

POLY(VINYL ALCOHOL) — SELECTED TOPICS ON ITS SYNTHESIS

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INTRODUCTION

Commercial poly(vinyl alcohol) is produced by the saponification of poly(vinyl acetate). In Japan, about 80 per cent of the total production of poly(vinyl acetate) is converted into poly(vinyl alcohol) (PVA) and is fabricated into synthetic fibres, adhesives, and warpsizing and papersizing materials, etc. The total production of poly(vinyl alcohol) amounts to about 80 000 tons per year. The major part of poly(vinyl acetate) is converted into poly(vinyl alcohol); the phenomenon seems to be an unique one in the world.

Although the source of raw materials in Japan is nowadays rapidly changing, because of the revolutionary development of the petrochemical industry, Japan was one of the top producers of calcium carbide from 1930 to 1960. This situation has not substantially changed even at the present, as is shown in Table 1¹.

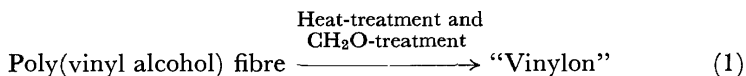
Table 1. Production and demand for calcium carbide (unit: 1000 tons/year)

Year	Japanese demand and production				U.S. Production	W. German Production	E. German Production	
	Production	Total	Demand For Ca(CN) ₂	Demand For Organics				Miscell- aneous
1955	674	681	363	182	136	794	822	812
1956	756	749	318	281	150	929	881	802
1957	822	879	318	378	183	922	960	799
1958	891	850	281	396	573	825	997	830
1959	948	1080	242	646	192	924	1031	887
1960	1210	1582	235	831	216	993	1101	923
1961	1518	1444	221	970	253	945	—	940
1962	1323	1381	209	940	232	983	—	—
1963	1555	1608	227	1143	238	—	—	—
1964	1766	1753	205	1308	240	—	—	—
1965†	1630	1550	250	1060	240	900	—	—
1970†	1680	1680	250	1180	250	—	—	—

† Estimate

From the point of view of the raw material, therefore, the development of the poly(vinyl alcohol) industry in Japan can be understood. Acetic acid, acetylene, and hence vinyl acetate were products of the acetylene industry. The other reason for this development lies in the fact that the work of Sakurada stimulated many research chemists to work in fundamental research on poly(vinyl alcohol).

The synthesis of poly(vinyl alcohol) was revealed for the first time in the patent literature of 1926 by German chemists, Herrmann and Haehnel². Academic reports by themselves and by Staudinger³ appeared soon after. It was already known at the time that poly(vinyl alcohol) is a water-soluble polymer with excellent properties for fibres and films. Stimulated by the discovery of nylon in 1938, Japanese industry was looking for a polymer with promising fibre properties. Taking advantage of the crystallinity of poly(vinyl alcohol) on the one hand, and the reactivity of the hydroxyl groups on the other, Sakurada at Kyoto University and independently Yazawa at Kanegafuchi Spinning Co. developed the methods of heat-treatment and formalization in order to make the fibre water-resistant. Thus, in 1938 a new synthetic fibre was born in Japan and latter given the general name "Vinylon"



Vinylon fibres are now produced mainly by Kurashiki Rayon Co. and Nichibo Co. at a rate of 100 and 60 tons per day, respectively. The production of poly(vinyl alcohol) is still increasing steadily with the parallel development of a wide variety of new applications.

Along with this industrial development, academic research on poly(vinyl alcohol) was actively promoted. Sakurada and his school and the late Tomonari and his research group at Kurashiki Rayon took the lead in this research. One can follow their activities in the reports of three "Symposium on Poly(vinyl alcohol)"; which were held in Japan in 1955, 1958 and 1963⁴, and also in some review articles which appeared afterwards⁵⁻⁸.

Marvel and Denon⁹ established in 1938, that poly(vinyl alcohol) is mainly composed of 1,3-glycol units. It was, however, an important problem academically, as well as industrially, to elucidate the reasons for the different properties observed in poly(vinyl alcohol) specimens prepared under different manufacturing conditions. In other words, the fundamental problem was to find out how differences in the polymer structure were reflected in its properties. The following structural characteristics must be considered: end groups⁵, 1,2-glycol units¹⁰, carbonyl groups in the main chain⁵, unsaturated bonds¹¹, cross-linking⁶, stereoregularity^{5, 12}, long and short branches^{7, 13}.

When we focus our attention on the stereoregularity, for example, we find that the following properties have been studied for possible relationships to this variable: the solid properties—swelling index^{12b, 14}, crystallinity^{12a, 15}, melting point^{15, 16} and dielectric property¹⁷. The solution properties—viscosity¹⁸, the gellation of concentrated solutions¹⁹, the I₂-colour reaction²⁰, the rate of acetalization and other reactions⁷, the molecular dimension of PVA²¹ and of acetalized PVA²² and the foaming property²³.

Since a physical property usually results from a combination of different structural factors, it is very difficult to decide which one of these structural changes is responsible for the variation of a physical property. Nevertheless, the problems are now being gradually solved. The author believes that an important remaining problem is the existence of short-chain branching and the frequency of its occurrence. The Kurashiki^{13c} and the Kyoto group^{13b},

independently, have insisted for several years on the existence of short branching.

