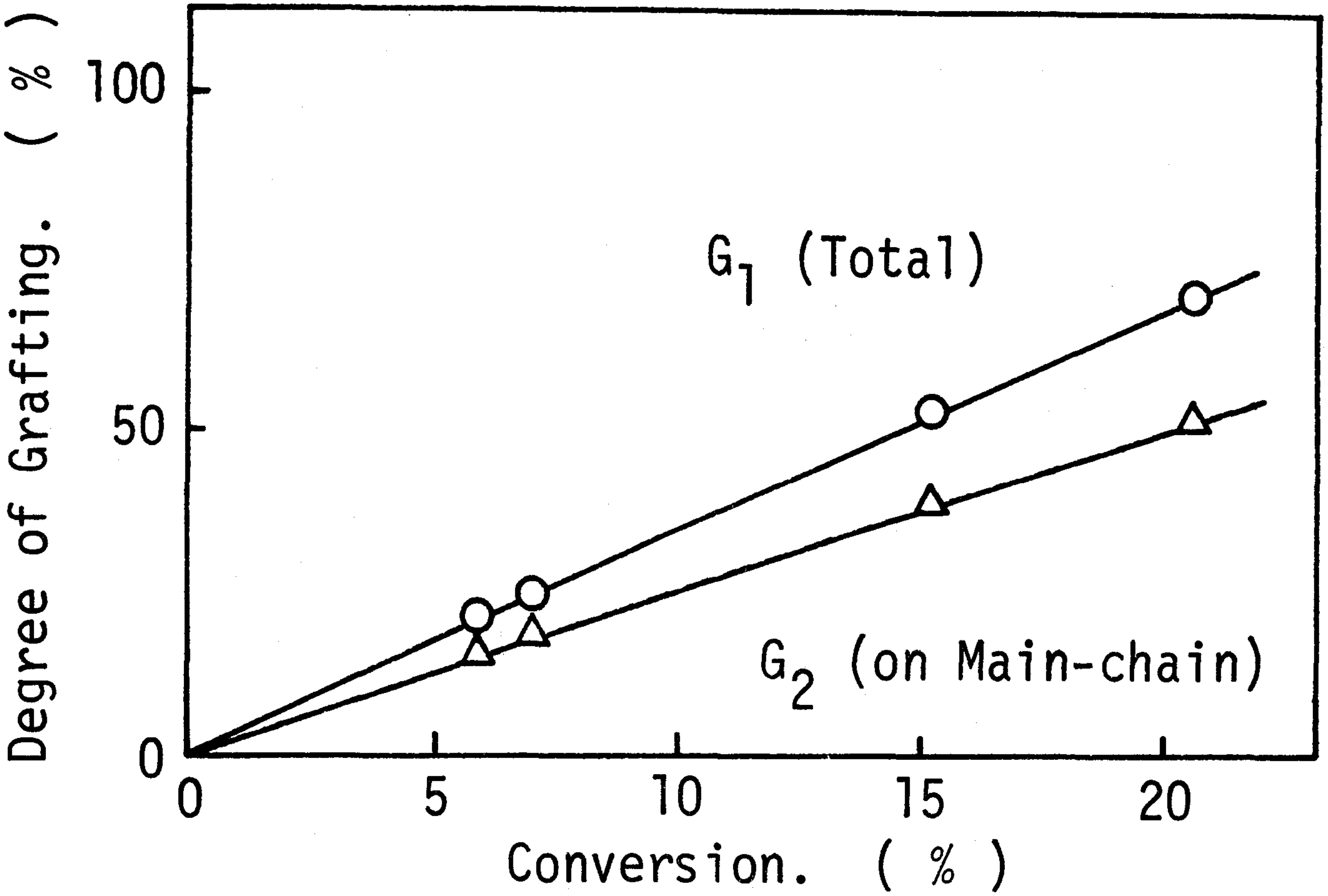


Figure 4. Relationship between degree of grafting and conversion: polymerization conditions; bulk, 0°C, AIBN 0.01 mol%/monomer + UV.

that onto the main chain, $(G_1/G_2) - 1$, were plotted against the conversion, as shown in Figure 5. These ratios increased gradually with the increase in conversion, and especially in the case of the polymerization at 60°C this tendency was more remarkable. This may be because the grafting takes place not only onto the initially added polymer chain but also onto the branches themselves, which are formed in the polymerization, at higher conversions. Even if such secondary branching is not hydrolyzable type and the primary branching has been attached to the acetoxy group of the parent polymer, the secondary branch will be removed along with the primary branch from the parent polymer in the deacetylation process and will not come into 4C fraction. Therefore it seems apparent that the amount of hydrolyzable branching increases more rapidly at higher conversions.

Consequently, the ratios of the chain-transfer constant to the acetoxy group of PVAc ($C_{p,1}$) to that to the main chain ($C_{p,2}$) were determined by the extrapolation to zero conversion in Figure 4:

$$C_{p,1}/C_{p,2} = 0.42 \quad \text{(at 60°C)}$$

$$C_{p,1}/C_{p,2} = 0.21 \quad \text{(at 0°C)}$$

These values show that, in the polymerization of vinyl acetate, the chain transfer to the polymer main chain takes place about 2.4 times as frequently as that to the acetoxy group at 60°C and about 4.8 times at 0°C.

According to chain transfer studies, the hydrogen atoms in the α-position are more reactive than those on the acetoxy methyl group[15].

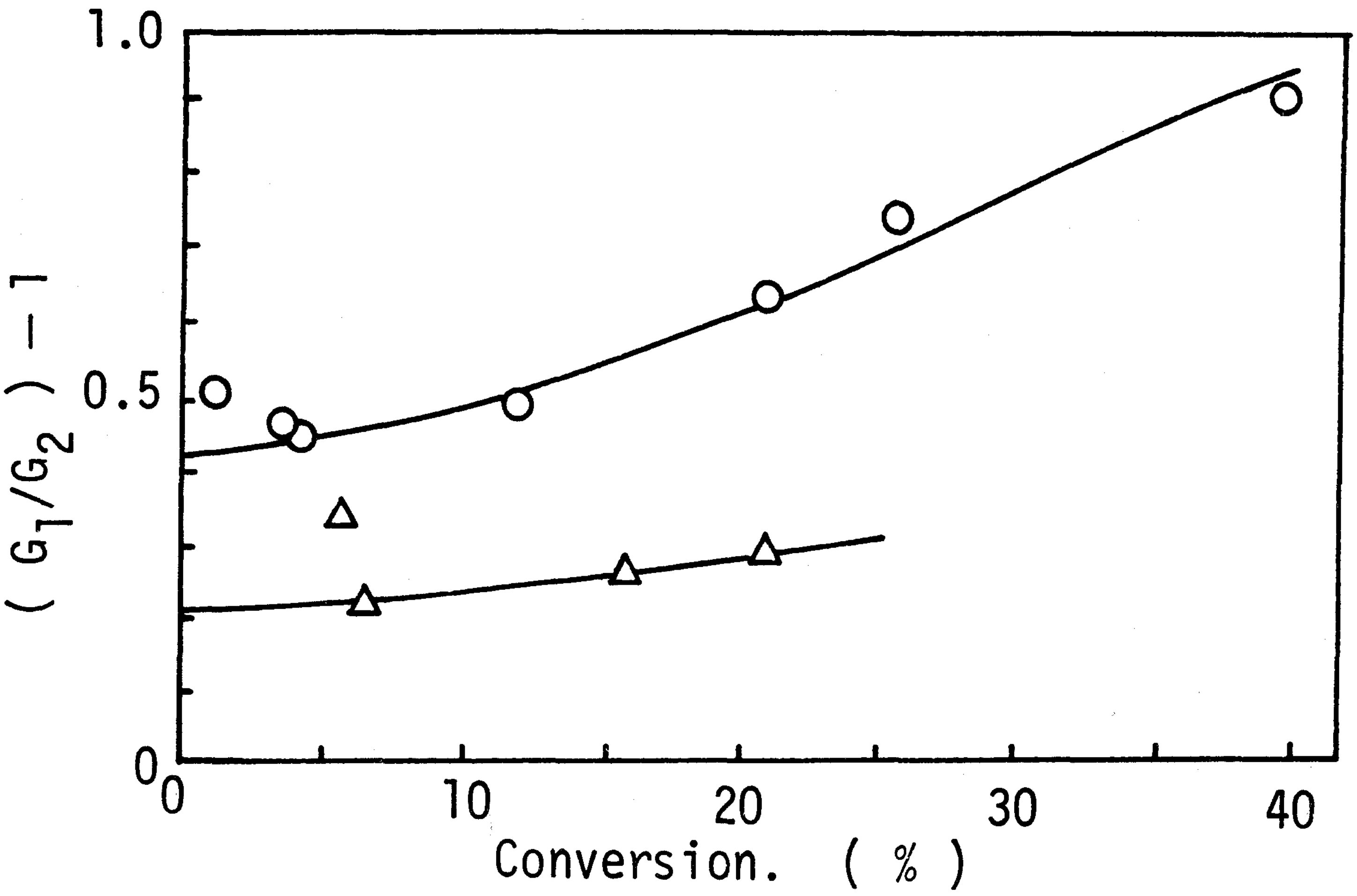
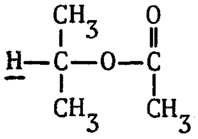


Figure 5. Plots of $(G_1/G_2) - 1$ against conversion: ○,bulk, 60°C, AIBN 0.01 mol%/monomer; △, bulk, 0°C, AIBN 0.01 mol%/monomer + UV.

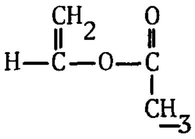
Chain-transfer constants in the polymerization of vinyl acetate at 60°C are given for the underlined hydrogen atoms in structures I,II.



$\underline{H}-C(CH_3)_2-O-C(=O)-CH_3$

8.0×10^{-4}

I



$H-C(=CH_2)-O-C(=O)-C\underline{H_3}$

2.5×10^{-4}

II

Therefore, one could expect the nonhydrolyzable branching by the chain transfer mechanism to occur in PVAc about three times as readily as the hydrolyzable type.

It is well known that the molecular weight of PVAc increases with conversion while that of the corresponding PVA is not almost affected by conversion. In Figure 6, the intrinsic viscosities of 1C fractions which homo polymerized in the presence of the PVAc gel, and those of 2C fractions which obtained from 1C fractions by saponification and reacetylation were plotted against conversion. The viscosities of branches themselves, 3C fractions, which had combined to the acetoxy methyl groups of the parent PVAc gel were also plotted by square symbols. All of the hydrolyzable bonds in 3C fractions should have been cleaved during the saponification process. As seen in Figure 6, the intrinsic viscosities of 2C fractions were quite identical. This fact indicates that the propagation of branch itself took place kinetically in a similar environment to the homo propagation In addition, to clarify this point the comparison of molecular weight

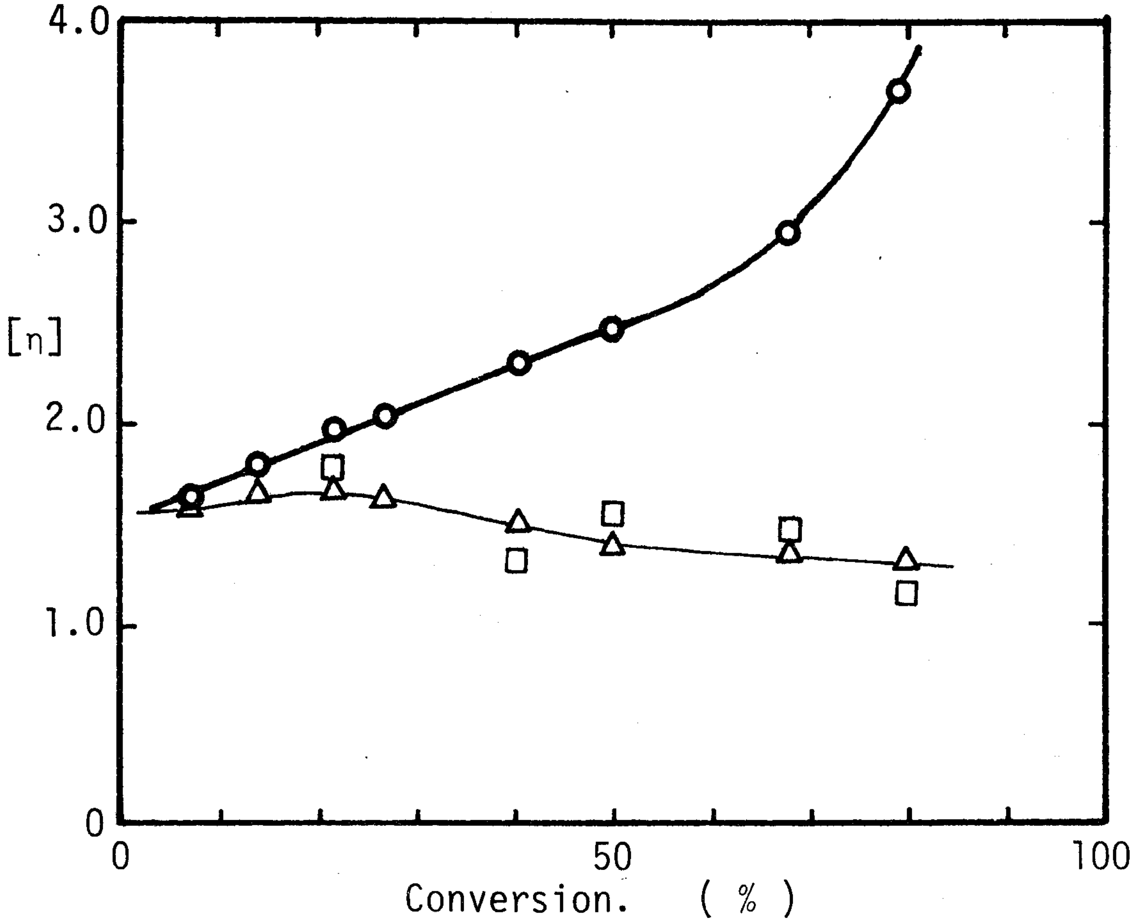


Figure 6. Relationship between intrinsic viscosity and conversion for 1C, 2C,and 3C fractions:polymerization; bulk, 60°C, AIBN 0.01 mol%/ monomer; ○, 1C; △, 2C; □,3C fraction.

distribution was made. GPC curves for the samples of 2C and 3C fractions at the conversion of 49.8% are shown in Figure 7. It is obvious, as seen in Figure 6 and 7, that these two fractions are fairly identical in the average molecular weight as well as the molecular weight distribution.

