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Stereospecific Polymerization of Allyl Vinyl Ether by $BF_3 \cdot OEt_2$

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The polymerization of allyl vinyl ether was carried out by means of $BF_3 \cdot OEt_2$. The reaction proceeded through the vinyl double bond, and a polymer with allyl ether side chains was obtained. The effects of the polymerization conditions on the stereoregularity of the polymer were studied by means of NMR spectroscopy using a spin decoupling technique. A highly isotactic polymer was obtained at $-78°C$ in toluene. The isotacticity of the polymer decreased slightly with a rise in the reaction temperature and with an increase in the initial monomer concentration. When the reaction was carried out in a mixture of toluene and nitroethane, a marked decrease in the isotacticity and the solution viscosity of the polymer was observed with an increase in the amount of nitroethane. The solution viscosity of the polymer decreased with an increase in the polymerization temperature and the catalyst concentration, and increased with an increase in the initial monomer concentration. The reaction between the polymer and HBr in acetic acid yielded a ternary copolymer consisting of vinyl alcohol, vinyl acetate, and vinyl bromide units.

Many papers have been published on the stereospecific polymerization of vinyl ethers.[1-6] However, only a few investigations have been done on the

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[1] C. E. Schildknecht, S. T. Gross, H. R. Davidson, J. M. Lambert and A. O. Zoss, *Ind. Eng. Chem.*, **40**, 2104 (1948).

[2] H. Yuki, K. Hatada, K. Ohta, I. Kinoshita, K. Ono, S. Murahashi and Y. Ito, *J. Polym. Sci.*, Part *A-1*, **7**, 1517 (1969).

[3] S. Murahashi, S. Nozakura and M. Sumi, *Polym. Lett.*, **3**, 245 (1965).

[4] S. Murahashi, S. Nozakura, M. Sumi and K. Matsumura, *ibid.*, **4**, 59 (1966).

[5] G. J. Blake and A. M. Carlson, *J. Polym. Sci.*, Part *A-1*, **4**, 1813 (1966).

[6] S. Okamura, T. Kodama and T. Higashimura, *Makromol. Chem.*, **53**, 180 (1962).

polymerization of allyl vinyl ether (AVE) by cationic catalysts,[7,8] and there have been no information concerning the stereospecific polymerization of this monomer.

The present authors studied the polymerization of AVE by $BF_3 \cdot OEt_2$ and found that the polymerization proceeded through the vinyl double bond and that a polymer containing one allyl double bond per monomer unit was obtained. The tacticity of the polymer were analyzed by means of NMR spectroscopy using a spin decoupling technique, and the effects of the polymerization conditions on the stereoregularity of the polymer were investigated. The reaction of poly(allyl vinyl ether) (PAVE) with hydrogen bromide was also studied.

Experimental

Reagents. AVE was prepared from isobutyl vinyl ether and allyl alcohol by transetherification using mercuric acetate as the catalyst.[9] The crude product was purified by refluxing it over calcium hydride and then over lithium aluminum hydride under nitrogen pressure, after which it was distilled *in vacuo*. Bp, 67.0°C. The purified AVE was sealed in an ampule under dry nitrogen and stored at −20°C.

The isobutyl vinyl ether was purified by shaking it several times with 5% aqueous sodium hydroxide, dried with anhydrous potassium carbonate, and then refluxed over calcium hydride. It was finally distilled from calcium hydride using an efficient column. Bp, 82.8—83.0°C.

The allyl alcohol was dried with molecular sieves 4A and distilled under nitrogen pressure. Bp, 96.0—97.0°C.

The toluene was purified and dried by a usual method and was distilled from calcium hydride. Then the distillate was mixed with a small amount of *n*-butyllithium in a toluene solution and distilled on a vacuum line before use.

The *n*-hexane and *n*-heptane were purified by usual methods and stored over calcium hydride. Each was mixed with a small amount of *n*-butyllithium in the same solvent and distilled on a vacuum line just before use.

The nitroethane was purified by distillation, dried with molecular sieves 4A, and distilled under a high vacuum just before use.

The methylene chloride was shaken with concentrated sulfuric acid, washed with aqueous sodium hydroxide and water, dried over calcium chloride, and distilled. The distillate was dried with a mixture of calcium hydride and molecular sieves 4A and then distilled again under a vacuum just before use.