I would like to discuss the results obtained by these research groups as well as our own, emphasizing how synthetic studies have contributed to the chemistry of poly(vinyl alcohol). The first topic is the synthesis of stereoregular poly(vinyl alcohol) and the second is the synthesis of poly(vinyl alcohol) which is unusually rich in the head-to-head structure.

If we were able to prepare isotactic and syndiotactic poly(vinyl alcohol), the stereochemical problems of the polymer, which have long been controversial, would be solved. What would then be the properties of heterotactic poly(vinyl alcohol)?

Concerning the problem of branching, there is the possibility that a different monomer and different polymerization conditions might give an unbranched polymer. Unfortunately, there is no suitable method for the detection of short branches so far. Synthetic approaches might be able to give a clue to this problem.

Poly(vinyl alcohol) usually contains a small amount of 1,2-glycol units which come from the abnormal head-to-head propagation of the polymerization. This is an established fact and there is a simple method for its determination¹⁰. A commercial product usually contains 1,2-glycol units in about 2 mole per cent, and this amount is considered to be of insignificant influence on the physical properties of poly(vinyl alcohol). As will be mentioned later, some polymerizations lead to specimens having more than 30 mole per cent 1,2-glycol units. Such a polymer shows unusual properties. What would then be the properties of a poly(vinyl alcohol) having 100 per cent 1,2-glycol units, as an extreme case? This kind of synthetic investigation is meant to contribute to the clarification of the structure-property relationships.

SYNTHESIS OF ISOTACTIC POLY(VINYL ALCOHOL)

We obtained isotactic poly(vinyl benzyl ether) by the cationic low temperature polymerization of vinyl benzyl ether. The latter was saponified into isotactic poly(vinyl alcohol)²⁴. It was easily soluble in cold water despite its high molecular weight and did not show any increase of crystallinity on heat-treatment, as is usually the case. These facts together with results

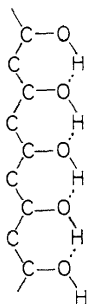
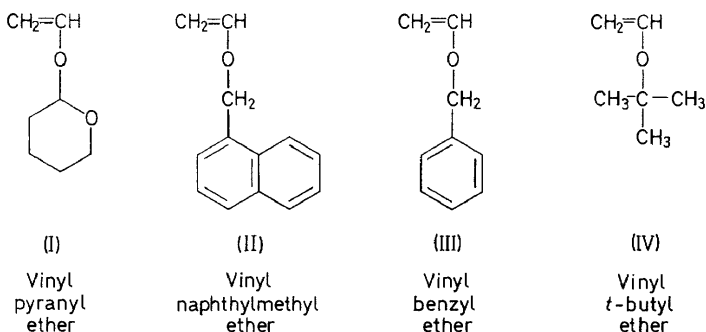


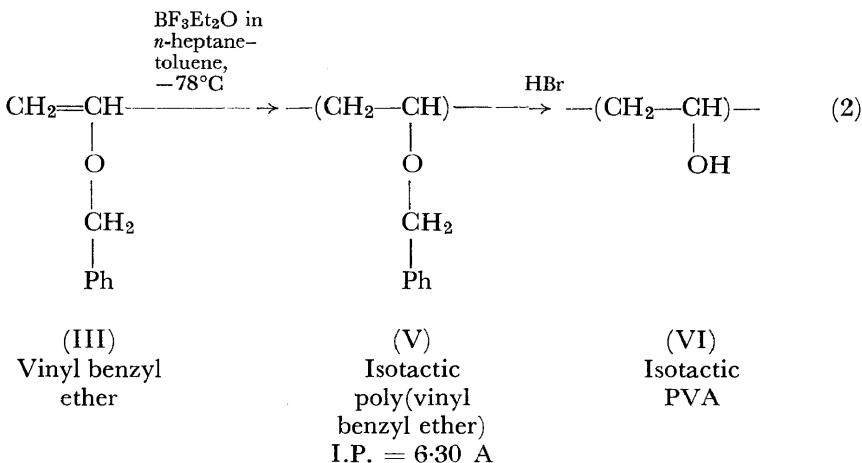
Figure 1. A possible model of the isotactic part of poly(vinyl alcohol) in the crystalline state. The projection on the plane of the C—O bonds

obtained from infrared dichroism studies made us conclude that the hydrogen bonds in isotactic poly(vinyl alcohol) are intramolecular as shown in *Figure 1*. Moreover, Kawakami at Nichibo Co., found that a fibre of isotactic poly(vinyl alcohol) can be drawn to very large extents²⁵. The fact seems to be compatible with the structure of *Figure 1*.

It is well known, from the work of Schildknecht²⁶ and Natta²⁷, that vinyl ethers yield crystalline isotactic polymers under suitable polymerization conditions. The conversion of poly(vinyl alkyl ether) into poly(vinyl alcohol), however, was known to be, in general, impractical. Therefore, we had to choose the following special vinyl ethers which were expected to be easily saponified.



