

MOLECULAR STRUCTURES AND FUNCTIONAL
MODIFICATIONS

OF

POLY(VINYL ALCOHOL)

BY

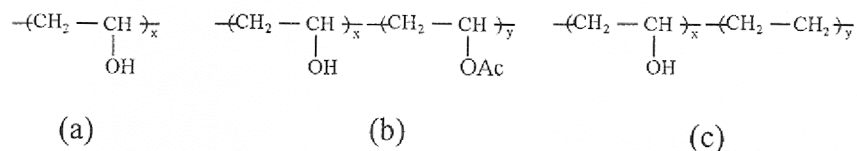
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MAY, 1998

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ABSTRACT

Poly(vinyl alcohol) (a), its partially hydrolyzed product or poly(vinyl alcohol-co-vinyl acetate) (b) and poly(ethylene-co-vinyl alcohol) (c) are all industrially significant polymers used mainly for fiber and film, size and emulsifier/stabilizer, and gas-barrier material, respectively.



In this thesis, these vinyl alcohol-based polymers have been discussed from two aspects: the molecular structures characterized by high resolution nuclear magnetic resonance spectroscopy (NMR) and functional modifications with ionic or crosslinkable groups by copolymerization.

Tacticity and Sequence Distribution The quantitative determination of tacticity for poly(vinyl alcohol) has been difficult using IR and $^1\text{H-NMR}$ before the present work because of severe overlapping of spectral lines. No attention has been paid to the hydroxyl proton of the polymer in $^1\text{H-NMR}$ because it can not be observed due to rapid exchange with water used as a usual solvent. In the present work it has been found that the hydroxyl proton can be observed as three well-separated lines assigned to the three triad sequences of tacticity when dimethyl sulfoxide is used as another solvent instead of water. This discovery has made it possible to determine the tacticity of the polymer easily and quantitatively.

To determine how acetyl group distributes along molecular chains for partially hydrolyzed products is also significant but no analytical method has been known so far.

This subject is industrially significant because the distribution is believed to affect the surface activity of aqueous solution. A direct and quantitative analytical method has been found using ^{13}C -NMR, where the methylene carbon has shown three well-separated lines assigned to the triad sequences of monomer units. Using this method, it has been quantitatively clarified how distribution is strongly dependent on the conditions of hydrolysis and alcoholysis. This method has become a new effective tool for designing emulsifier/stabilizer as well as for investigating the polymer reaction.

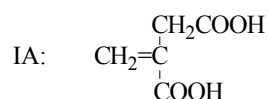
^{13}C -NMR has also been found to be useful for the investigation of anomalous structures generated in polymerization. It was reported in the literature that monomer inversion (head-to-head addition) occurred so frequently at ethylene radical chain ends in the copolymerization of ethylene and vinyl monomer as the normal (head-to-tail) addition did. In the ^{13}C -NMR spectra of poly(ethylene-co-vinyl alcohol) prepared from the hydrolysis of poly(ethylene-co-vinyl acetate), it has been found that the line of 1,4-glycol arising from monomer inversion can be clearly observed and its amount can precisely be determined. From the present analysis, the frequency fraction of monomer inversion of vinyl acetate at ethylene radical chain ends has been determined as 2 to 6.5%, which is apparently more than the fraction in homopolymerization, 1 to 2%, but the normal head-to-tail linkage is still predominant.

Conformational Analysis A new analytical method for determining the conformation of model compounds for vinyl polymers in solution has been developed. In the simplest model compounds, 2,4-disubstituted pentanes with two stereoisomers, there are twelve distinguishable conformers while only four observable values can be obtained for spin-spin coupling constants in ^1H -NMR. In order to avoid this basic difficulty in analysis, only a few limited "preferred conformers" were taken into consideration so far. In the present new analytical method, the number of unknowns is reduced due to the assumption that every conformational energy can be expressed as a sum of five energy parameters concerning local conformation. Usefulness of this method has been typically demonstrated for the conformational analysis of pentane-2,4-diol, a model compound for poly(vinyl alcohol). The fractions of twelve conformers have been determined using the published data on solvent effects and temperature dependence of coupling constants. Other significant results have been found by chance concerning the standard coupling constants for the positions of trans and gauche, J_t and J_g , essential parameters in NMR conformational analysis. From the

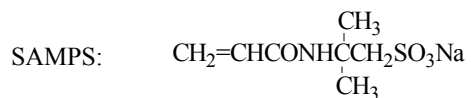
data on pentane-2,4-diol, they have been determined experimentally now as $J_t = 11.5 \pm 1.0$ and $J_g = 2.1 \pm 1.0$ Hz. This is the first determination for chain molecules although they were obtained for ring compounds so far. The new method of conformational analysis has also been applied to the model compounds of poly(vinyl chloride) and polystyrene. The energy parameters used in the present analysis are conceptually the same as those adopted in a statistical method calculating conformation for polymer chain using multiplication of matrices. Therefore, the parameters determined experimentally in the present method can directly be used for the calculation.

Functional Modifications of Poly(vinyl alcohol) Extensive studies have been made for the functional modifications of poly(vinyl alcohol) with carboxylate, sulfonate, cationic or crosslinkable groups by copolymerization method. The examples of comonomers suitable for copolymerization with vinyl acetate for industrial production are shown below. All the copolymers with vinyl alcohol are novel substances, which have not been reported in the literature before the present work.

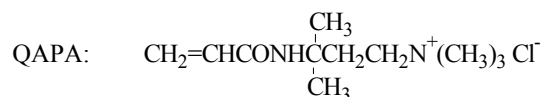
Carboxylic group : Itaconic acid (IA)



Sulfonate group : Sodium 2-acrylamide-2-methyl sulfonate (SAMPS)



Cationic group : Trimethyl-(3-acrylamide-3,3-dimethylpropyl)ammonium chloride (QAPA)



Crosslinkable group : N-(n-butoxymethyl)-acrylamide (BMAM)



In the modification with carboxylic group, specific and practical problems were the

formation of intramolecular ester or inactive lactone and intermolecular ester or crosslinking instead of functionally active carboxylate. It has been found that the problems are dependent on comonomers used and IA has been found to be the most useful because sodium γ, δ -hydroxycarboxylate groups are formed directly in alcoholysis without any risk of crosslinking. By using IA, modified poly(vinyl alcohol)s of lower degrees of hydrolysis, even 80 to 50 mol%, have become possible to be used as water-soluble polymers. In contrast, maleic anhydride can not be applied to the production of partially hydrolyzed products due to crosslinking problem. The formation of crosslinking can be explained by the ring-opening reaction of δ -lactone formed in alcoholysis. Other eight carboxylic monomers have also been studied.