The molecular weight of 4C fraction should be larger than the initial PVAc (0C) because of grafting onto its main chain. Figure 8 and 9 show the relations between the degree of grafting onto the main chain and the number average molecular weight or the intrinsic viscosity at the polymerization temperatures of 60°C and 0°C respectively. The molecular weight and intrinsic viscosity increased with the degree of grafting onto the main chain. GPC curves are given in Figure 10 for the initial PVAc with the average molecular weight of 1.78×10^5 and the branched PVAc in which the number-average molecular weight increased to 2.50×10^5 because of the degree of grafting of 52.9% by weight onto the main chain. It is noticeable that, in the GPC curve of branched PVAc, a new peak appeared at higher molecular weight and the molecular weight distribution was broadened considerably only in the higher molecular weight range. This fact shows that the branching frequency due to the chain transfer to polymer may be fairly small, although the value of the degree of grafting represented by weight per cent is considerably large.

It may be concluded that the chain transfer to polymer takes place more frequently at the main chain than at the acetoxy methyl group in the radical polymerization of vinyl acetate and that

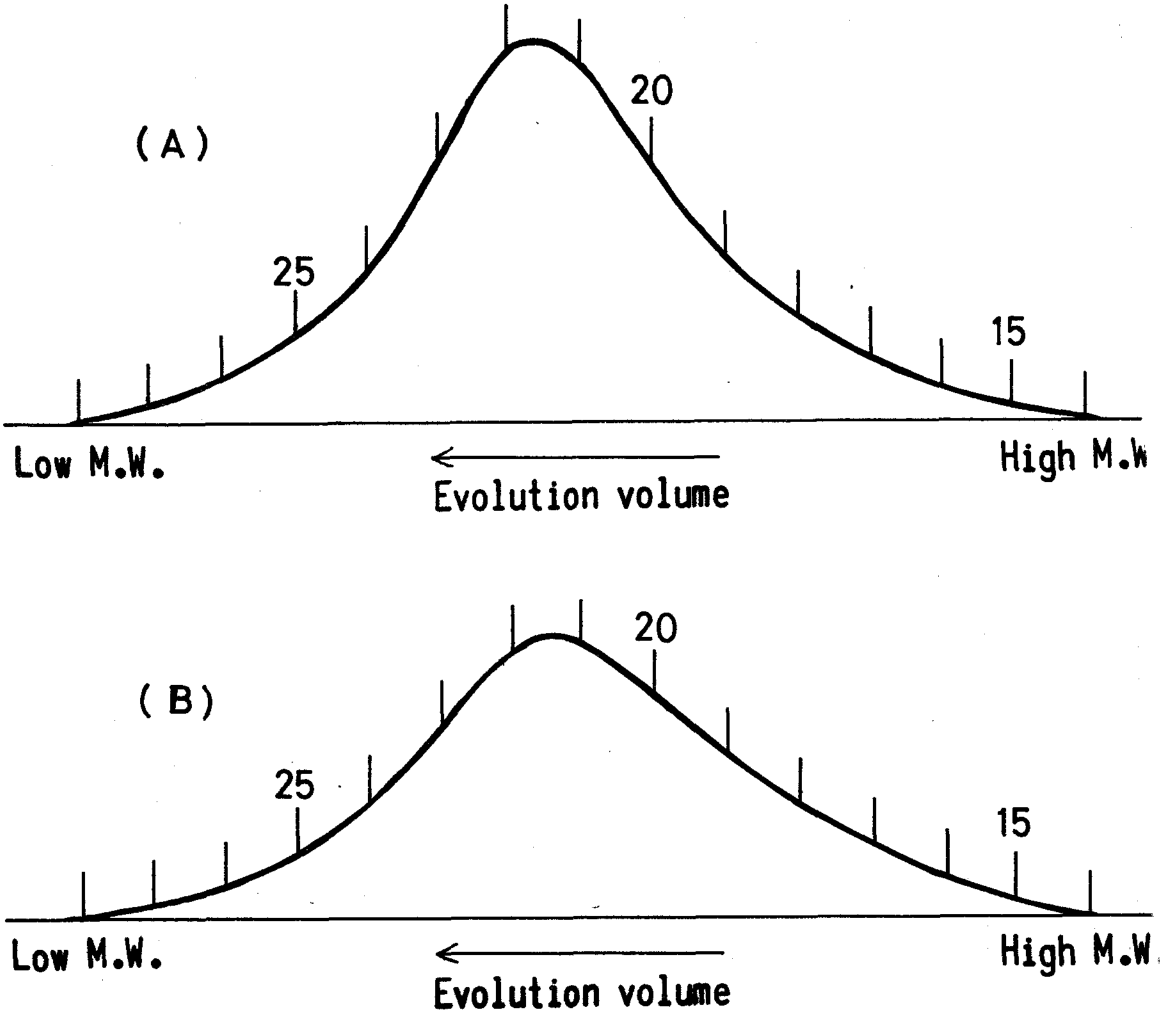


Figure 7. Gel-permeation chromatogram of (2C) and (3C) fractions; (A), (2C) fraction; (B), (3C) fraction; polymerization condition, bulk, 60 °C, AIBN 0.01 mol%/monomer; conversion, 49.8 %.

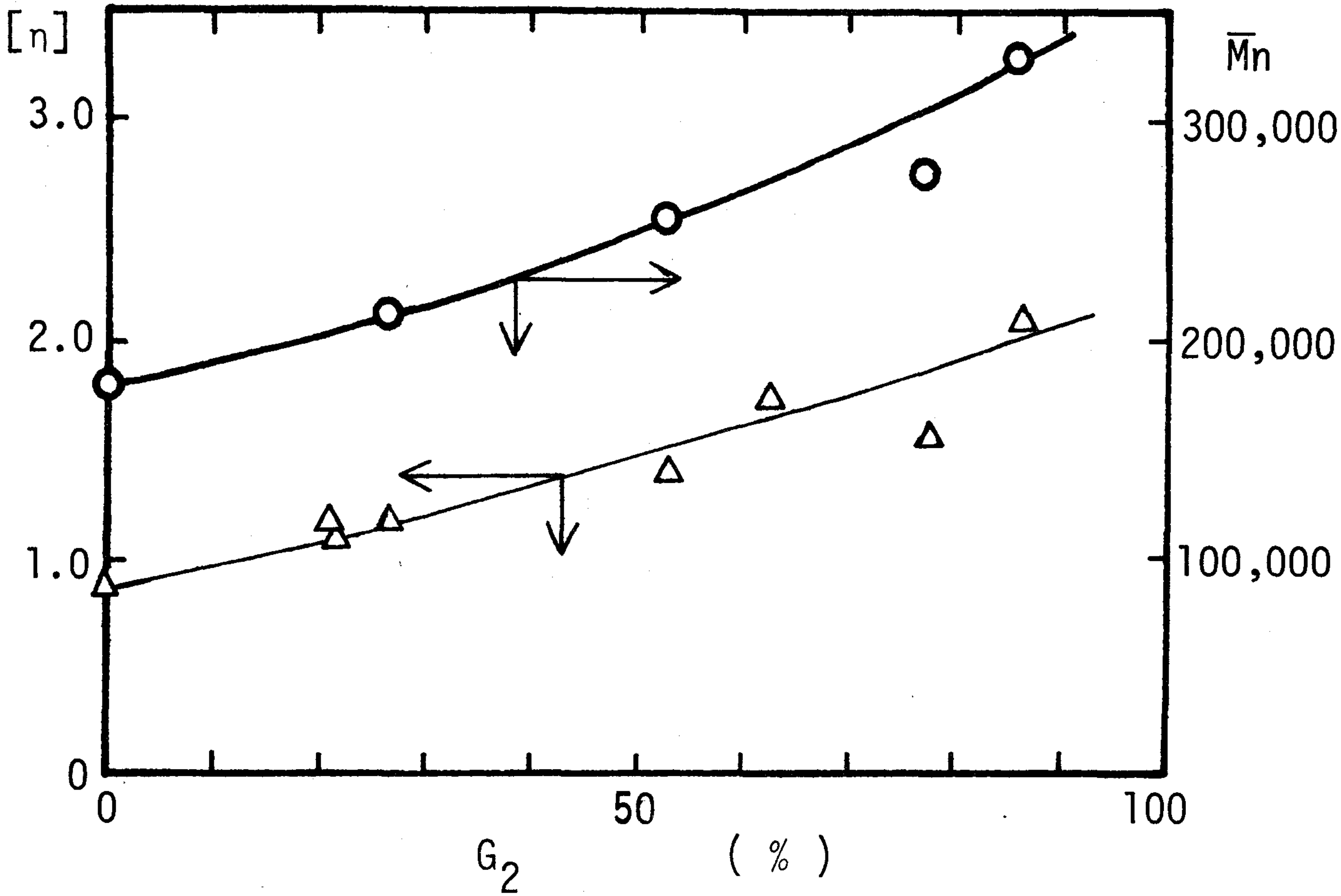


Figure 8. Intrinsic viscosities and number-average molecular weights for 4C fraction vs. degree of grafting onto main chain (G_2): polymerization; bulk, 60°C, AIBN 0.01 mol%/monomer.

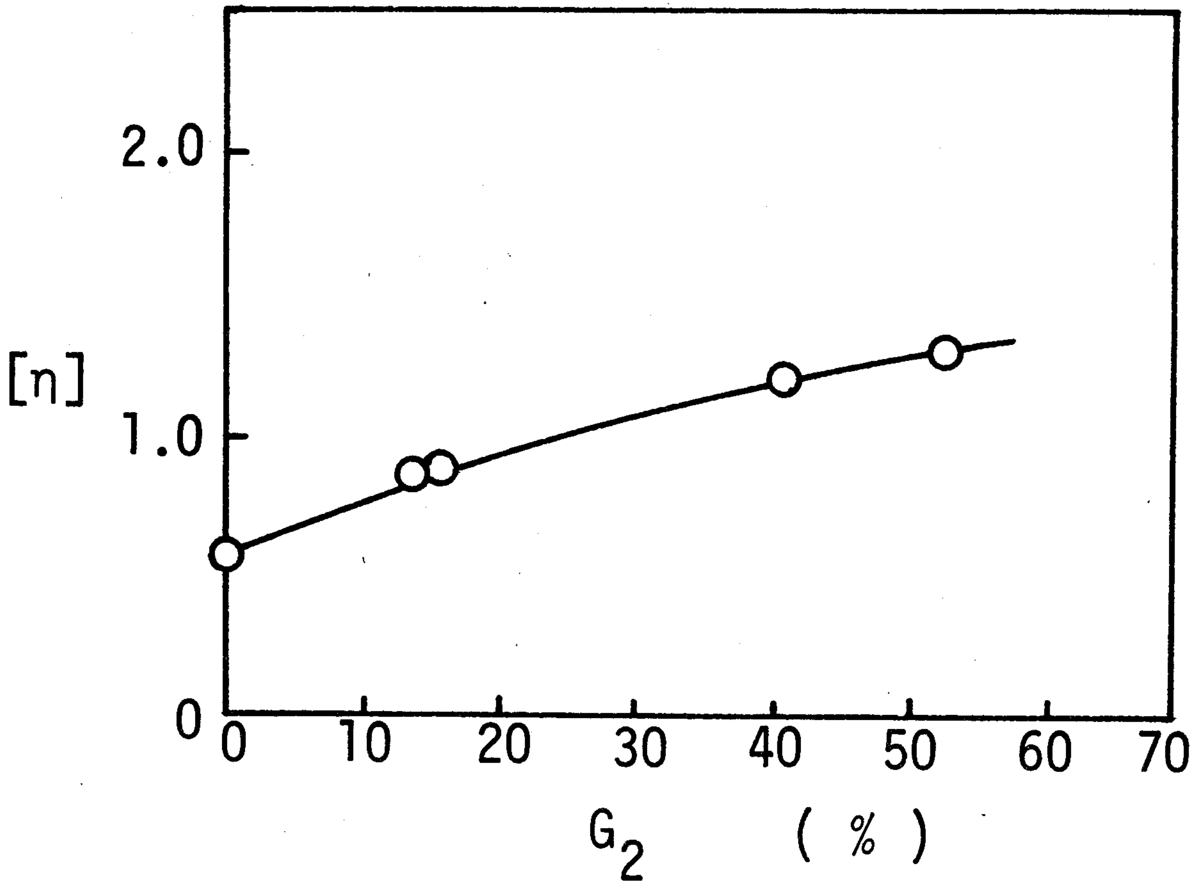


Figure 9. Intrinsic viscosities for 4C fraction vs. degree of grafting onto main chain(G_2): polymerization; bulk, 0°C, AIBN 0.01 mol%/monomer + UV.