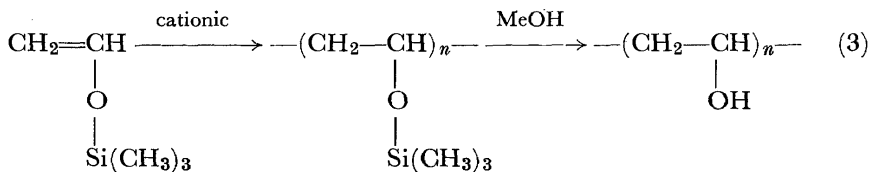
Among these monomers, vinyl benzyl ether (III) was found to give a crystalline polymer (V) and its isotactic structure was established by an x-ray study.



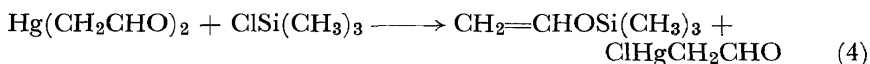
The identity period was 6.3 Å. The saponification was carried out with anhydrous hydrogen bromide to yield a colourless isotactic poly(vinyl alcohol) (VI). We deduced its isotactic structure from the synthetic route and a study of the infrared dichroism²⁴. The structure was then unambiguously established by an x-ray analysis of the derived formate²⁸ by the

Kurashiki group. Vinyl *t*-butyl ether (IV) was later converted into isotactic poly(vinyl alcohol), in a similar way, by Okamura²⁹.

Vinyloxytrimethylsilane is another interesting monomer. It was found that this monomer is an excellent starting material for the laboratory preparation of stereoregular poly(vinyl alcohol)³⁰.



This monomer is unique in the ease of solvolysis of the resulting polymer and stereoregulation is favoured, probably because of the bulkiness of the trimethylsilyl group. By using this monomer, we were able to obtain a series of poly(vinyl alcohols) of different tacticities, from isotactic to syndiotactic specimens. The study of the stereochemistry of poly(vinyl alcohol) thus made significant progress. The synthesis of vinyloxytrimethylsilane is shown by equation (4). The method was discovered by Nesmeyanov in 1959³¹.



The polymerization behaviour of this monomer is similar to the usual vinyl ethers, as seen from the *Q* and *e* values in Table 2³²; this monomer undergoes cationic polymerization. The solvolysis takes place readily at room temperature. The intermediate polymer is usually converted *in situ* into poly(vinyl alcohol) without isolation.

Table 2. *Q* and *e* values of vinyloxytrimethylsilane and vinyl isobutyl ether

Vinyl ethers	<i>Q</i> †	<i>e</i> †
Vinyloxytrimethylsilane	0.018	-2.39
Vinyl isobutyl ether	0.019	-2.11

† Average values obtained from their copolymerization with acrylonitrile, methacrylonitrile, vinylacetate and methyl methacrylate

When the cationic polymerization was carried out in a non-polar solvent, for example in toluene, using ethylaluminum dichloride as a catalyst at low temperature, we obtained an isotactic polymer. The isotacticity of this polymer was higher than that obtained previously with vinyl benzyl ether. The polymerization at low temperature in a polar solvent, for instance in nitroethane, yielded a poly(vinyl alcohol) with an infrared spectrum which was very much different from that obtained from the isotactic polymer³³. This polymer will later be shown to have high syndiotacticity³⁴. Figure 2 shows

the infrared spectra of poly(vinyl alcohols) which were derived from vinyloxy-trimethylsilane under various conditions. There are large variations of intensity at 916 and 849 cm^{-1} and other minor variations.

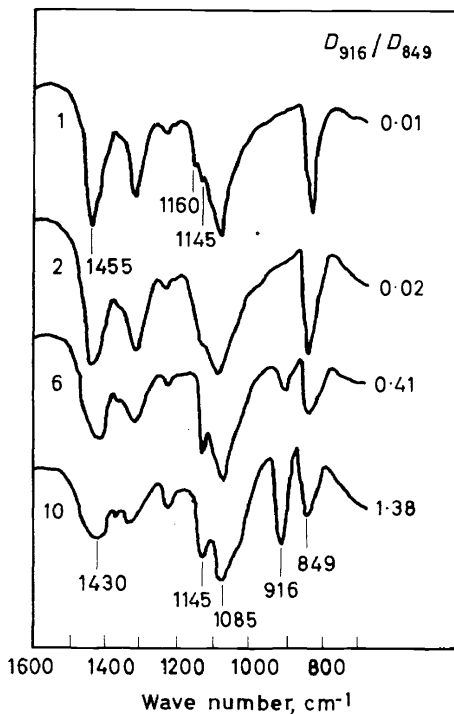


Figure 2. Infrared spectra of stereoregular poly(vinyl alcohols)

Mention must be made here about the tacticity measurements of poly(vinyl alcohol). The Kurashiki group compared four specimens of poly(vinyl alcohol), together with the corresponding formed polymers, by x-ray analysis and infrared spectroscopy. These four specimens include polymers derived from poly(vinyl formate), poly(vinyl trifluoroacetate), poly(vinyl acetate), and poly(vinyl ether), as shown in Table 3.