SAMPS has been found to be convenient for making poly(vinyl alcohol)s modified with sulfonate group. By this modification, poly(vinyl alcohol)s of much lower degrees of hydrolysis can also be used as water-soluble polymers. In comparison with the modification using carboxylic monomers, the solubility of poly(vinyl alcohol)s modified with SAMPS are less sensitive to pH or to the presence of inorganic salts.

Among the ten cationic reagents investigated, the acrylamide and methacrylamide derivatives such as QAPA have been found to be useful to produce cationically modified poly(vinyl alcohol)s because of their much higher reactivity in copolymerization, and because of the good stability of amido linkage in alkaline alcoholysis. The cationically modified poly(vinyl alcohol)s show specific functions such as high adsorption to fibrous pulp dispersed in water, formation of polyelectrolyte complex and emulsifying ability to make cationic emulsion.

BMAM has been found to be useful for producing self-crosslinkable poly(vinyl alcohol)s where timing of crosslinking is controllable: no crosslinks is included in powder as well as in aqueous solution, and crosslinking can be generated in the dry state as the aid of ammonium chloride. From a modified PVAL containing 1.0 mol% of BMAM units, crosslinked film of high boiling-water resistance has been obtained: 0.8 % of the sol fraction and 2.4 wt/wt of the swelling degree.

Analysis of Gel Crosslinked films have been obtained from modified poly(vinyl alcohol)s containing 0.025 to 5 mol% of BMAM units. Sol fraction of the crosslinked films and average degree of polymerization for sol molecules have been determined experimentally. For the samples with crosslinkage below 2 mol%, excellent agreement has been found

between experiment and the gel network formation theory developed by Flory and Charlesby. This means that “ideal gel” has been realized for the present samples probably because crosslinking occurs in the solid state and therefore intramolecular crosslinking or loop formation is negligible and because no molecular scission is accompanied by crosslinking. Using the crosslinked film, the polymer-solvent interaction parameter, χ , has been obtained from swelling experiment in water. The χ value extrapolated to pure poly(vinyl alcohol) has been determined as 0.47 (volume fraction of polymer =0, 20°C). This shows a good agreement with the reported values obtained by osmometry or intrinsic viscosity. This is the first experiment for determining χ parameter solely from swelling experiment: a calibration standard has been used in usual swelling experiments so far. High-swelling films have been obtained from poly(vinyl alcohol)s modified with BMAM as a crosslinkable monomer and with ionic monomers like maleic anhydride, acrylic acid, SAMPS and QAPM. The crosslinked poly(vinyl alcohol) films show high swelling degrees, about 400 in distilled water and about 60 in 0.1M sodium chloride aqueous solution. Theoretical calculation has also been carried out for obtaining volumetric swelling degree of polyelectrolyte gels using the theories presented in the literature. Most of the observed data have been regarded as almost consistent with theoretical calculation results, and thus the theoretical calculation can be used as a tool for designing the present high-swelling materials.

The analytical determination methods established in this thesis for tacticity, sequence distribution of acetyl group, monomer inversion and conformation in solution have been being used practically. Concerning the functionally modified poly(vinyl alcohol)s, modifications with carboxylic, sulfonate and cationic monomers have already been commercialized and used to extensive applications.

TABLE OF CONTENTS

Abstract

i

Table of Contents

vi

Chapter 1 General Introduction

1

Chapter 2 Methodology

23

PART A MOLECULAR STRUCTURES CHARACTERIZED BY NMR

30

**Chapter 3 Tacticity of PVAL
Studied by NMR of Hydroxyl Proton**

31

**Chapter 4 Sequence Distribution of Acetyl Group
in Partially Hydrolyzed PVAL (PVAL-AC)**

44

**Chapter 5 Monomer Inversion in Ethylene-
Vinyl Alcohol Copolymer (EVOH)**

58

| | | |
|--|---|------------|
| Chapter 6 | Conformational Analysis in Model Compounds of Vinyl Polymers | 82 |
| PART B FUNCTIONAL MODIFICATIONS BY COPOLYMERIZATION | | 115 |
| Chapter 7 | Modification with Carboxylic Monomers | 116 |
| Chapter 8 | Modification with a Sulfonate Monomer | 141 |
| Chapter 9 | Modification with Cationic Monomers | 151 |
| Chapter 10 | Self-Crosslinkable PVAL | 173 |
| Chapter 11 | Analysis of Crosslinked PVAL | 191 |
| Chapter 12 | Highly-Swelling PVAL Films | 225 |
| Chapter 13 | Conclusions | 244 |
| | List of Publications | 249 |
| | Acknowledgment | 255 |

CHAPTER 1

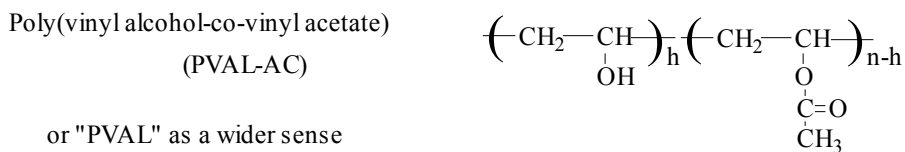
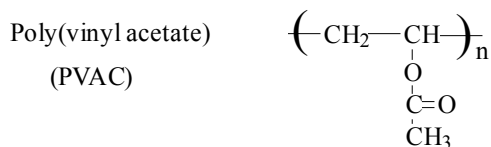
GENERAL INTRODUCTION

1.1 “PVAL” INCLUDING PARTIALLY HYDROLYZED PRODUCT

Poly(vinyl alcohol) (PVAL) is a typical synthetic water-soluble polymer with the following chemical formula:



As PVAL is industrially produced by hydrolysis or alcoholysis of poly(vinyl acetate) (PVAC), usually the term “PVAL” includes partially hydrolyzed product as a wider sense for convenience, although it should be called poly(vinyl alcohol-co-vinyl acetate) (PVAL-AC) to substitute a strict chemical nomenclature.