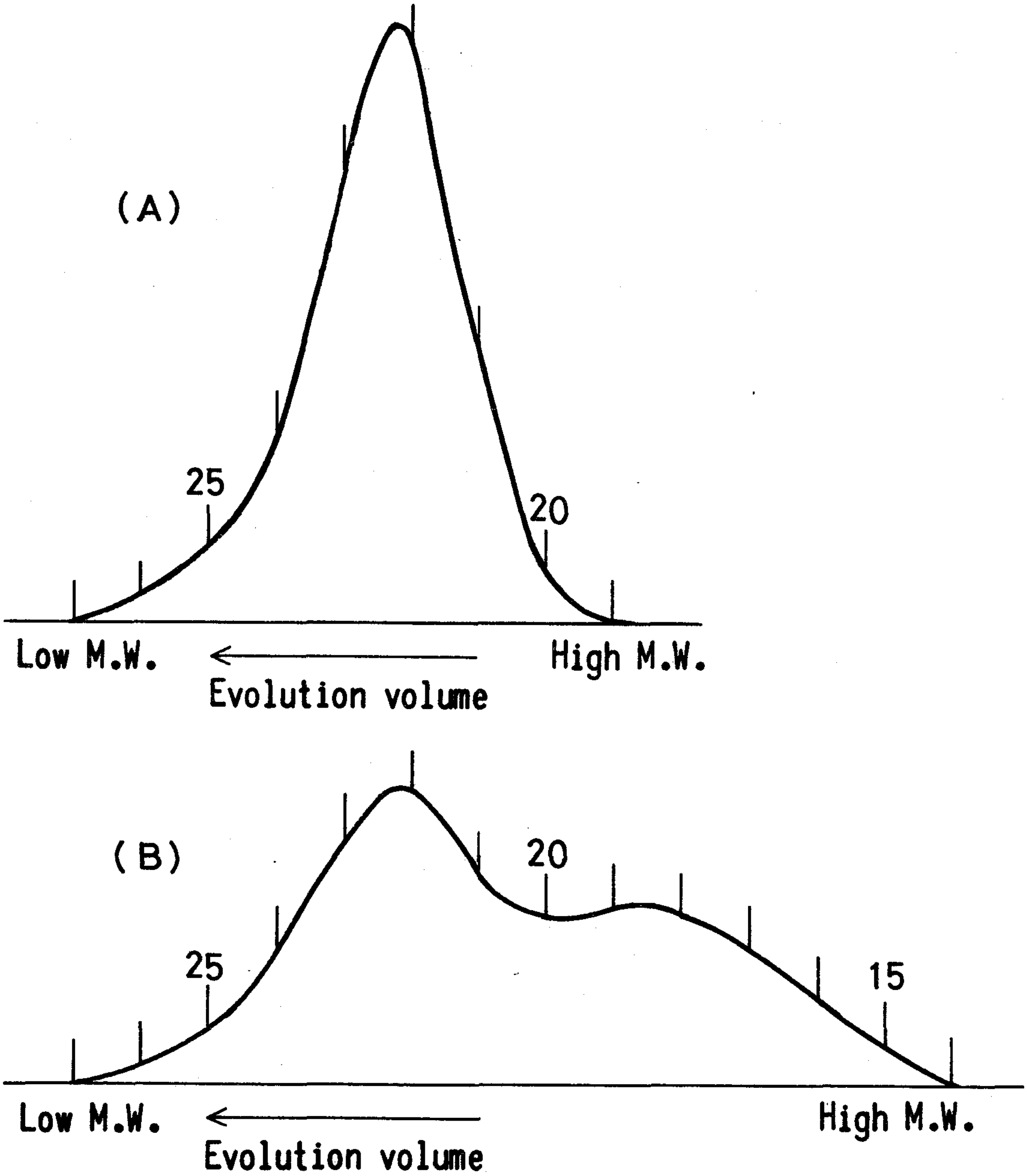


Figure 10. Gel-permeation chromatogram of initial PVAc and grafted PVAc: (A), Initial PVAc ($\overline{Mn} = 1.78 \times 10^5$); (B), grafted PVAc (degree of grafting onto main chain = 52.9 %, $\overline{Mn} = 2.50 \times 10^5$); polymerization , bulk, 60°C, AIBN 0.01 mol%/monomer.

consequently the presence of long branching in PVA is proved. On the other hand, considering the appreciable decrease in molecular weight caused by saponification, PVAc should have more hydrolyzable branches than that expected from the chain transfer to polymer. These problems will be discussed in more detail in the subsequent paper.

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16. Chapter I.

Chapter III

Kinetic Study of Branching Reaction in the Radical Polymerization of Vinyl Acetate

ABSTRACT

The branching reaction in the radical polymerization of vinyl acetate was studied kinetically. Branching occurs by the polymer transfer as well as the terminal double bond copolymerization. The chain-transfer constants to the main chain ($C_{p,2}$) and to the acetoxy methyl group ($C_{p,1}$) on the polymer were kinetically calculated on the basis of the experimental data described in the preceding paper giving $C_{p,2} = 3.03 \times 10^{-4}$, $C_{p,1} = 1.27 \times 10^{-4}$ at 60°C and $C_{p,2} = 2.48 \times 10^{-4}$, $C_{p,1} = 0.52 \times 10^{-4}$ at 0°C. The chain transfer to monomer is important with respect to the formation of the terminal double bond. The total values of transfer constants to the α- or β-position in the vinyl group and the acetoxy methyl group in vinyl acetate was determined to be 2.15×10^{-4} at 60°C. The transfer constant to the acetyl group in the monomer ($C_{m,1}$) was also evaluated to be 2.26×10^{-4} at 60°C from the quantitative determination of the carboxyl terminals in PVA. These facts suggest that the chain-transfer constant to the α- or β-position in the monomer ($C_{m,2}$) is nearly equal to zero within the experimental errors. Copolymerization reactivity parameters of the terminal double bond were also estimated. As a conclusion, it has become clear that the formation of nonhydro-

lyzable branching by the terminal double bond reaction can be almost neglected, and hence that all of the long branching in PVA are formed only by the polymer transfer mechanism. On the other hand, a large number of hydrolyzable branching in PVAc are prepared by the terminal double bond reaction rather than by the polymer transfer.

INTRODUCTION

It has been well known that branched polymers are formed during the radical polymerization of vinyl acetate. A chain transfer to polymer leads to a long-chain branching. It is a common view that such branching occurs in poly(vinyl acetate)(PVAc) quite readily at the acetoxy methyl group[1-3]. This reaction involves the hydrogen abstraction and a further polymerization at the acetoxy methyl group. The result is a hydrolyzable branch, so named because during hydrolysis of the PVAc to PVA the branched chain is released. Thus a decrease in molecular weight results upon saponification[1-6] and the branching of this type during the polymerization does not result in the branching on poly(vinyl alcohol)(PVA). On the other hand, the abstraction of an α-hydrogen would result in a nonhydrolyzable long-chain branch that remains in the derived PVA.

In the previous paper[7], it was reported that the cross-linked PVAc gel which was able to be decross-linked to give soluble polymers could be prepared by the reaction of partially hydrolyzed PVAc and toluylene diisocyanate. The polymerization of radioactively labelled vinyl acetate in the presence of such a gel PVAc was described in the preceding paper[8], and it was found that the hydrogen atoms in the α-position are more reactive than those on the acetoxy methyl group.

On the other hand, a monomer transfer results in a polymer molecule with a terminal double bond. The copolymerization of the terminal double bond gives a trifunctional branch point. Therefore, the chain transfer reactions to polymer and to monomer are both important with respect to branching in the radical polymerization of vinyl acetate.

A number of studies have been reported[5,6,9-17] in which the determination of these chain-transfer constants were tried. In the case of the chain-transfer constant to monomer, these reported values are relatively in good agreement with each other, that is 2—3 x 10^{-4} at 60°C. Chain-transfer constants to polymer are not so easily measured as those to monomer or solvent and the proposed values are quite different from each other. One could obtain the polymer transfer constant by knowing the degree of polymerization of the newly formed polymer in the presence of relatively short chain added polymer[13,16,17]. The polymer-transfer constant could also be obtained by the determination of the molecular weight change upon saponification[10,14] as well as by the quantitative determination of the carboxyl terminals in the corresponding PVA[11]. The chain-transfer constant obtained by these methods, however, should be one to the acetoxy methyl group of PVAc.

In the present study, the chain-transfer reaction to polymer and the copolymerization of the terminal double bond were analyzed kinetically and kinetic parameters were estimated based on the experimental results described in the preceding paper.

EXPERIMENTAL

Purification of Monomer

An especially pure vinyl acetate was prepared as follows. Vinyl acetate obtained commercially was washed successively with a 5-% $NaHSO_3$ aqueous solution, a 5-% $NH_2OH \cdot HCl$ aqueous solution, and water, dried with $CaCl_2$, and then distilled through a Widmer column three times and a fraction distilling at 72—73°C was collected. The samples were degassed, polymerized to the extent of 10% conversion, and the residual monomer was distilled. The purified monomer was then stored at -78°C until required.

Polymerization Procedure

A known volume of freshly distilled vinyl acetate was distilled into an ampoule containing 2,2'-azobisisobutyronitrile under high vacuum and the ampoule was sealed off. The initiator concentration was 0.01 mol% of the monomer. The ampoules were immersed in a thermostat at 60°C. After the required time of polymerization, the ampoule was opened and the content was diluted with acetone and allowed to pour into n-hexane under stirring to precipitate the polymer. The precipitated polymer was washed with n-hexane, dried, dissolved in benzene and recovered by the freeze-drying technique.

Saponification of PVAc

PVAc was saponified by treating a methanolic polymer solution (1-g PVAc in 100-ml methanol) with 1 ml of a 23.2-% NaOH aqueous solution. The reaction mixture was held at room temperature for about 15 hr until the precipitation of PVA was completed. The PVA was separated, washed with methanol, and then dried in vacuo. In order to complete the saponification, PVA was further treated with NaOH in an aqueous solution in the following way. Into a 3-% PVA aqueous solution NaOH was added with the proportion of 0.2 mol NaOH to unit mol of PVA and the solution was kept at 80°C for several hours. PVA was separated by pouring the solution into a large excess of methanol, purified by reprecipitation into methanol from an aqueous solution, washed with methanol by a Soxhlet extractor for a week, and then dried in vacuo.

Reacetylation of PVA

One gram of PVA was added into 40 ml of a mixture of acetic anhydride and pyridine (1/2,v/v). The mixture was held at 70°C for a few days and then poured into a large excess of water to precipitate PVAc. The product was washed with water, purified by reprecipitation into water from an acetone solution, and dried overnight under vacuum at about 40°C. The purified PVAc was then dissolved in benzene and freeze-dried.

Viscosity

The viscosity measurements were made with a modified Ubbelohde viscometer. Flow time measurements were carried out at 30°C in acetone as solvent and at five solution concentrations. Intrinsic viscosities were obtained from the double plots[18].