Table 3. X-ray crystallinity of poly(vinyl alcohol) and its derivatives

Polymer	Isotactic	Atactic	Syndiotactic (from VF)
PVAc	amorph.	amorph.	amorph.
PVF	cryst.(6.55A)†	amorph.	cryst.(5.0A)
PVTFAc	cryst.(4.8A)	cryst.(4.8A)	cryst.(4.8A)
PVA	low cryst.(2.5A)	cryst.(2.5A)	cryst.(2.5A)

† Identity period in A

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As a result, they proposed, in 1962 the use of the optical density ratio of infrared absorptions at 916 and 850 cm^{-1} , D_{916}/D_{850} , as a measure of the syndiotacticity of poly(vinyl alcohol)^{12a}. The ratio is close to zero in the case of the isotactic polymer and becomes larger than 0.5 for syndiotactic specimens. Although the so-called "syndiotactic" polymer in that investigation, which was obtained from vinyl trifluoroacetate, turned out to be not typically syndiotactic, this qualitative measure of tacticity was found to be applicable to the determination of a wide range of tacticities up to high syndiotacticity.

Using these criteria of i.r. spectroscopy and x-ray analysis, the polymers obtained with vinyloxytrimethylsilane were found to vary widely in tacticity. In the next step, we tried to correlate the above-mentioned qualitative measure with the more quantitative one of n.m.r. spectroscopy³⁴. In their pioneering work, Bovey and coworkers found in 1963 that the acetoxy methyl protons of poly(vinyl acetate) were split into three peaks and suggested the determination of the tacticity in triads³⁵. We converted a series of poly(vinyl alcohols) having a wide variety of tacticities into poly(vinyl acetates) and observed the n.m.r. spectra in chloroform at 60°C and at 100 Mc/s . The results are shown in *Figure 3*. Thus, the three peaks at $\tau 7.98$, 8.00 and 8.02 were assigned to the isotactic, heterotactic and syndiotactic triad. The Kurashiki group independently studied model compounds, i.e. stereoisomeric 2,4,6-heptanetriol triacetates, and obtained results which are in good agreement with our assignment³⁶. The assignment of the n.m.r. spectra of

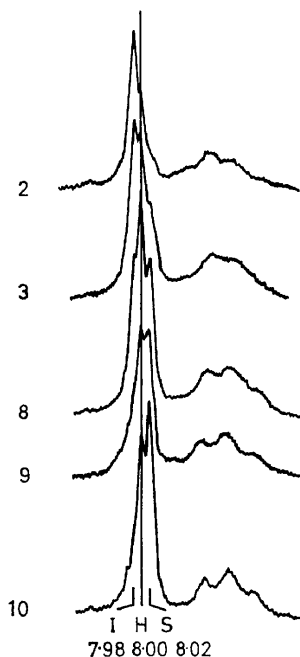


Figure 3. N.m.r. spectra of poly(vinyl alcohols) in chloroform solutions at 60°C — slow sweep of the methyl resonance

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poly(vinyl acetates) is thus established. Several other methods have been proposed for the n.m.r. determination of tacticity, including poly(vinyl alcohol) in phenol³⁷ or in deuterium oxide^{38, 39}, poly(vinyl trifluoroacetate) in deuterated acetone³⁹ or in acetone⁴⁰, and poly(vinyl acetate) in CH_2Cl_2 ³⁹. Some of our observed values are compared with, and found to be in good agreement with, those obtained with the same specimens by the method of Bargon and others³⁷, i.e., the decoupled α -proton resonance of poly(vinyl alcohol) in phenol at 120°C (*Table 4*).

Table 4. Estimation of the tacticity from decoupled α -proton spectra of poly(vinyl alcohol)

No.	Triads			Diads†	
	<i>I</i>	<i>H</i>	<i>S</i>	<i>i</i>	<i>s</i>
1	85	10	5	90	10
4	30	46	24	53	47
10	10	36	54	28	72

† Calculated from triads

The correlation between the optical density ratio and the tacticity, determined by n.m.r., is shown in *Figure 4*. The relationship is represented by equation (5). It has thus been made possible to estimate the tacticity from the infrared spectra.

$$\text{Syndiotacticity in diads, \%} = 72.4(D_{916}/D_{849})^{0.43} \quad (5)$$

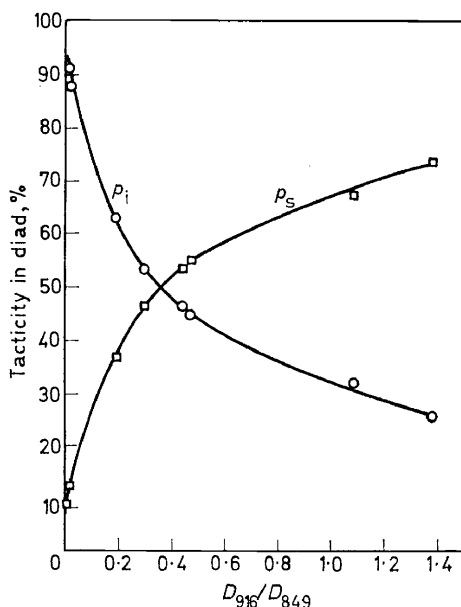


Figure 4 The correlation between tacticity of poly(vinyl acetate) and the ratio D_{916}/D_{849} of the parent poly(vinyl alcohol)

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Table 5 shows the tacticity values of various samples which were obtained from vinyloxytrimethylsilane. The number 4 and 6 samples of the table were derived from the radical polymerization of vinyl acetate and vinyl trifluoroacetate, respectively. It can be seen that we have obtained an isotactic polymer of considerable tacticity while the tacticity in the syndiotactic polymer is rather low. Another interesting fact is that poly(vinyl alcohol) derived

Table 5. Estimation of the tacticities of various poly (vinyl acetates) by n.m.r.