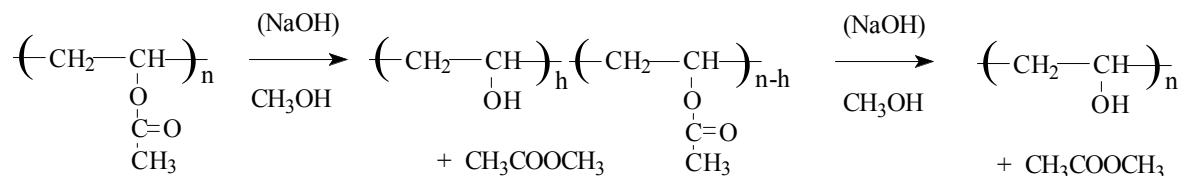


or "PVAL" as a wider sense
or "Partially hydrolyzed PVAL" as a conventional term

This is also called “partially hydrolyzed PVAL” conventionally. It is chemically incorrect and the term “partially hydrolyzed PVAC” must be more appropriate. In this thesis,

however, the term “partially hydrolyzed PVAL” is used because it is convenient for expressing PVAL as a wider sense.

The industrial process of converting PVAC to PVAL consists mainly in alcoholysis or ester interchange reaction of PVAC with alcohol as a solvent using alkali as a catalyst. It is shown by the following equation:



This process is sometimes called “saponification” traditionally in the industrial literature. The term is not used in this thesis because it is inadequate chemically and inconvenient for the chemical discussion of the process. For expressing the process, terms like “alcoholysis” and “hydrolysis” are used depending on actual process. On the other hand the term “hydrolysis” is used when the process itself is not concerned, like “the degree of hydrolysis”. The degree of hydrolysis (DH) of PVAL-AC or “PVAL” is defined using the number of

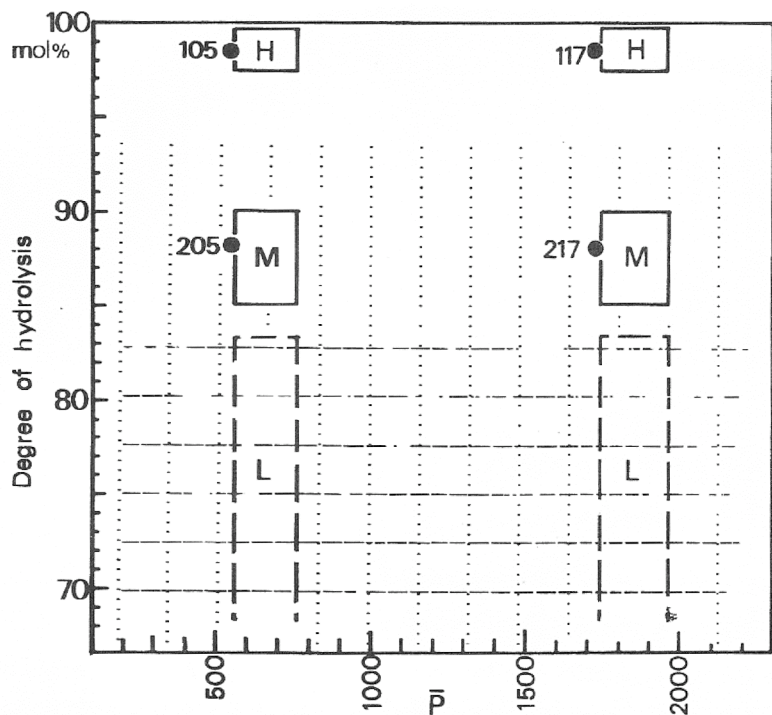


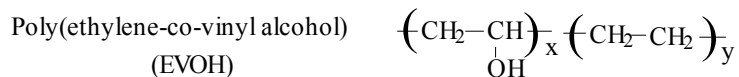
Figure 1 Typical grades of PVAL as expressed by degree of polymerization, \bar{P} , and degree of hydrolysis, DH.

original vinyl acetate units, n, and that of hydrolyzed units, h, by the following equation:

$$\text{DH (mol\%)} = 100 \cdot h/n$$

Basic grades of PVAL have traditionally been designed from the combination of degree of polymerization (\bar{M}_n) and DH, as shown in Figure 1. The production of PVAL was started originally as a raw material for making man-made fiber or vinylon. Later it was applied to making film. For these applications, fully hydrolyzed product has been used. Next it has been applied to wide applications like paper sizing, textile sizing, binder, adhesive, emulsifier and others due to the unique properties of PVAL, water-solubility. Approximately 800,000t of PVAL is now produced in 1995 in the world. Major grades of PVAL used as size and emulsifier are those of partially hydrolyzed one, typically 98 and 88 mol% of DH. PVALs of further lower DH than 80 mol% can not be used as usual size and emulsifier due to insolubility in water although they are used as a stabilizing agent in suspension polymerization of poly(vinyl chloride).

In relation to PVAL industry, the copolymer of vinyl alcohol and ethylene, EVOH, has been developed as a "gas barrier resin" or thermoplastic material having the characteristics of low permeability of gas; it is used mainly for plastic food packaging.