The tetralin, dioxane, and acetic acid were purified and dried by usual methods.

The hydrogen bromide was prepared by dropping dry bromine into tetraline at 60°C under nitrogen pressure.

The nitrogen was dried by being passed through molecular sieves 4A cooled at −78°C.

The boron trifluoride etherate ($BF_3 \cdot OEt_2$) was purified by distillation under reduced nitrogen pressure and was used as a toluene solution.

Polymerization. A vessel equipped with a three-way stop-cock was flushed with dry nitrogen. The monomer and a solvent were introduced with hypodermic syringes. To this solution, cooled at a given temperature, the catalyst solution was then added, drop by drop, using a syringe. The polymerization was stopped by adding a small amount of ammoniac methanol which had been cooled at the same temperature as the reaction mixture. The mixture was then poured into a large amount of methanol containing a small amount of phenyl-β-naphthylamine. The precipitated polymer was collected by filtration, washed thoroughly with the same methanol, and dried *in vacuo* at room temperature for 2 days. The polymer was stored under nitrogen atmosphere at −20°C to avoid the formation of cross-linked insoluble polymer. When the polymer was low-molecular and was soluble in methanol, the solution was concentrated to dryness under a high vacuum; the residual polymer was then redissolved in benzene in order to free it from inorganic materials and dried by the freeze-drying method.

Reaction of PAVE with HBr. Dry hydrogen bromide was bubbled through a solution of PAVE in toluene at room temperature under nitrogen pressure. After the reaction has been completed, dry nitrogen was passed through the reaction mixture in order to remove the excess hydrogen bromide, and then the mixture was poured into a large amount of methanol in order to precipitate the product. After the mixture had stood overnight, the resultant polymer was collected, washed with methanol, and dried *in vacuo*.

When the reaction was carried out in acetic acid, the polymer was not completely soluble in the medium at the begining, but it was gradually dissolved in the course of the reaction. In the reaction the formation of poly(vinyl acetate) was expected. However, the reaction product did not contain a methanol-soluble part.

Measurements of NMR Spectra. NMR spectra were obtained with a JEOL JNM-4H-100 spectrometer at 100 MHz by using a 5 w/v% solution containing a small amount of tetramethylsilane as an internal standard. The spectra of the polymer and AVE were measured in carbon tetrachloride at 60°C and in chloroform at 22.5°C respectively.

Measurements of IR Spectra. The IR spectra of the polymer were taken on a JASCO IR-S spectrometer, casting the polymer film on a rock salt plate from a benzene solution.

Viscosity Measurements. The solution viscosity of the polymer was measured on its benzene solution (0.1 g/d*l*) at 30.0±0.03°C using an Ostwald viscometer.

Results

NMR Spectra and Structure of PAVE. Figure 1 shows the NMR spectrum of PAVE obtained at −78°C in toluene, together with the spectrum of AVE. The spectrum of PAVE consists of five peaks which correspond to the β-methylene, α-methine, allyl methylene protons, and terminal methylene and methine protons in an allyl double

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[7] R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. Soc. Chim. Fr.*, **1950**, 121.

[8] J. Lal, *J. Polym. Sci.*, **31**, 179 (1958).

[9] W. H. Watanabe and L. E. Conlon, *J. Amer. Chem. Soc.*, **79**, 2828 (1957).