No.	D_{916}/D_{849} of PVA	Tacticity				
		Triads			Diads†	
		P_I	P_H	P_S	P_i	P_s
1	0.01	86	10	4	91	9
2	0.02	79	17	4	87	13
3	0.19	46	34	20	63	37
4(R)	0.27	32	46	22	55	45
5	0.29	33	41	26	53	47
6(R)	0.41	25	48	27	48	52
7	0.44	24	45	31	46	54
8	0.47	23	44	33	45	55
9	1.08	11	43	46	32	68
10	1.38	6	40	54	26	74

† Calculated from triads

from vinyl trifluoroacetate had for some years been considered to be the most syndiotactic, but it turns out to be atactic. It has also to be noticed that there is essentially no difference in tacticity between a commercial sample and the one derived from vinyl trifluoroacetate. This observation is consistent with Sakaguchi's earlier suggestion which was presented on the basis of a study of the rate of saponification of poly(vinyl acetate)⁷. There is, however, a large difference in their physical properties⁴¹.

Table 6. Solubility of poly(vinyl alcohol) in water

Sample No.	Isotactic % in diad	Solubility in water
1	91	Insol. in cold; sol. at 100°
2	87	Sol. in cold
4 (Commercial)	55	Insol. in cold; sol. at 100°
6	48	Insol. in cold; sol. at 100°
10	26	Insol. at 150°; sol. at 160°

As shown in Table 6, a moderately isotactic polymer was soluble in cold water, while a higher isotacticity made it insoluble^{33b}. A similar phenomenon can be seen in the melting point which was measured by differential thermal analysis (Figure 5). It may be interesting to try to obtain more highly isotactic polymer, since an extremely high isotacticity might display some unexpected properties. It seems even more interesting to attempt to obtain a high

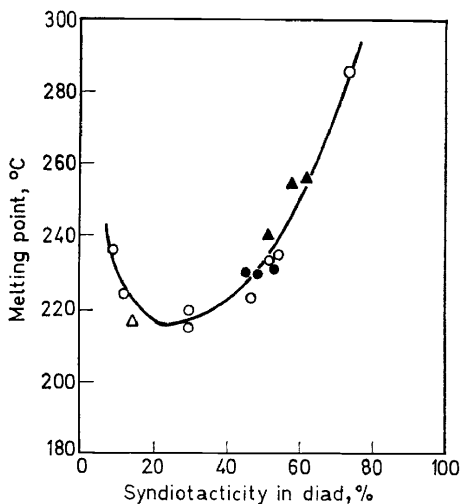


Figure 5. Variation of melting point of poly(vinyl alcohol) with tacticity [○, vinyloxytrimethylsilane; ●, vinyl acetate; △, vinyl *t*-butyl ether; ▲, vinyl trifluoroacetate]

syndiotacticity for the elucidation of a structure–property relationship. The synthesis of syndiotactic poly(vinyl alcohol) appears to have industrial importance as well.

SYNDIOTACTIC POLY(VINYL ALCOHOL)

We were hoping to obtain a syndiotactic polymer of high tacticity by modifying the starting monomers and by varying the polymerization conditions. On modifying vinyl monomers, such variables as bulkiness and the polarity of the substituents first occurred to us. Some results of our attempts in this line will be illustrated in the following paragraphs.

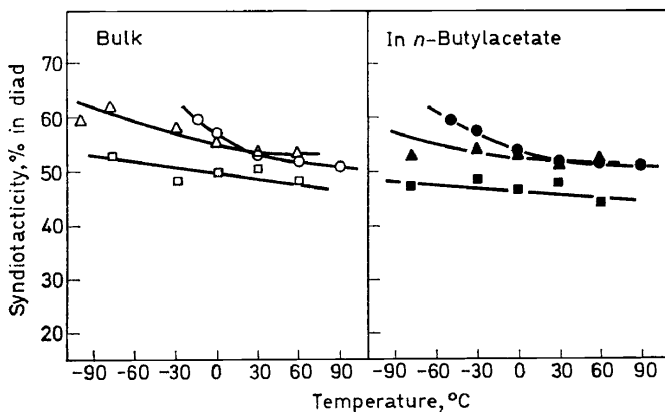


Figure 6. Tacticity vs. polymerization temperature in the polymerization of vinyl acetate derivatives [□, ■ CH₂=CHOCOCH₃; △, ▲ CH₂=CHOCOCF₃; ○, ● CH₂=CHOCOCCl₃]