Many reviews have been published concerning chemistry and industry of PVAL and EVOH in the literature so far.¹⁻¹¹

The author of this thesis has been working for the industry of PVAL and EVOH. Based on his activities, the following two subjects have been focused in this thesis:

Part A: Molecular structures characterized by NMR

Part B: Functional modifications by copolymerization

1.2 MOLECULAR STRUCTURE DETERMINATIONS

In Part A, the author intended to establish some new methods for determining the molecular structures of PVAL such as tacticity, the distribution of acetyl group, the monomer inversion in EVOH and conformation in solution. The former three subjects are basically significant in polymer science because the difference of such chemical structure

can make large difference in properties of polymers. The last subject, conformational analysis, is also significant for investigating polymers from physical and theoretical aspects. The molecular structure determinations have mainly been made using high resolution nuclear magnetic resonance spectroscopy (NMR) because it has been known as a powerful tool for analyzing the structures of polymers.^{12,13}

1.3 TACTICITY DETERMINED BY HYDROXYL PROTON AS A USEFUL PROBE

Figure 2 shows three stereochemical structures of sequence, “triads”, in PVAL chain. The mole fractions of the triads define the tacticity of PVAL. Investigation of tacticity has been made using X-ray diffraction,¹⁴ IR spectroscopy¹⁴⁻¹⁶ and NMR spectroscopy of methine and methylene proton¹⁷⁻²⁰ but quantitative determination has been difficult before the present work as shown in Chapter 3. The new method is based on hydroxyl proton, which has been neglected in ¹H-NMR due to the fast exchange between hydroxyl group and water as a solvent. Adopting dimethyl sulfoxide as another solvent made it possible to observe hydroxyl proton as a useful probe.

1.4 THE SEQUENCE DISTRIBUTION OF ACETYL GROUP

Figure 3 shows how acetyl group, $-\text{OCOCH}_3$ or $-\text{OAc}$, distributes along the chains of partially hydrolyzed PVAL. It has been qualitatively assumed that the distribution is blockier for PVAL produced by alcoholysis or hydrolysis.²¹⁻²³ The reason for causing such blockier distribution has been explained by the mechanism that the rate of hydrolysis is higher for the acetyl group neighboring to hydroxyl group. Therefore the hydrolysis reaction proceeds mainly along the chain like opening zipper. As the emulsifying ability of PVAL has been assumed to increase with increasing blockier character, various methods to control the distribution have been investigated industrially. No direct and precise method has been presented for the determination of sequence distribution, although practical methods of evaluation have been known: IR spectroscopy,²⁴ melting point²⁵ and iodine color reaction.²⁶ The ¹³C-NMR work in Chapter 4 is the first and only direct analytical method for determining the distribution.

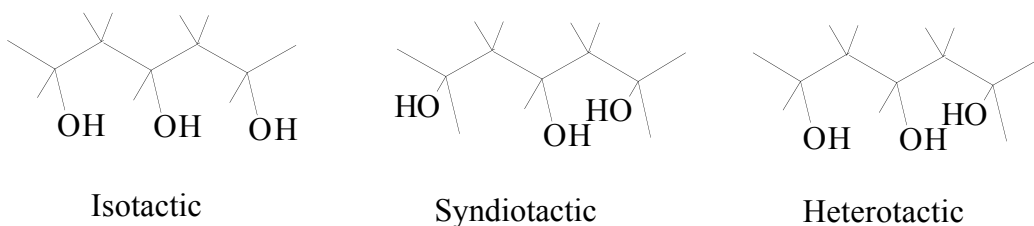
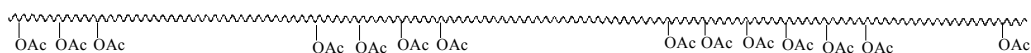


Figure 2 Three stereochemical structures of sequence in poly(vinyl alcohol).

A) Blockier



B) Random

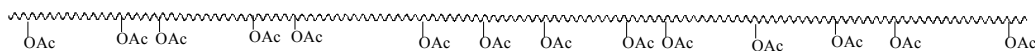


Figure 3 Sequence distribution of acetyl group in poly(vinyl alcohol-co-vinyl acetate).

1.5 MONOMER INVERSION AT ETHYLENE RADICAL CHAIN ENDS

Investigation on anomalous linkage is another significant subject in the analysis of polymers. Predominance of head-to-tail linkage in radical polymerization of vinyl monomers has generally been accepted, although there has been observed a small amount of head-to-head linkage due to inversion of monomer in polymerization as shown by an equation in Figure 4. The amount of 1,2-glycol structure in PVAL has been reported as 1.5% at a polymerization temperature of 60°C and 2.0% at 100°C by the

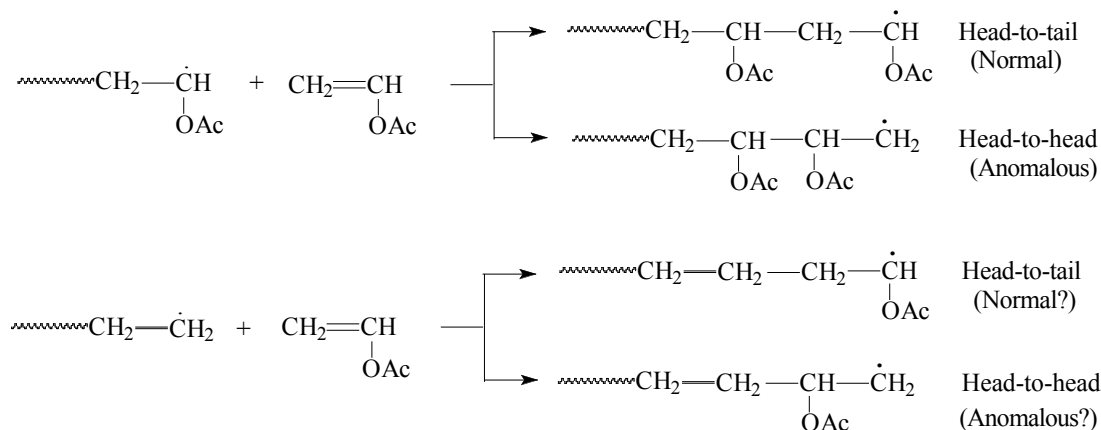


Figure 4 Normal and anomalous additions of vinyl acetate in propagation step for the copolymerization of ethylene and vinyl acetate.

oxidation method.^{27,28} More frequent occurrence of monomer inversion could be expected for ethylene-vinyl monomer copolymerization because a steric hindrance between substituents is apparently absent for the inverted addition of a vinyl monomer at ethylene radical chain ends. Actually much amount of the anomalous linkage, 1,4-structure, resulting from such monomer inversion, has been suggested for poly(ethylene-co-vinyl acetate), about 45% from IR spectroscopy²⁹ and 4 to 13% from ¹H-NMR spectroscopy.³⁰ If this is the case, the amount of monomer inversion can have great influence on properties of EVOH. Thus the development of quantitative analytical method determining the monomer inversion in EVOH has been strongly needed since oxidation method can not be applied to the analysis of 1,4-glycol. In Chapter 5, the investigation has been made using ¹³C-NMR, in which 1,4-glycol structure has been clearly observed. For quantitative discussion on monomer inversion, calculation was necessary using kinetics of terpolymerization based on the first-order Markofian statistics.