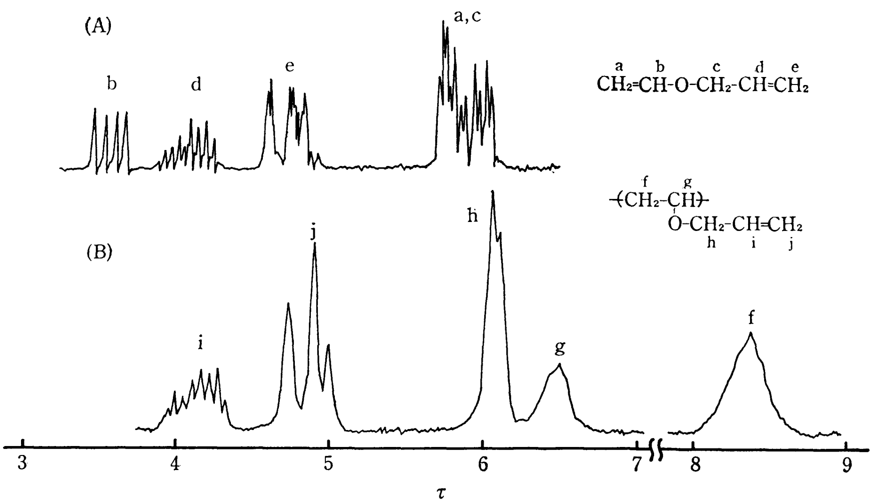

Fig. 1. NMR spectra of allyl vinyl ether (A) and poly (allyl vinyl ether) polymerized by $BF_3 \cdot OEt_2$ at −78°C in toluene (B).

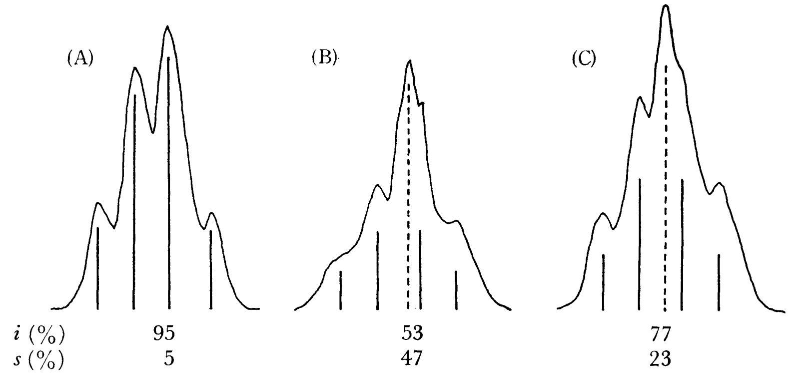

Fig. 2. β-Proton resonance spectra decoupled from α-proton of poly (allyl vinyl ether)s prepared at −78°C by $BF_3 \cdot OEt_2$ in toluene (A), by $BF_3 \cdot OEt_2$ in nitroethane (B) and by $EtAlCl_2$ in toluene (C).
——— isotactic dyad, - - - - - syndiotactic dyad

bond with a decrease in the magnetic field. The intensity ratio of these five peaks is 2.1 : 1.0 : 2.0 : 1.9 : 1.1. There is no resonance at about 3.6 and 5.6—6.0 τ, where the resonances due to the protons of vinyl group in the polymer may appear, if they exist, as is observed in the spectrum of AVE. These results suggest that AVE polymerizes exclusively through the vinyl double bond and that the polymer contains one pendant allyl group per monomer unit.

The polymers obtained under various conditions showed the same spectra as that of PAVE obtained at −78°C in toluene, suggesting that the mode of polymerization did not depend on the reaction conditions.

Determination of Tacticity of PAVE. In the undecoupled spectrum of PAVE (Fig. 1B) it was impossible to discriminate the respective multiplets arising from the nuclei in different stereochemical sequences because the spin-spin coupling complicated the spectrum greatly. However, the resonance of the β-protons appeared to be sensitive to the stereochemical configuration in the spin decoupled spectrum, as is shown in Fig. 2.

The β-proton resonance of PAVE obtained at −78°C in toluene showed a typical AB quartet (Fig. 2A) when decoupled from the α-proton, suggesting that the polymer is highly isotactic.

On the other hand, the decoupled resonance of PAVE obtained in nitroethane exhibited five components, as is shown in Fig. 2B. Generally in cationic polymerization vinyl ether gives a less isotactic polymer as the reaction medium is more polar.[10-12] Therefore, the above resonance may

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[10] T. Higashimura, T. Watanabe, K. Suzuoki and S. Okamura, *J. Polym. Sci.*, **C, No. 4,** 361 (1963).

[11] T. Higashimura, K. Suzuoki and S. Okamura, *Makromol. Chem.*, **86,** 259 (1965).