Determination of Carboxyl Group in PVA

PVA molecules obtained by saponification of PVAc have a carboxyl group as the end group. The determination of the carboxyl group in PVA was studied by the conductometric titration. Accurately weighed 0.5-g PVA was dissolved in 150 ml of deionized water in which 0.5—1.5 ml of 0.01-N HCl aqueous solution was added. After leaving the solution for about 30 minutes, it was titrated with 0.01-N NaOH aqueous solution. The conductivity was plotted as a function of the volume of titer. As a blank test, a solution without containing PVA was also titrated and plotted in a similar manner. The electric conductivity of the solution decreased initially with titer, because of the neutralization of the excess of HCl by titrant. And then the conductivity became almost constant irrespective of the amount of titer. The quantity of caroxyl group was obtained from the amount of consumption of NaOH corresponding to the portion of almost constant conductivity in the titration curve by substracting the blank value. The conductivity was measured at 20°C by the use of a Yanagimoto Conductivity Outfit Model MY-7: cell volume, 200 ml; electrode size, $1^{cm} \times 1^{cm}$; electrode intervals, 2 cm.

RESULTS AND DISCUSSION

Determination of the Number-average Degree of Branching and the Chain-transfer Constant to Polymer

The rate of formation of branching point by polymer transfer and the rate of polymerization are represented below.

$$\frac{d\nu}{dt} = k_{t,p}[R\cdot][P] \qquad (1)$$

$$\frac{dx}{dt} = k_p[R\cdot][1 - x] \qquad (2)$$

where ν is the average concentration of branching point, $k_{t,p}$ is the rate constant of the chain transfer to polymer, k_p is the rate constant of propagation, x is the fractional conversion, [R·] is the concentration of the growing chain radical, and [P] is the concentration of unit moles of polymer respectively. Dividing eq 1 by eq 2 and integrating,

$$C_p = \frac{1}{-\ln(1 - x)} \cdot \frac{\nu}{[P]} \qquad (3)$$

where $C_p = k_{t,p}/k_p$, and $\nu/[P]$ is the number-average branching density per unit mole of polymer which can be obtained from the degree of grafting (G), $(W - W_0)/W_0$, and the number average degree of polymerization of branch itself (P_B) as below. W and W_0 are weight of the grafting and the original polymer respectively.

$$\frac{\nu}{[P]} = \frac{G}{P_B} \qquad (4)$$

In the preceding study[8], the polymerization of radioactive vinyl acetate in the presence of a cross-linked PVAc gel was investigated in order to elucidate the branching formation caused by the polymer transfer, and the total degree of grafting(G_1) and the degree of grafting onto the main chain (G_2) were determined at various conversions.

In the present study the chain-transfer constants to the polymer and the number-average branching densities were calculated from eq 3 and 4 on the basis of the experimental data described in the preceding paper[8]. The results of the calculation are listed in Table I. As mentioned in the preceding paper, since the branch itself (3C fraction) and the "homo polymer" (2C fraction) were identical not only in the average molecular weight but also in the molecular weight distribution, one could use the degree of polymerization of 2C fraction instead of 3C fraction as P_B in the calculation of branching density according to eq 4. It was found difficult to measure the number-average molecular weight by osmotic pressure with the unfractionated sample of 2C fraction because some of the low molecular weight polymers in the sample permeated through a membrane. Therefore, the authors were forced to measure viscosity to estimate the molecular weight. For the calculation of the number-average molecular weight from intrinsic viscosity, the equation propsed by Matsumoto et al.[19] for the unfractionated PVAc of

Table I. The number-average branching densities($\nu/[P]$) and chain-transfer constants to main chain of polymer($C_{p,2}$)

No.	Temp. °C	x	G_2	Branch[a] $[\eta]$	Branch[a] $P_b \times 10^{-3}$	[b] $(\nu/[P]) \times 10^5$	$C_{p,2} \times 10^4$
117	60	0.0435	0.0506	1.55	3.86	1.31	2.94
121	60	0.140	0.206	1.65	4.22	4.88	3.23
119	60	0.215	0.266	1.65	4.22	6.30	2.60
120	60	0.263	0.394	1.63	4.15	9.50	3.11
114	60	0.402	0.622	1.50	3.67	17.0	3.29
						Aver.	3.03
123	0	0.0662	0.179	2.81	8.81	2.03	2.22
124	0	0.154	0.418	2.95	9.40	4.44	2.66
125	0	0.208	0.563	2.97	9.50	5.93	2.55
						Aver.	2.48

a) The degree of polymerization of branches(P_B) were calculated from the intrinsic viscosities of 2C fraction by $[\eta] = 4.10 \times 10^{-3} P^{0.72}$.

b) The number of nonhydrolyzable branches per monomer unit of back bone.

low conversion was used. As seen in Table I, the order of values of the number average branching densities are in the range of 10^{-5}—10^{-4}. These considerably small values indicate that the length of the branches formed by the polymer transfer is significantly long, which is supported by the GPC data of the sample shown in the preceding paper[8]. The values of the chain-transfer constants to the main chain of polymer ($C_{p,2}$) which was calculated from eq 3 using the values of the number-average branching densities are also shown in Table I. The ratios of the chain-transfer constant to the acetoxy methyl group on the polymer and that to the main chain, $C_{p,1}/C_{p,2}$, were precedingly estimated[8] to be 0.42 at 60°C and 0.21 at 0°C. Using these ratios, the values of the chain-transfer constants to the acetoxy methyl group on the polymer are estimated. Table II shows the polymer transfer constants $C_{p,1}$ and $C_{p,2}$ at 0°C and 60°C, and the activation energy differences between the polymer transfer and the propagation.

According to chain transfer studies of vinyl acetate to low molecular compounds such as isopropyl acetate, the hydrogen atoms in the α-position are more reactive than those on the acetoxy methyl group[9]. Therefore, the chain transfer to the main chain of PVAc might well have occurred dominantly at the α-position. It is generally considered that the energy of activation for the chain transfer is greater than that for the propagation and hence the transfer is less important at low temperatures. As seen in Table II, however, the activation energy for the chain transfer to the main chain of polymer are only slightly larger than that for the propagation. This fact

Table II. Chain-transfer constants to polymer and activation parameters

	60°C	0°C
$C_{p,1}$ (to acetyl group)	1.27×10^{-4}	0.52×10^{-4}
$C_{p,2}$ (to main chain)	3.03×10^{-4}	2.48×10^{-4}
C_p (total)	4.30×10^{-4}	3.00×10^{-4}
$E_{t,p1} - E_p$	2.70 Kcal/mol	
$E_{t,p2} - E_p$	0.60 "	
$E_{t,p1} - E_{t,p2}$	2.10 "	

suggests that in the radical polymerization of vinyl acetate the chain transfer to the α-position of the polymer may take place appreciably at low temperature and hence the presence of branching in the PVA derived from PVAc polymerized at low temperature can not be negligible.

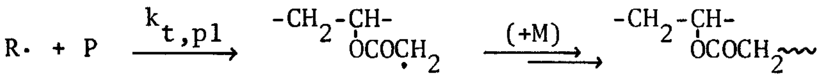
Kinetic Analysis of Branching Reactions

The polymerization of vinyl acetate is understood as such that branching occurs by a few relatively simple reactions. These reactions are propagation, monomer transfer which results in a polymer molecule with a terminal double bond, polymer transfer which yields a trifunctional branch point in the polymer molecule, and the terminal double bond copolymerization in which an entire polymer molecule is incorporated into a growing radical. These reactions are illustrated in eq 5 through 11.

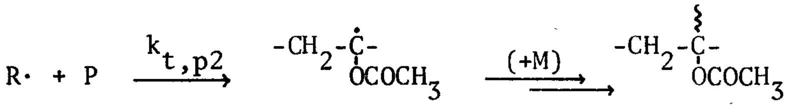
Propagation:

$$R\cdot + M \xrightarrow{k_{p,0}} R\cdot \qquad (5)$$

Transfer to polymer:

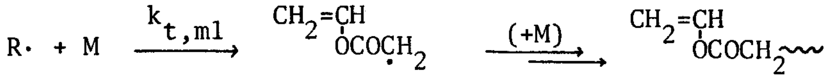


$$R\cdot + P \xrightarrow{k_{t,p1}} \underset{OCO\dot{C}H_2}{-CH_2-CH-} \xrightarrow{(+M)} \underset{OCOCH_2\sim}{-CH_2-CH-} \qquad (6)$$



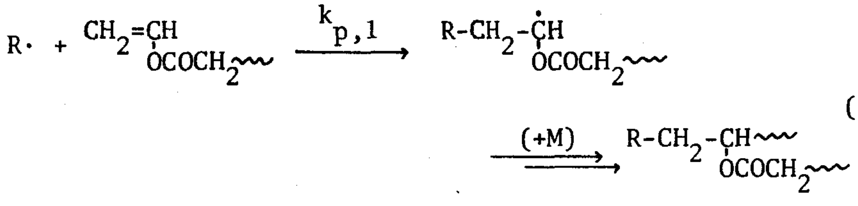
$$R\cdot + P \xrightarrow{k_{t,p2}} \underset{OCOCH_3}{-CH_2-\dot{C}-} \xrightarrow{(+M)} \underset{OCOCH_3}{-CH_2-\overset{\wr}{C}-} \qquad (7)$$

Transfer to monomer:



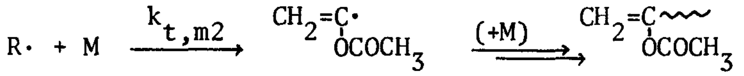
$$R\cdot + M \xrightarrow{k_{t,m1}} \underset{OCO\dot{C}H_2}{CH_2=CH} \xrightarrow{(+M)} \underset{OCOCH_2\sim}{CH_2=CH} \qquad (8)$$

Terminal double bond copolymerization:



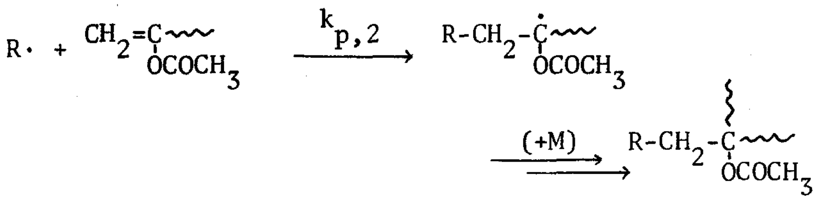
$$R\cdot + CH_2{=}\underset{OCOCH_2\sim\sim}{CH} \xrightarrow{k_{p,1}} R{-}CH_2{-}\underset{OCOCH_2\sim\sim}{\dot{C}H} \xrightarrow{(+M)} R{-}CH_2{-}\underset{OCOCH_2\sim\sim}{CH}\sim\sim \qquad (9)$$

Transfer to monomer:



$$R\cdot + M \xrightarrow{k_{t,m2}} CH_2{=}\underset{OCOCH_3}{C\cdot} \xrightarrow{(+M)} CH_2{=}\underset{OCOCH_3}{C}\sim\sim \;. \qquad (10)$$

Terminal double bond copolymerization:



$$R\cdot + CH_2{=}\underset{OCOCH_3}{C}\sim\sim \xrightarrow{k_{p,2}} R{-}CH_2{-}\underset{OCOCH_3}{\dot{C}}\sim\sim \xrightarrow{(+M)} R{-}CH_2{-}\underset{OCOCH_3}{\overset{\wr}{C}}\sim\sim \qquad (11)$$

where R· is the usual growing chain radical, P is a polymer molecule, M is a monomer molecule, and k's are the rate constants.

These reactions are so frequent that the effects of radical initiation and termination on average chain length can be made negligible by operating at low but still reasonable rates of polymerization. Hence, under the polymerization conditions with a small amount of initiator in bulk at 60°C, the molecular weight of the polymer at any point in the conversion should, for the most part, be determined by the above reactions.

According to these elementary reactions, one could calculate kinetically the quantity of the hydrolyzable and nonhydrolyzable branching caused by the polymer transfer or the terminal double bond copolymerization, and the degree of polymerization before and after saponification. The rate of propagation is represented as,

$$-\frac{d[M]}{dt} = k_{p,0}[R\cdot][M] \tag{12}$$

where [M] and [R·] denote the monomer and growing chain radical concentration at time t, and $k_{p,0}$ is the rate constant of propagation. The rate of the formation of hydrolyzable branching point by polymer transfer can be represented by eq 13.

$$\frac{d[HBg]}{dt} = k_{t,p1}[R\cdot][P] \tag{13}$$

where [HBg] denotes the concentration of hydrolyzable branching point formed by polymer transfer, [P] is the concentration of the base mole of polymer and $k_{t,p1}$ is the rate constant of the reaction 6. Combination of eq 12 and 13 gives eq 14.

$$-\frac{d[HBg]}{d[M]} = C_{p,1}\frac{[M]_0 - [M]}{[M]} \tag{14}$$

where $[M]_0$ is the initial concentration of monomer, and $C_{p,1} = k_{t,p1}/k_{p,0}$. Upon integration of eq 14, the number of hydrolyzable branches per monomer unit of back-bone caused by the polymer transfer mechanism is obtained by formula,

$$\frac{[HBg]}{x[M]_0} = C_{p,1}\left(-\ln\frac{1}{x}\frac{1}{1-x} - 1\right) \tag{15}$$

where $x = ([M]_0 - [M])/[M]_0$. Expression for nonhydrolyzable branches can be obtained in a similar manner,

$$\frac{[\mathrm{NBg}]}{x[\mathrm{M}]_0} = C_{p,2}\left(-\frac{1}{x}\ln\frac{1}{1-x} - 1\right) \qquad (16)$$

where [NBg] is the concentration of nonhydrolyzable branching point, and $C_{p,2} = k_{t,p2}/k_{p,0}$.