According to Fordham's theoretical treatment of radical polymerization⁴², the syndiotactic propagation is favoured over the isotactic owing to the steric and electrostatic effects of the substituents. As mentioned before, the so-called syndiotactic polymer derived from vinyl trifluoroacetate at 60°C, turned out to be atactic according to n.m.r. analysis. The effect of substituents on the tacticity of vinyl acetate derivatives, obtained by radical polymerization, was pursued using these quantitative measurements of tacticity. Figure 6 shows the effect of the polymerization temperature on the tacticity of three acetate derivatives⁴³. In bulk, as well as in the *n*-butyl acetate solution, syndiotacticity tends to increase at lower polymerization temperatures. A maximum syndiotacticity of 62 per cent was obtained in this way in the bulk polymerization of vinyl trifluoroacetate. In general, the effect of temperature on tacticity can be represented by equation (6)⁴⁴.

$$\log(p_i/p_s) = \frac{\Delta S_i^\ddagger - \Delta S_s^\ddagger}{R} - \frac{\Delta H_i^\ddagger - \Delta H_s^\ddagger}{RT}$$

- p_i and p_s : probability of isotactic and syndiotactic propagation
 ΔS_i^\ddagger and ΔS_s^\ddagger : activation entropy for isotactic and syndiotactic propagation
 ΔH_i^\ddagger and ΔH_s^\ddagger : activation enthalpy for isotactic and syndiotactic propagation

Thus, we can calculate differences of activation parameters for isotactic and syndiotactic propagations.

Table 7. Activation parameters for the radical polymerization of vinyl acetate derivatives, $\text{CH}_2=\text{CHOCOR}$

<i>R</i>	Solvent	$\Delta H_i^\ddagger - \Delta H_s^\ddagger$ (cal/mole)	$\Delta S_i^\ddagger - \Delta S_s^\ddagger$ (cal/deg. mole)
CH ₃	—	170	0.6
	<i>n</i> -BuOAc	60	0.5
CF ₃	—	380	1.0
	<i>n</i> -BuOAc	210	0.5
CCl ₃	—	700	2.0
	<i>n</i> -BuOAc	430	1.1

As shown in Table 7 the temperature dependency increases in the order: methyl < trifluoromethyl < trichloromethyl. The largest value is 700 cal/mole for vinyl trichloroacetate in bulk which is the same order of magnitude as for methyl methacrylate⁴⁴. Vinyl trichloroacetate seemed to be one of the more promising monomers among these monomers. Unfortunately, however, the polymerization of this monomer at very low temperatures was almost impractical because of the high melting point of the monomer (−25°C) and the low rate of polymerization.

As shown earlier in Table 5, vinyloxytrimethylsilane gave a wide variety of tacticities depending upon the polymerization conditions. Poly(vinyl

alcohol), obtained from the cationic polymerization of vinyloxytrimethylsilane at -78° in nitroethane, has a syndiotacticity of 74 per cent. This is the highest syndiotacticity we have ever obtained. The temperature-dependency of the tacticity in the isotactic, atactic, and syndiotactic polymerization systems is shown in *Figure 7* and *Table 8*⁴⁵.

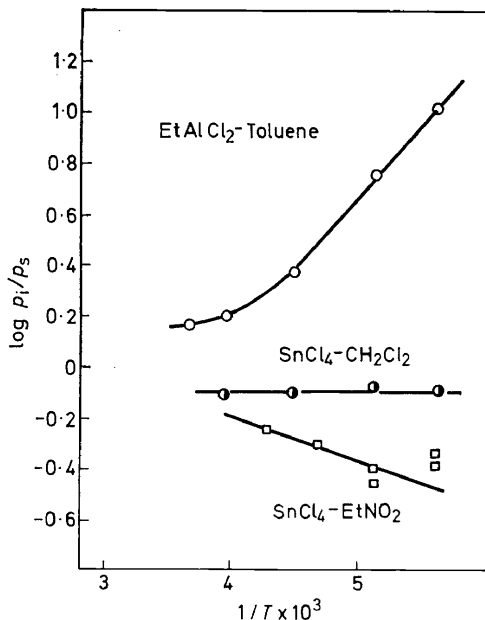


Figure 7. Dependency of tacticity on the polymerization temperature

Table 8. Activation parameters in isotactic and syndiotactic polymerization of vinyloxytrimethylsilane

Polymerization system	$\Delta H_1 - \Delta H_s$ (cal/mole)	$\Delta S_1 - \Delta S_s$ (cal/deg. mole)
EtAlCl ₂ -toluene	-2600	-9.8
SnCl ₄ -CH ₂ Cl ₂	0	-0.4
SnCl ₄ -NO ₂ Et	780	2.1

It is interesting that the difference in the activation enthalpies for the syndiotactic polymerization (780 cal/mole) is of the same order as those for the radical polymerization of methyl methacrylate and vinyl trichloroacetate; little difference in the activation entropies was found. These facts seem to suggest a similar mechanism of stereoregulation for the cationic and radical syndiotactic polymerizations. In other words, these data are consistent with the free ion mechanism of the cationic polymerization in polar solvents⁴⁶. On the other hand, the isotactic polymerization showed a large temperature dependency of tacticity and a large negative value for the

activation entropy differences. This might suggest a special molecular orientation in the transition state of the isotactic propagation and would be consistent with some of the hypotheses of cyclic transition states⁴⁷.