[12] M. Sumi, S. Nozakura and S. Murahashi, *Kobunshi Kagaku*, **24,** 424 (1967).

be considered to be the overlap of an AB quartet due to the isotactic methylene and a singlet due to the syndiotactic methylene, which are equivalent. Although the spectral resolution was not sufficient, the fraction of the tactic dyad can be estimated from the relative areas of the AB quartet and singlet within an error of $\pm 5\%$.

The resonance of the α-proton seems not to be so sensitive to the stereochemical configuration of the polymer chain that the fraction of the tactic triad can not be determined by NMR spectroscopy.

Effect of Polymerization Temperature. The polymerizations were carried out in toluene at various temperatures ranging from -78 to 0°C. The results are shown in Fig. 3. The polymerization was always almost completed within one hour even at -78°C. The isotacticity of the polymer decreased slightly with a rise in the polymerization temperature. On the other hand, a marked decrease was observed in the molecular weight of the polymer at higher polymerization temperatures. The polymer obtained at 0°C was a viscous oil and was soluble in methanol.

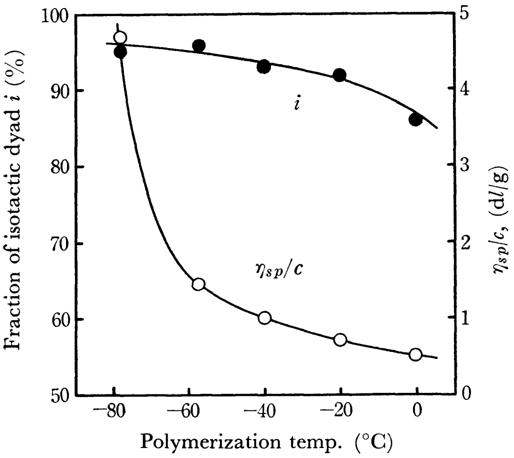


Fig. 3. Effect of temperature on the polymerization of allyl vinyl ether by $BF_3 \cdot OEt_2$ in toluene for 1 hr. Monomer 20 mmol, $BF_3 \cdot OEt_2$ 0.1 mmol, total volume of the system 22 m*l*

Effect of Catalyst Concentration. Figure 4 shows the results of the polymerizations carried out with various catalyst concentrations at -78°C in toluene. The polymerization was always almost completed in one hour at any catalyst concentration above 4.6×10^{-3} mol/*l*. The solution viscosity of the polymer remarkably decreased with an increase in the catalyst concentration.

Effect of Monomer Concentration. The polymerization was carried out at various monomer concentrations in toluene at -78°C. The results are given in Fig. 5. The isotacticity of the polymer was enhanced with a decrease in the initial monomer concentration. The solution viscosity of the polymer increased with an increase in the initial monomer concentration.

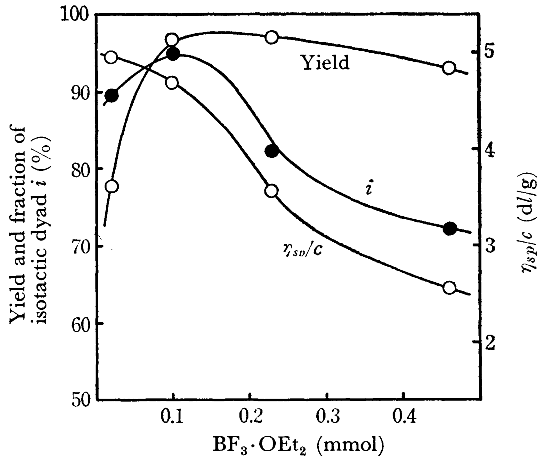


Fig. 4. Effect of catalyst amount on the polymerization of allyl vinyl ether by $BF_3 \cdot OEt_2$ in toluene at -78°C for 1 hr.
Monomer 20 mmol, total volume of the system 22 m*l*