The rate of formation of the hydrolyzable branch by the copolymerization mechanism of the terminal double bond can be represented by the formula,

$$\frac{d[\mathrm{HBc}]}{dt} = k_{p,1}[\mathrm{R}\cdot]\left[\mathrm{CH_2{=}}\underset{\mathrm{OCOCH_2}\sim\sim}{\mathrm{CH}}\right] \qquad (17)$$

where [HBc] is the concentration of hydrolyzable branching point formed by the copolymerization of the terminal double bond. The rate of formation of the terminal double bond is given by eq 18.

$$\frac{d}{dt}\left[\mathrm{CH_2{=}}\underset{\mathrm{OCOCH_2}\sim\sim}{\mathrm{CH}}\right] = k_{t,m1}[\mathrm{R}\cdot][\mathrm{M}] - k_{p,1}[\mathrm{R}\cdot]\left[\mathrm{CH_2{=}}\underset{\mathrm{OCOCH_2}\sim\sim}{\mathrm{CH}}\right] \qquad (18)$$

Combination of eq 12 and 18 gives eq 19,

$$-\frac{d}{d[\mathrm{M}]}\left[\mathrm{CH_2{=}}\underset{\mathrm{OCOCH_2}\sim\sim}{\mathrm{CH}}\right] = C_{m,1} - K_1\frac{\left[\mathrm{CH_2{=}}\underset{\mathrm{OCOCH_2}\sim\sim}{\mathrm{CH}}\right]}{[\mathrm{M}]} \qquad (19)$$

where $C_{m,1} = k_{t,m1}/k_{p,0}$ and $K_1 = k_{p,1}/k_{p,0}$. Upon integration,

$$\frac{\left[\mathrm{CH_2{=}}\underset{\mathrm{OCOCH_2}\sim\sim}{\mathrm{CH}}\right]}{x[\mathrm{M}]_0} = \frac{C_{m,1}}{1-K_1}\left\{\frac{(1-x)^{K_1}}{x} - \frac{1}{x} + 1\right\} \qquad (K_1 \neq 1) \qquad (20)$$

Combination of eq 12, 17, and 20 gives the number of hydrolyzable branches per monomer unit of the back bone caused by the copolymerization of the terminal double bond by formula,

$$\frac{[\mathrm{HBc}]}{x[\mathrm{M}]_0} = \frac{C_{m,1}}{1 - K_1}\left\{\frac{1}{x} - \frac{(1 - x)^{K_1}}{x} - K_1\right\} \qquad (K_1 \neq 1) \qquad (21)$$

Expression for nonhydrolyzable branches can be obtained in a similar manner,

$$\frac{[\mathrm{NBc}]}{x[\mathrm{M}]_0} = \frac{C_{m,2}}{1 - K_2}\left\{\frac{1}{x} - \frac{(1 - x)^{K_2}}{x} - K_2\right\} \qquad (K_2 \neq 1) \qquad (22)$$

where [NBc] is the concentration of the nonhydrolyzable branching point formed by the copolymerization of the terminal double bond, $C_{m,2} = k_{t,m2}/k_{p,0}$ and $K_2 = k_{p,2}/k_{p,0}$.

The reciprocal of the number-average degree of polymerization of trifunctionally branched polymer is given by

$$\frac{1}{P} = \frac{\Sigma[\mathrm{E}] - \Sigma[\mathrm{B}]}{2x[\mathrm{M}]_0} \qquad (23)$$

where $\Sigma[\mathrm{E}]$ and $\Sigma[\mathrm{B}]$ represent the sum of polymer ends and branching points, respectively. Under the polymerization condition of vinyl acetate which is employed with a small amount of initiator in bulk, as mentioned above, $\Sigma[\mathrm{E}]$ is approximately given as,

$\Sigma[E] = \Sigma[\text{chain transfer to polymer}] + 2\Sigma[\text{chain transfer to monomer}] - \Sigma[\text{branch point formed by the terminal double bond copolymerization}]$ (24)

Combination of eq 15,16,21,22,and 23 gives the reciprocal of the number average degree of polymerization of branched PVAc as a function of fractional conversion x.

$$\frac{1}{P} = \frac{C_{m,1}}{1 - K_1}\left\{\frac{(1 - x)^{K_1}}{x} - \frac{1}{x} + 1\right\} + \frac{C_{m,2}}{1 - K_2}\left\{\frac{(1 - x)^{K_2}}{x} - \frac{1}{x} + 1\right\} \quad (25)$$

The number-average degree of polymerization P' for the polymer after hydrolysis can be calculated from the sum of polymer ends $\Sigma[E']$ and that of branching points $\Sigma[B']$ after hydrolysis. These sums are represented as follows:

$$\Sigma[E'] = \Sigma[E] + \Sigma[\text{hydrolyzable branch point}] \quad (26)$$

$$\Sigma[B'] = \Sigma[NBg] + \Sigma[NBc] \quad (27)$$

Using eq 23, the reciprocal of P' is obtained by the formula,

$$\frac{1}{P'} = C_{m,1} + \frac{C_{m,2}}{1 - K_2}\left\{\frac{(1 - x)^{K_2}}{x} - \frac{1}{x} + 1\right\} + C_{p,1}\left(-\frac{1}{x}\ln\frac{1}{1 - x} - 1\right) \quad (28)$$

The total number of hydrolyzable branching points are given by (1/P') - (1/P) from eq 25 and 28.

$$\frac{1}{P'} - \frac{1}{P} = C_{p,1}\left(-\frac{1}{x}\ln\frac{1}{1 - x} - 1\right) + \frac{C_{m,1}}{1 - K_1}\left\{\frac{1}{x} - \frac{(1 - x)^{K_1}}{x} - K_1\right\}$$

$$= \frac{[HBg]}{x[M]_0} + \frac{[HBc]}{x[M]_0} \tag{29}$$

And the sum of the chain-transfer constants to monomer $(C_{m,1} + C_{m,2})$ is obtained by

$$\lim_{x \to 0} \frac{1}{P} = \lim_{x \to 0} \frac{1}{P'} = C_{m,1} + C_{m,2} \tag{30}$$

Table III shows the degree of polymerization before and after saponification and the number of hydrolyzable branching point per polymer base mole, which is formed by the polymer transfer and the terminal double bond copolymerization, of the PVAc samples polymerized to various conversion. Total number of the hydrolyzable branching points per polymer base mole were obtained from eq 29 and number of that formed by the polymer transfer were calculated from eq 15 using the value of $C_{p,1}$ shown in Table II. Substracting the latter value from the former, number of hydrolyzable branching points formed by the terminal double bond copolymerization were also determined. It is noticeable, as seen in Table III, that the branching at the acetoxy group on the polymer is formed much more by the terminal double bond copolymerization than by the polymer transfer at higher conversions. The degree of polymerization P increases with conversion and, in contrast, that of saponified sample decreases. The reciprocal values of these degree of polymerization were plotted against the fractional conversion in Figure 1. From the intercept of the curves at zero conversion, the total value of the monomer transfer constants

Table III. The number of hydrolyzable branches formed by chain transfer to polymer and terminal double bond copolymerization$^{a)}$

No.	x	$P \times 10^{-3}$ $^{b)}$	$P' \times 10^{-3}$ $^{b)}$	$(1/P')-(1/P)$ $\times 10^4$	$\frac{[HBg]^{c)}}{x[M]_0} \times 10^4$	$\frac{[HBc]}{x[M]_0} \times 10^4$
1	0.0258	4.66	-	-	0.017	-
2	0.0528	4.71	4.61	0.045	0.034	0.011
3	0.0770	4.82	4.57	0.115	0.047	0.068
4	0.149	4.98	4.50	0.215	0.102	0.113
5	0.200	5.15	4.43	0.313	0.146	0.164
6	0.255	5.27	4.29	0.432	0.195	0.237
7	0.313	5.39	4.15	0.555	0.252	0.303
8	0.406	6.39	4.21	0.810	0.357	0.453

a) Polymerization; bulk, 60°C, AIBN 0.01 mol%/monomer.

b) The degree of polymerization(P & P') was calculated from $[\eta] = 4.10 \times 10^{-3} P^{0.72}$.

c) Calculated from eq 15 using $C_{p,1} = 1.27 \times 10^{-4}$.

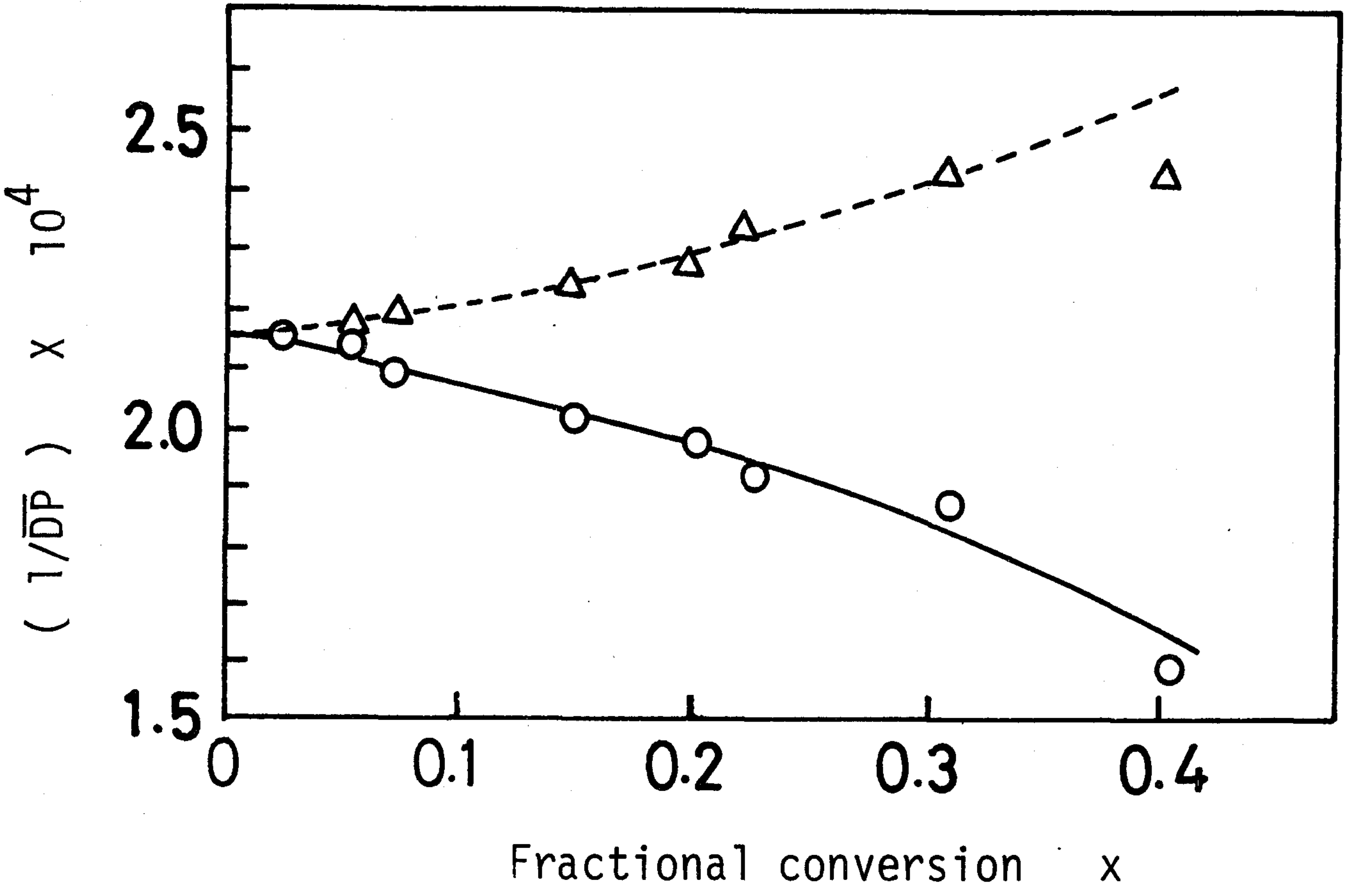


Figure 1. Dependency of the reciprocal of the degree of polymerization on the fractional conversion: ○ , original; △ , after hydrolysis and reacetylation: polymerization; bulk, 60°C, AIBN 0.01 mol%/monomer.