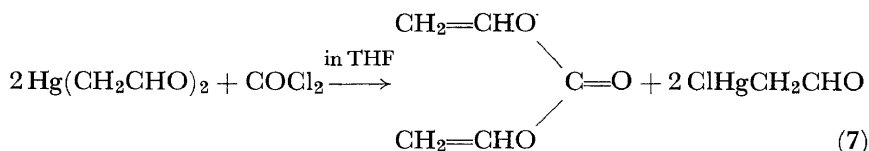
Since vinyl *t*-butyl ether, which is structurally similar to vinyloxytrimethylsilane, does not give such a high syndiotacticity as the latter does³⁶, it is conceivable that the bulkiness of the trimethylsilyl group plays an important role. However, the bulkier triethylsilyl and tri-*n*-propylsilyl groups did not favourably effect the stereoregulation, suggesting a complex effect of the substituent⁴⁸.

HEAD-TO-HEAD POLY(VINYL ALCOHOL)

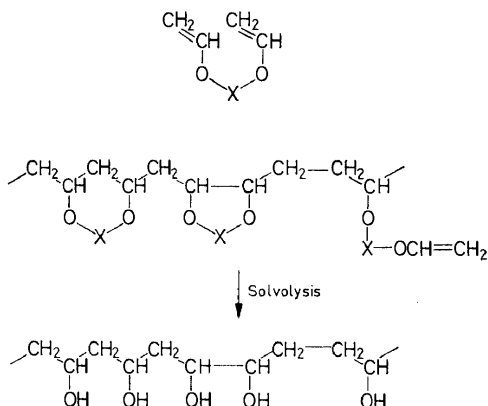
Another route to poly(vinyl alcohol) is the intra-intermolecular polymerization of divinyl compounds, the principle of which was discovered by Butler in 1957⁴⁹. Application of the principle to the synthesis of poly(vinyl alcohol) was reported in 1961 by Matsuyan, who hydrolyzed the cyclized polymer of divinyl formal⁵⁰.

It was found that divinyl carbonate⁵¹ and divinylxydimethylsilane⁵² gave partially cyclized polymers, and their hydrolysis lead to a new type of poly(vinyl alcohol) containing 30 to 37 per cent of 1,2-glycol units. Divinyl carbonate was picked since this is the carbonic acid ester of enolized acetaldehyde, and might be synthesized from acetaldehyde and carbon dioxide in the future. Divinylxydimethylsilane was chosen as a part of a series of investigations on the polymerizability of vinyloxysilanes.

Divinyl carbonate is a new monomer and is synthesized according to equation (7)⁵¹.



Divinylxydimethylsilane is a known compound and was prepared by Nesmeyanov in 1959³¹. The polymers of these monomers can be represented by the following general formula.



The formula may contain cyclized structures and pendant unsaturation. We studied in detail the structure of poly(vinyl carbonate) using i.r. spectroscopy and thus confirmed the presence of the two types of cyclization. The derived poly(vinyl alcohol) has the structure corresponding to the structure of the parent polymer. A 6-membered ring will give a 1,3-glycol unit and a 5-membered ring will give a 1,2-glycol unit. Thus, the poly(vinyl alcohol) was found to contain 30 to 37 mole per cent of 1,2-glycol units. The i.r. spectrum of this polymer is very different from that of the normal polymer, as shown in *Figure 8*.

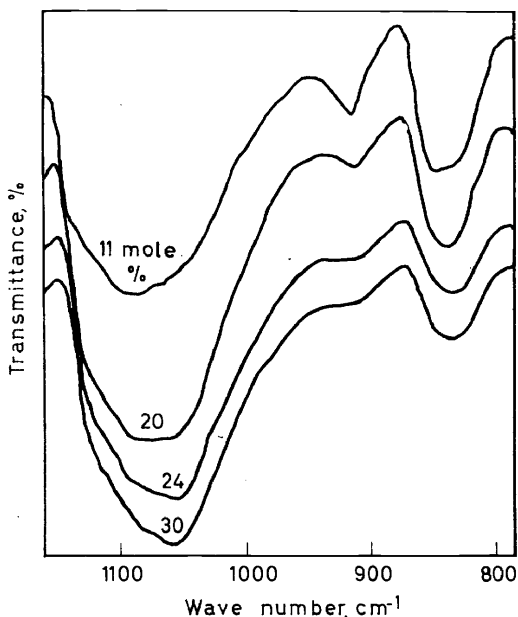


Figure 8. Infrared spectra of poly(vinyl alcohol) having various amounts of 1,2-glycol units

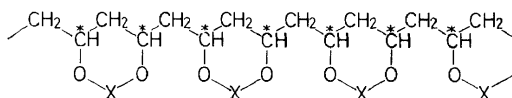
The band at 916 cm^{-1} is very small and the band at 1090 is shifted to 1060 cm^{-1} . The melting point of the polymer decreased with increasing amounts of 1,2-glycol units. Melting points varied from 207° to about 120°C (*Figure 9*)⁵³.

Poly(vinyl alcohol) derived from divinyl oxalate⁵⁴, divinyl formal⁵⁵, and other divinyl acetals⁵⁶ were reported to contain a large amount of 1,2-glycol units.