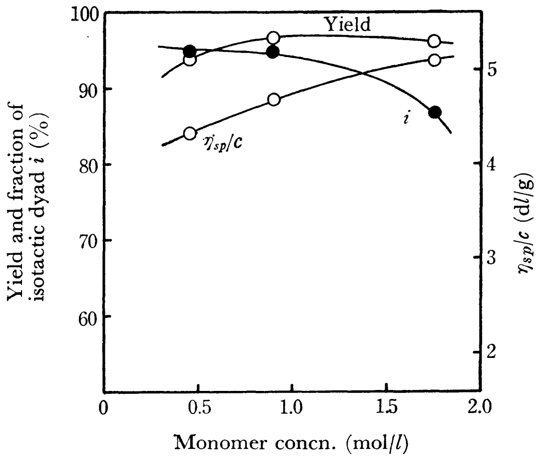


Fig. 5. Effect of monomer concentration on the polymerization of allyl vinyl ether by $BF_3 \cdot OEt_2$ in toluene at -78°C for 1 hr.
$BF_3 \cdot OEt_2$ 0.1 mmol, total volume of the system 22 m*l*

Polymerization in Various Solvents. The results of polymerizations in various solvents at -78°C are listed in Table 1. The isotacticity of the polymer was lowered in a polar solvent. In the polymerization in *n*-hexane or *n*-heptane, the polymer produced was precipitated during the course of the reaction, and the yield and the isotacticity of the polymer were both lowered.

The polymerization was carried out in toluene-nitroethane mixtures at -78°C. The results are shown in Fig. 6. A gradual decrease in the isotacticity and a rapid decrease in the solution viscosity of the polymer were observed with an

TABLE 1. POLYMERIZATION OF ALLYL VINYL ETHER IN VARIOUS SOLVENTS AT −78°C FOR 1 hr
Monomer 20 mmol, $BF_3 \cdot OEt_2$ 0.1 mmol, total volume of the system 22 m*l*

Solvent	Polymer			
	Yield (%)	Tacticity (%) *i*	Tacticity (%) *s*	η_{sp}/C^a (d*l*/g)
Toluene	96.6	95	5	4.70
$EtNO_2$	94.1	53	47	0.55
CH_2Cl_2	82.6	87	13	1.81
n-Hexane	37.4	69	31	2.05
n-Heptane	47.8	63	37	3.45

a) Determined at 30.0°C with a benzene solution at 0.1 g/d*l*

increase in the fraction of nitroethane in the medium.

Reaction of PAVE and HBr. The reactions of PAVE with HBr were carried out in toluene, dioxane, and acetic acid. The results are given in Table 2. The reaction products in toluene and dioxane were not soluble in usual organic solvents and contained a considerable amount of bromine.

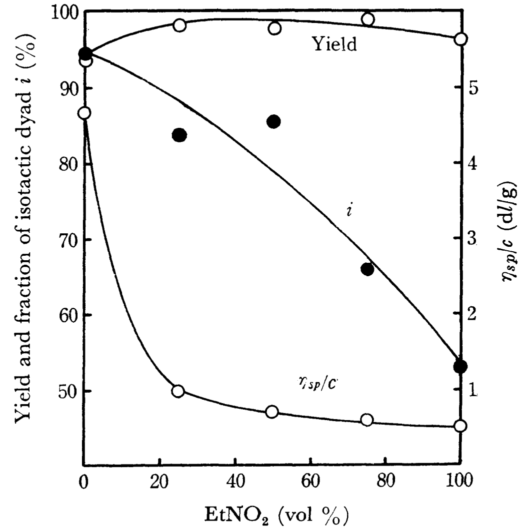


Fig. 6. Polymerization of allyl vinyl ether by $BF_3 \cdot OEt_2$ at −78°C for 1 hr in toluene-nitroethane mixed solvent.
Monomer 20 mmol, $BF_3 \cdot OEt_2$ 0.1 mmol, total volume of the system 22 m*l*

TABLE 2. REACTION OF PAVE WITH HBr IN VARIOUS SOLVENTS

No.	Solvent	(m*l*)	PAVE		Reaction time (hr)	Reaction product				
			(g)	η_{sp}/C (d*l*/g)		Yield (g)	Elementary analysis (%) C	H	O	Br
A-82	Toluene	60	0.957	2.7	1	0.788	48.77	7.54	20.74	22.95
B02	Toluene	150	1.448	2.6	5	1.103	48.08	7.68	24.49	19.75
B03	Dioxane	200	1.460	2.6	5	0.959	55.63	8.03	23.72	12.62
B04	Acetic acid	80	0.783	1.2	3	0.684	38.83	5.09	16.99	39.09
K-15	Acetic acid	110	1.010	—	2.5	1.163	37.85	4.81	15.85	41.49