$(C_{m,1} + C_{m,2})$ of 2.15×10^{-4} was obtained.

The branches attached to the acetoxy group and terminal double bond combined with parent polymer by ester linkage, which are formed by the reactions 6, 8, and 9, should be released from the parent polymer upon saponification, giving PVA with a terminal carboxyl group. Since the presence of carboxyl terminals in PVA was first pointed out by Sakurada and Inoue[20], its quantitative estimation has been studied by Sakurada and Yoshizaki[21] using conductometric titration and Ukida et al.[11] using polarography. Under the polymerization conditions that the effects of radical initiation and termination on average chain length can be neglected, number of carboxyl terminal group per polymer base mole in PVA may be represented as eq 31.

$$\frac{[\mathrm{COOH}]}{x[\mathrm{M}]_0} = \frac{\left[\begin{matrix}\mathrm{CH_2=CH} \\ \quad\;\; | \\ \quad\;\; \mathrm{OCOCH_2}\!\sim\end{matrix}\right]}{x[\mathrm{M}]_0} + \frac{[\mathrm{HBc}]}{x[\mathrm{M}]_0} + \frac{[\mathrm{HBg}]}{x[\mathrm{M}]_0}$$

$$= C_{m,1} + C_{p,1}\left(\frac{1}{x}\ln\frac{1}{1-x} - 1\right) \qquad (31)$$

Therefore, the quantitative determinations of the carboxyl terminal group in PVA samples which are derived from PVAc polymerized to various conversions make it possible to estimate the chain-transfer constants to the acetoxy methyl group both in monomer and polymer.

In the present work, the quantitative estimation of the carboxyl terminals in highly purified PVA samples derived from PVAc at several conversions was carried out employing the conductometric titration for the purpose of estimation of $C_{m,1}$ and $C_{p,1}$. The results are shown in Table IV. Figure 2 shows an example of the titration curves. The number of carboxyl terminals per polymer base mole were plotted in Figure 3 according to eq 31. From the intercept and the slope of the straight line $C_{m,1} = 2.26 \times 10^{-4}$ and $C_{p,1} = 1.17 \times 10^{-4}$ were determined , respectively using a least squares method. These values are in good agreement with those reported by Ukida et al.[11] who used polarography for the quantitative estimation of the carboxyl group in PVA. This $C_{p,1}$ value also agrees approximately with that shown in Table II. The value of $C_{m,1}$ is somewhat larger than the value of $(C_{m,1} + C_{m,2})$ obtained previously. This fact suggests that the chain-transfer constant to α- or β-position in vinyl acetate $(C_{m,2})$ is nearly equal to zero within the experimental error. As the abstraction of hydrogen atoms from α- or β-position of the vinyl group is generally considered to rarely happen, it may be concluded that the chain transfer to monomer takes place almost dominantly at the acetoxy methyl group which is susceptible to a radical attack by virture of the adjacent carbonyl group. It is somewhat interesting that the observed value of the chain-transfer constant to the acetoxy methyl group in monomer $(C_{m,1})$ is a little larger than that to the acetoxy methyl group in polymer $(C_{p,1})$. The reason for this fact is obscure, but the possibility that the diffusion factors contribute to some extent to the polymer transfer reaction which is the reaction between two macromolecules can not be neglected.

Table IV. The amount of carboxyl groups in PVA [a)]

Sample No.	Fractional conv. x	$\frac{[COOH]}{x[M]_0} \times 10^4$
9	0.0685	2.24
10	0.0930	2.39
11	0.105	2.38
12	0.185	2.52
13	0.325	2.59
14	0.382	2.74

a) Polymerization condition of PVAc: bulk, 60°C, AIBN 0.01 mol%/monomer.

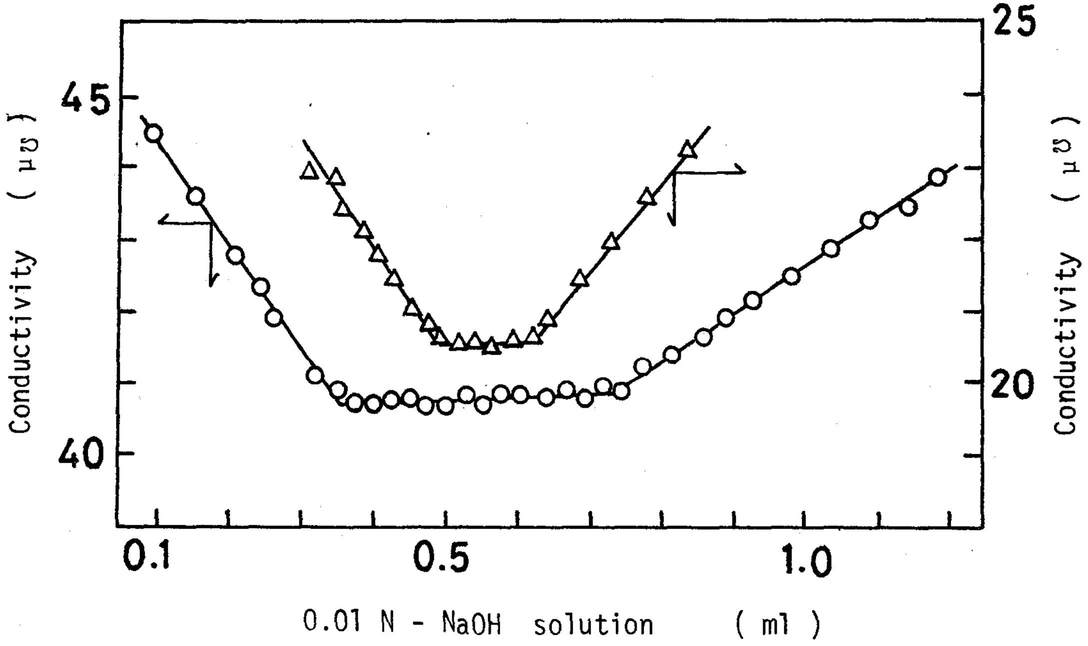


Figure 2. Examples of conductometric titration curves for PVA:
○, sample No.12; △, blank.

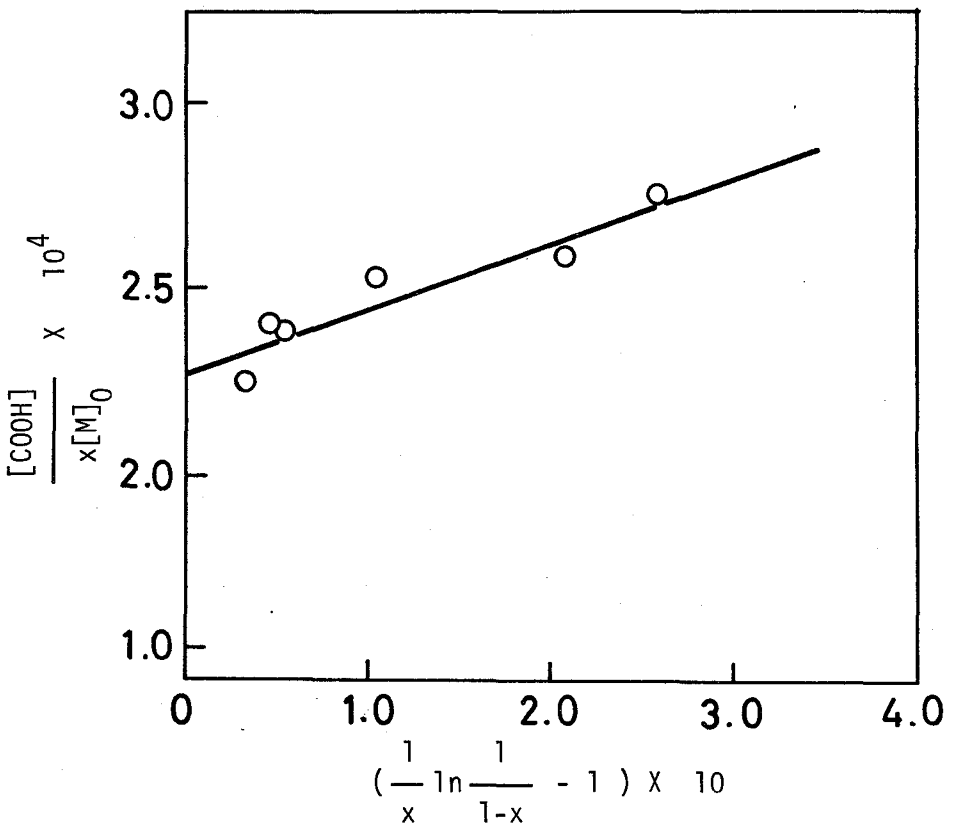


Figure 3. Correlation between conversion and the amount of carboxyl group in PVA.

As mentioned above, all of the transfer constants, $C_{m,1}$, $C_{m,2}$, $C_{p,1}$, and $C_{p,2}$ were successfully estimated. The next problem is to evaluate the reactivity parameters of K_1 and K_2 in the terminal double bond copolymerization. Eq 21 shows that the amount of hydrolyzable branches prepared by the terminal double bond copolymerization depends on the parameters $C_{m,1}$ and K_1. In order to evaluate the parameter K_1, the amount of hydrolyzable branches formed by the terminal double bond reaction (Table III) was plotted as a function of fractional conversion in Figure 4. The curves shown in the figure are obtained by the calculation from eq 21 using $C_{m,1}$ value of 2.26×10^{-4} and various K_1 values. When the value of K_1 is taken to be 0.7—0.8, the experimental data fit best the theoretical curve over the wide range. Stein[22] and Graessley et al.[15] deduced 0.8 for parameter K_1, the agreement with ours being fairly well.

In Figure 5, curves represent the relations between the calculated degree of polymerization before and after saponification according to eq 25 and 28 and the fractional conversion, and plots represent the experimental values. Close agreements between observed and calculated values were obtained.

The value of parameter K_2 could not be estimated. When the chain transfer to α- or β-position of the vinyl group in vinyl acetate can be neglected, the value of K_2 is not important with respect to branching reactions. Supposing that the terminal double bond was formed by reaction 10, its reactivity for copolymerization should be markedly low because of the allylic double bond.

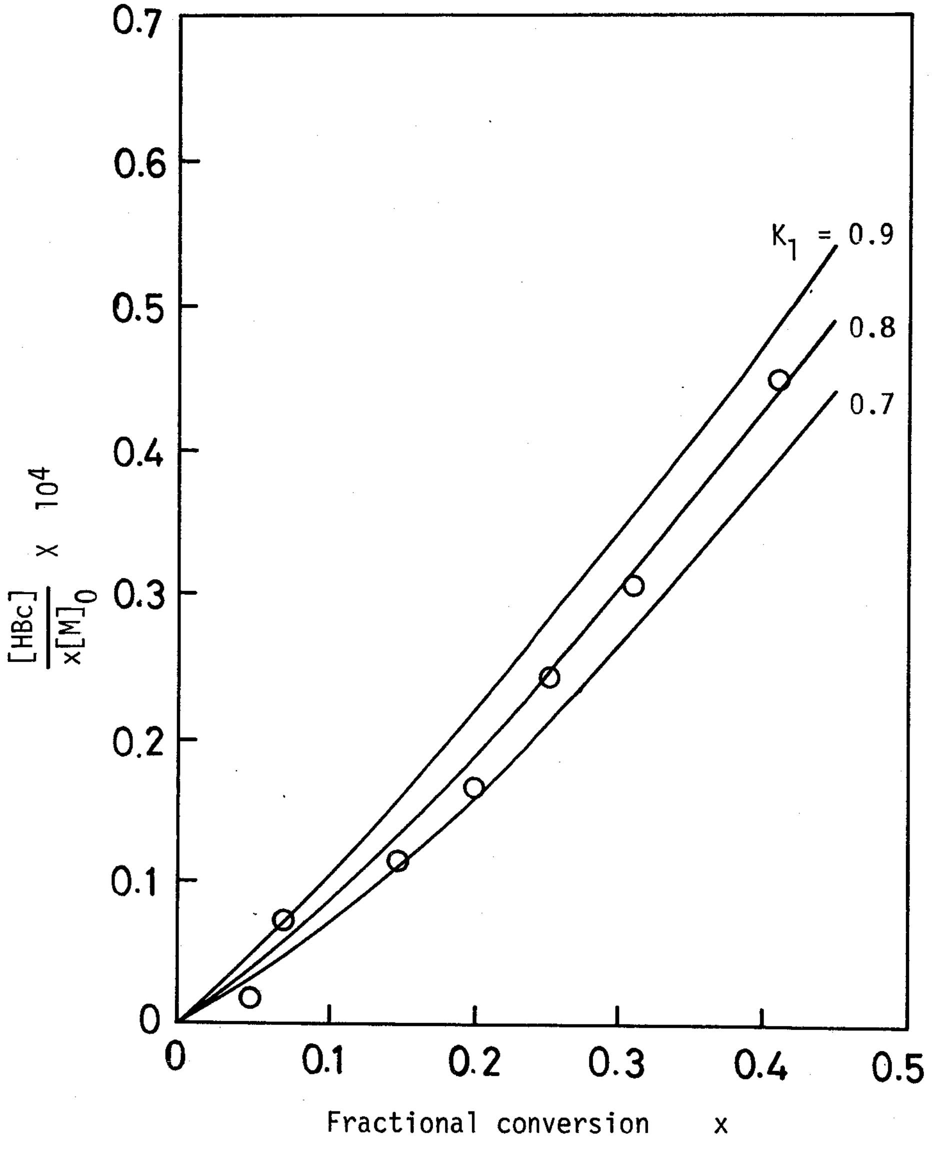


Figure 4. The amount of hydrolyzable branching formed by terminal double bond copolymerization mechanism vs. fractional conversion. The curves were calculated for $C_{m,1} = 2.26 \times 10^{-4}$ from eq(21).