It may be worthwhile to mention that divinyl oxydimethylsilane showed different cyclopolymerization behaviour when polymerized by the radical and the cationic mechanisms. Radical polymerizations yielded polymers rich in 1,2-glycol units, whereas cationic polymerizations gave normal polymers with no enhanced amounts of 1,2-glycol units⁵².

Let us consider the problem of the tacticity in the cyclopolymerization. As a simple example, let us now assume the case of 100 per cent cyclization to a 6-membered ring.

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(11)	(11)	(11)	(11)	(11)	(11)	100 % I
(11)	(dd)	(11)	(dd)	(11)	(dd)	100% H
(11)	(11)	(dd)	(11)	(dd)	(dd)	50% I + 50% H

The group X might have an influence on the steric structure of the ring so that the two asymmetric carbons in the ring might have the same configuration (11) or (dd). It is found in the case of a formal ring⁵⁷ that the ring conformation having the placement of two side chains in two equatorial positions is favoured over that in which the groups have an equatorial and an axial position. Stereoregularity between the rings might result in all isotactic

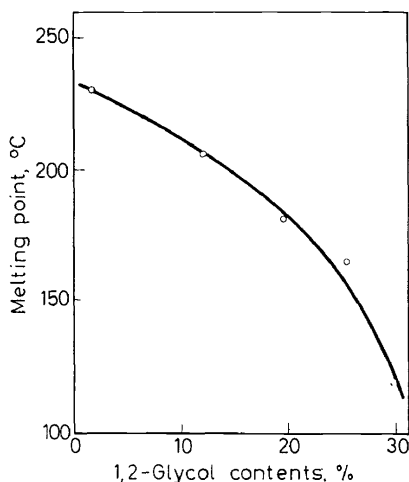


Figure 9. Variation of the melting point of poly(vinyl alcohol) with the content of 1,2-glycol units

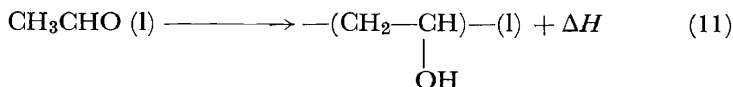
or all heterotactic polymer in terms of triads. The absence of regularity between the rings might give 50 per cent isotactic and 50 per cent heterotactic samples. Actually, methacrylic anhydride was reported to give a polymer rich in both syndiotactic and heterotactic triads. An all-syndiotactic polymer will be obtained in another extreme case. One has to add that it would be rather difficult to attain high stereoregularity in this fashion.

DIRECT SYNTHESIS OF POLYVINYL ALCOHOL FROM ACETALDEHYDE

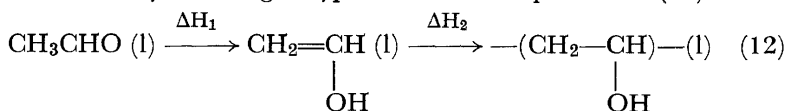
Mention will be made briefly of the possibility of a synthesis of poly(vinyl alcohol) directly from acetaldehyde. As Staudinger pointed out in his first paper on poly(vinyl alcohol) in 1927³, this has been the most important synthetic problem from the very beginning. The problem still remains unsolved after the lapse of about 40 years. The synthesis of polymers has

made a remarkable progress in 20 years. It seems to me that the time has come to reconsider this old problem, applying the present knowledge of polymer synthesis.

Let us roughly estimate the heat of polymerization for the hypothetical direct polymerization (11):



This can be done by assuming a hypothetical two-step reaction (12):



We already know the theoretical value for the heat of enolization of acetaldehyde, ΔH_1 , to be + 10.0 kcal/mole⁵⁸. It may not be unreasonable to assume that the heat of vinyl polymerization of vinyl alcohol into poly(vinyl alcohol), ΔH_2 , can be approximated by that of vinyl acetate: that is -21.3 kcal/mole⁵⁹. The acetyl group of vinyl acetate will not impose significant steric or electronic effects on the heat of polymerization. Since $\Delta H = \Delta H_1 + \Delta H_2$, ΔH is estimated to be around -11.3 kcal/mole. An experimental verification from the heat of combustion of poly(vinyl alcohol) would be very interesting. The value suggests that the direct synthesis of equation (11) is moderately exothermic.

One might consider three possible mechanisms. The first one is successive aldol condensations. The second is a vinyl polymerization in the enolized form. The third is a synthesis via vinyloxymetal compounds. The first method is being actively investigated by T. Imoto and his group at Osaka City University⁶⁰. They got a poly(vinyl alcohol)-like polymer of low molecular weight, using sodium amalgam as a catalyst under high pressures. The difficulty seems to lie in the presence of side reactions such as dehydration, cyclization, and acetalization, which are known to be characteristic of the aldol synthesis. There has recently been a report which disagrees with the poly(vinyl alcohol) structure of the polymer⁶¹.

As you have seen in the case of vinyloxysilanes, there has been some success in using vinyloxymetal compounds as monomers. It is known that some vinyloxymetal compounds can be prepared directly from acetaldehyde⁶². Therefore, once their polymerizability is known, a new method would be available. A more attractive possibility seems to be the vinyl polymerization of the enol form of acetaldehyde; especially the surface complex of the enol form with metal compounds. This type of complex was shown for iron⁶³.

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