1.6 CONFORMATIONAL ANALYSIS OF MODEL COMPOUNDS

Conformation of a polymer chain in solution, schematically shown in Figure 5-a, is the subject discussed in Chapter 6. So far this subject has been investigated from three standpoints: the first is classical measurements such as light scattering and viscosity

measurement, the second is conformational analysis by using vicinal coupling constants in NMR and the last is theoretical calculation. The first gives information concerning the overall extension of polymer chain commonly expressed as the mean square end-to-end distance $\langle r^2 \rangle_0$. In contrast, the second provides information concerning local conformation of model compounds like 2,4-disubstituted pentanes shown in Figure 5-b.¹² The last is theory which connects local conformation and overall extension.

The second approach on model compounds is significant, but it involved basic difficulty in analysis. The mole fractions of so many conformers, ten even in 2,4-disubstituted pentanes as the simplest model, were required to be determined from only four observable spin-spin coupling constants.

In order to solve the problem, the new method using the "local interaction model" has been applied in the analysis of experiments. The model has already been adopted in the theories³¹⁻³⁵ for connecting model to polymer. The new method reported in this thesis has been found to be useful in NMR conformational analysis of 2,4-disubstituted pentane because smaller numbers of parameters, usually five intramolecular interaction energies, can be determined from the temperature dependence of four vicinal coupling constants. Practical applications and the usefulness of the new method have been demonstrated for pentane-2, 4-diol as a model of PVAL as well as 2,4-dichloropentane as a model of poly(vinyl chloride) and 2,4-diphenylpentane as a model of polystyrene. Furthermore, the parameters determined experimentally in this method can directly be applied to the conformational calculation of polymer using the multiplication of matrices as statistical weight parameters.

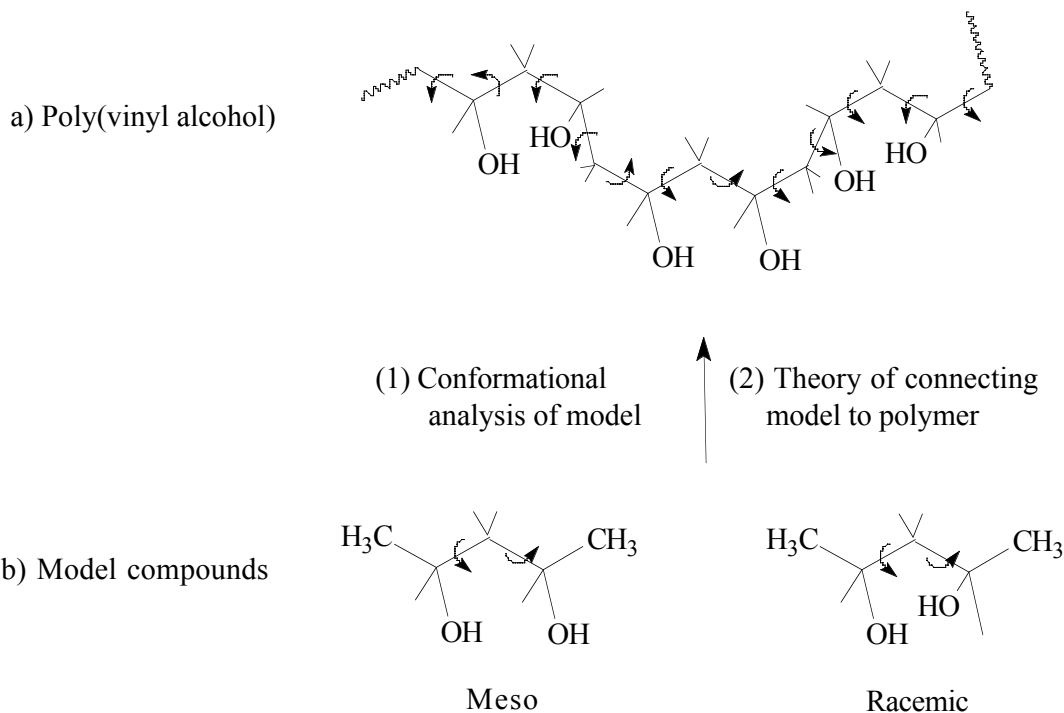


Figure 5 The determination of conformation for polymer from the conformational analysis of model compounds and theoretical calculation

1.7 FUNCTIONAL MODIFICATION BY COPOLYMERIZATION

In contrast to Part A where the precise structural determination of fundamental PVAL and EVOH has been studied, the functional modification of PVAL or introducing functional groups into the polymer chain by copolymerization has been discussed in Parts B. Many works are known concerning the modification of PVAL by polymer reaction³⁶⁻³⁹ and by copolymerization⁴⁰ for the purposes of expanding application field. There have been some ideas of modification as shown in Figure 6. Higher or lower degrees of polymerization are simple ideas (a and b). Changing distribution of acetyl group along chains (c) has already been applied for emulsifier/stabilizer.⁶ Modification of end group⁴¹ (d) and with hydrophobic group⁴² (e) has also been investigated mainly from the interests in interfacial activities. Modification with ionic groups (f and g) and crosslinkable groups (h) has been

believed to be basically significant for expanding fields of PVAL. Therefore extensive studies have been made on the modification and reported in this thesis. In spite of the significance, such modified PVALs have not been commercialized before the present work except for the PVALs modified with methyl (meth)acrylate or maleic anhydride.