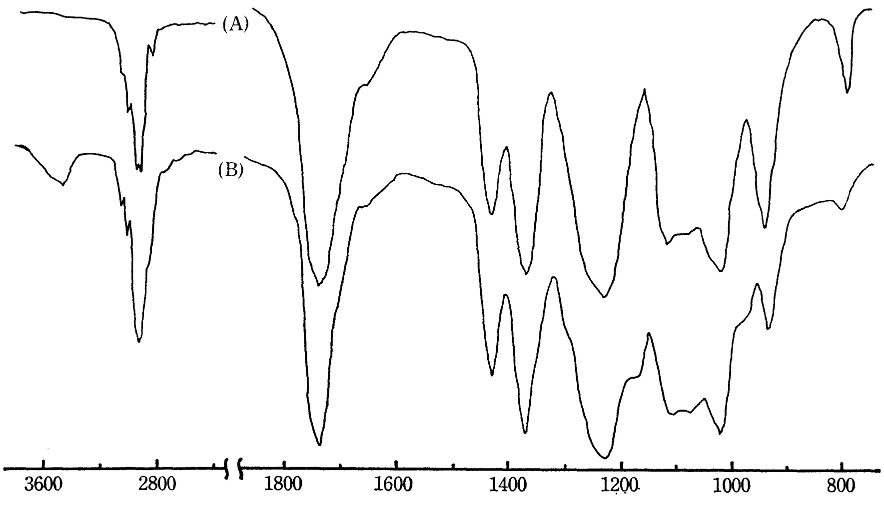
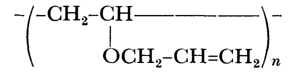
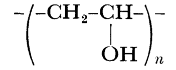
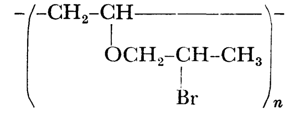
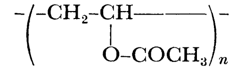
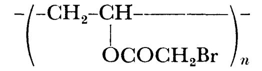
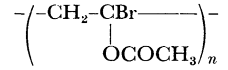
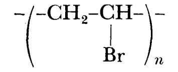


Fig. 7. Infrared spectra of PVAc polymerized by AIBN (A) and reaction product of PAVE with HBr in glacial acetic acid (B).

Table 3. Possible structural units for the reaction product of PAVE and HBr

	Structure	Mol. formula	C (%)	H (%)	O (%)	Br (%)
I	 $-\left(-CH_2-\underset{OCH_2-CH=CH_2}{\underset{\vert}{CH}}-\right)_n-$	C_5H_8O	71.39	9.59	19.02	0
II	 $-\left(-CH_2-\underset{OH}{\underset{\vert}{CH}}-\right)_n-$	C_2H_4O	54.52	9.17	36.31	0
III	 $-\left(-CH_2-\underset{OCH_2-\underset{Br}{\underset{\vert}{CH}}-CH_3}{\underset{\vert}{CH}}-\right)_n-$	C_5H_9OBr	36.40	5.50	9.70	48.43
IV	 $-\left(-CH_2-\underset{O-COCH_3}{\underset{\vert}{CH}}-\right)_n-$	$C_4H_6O_2$	55.80	7.03	37.17	0
V	 $-\left(-CH_2-\underset{OCOCH_2Br}{\underset{\vert}{CH}}-\right)_n-$	$C_4H_5O_2Br$	29.12	3.05	19.39	48.43
VI	 $-\left(-CH_2-\underset{OCOCH_3}{\underset{\vert}{CBr}}-\right)_n-$	$C_4H_5O_2Br$	29.12	3.06	19.39	48.43
VII	 $-\left(-CH_2-\underset{Br}{\underset{\vert}{CH}}-\right)_n-$	C_2H_3Br	22.45	2.83	0	74.73

When the reaction was performed in acetic acid, the product was not soluble in methanol, but it was soluble in toluene, benzene, acetone, and chloroform. It also contained about 40% of bromine. As is shown in Fig. 7 the infrared spectrum of this product was almost identical with that of poly(vinyl acetate) except for an absorption at 3490 cm^{-1} due to an OH group. These results suggest that the product was composed of vinyl acetate and vinyl alcohol units, plus a unit containing bromine. The possible structures for the constituent units are summarized in Table 3. Among the bromine-containing units, the vinyl bromide unit is most relevant because the other three units have a bromine content close to that of the product, which may be assumed to contain considerable amounts of vinyl acetate and vinyl alcohol units.