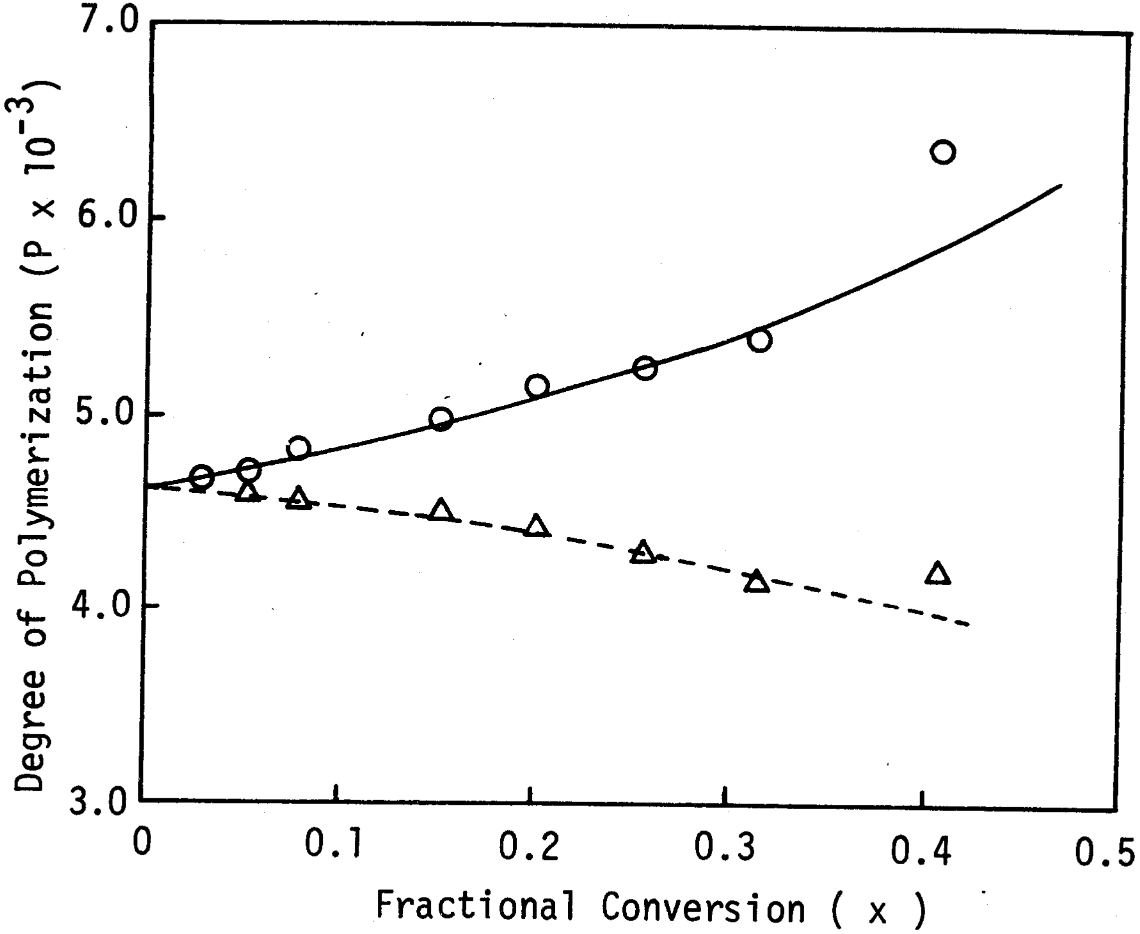


Figure 5. Calculated and observed change in degree of polymerization upon hy hydrolysis and reacetylation: curve, calculated; ○, original; △,after hydrolysis and reacetylation: polymerization; bulk, 60°C, AIBN 0.01 mol%/monomer.

Consequently, it has become clear that the chain transfer to monomeric vinyl acetate occurs almost dominantly at the acetoxy methyl group and hence the formation of nonhydrolyzable branches by the terminal double bond reaction can be neglected. This fact indicates that all of the long branching in PVA are prepared by the polymer transfer mechanism. On the other hand, a large number of hydrolyzable branches in PVAc are formed by the terminal double bond copolymerization mechanism rather than by the polymer transfer.

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Chapter IV

Polymerization of Vinyl Trimethylacetate in the Presence of Cross-linked Poly(vinyl acetate)

ABSTRACT

In order to clarify the grafting behavior of vinyl trimethylacetate(VTMAc) onto poly(vinyl acetate)(PVAc), the polymerization of a radioactive VTMAc in the presence of a cross-linked PVAc gel was studied in accordance with the experimental technique described in the previous papers. It was found that, contrary to the result by Imoto et al., the grafting onto the main chain of PVAc takes place about 2.8 times as readily as that onto the acetyl side group on PVAc at 60°C.

INTRODUCTION

In previous papers[1-3], it was clarified that, in the polymer transfer reaction during the radical polymerization of vinyl acetate, the hydrogen atoms in the α-position of the main chain are more reactive than those on the acetoxy methyl group, and that consequently long chain branches are present in the derived poly(vinyl alcohol) (PVA). In addition, from the kinetic analysis of the reaction of branch formation[3], it turned out that all the long branching in PVA are formed solely by the chain transfer to polymer (accumulated in the polymerization system during the radical polymerization of vinyl acetate), and that terminal double bond copolymerization mechanism is not important with respect to the formation of branch in PVA.

It had been a common view that poly(vinyl acetate)(PVAc) had many branches at the acetyl group but that the derived PVA had little branching.

In order to study the branching in PVAc and PVA, Imoto, Ukida, and Kominami[4] investigated the polymerization of vinyl trimethylacetate(VTMAc) in the presence of PVAc. The isolated graft polymers were saponified with methanolic sodium hydroxide. Only PVAc was converted to PVA, the poly(vinyl trimethylacetate)(PVTMAc) remaining intact, because the rate of alkali-catalyzed saponification of PVTMAc was remarkably slower than that of PVAc. After removal of the PVTMAc side branch by repeated extraction, the number of PVTMAc units remaining in the PVA was determined by infrared analysis. They deduced that most of the branching occurred at the acetoxy methyl group of

PVAc and only a very little at the main chain, estimating the ratio of the numbers of both branches to be 40:1 at 60—70°C.

According to the previous paper[2], the chain transfer to the polymer main chain, during the radical polymerization of radioactive vinyl acetate in the presence of PVAc gel, took place about 2.4 times as readily as that to the acetoxy methyl group at 60°C.

These two results are quite in conflict with each other, in spite of considering the similar reactivity of VTMAc and vinyl acetate. In order to inspect this discrepancy, the polymerization of radioactive VTMAc in the presence of PVAc gel was studied in the present work.

EXPERIMENTAL

Materials

Vinyl-1,2-^{14}C trimethylacetate(V*TMAc) was synthesized from trimethylacetic acid and vinyl-1,2-^{14}C acetate by transesterification in accordance with the Adelman's method[5]. The monomer was washed successively with a 5-% Na_2CO_3 aqueous solution, water, dried with $CaCl_2$, and then distilled through a Widmer column: bp 110—111°C; specific radioactivity, 10.4 μCi/mol.

A PVAc gel used for the present study was prepared according to the previous paper[2]. The intrinsic viscosity and number average molecular weight of the initial PVAc (before cross-linking) were 0.54 and 1.18×10^5 respectively.

Polymerization Procedure

An ampoule containing a PVAc gel, radioactive V*TMAc, and 2,2'-azobisisobutyronitrile(0.05 mol% of monomer) was degassed seven times in a high-vacuum system(<10^{-3} mmHg) and then sealed. Polymerizations were carried out by keeping the ampoules in a thermostat at 60°C for certain periods. The polymers were separated by pouring the reaction mixtures into a large excess of n-hexane, washed by petroleum ether, added into benzene, and then recovered by the freeze-drying technique.

Separation Procedures

Separation procedures for the polymerization products are shown in a block diagram in Figure 1. Soluble radioactive PV*TMAc, termed 1T fraction, which was formed in the polymerization of V*TMAc in the presence of a PVAc gel was separated by repeated extraction with acetone. This procedure was carried out in a similar manner to the previous paper[2]. The end point of the extraction was checked by the radioactivity measurement of the supernant solution and was reached in about five days. The residual gel onto which radioactive PV*TMAc should have grafted was saponified by a MeOH—NaOH system[1] and divided into two parts. One of these was allowed to be decross-linked by treatment with 3-N HBr aqueous solution according to the previous paper[1] and then acetylated by the pyridine—acetic anhydride system giving fraction 34T as shown in Figure 1. This fraction should have radioactivity which is based on the grafting of PV*TMAc both on the acetoxy methyl and on the main chain of PVAc. Another part was

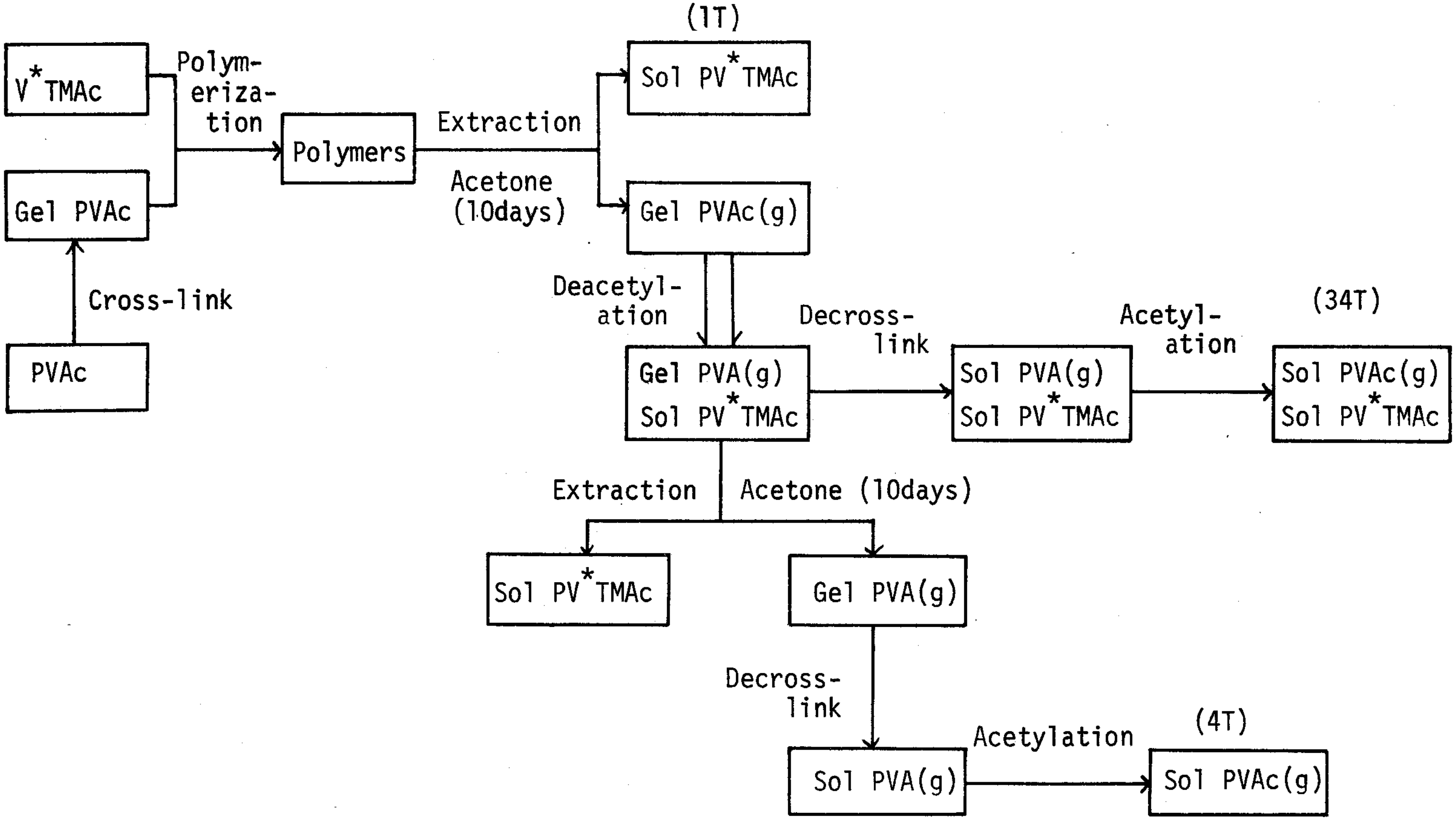

Figure 1. Block diagram of the separation procedures for V* TMAc - PVAc gel system: (g), grafted.

subjected extensive separation by extraction with acetone into a soluble PV*TMAc which had been removed from the side chain group of PVAc and a PVA gel on which PV*TMAc should have grafted. This PVA gel was decross-linked by 3-N HBr and acetylated to give the 4T fraction. It was checked by infrared spectra that PVTMAc was not hydrolyzed at all under the same reaction condition as those for the saponification and the decross-linking.