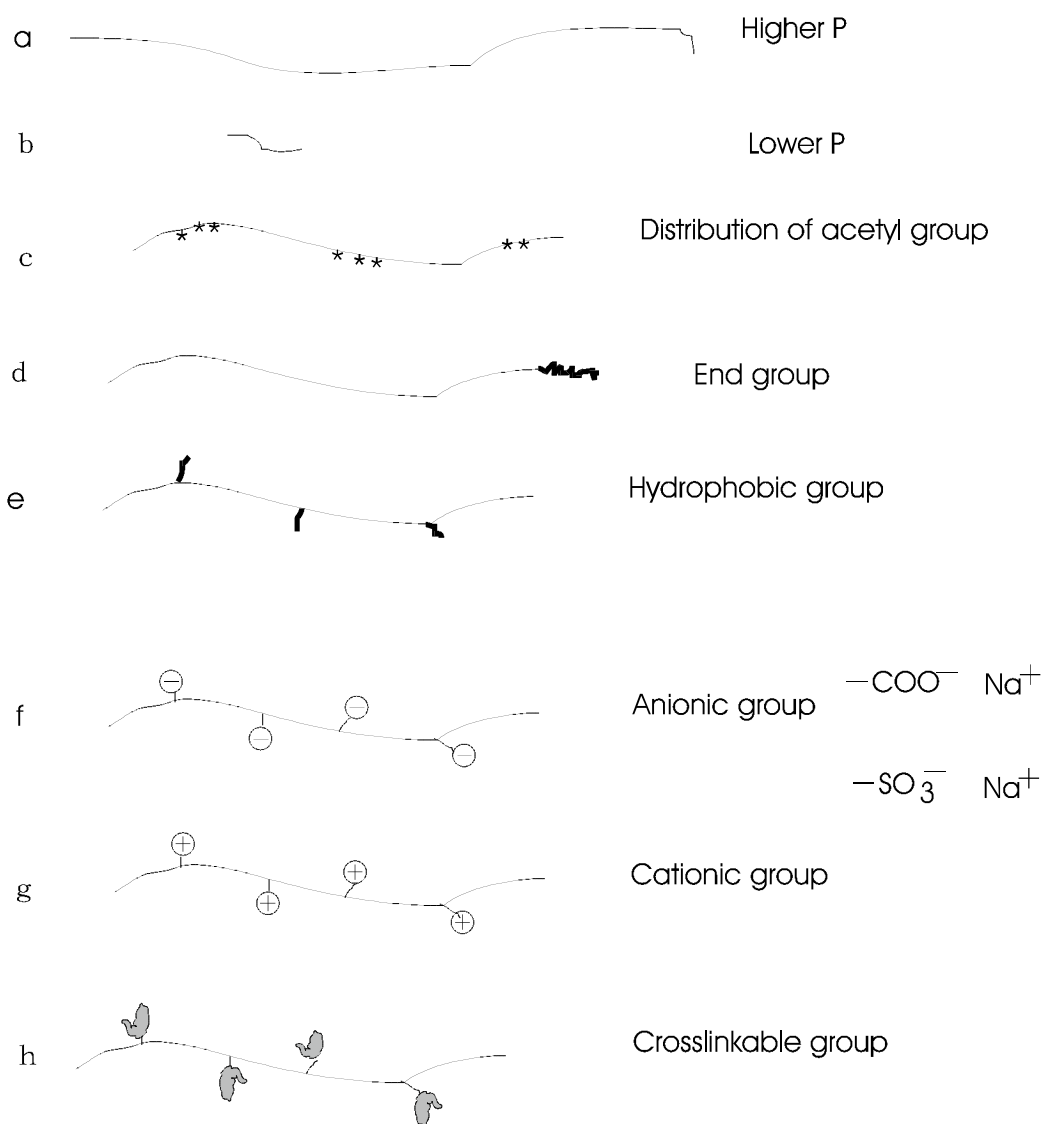
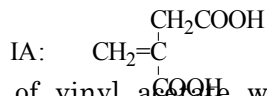


Figure 6 Ideas for the modification of PVAL.

1.8 MODIFICATION WITH CARBOXYLIC MONOMERS

Modification with carboxylic monomers has first been studied extensively in Chapter 7. It is the main purpose naturally to obtain PVALs containing sodium carboxylate groups, COONa , in polymer chains. In practice, however, much complexity has been observed like the formations of lactone, ^{37,43-58} and crosslinking in the modification processes, typically for partially hydrolyzed products. Lactone formation deactivates carboxylic group and crosslinking makes the product not usable. These two problems are caused by the fact that polymer system contains two classes of chemical groups, hydroxyl and carboxyl, reactive each other. Lactone formation and crosslinking, as shown in Figures 7 and 8, have typically been observed in the modification with methyl (meth)acrylate and maleic anhydride or monomethyl maleate in methanol, respectively. In contrast, dibasic acidic monomers, itaconic acid (IA) in particular, have been found to be useful for producing modified PVALs showing the functions targeted without any risk of crosslinking.



No reports on copolymerization of vinyl acetate with dibasic acidic monomers like itaconic, fumaric and maleic acid has been known so far. This must be due to the insolubility of the dibasic acidic monomers in vinyl acetate itself. Copolymerization can be performed in the presence of methanol. These dibasic monomers have been found to be useful for producing PVAL modified with sodium carboxylate, as shown in Figure 9. By modification with itaconic acid, PVALs of lower DS, less than 80 mol% and even less than 50 mol%, have become possible to be used as water-soluble polymers. The modified PVAL shows strong reactivity to polyvalent inorganic salts like alum.

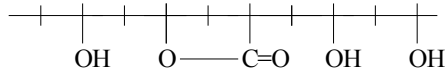


Figure 7 Modified PVAL containing lactone, typically produced by alcoholysis of the copolymer of vinyl acetate and methyl acrylate.

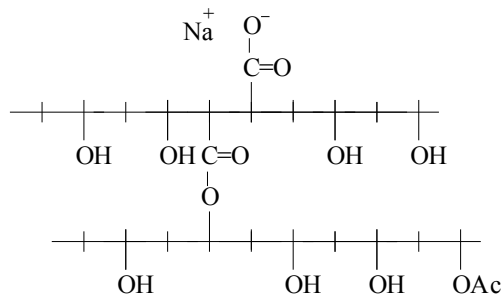


Figure 8 Modified PVAL including crosslinking by intermolecular ester linkage, typically produced by partial alcoholysis of the copolymer of vinyl acetate and maleic anhydride. Crosslinking makes the modified PVAL insoluble.

