

CHAPTER 13

CONCLUSIONS

In the present thesis the author intended to investigate PVAL concerning two aspects, molecular structure determinations (Part A) and functional modifications (Part B).

In Part A, new several analytical methods have been clarified for the determinations of basic molecular structures using NMR.

For the determination of tacticity, it has been shown that the hydroxyl proton has been observed as three well-separated lines assigned to the three sequences of tacticity when dimethyl sulfoxide is used as a solvent. This method using hydroxyl proton as a probe has been used as a convenient and effective analytical method although another analytical method, ^{13}C -NMR, is now available for the determination of tacticity.

^{13}C -NMR has been found to be useful for the distribution determination of acetyl group in partially hydrolyzed PVAL. The methylene carbon has shown three well-separated lines assigned to the three sequences of the copolymer. This is the first and only method for the direct and quantitative determination of acetyl group distribution in the polymer. It has been clarified that the distribution is strongly dependent on the conditions of making the copolymer, hydrolysis, alcoholysis or re-acetylation. This method has become a new effective tool for designing emulsifier/stabilizer using partially hydrolyzed PVAL, in which the distribution of acetyl group affects the surface activity of aqueous solution.

^{13}C -NMR has also been a powerful tool for the determination of anomalous structures generated in polymerization, for the subject of monomer inversion in EVOH in this thesis. This subject has been investigated because IR and ^1H -NMR studies in the literature suggested much frequent occurrence of monomer inversion (head-to-head addition) in ethylene radical chain ends for the copolymerization of ethylene and vinyl monomer. In

^{13}C -NMR spectra of EVOH, it has been found that 1,4-glycol structure arising from monomer inversion can be observed clearly and analyzed quantitatively. For the quantitative discussion of monomer inversion, it has been necessary to use the numerical calculation of "terpolymerization" based on the first-order Markoffian statistics. From the experimental data and the calculation, it can be concluded that the frequency fraction of monomer inversion of vinyl acetate in ethylene radical chain ends is 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. This must mean that the main factor for determining the predominance of head-to-tail addition for the radical polymerization of vinyl acetate is not steric hindrance but other factors like resonance effects stabilizing radical.

The progress of this thesis in the field of polymer conformation is in the new calculation process for observed spin-spin coupling constants of model compounds, 2,4-disubstituted pentanes as the simplest models for vinyl polymer. In the new method, five energy parameters concerning local conformation has been adopted instead of ten independent conformers for two stereoisomers in the usual method. The new method has been applied to the reported data on models for PVAL, poly(vinyl chloride) and polystyrene. The method removes ambiguity in conformational analysis and has made it possible to determine the fractions of twelve conformers. Furthermore it has been found by chance that the standard coupling constants for the positions of trans and gauche, J_t and J_g , can be determined experimentally as $J_t = 11.5 \pm 1.0$ and $J_g = 2.1 \pm 1.0$ Hz from the data on solvent effects of pentane-2,4-diol. This is the first data determined for chain molecules although they were obtained for ring compounds so far. Another advantage of the new method is in that the parameters obtained can be used for calculating conformation of polymer chain in the statistical method using multiplication of matrices. Such calculations have been demonstrated for stereo-regular PVAL chains and for analyzing spin-spin splitting of hydroxyl protons.

In Part B, extensive studies have been made for the functional modification of PVAL with carboxylate, sulfonate, cationic and self-crosslinkable groups by copolymerization method. The studies have been carried out from the standpoint of commercialization of new modified PVALs containing the functional groups. Therefore, the main purpose of the work is finding the best functional comonomers concerning convenience in production,

performance in product and economy. Typical examples of the functional comonomers selected as the result of these studies are: itaconic acid (IA) for carboxylic group, sodium 2-acrylamide-2-methyl sulfonate (SAMPS) for sulfonate group, trimethyl-(3-acrylamide-3,3-dimethylpropyl)ammonium chloride (QAPA) for cationic group and N-(n-butoxymethyl)-acrylamide (BMAM) for crosslinkable group. The copolymers of these comonomers with vinyl alcohol are novel substances, which have not been reported in the literature before the present work.

In the modification with carboxylic comonomers, a specific and practical problem was the formation of intramolecular ester or inactive lactone and intermolecular ester or crosslinking instead of functionally active carboxylate. It has been found that the problem is dependent on comonomers used and IA has been found to be the most useful because sodium carboxylate, γ , δ -hydroxycarboxylate in particular, is 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. This property has been found to be useful for some applications like specialty films with highly solubility.

Among the ten cationic reagents investigated, the acrylamide and methacrylamide derivatives such as QAPA have been found to be useful to produce cationically modified PVALs because of their much higher reactivity in copolymerization, and because of the good stability of amido linkage in alkaline alcoholysis. The cationically modified PVALs 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 the timing of crosslinking is controllable. Controlling the timing is a key for crosslinking polymers: crosslinking sometimes can make polymers unusable due to

increasing viscosity and generating gel. The modified PVAL with BMAM has been found to be controllable because 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.

More detailed study has been made for crosslinking with BMAM. Crosslinked films have been obtained from modified PVALs containing 0.025 to 5 mol% of BMAM units. Sol fraction of the crosslinked films and average degree of polymerization for sol molecules has been determined experimentally. Calculation based on the gel network formation theory developed by Flory and Charlesby has also been carried out. For the samples with crosslinkage below 2 mol%, excellent agreement has been found between experiment and calculation. 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 PVAL 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 PVALs modified with BMAM as a crosslinkable monomer and with ionic monomers like maleic anhydride, acrylic acid, SAMPS and QAPM. The crosslinked modified PVAL 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 PVALs, modifications with carboxylic, sulfonate and cationic monomers have already been commercialized and used to extensive applications.

LIST OF PUBLICATIONS

Original Papers

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