Radioactivity Measurement

About 0.1 g of polymer was dissolved into 10 ml of toluene containing scintillators(5-g PPO and 0.3-g dimethyl POPOP in 1-l toluene). Radioactivity of the solution was measured using a Tri-Carb Scintillation Spectrometer Model 3002. Counting efficiency was about 78%.

Viscosity

Intrinsic viscosities of acetone solutions of polymer were measured at 30°C in a modified Ubbelohde type viscometer having a solvent flow time of 147 sec.

RESULTS AND DISCUSSION

Copolymerization of Vinyl Acetate and VTMAc

To compare reactivity of VTMAc with vinyl acetate, the copolymerization of vinyl-1,2-^{14}C acetate and VTMAc was examined at 60°C. The copolymer compositions were determined by radioactivity measurements. A copolymer composition curve for vinyl acetate(M_1) and VTMAc (M_2) is shown in Figure 2. It suggests a similar reactivity of these two monomers. The monomer reactivity ratios determined from Fineman—Ross plot are

$$r_1 = 0.83 \pm 0.03$$
$$r_2 = 1.10 \pm 0.05$$

And the values of $Q = 0.024$, $e = -0.62$ were obtained for VTMAc using the values of $Q = 0.027$, $e = -0.3$ for vinyl acetate.

Imoto, Ukida, and Kominami[4] had examined the copolymerization of the same system determining the copolymer composition by infrared spectra and reported the values of $r_1 = 0.75 \pm 0.04$, $r_2 = 0.43 \pm 0.05$, $Q = 0.05$, and $e = -1.3$. This disagreement is considered to be due to the accuracy of the determination of copolymer composition.

The reactivity of VTMAc is so close to that of vinyl acetate that it can be reasonably used as a model monomer of vinyl acetate.

Polymerization of V*TMAc in the Presence of PVAc Gel

The experimental results are summerized in Table I. From the radioactivities of fraction 34T and 4T, the total degree of grafting (G_1) and the degree of grafting onto the main chain of PVAc (G_2) are obtained as shown in Figure 1. As the rates of alkali- and acid-catalyzed saponification of PVTMAc is remarkably slower than that of PVAc, the grafted VTMAc units were not hydrolyzed at all under the

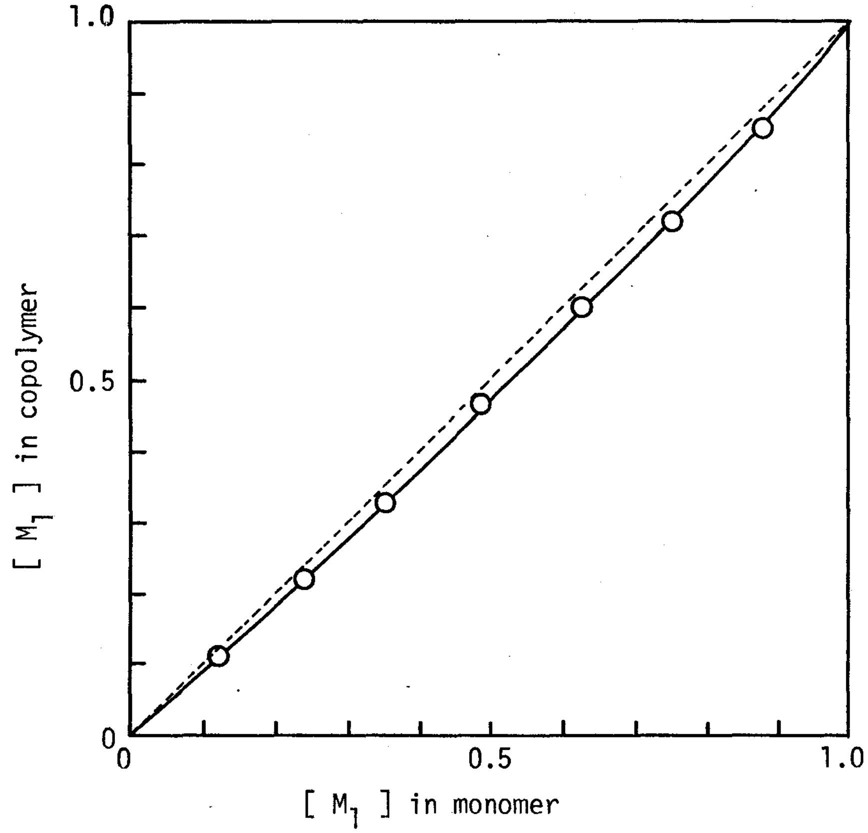

Figure 2. Copolymer composition curve for vinyl acetate (M_1) and vinyl trimethylacetate (M_2): $[M_1] + [M_2] = 52$ mmol, bulk, at 60°C, AIBN 0.05 mol%/monomer.

Table I. Total degree of grafting (G_1) and degree of grafting on main chain (G_2) for V^*TMAc - PVAc gel system

Expt No.	V^*TMAc/Gel (wt.)	Conversion (%)	Radio activity (cpm/0.1g.)		Degree of grafting (%)	
			(34T)	(4T)	G_1	G_2
5	14.0	8.33	353	306	3.39	2.93
1	14.5	17.3	900	589	9.12	5.78
6	14.0	21.4	1084	904	11.19	9.17
7	14.0	26.9	1529	1270	16.55	13.37
3	14.2	56.7	2784	1901	34.88	21.44
2	13.4	62.8	—	2225	—	26.06
4	14.1	86.3	—	2648	—	32.61

Polymerization conditions: bulk, 60°C, AIBN 0.05 mol%/monomer.

Specific activity of PV^*TMAc: 10767 cpm/0.1g.

conditions of the saponification and decross-linking of the PVAc gel. Therefore fraction 4T should be constituted of a PVAc having grafted PV*TMAc chains on its main chain. Figure 3 shows the increase in the total degree of grafting and in the degree of grafting onto the main chain with conversion. The both degree of grafting, G_1 and G_2, increased with conversion. It should be noted that the grafting has occurred to a significant extent onto the main chain of PVAc. The ratio of the chain transfer to the acetoxy methyl group to that to the main chain, which was obtained from the slopes of the initial stage in the curves shown in Figure 3, was 0.36. This value is approximately in agreement with the value of 0.42 in the case of vinyl acetate polymerization[2]. This fact indicates that the chain transfer to the polymer main chain takes place about 2—3 times as frequently as that to the acetyl group on PVAc in the case of the polymerization of VTMAc, as similar to the case of vinyl acetate.

Table II shows the intrinsic viscosities of PV*TMAc of fractions 1T which homo polymerized in the presence of PVAc gel. According to Imoto et al.[4], the reported values of the intrinsic viscosity were considerably smaller (0.006—0.059, in acetone, at 30°C).

Consequently there are many apparent inconsistensies between the experimental results mentioned in the present paper and those in the literature[4]. The reason for these discrepancies are not clear, but the following may be supposed for the results of the literature: the separetion of the PVAc—PVTMAc graft polymer and the PVTMAc homo polymer, the latter of which was reported to be considerably low

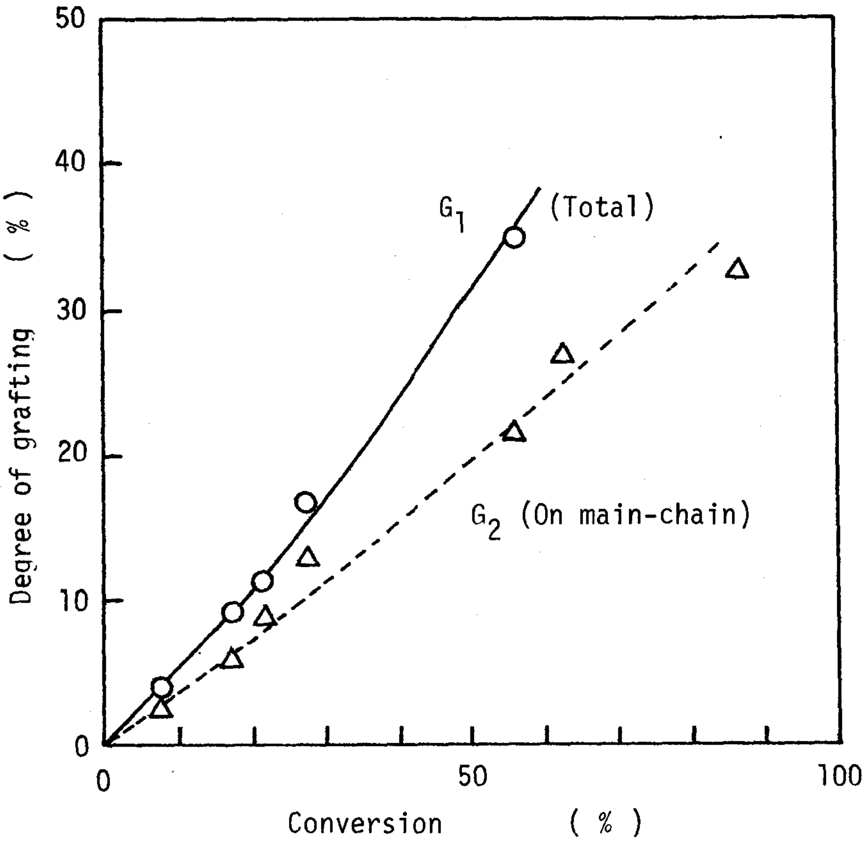

Figure 3. Relationship between degree of grafting and conversion for V*TMAc - PVAc gel system. Polymerization; bulk, 60°C, AIBN 0.05 mol%/monomer.

Table II. Intrinsic viscosities of PV*TMAc (1T) fractions$^{b)}$

Expt No.	$[\eta]^{a)}$	k'
5	0.93	0.36
1	1.09	0.42
6	1.65	0.43
7	1.85	0.41
3	1.31	0.43
2	1.27	0.39
4	1.64	0.42

a) acetone solution, at 30°C, 100ml/g.

b) Polymerization conditions: bulk, 60°C, AIBN 0.05mol%/monomer molecular weight, might be incomplete, and the infrared spectroscopic determination of the degree of grafting might practically be difficult. In the literature, the separation was carried out by extraction of graft polymer with 25% aqueous methanol. PVTMAc is usually insoluble in such a solvent, however, PVTMAc with such considerably low molecular weight should not be thoroughly insoluble in it. Therefore the separated graft polymer fraction might contain the PVTMAc homo polymer to some extent. The infrared absorption band at 12.49 μ for PVAc and the band at 13.05 μ for PVTMAc were used for the key bands in the determination of the chemical composition of graft polymer. However these key bands seem practically too week in absorption intensity to be used for the quantitative analysis.

On the other hand, employing the procedures as described in the present study, the separation into the individual components can be considered to be almost perfect. The quantitative analysis by radioactivity employed in the present work will give the chemical composition with a higher accuracy. Therefore, considering the similar reactivities of VTMAc and vinyl acetate, it may be concluded that VTMAc behaves very like vinyl acetate in the chain transfer reaction to PVAc.

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ACKNOWLEDGEMENT

This investigation has been carried out at Department of Polymer Science, Faculty of Science, Osaka University under the direction of Professor Shun-ichi Nozakura and emeritus Professor Shunsuke Murahashi. The author would like to express his deep gratitude to them for constant guidance in the cause of the work, and also wish to express his heartly thanks to Dr. Norio Sagane and Mr. Hiroshi Harayama for their helpful suggestions and encouragement. The auther is also grateful to Professor Yuji Tonomura and Dr. Yoshinobu Sugino for the measurement of radioactivity.

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