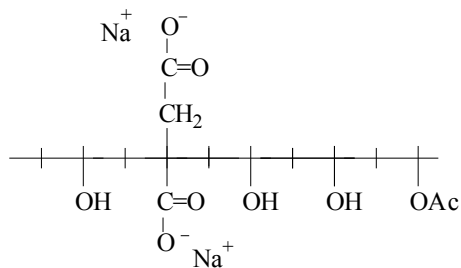
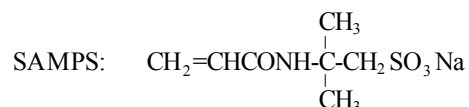


Figure 9 Modified PVAL with sodium carboxylate and without crosslinking, typically produced by alcoholysis of the copolymer of vinyl acetate and itaconic acid.

1.9 PVAL CONTAINING ANOTHER ANIONIC GROUP, SULFONATE

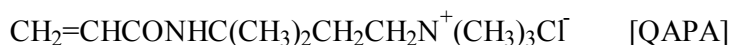
Next in Chapter 8, PVAL modified with sodium sulfonate group, another anionically active group, has been prepared by the copolymerization with a new sulfonate monomer, sodium 2-acrylamide-2-methylpropane sulfonate (SAMPS).



It was reported so far that PVALs modified with sulfonate $-\text{SO}_3\text{M}$ or sulfuric $-\text{OSO}_3\text{M}$ groups could be prepared by the polymer reaction with chromosulfuric acid or by copolymerization with a monomer like sodium allyl sulfonate,^{59,60} although these methods had difficulties of easiness for hydrolysis of the sulfuric group or those of low rate of copolymerization, respectively. The copolymerization of vinyl acetate and SAMPS has been found to be more convenient in easiness of synthesis for obtaining modified PVAL with sulfonate group. It shows strong hydrophilic properties, which permits PVALs of much lower DS less than 80 mol% to dissolve in water, as observed in the modification with IA. The PVALs modified with the two types of anionic groups, carboxylate and sulfonate, have been compared concerning the aqueous solution, sensitivity to pH and to the presence of inorganic salts, in particular.

1.10 PVAL MODIFIED WITH CATIONIC GROUP

Cationic modification for PVAL, written in Chapter 9, is significant in the fact that this is the first practical method for producing cationically active PVAL. The cationic monomers used are acrylamide and methacrylamide derivatives such as N-(1,1-dimethyl-dimethylaminopropyl)acrylamide (APA) and its quaternary ammonium salts (QAPA)



Typical advantages using these cationic monomers in copolymerization are higher rate in polymerization and structural stability in alcoholysis. The specific functions based on cationic group has been investigated by high adsorption to fibrous pulp dispersed in water, formation of polyelectrolyte complex and emulsifying ability to make cationic emulsion.

1.11 SELF-CROSSLINKABLE PVAL, WHERE THE TIMING OF CROSSLINKING CAN BE CONTROLLED

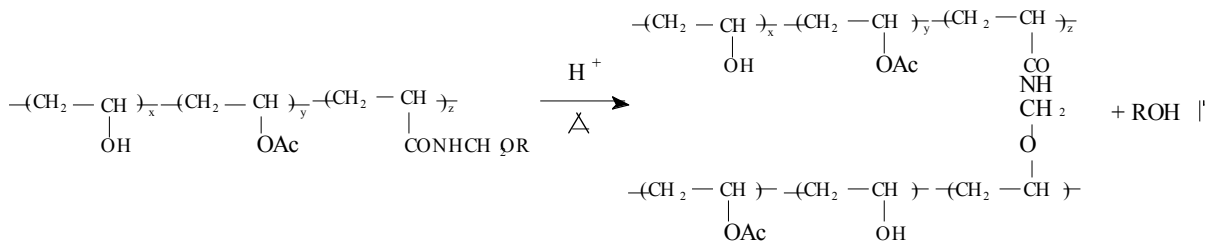
Insolubilization by crosslinking, or increasing water-resistance, is practically significant in the applications of PVAL. For this purpose, various types of crosslinking agents reacting with hydroxyl group have been proposed,⁶¹ for example, urea- and melamine-formaldehyde resins, dialdehydes like glyoxal and glutaraldehyde, and other organic compounds.⁶²⁻⁶⁹ Inorganic salts have also been proposed for this purpose, for example, boron compounds like boric acid, sodium borate, and other compounds containing titanium,⁷⁰ zirconium, vanadium⁷¹ or chromium. Using such crosslinking agent shows sometimes difficulties in controlling the viscosity of the aqueous solution of PVAL because crosslinking reaction proceeds in aqueous mixture.

In Chapter 10, a new functional PVAL modified with crosslinkable monomer has been investigated by copolymerization of VAc and an N-(alkoxymethyl)-acrylamide shown below, followed by alcoholysis:

N-(Methoxymethyl)-acrylamide (MMAM): $\text{CH}_2=\text{CH}-\text{CONH}-\text{CH}_2\text{OCH}_3$

N-(n-Butoxymethyl)-acrylamide (BMAM): $\text{CH}_2=\text{CH}-\text{CONH}-\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

The present work has been done for the purpose of making new “self-crosslinkable and controllable” PVAL. It contains crosslinkable group in the chain. It can be produced as powder, perfectly soluble in water and usable for applications like size, emulsifier, fiber and film. In these stages no crosslinking reaction occurs. Crosslinking can be formed as shown by the equation shown below in the dry state with the aid of a curing agent. The crosslinked materials show high water-resistance. By this means, the timing of crosslinking is controllable for the modified PVALs.