The NMR spectrum of the reaction product of PAVE and HBr is shown in Fig. 8 and compared with that of poly(vinyl acetate). In the spectrum there are a sharp singlet resonance of the acetoxy methyl proton, a broad multiplet probably due to the β-methylene proton overlapping with the methyl resonance, and three peaks, at 6.40, 5.93, and 4.93 τ, in the region of the methine proton resonance. The literature[13] indicates that the τ values corresponding to the methine protons in the structures of $-CH(OH)-$, $-CHBr-$, and $-CH(OCOCH_3)-$ are 6.4, 5.9, and 5.0 τ respectively. Therefore, the three peaks at 6.40, 5.93, and 4.93 τ may be tentatively assigned to the methine protons in the structural units of vinyl alcohol, vinyl bromide, and vinyl acetate respectively.

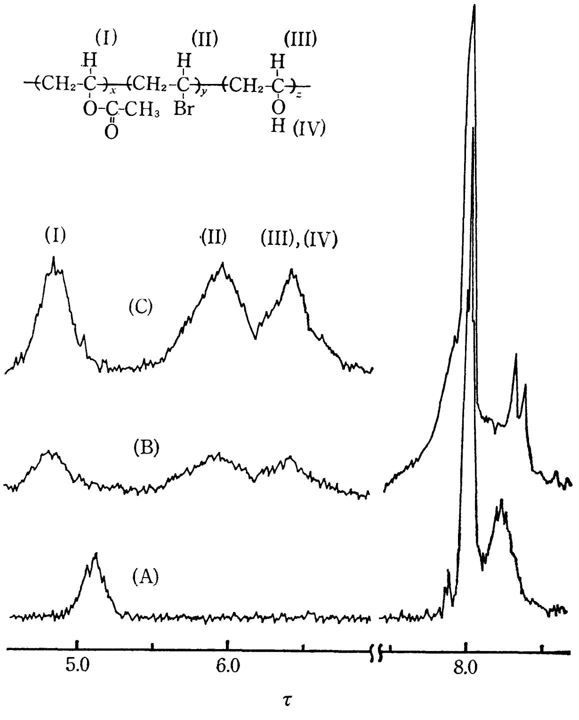


Fig. 8. NMR spectra of (A) PVAc prepared by AIBN, (B) reaction product of PAVE with HBr in AcOH and (C) the slow sweep of B.

On the basis of this assignment, the fraction of the three structural units in the reaction product can be estimated from the intensity ratio of these three methine resonances, assuming that the resonance of the hydroxy proton in the vinyl alcohol

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[13] R. M. Silberstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd Ed., John Wiley & Sons Inc., N. Y. (1963). p. 137.

TABLE 4. COMPOSITION OF THE REACTION PRODUCT OF PAVE AND HBr

No.	$-\left(-CH_2-\underset{OCOCH_3}{CH}-\right)_x-\left(-CH_2-\underset{Br}{CH}-\right)_y-\left(-CH_2-\underset{OH}{CH}-\right)_z-$			Elementary Analysis* (%)		
	x	y	z	C	H	Br
K-15	1	1.38	0.67	36.99 (37.40)	4.92 (4.99)	41.88 (40.88)
B04	1	1.34	0.60	36.99 (38.19)	4.90 (5.10)	41.85 (39.11)

* Values in parentheses are calculated for the ratio x, y, and z determined.

unit overlaps with its methine resonance at 6.40 τ. The results are shown in Table 4. The elementary compositions calculated for the determined ratio of the three structural units is in good agreement with that observed by the analysis. This shows the validities of the assignment of the NMR spectrum and the structure of the reaction product presumed to be a ternary copolymer of vinyl acetate, vinyl alcohol, and vinyl bromide.