1.12 ANALYSIS OF CROSSLINKED PVAL ON GEL NETWORK FORMATION AND SWELLING

In Chapter 11, gel network formation and swelling have been systematically investigated from experimental and theoretical points of view using the self-crosslinkable PVAL. Samples of the self-crosslinkable PVAL with various degrees of crosslinkable group have been synthesized. Crosslinked films have been formed and analyzed concerning the mole fraction of crosslinkage, the degree of polymerization of sol molecules and the swelling degree of gel part, as schematically shown in Figure 10. Theoretical calculation has also been made based on gel network formation theory established by Flory,^{72,73} Stockmayer,⁷⁴ Charlesby,⁷⁵ Scott⁷⁶ and others.⁷⁷⁻⁷⁹ Calculation based on swelling theories^{72,80-82} has also been carried out.

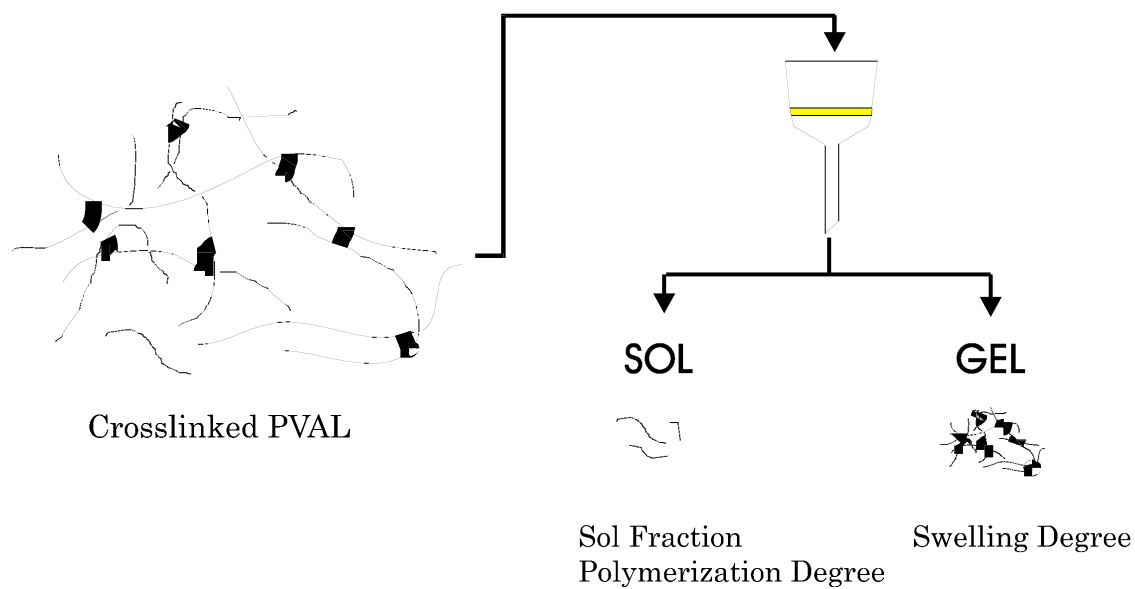


Figure 10 Analysis of crosslinked gel, sol fraction, polymerization degree of sol part and swelling degree of gel part.

1.13 HIGH-SWELLING MODIFIED PVAL FILMS

In Chapter 12, modified PVAL films having highly swelling ability have been investigated. Modified PVALs containing both the functional groups, ionic and crosslinkable, have been synthesized by ternary copolymerization of vinyl acetate, BMAM and ionic monomer like maleic anhydride(MAn), acrylic acid(AA), sodium 2-acrylamide-2-methyl propane sulfonate (SAMPS) and trimethyl-(3-methacrylamidopropyl)ammonium chloride (QAPM) and by succeeding alcoholysis of the copolymers. The swelling behavior in water for the crosslinked films made of the modified PVALs has been analyzed.

On the other hand, theoretical calculation has been carried out regarding swelling of polyelectrolyte gels in order to compare with the experiments. The calculation is based on the theories presented by Flory,⁸³ Katchalsky and Michaeli,⁸⁴ Hasa, Ilavský and Dusek,⁸⁵

and Ilavský.⁸⁶ Similar comparisons of experiment with theory for polyelectrolyte gels have already been reported before in the literature concerning poly(methacrylic acid),^{84,87-89} poly(acrylic acid)⁹⁰ or acrylamide⁹¹⁻⁹⁵ crosslinked with divinyl monomers: these hydrogels reported so far were prepared from the polymer crosslinked in copolymerization process. In contrast, crosslinking is formed under solid state in the present case of modified PVALs.

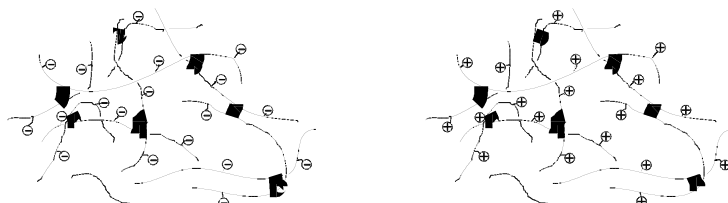


Figure 11 PVALs containing ionic groups and crosslinkage.

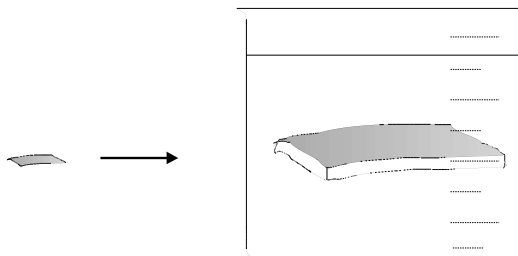


Figure 12 Highly swelling PVAL.

1.14 PRACTICAL USEFULNESS

It should be emphasized that almost all the subjects in this thesis were based on the practical needs in industry. Actually, the analytical methods presented here, tacticity, distribution of acetyl group and anomalous linkage, have long been applied practically.

In the development of modified PVALs, all the functional monomers available have been tried and compared each other from various standpoints, practical usefulness, stability, easiness of production and mechanism of problems. The problems and phenomena observed in synthesis have been investigated from the chemical structural points of view. In selecting the best method for commercial production, the significance of basic and extensive studies has been shown. Typical examples are shown for lactone formation and crosslinking problems in the modification with carboxylic monomers.

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