Discussion

Two double bonds in AVE are expected to participate in the polymerization reaction, either independently or together as in the cyclopolymerization of α,ω-diolefin.[14] However, all the PAVEs obtained by $BF_3 \cdot OEt_2$ under various conditions gave NMR spectra in which the resonances characteristic of the vinyl protons disappeared and the peaks due to the protons of the allyl double bond remained unchanged (Fig. 1). This shows that, by means of the $BF_3 \cdot OEt_2$ catalyst, this monomer polymerized exclusively through the vinyl double bond, leaving the allyl double bond unaffected during the polymerization. The polymer could subsequently be cross-linked through the allyl side chains over a long period at room temperature.

The solution viscosity of the PAVE obtained in toluene at −78°C increased with the increase in the monomer concentration (Fig. 5). This suggests that there is no or only a little chain-transfer reaction to the monomer in the polymerization. The marked decrease in the viscosity of the polymer with a rise in the polymerization temperature (Fig. 3) indicates that the contribution of the chain-transfer or termination reaction becomes greater at elevated temperatures. The decrease in the viscosity with an increase in the catalyst concentration (Fig. 4) will indicate the existence of a chain-transfer reaction to the catalyst. However, this is not conclusive, because a temporary elevation of the temperature in the reaction mixture was observed at a higher concentration of catalyst; this may cause the depression of the molecular weight of the polymer.

A number of NMR studies of poly(alkyl vinyl ether) have been reported, and the tacticity of polymer has been determined with[15] and without[2,16,17] the spin decoupling technique. In this work we have determined the fraction of the tactic dyad in PAVE by analysis of the decoupled spectrum, in which the resonance of β-protons decoupled from the α-proton was sensitive to the stereochemical configuration.

Generally the cationic polymerization at a low temperature gave an isotactic polymer in a non-polar solvent and a syndiotactic one in a polar solvent. This was explained by the ion-pair mechanism in a non-polar system and by the free-ion propagation in a polar system.[11,3] *t*-Butyl vinyl ether[11] and trimethylsilyl vinyl ether[18] gave isotactic polymers in toluene and rather syndiotactic polymers in nitroethane or methylene chloride. On the other hand, in the polymerization of benzyl vinyl ether[2] a fairly isotactic polymer was obtained even in a polar solvent and the isotacticity of the polymer decreased only slightly at elevated temperatures. The specific participation of the benzyl group was suggested in this stereoregulated polymerization.

Allyl vinyl ether gave a highly isotactic polymer at −78°C in toluene, and the decrease in the isotacticity was very small at higher temperature (Fig. 3), although it was observed remarkably in a polar medium (Table 1 and Fig. 6). This behavior of AVE may be attributable to the similarity between the allyl group and the benzyl group in benzyl vinyl ether.

It has been previously reported that an isotactic poly (benzyl vinyl ether) gave an isotactic poly(vinyl alcohol) by debenzylation reaction with HBr in toluene.[19] The reaction of PAVE with HBr in

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14) N. D. Field, *J. Org. Chem.*, **25**, 1006 (1960).

15) K. C. Ramey, N. D. Field and A. E. Borchert, *J. Polym. Sci.*, **A3**, 2885 (1965).

16) S. Brownstein and D. M. Wiles, *ibid.*, **A2**, 1901 (1964).

17) K. C. Ramey, N. D. Field and I. Hasegawa, *ibid.*, **B2**, 865 (1964).

18) S. Murahashi, S. Nozakura, M. Sumi, H. Yuki and K. Hatada, *Kobunshi Kagaku*, **23**, 605 (1966).

19) S. Murahashi, H. Yuki, T. Sano, U. Yonemura. H. Tadokoro and Y. Chatani, *J. Polym. Sci.*, **62**, No. 174, S 77 (1962).

toluene or dioxane gave an insoluble product containing a considerable amount of bromine. It was probably cross-linked through the allyl side chains by a cationic mechanism. In the reaction in acetic acid, the product was revealed to be a ternary copolymer of vinyl alcohol, vinyl acetate, and vinyl bromide by IR and NMR spectroscopies. The vinyl acetate unit must have been produced by a further reaction of the vinyl alcohol unit and acetic acid. It is not certain at present whether the vinyl bromide unit was formed by the reaction of the vinyl alcohol unit and HBr or by the cleavage of the ether linkage by HBr on the opposite side.

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