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Short Branching in Poly(vinyl alcohol). I. Syntheses of the Model Polymers

Yotaro MORISHIMA, Yoshio IRIE, Hiroyuki IIMURO, and Shun-ichi NOZAKURA

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka 560, Japan.

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ABSTRACT: Syntheses of model polymers of poly(vinyl alcohol)(PVA) having short branches are described. The copolymerization of vinyl acetate(VAc) and 2,4-diacetoxy-1-butene(DAB) followed by subsequent hydrolysis gave a model PVA with short branches of one monomer unit in length. In the same manner, a model PVA having short branches of two monomer units in length was obtained from the copolymer of VAc and 1,3,5-triacetoxy-5-hexene(TAH). The monomer reactivity ratios are $r_{VAc}=1.63\pm0.07$ and $r_{DAB}=0.52\pm0.13$ for the VAc—DAB copolymerization at 0°C, and $r_{VAc}=1.49\pm0.03$ and $r_{TAH}=0.67\pm0.14$ for VAc—TAH at 60°C.

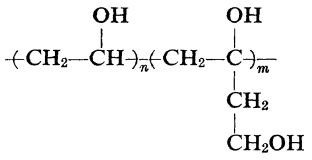
KEY WORDS Poly(vinyl alcohol) / Short Branching / Copolymerization / 2,4-Diacetoxy-1-Butene / 1,3,5-Triacetoxy-5-Hexene /

Among the structural characteristics such as molecular weight and its distribution, head-to-tail structures, terminal groups, stereoregularity, and branching of poly(vinyl alcohol)(PVA), many points still remain unsolved and ambiguous with reference to the problem of branching. The branches in PVA may be of two types, *i.e.*, long branches of an average size comparable with that of the main chain, and short branches of only a few monomeric units in length. The formation of the long branches in PVA was investigated kinetically by the present authors[1,2] and its presence was established experimentally. With regard to short branching however, no experimental techniques to prove its existence in PVA are known. There is no doubt that the short branches in PVA might affect its properties and, when some properties of PVA cannot be accounted for by the known structural factors as mentioned above, short branches have often been discussed as a possible factor.[3,4]

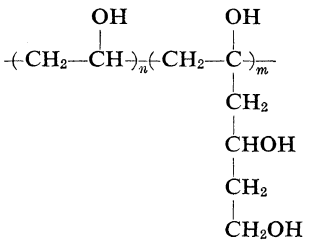
This work was undertaken to develop methods of measuring the amount of short chain branching in PVA and to clarify its effects on the polymer properties. The first approach is to synthesize a model PVA having a known amount of branches of known length.

The back-biting mechanism was proposed by Roedel[5] to explain the formation of short branches in polyethylene, being due to an intramolecular hydrogen-transfer reaction occurring *via* the transient 6-membered ring formation. This mechanism could be specific in favor of short branches of the butyl type. The double back-biting mechanism was also proposed[6] in which 1,5 back-biting is followed by addition of one monomer and by subsequent 1,5 back-bitting. This route would lead to polyethylene with short branches of the ethyl type.

It is assumed by analogy with the ethylene polymerization that the probable short branching structures in PVA are one or two monomer units in length. In this paper, the syntheses of the following model polymers are described.

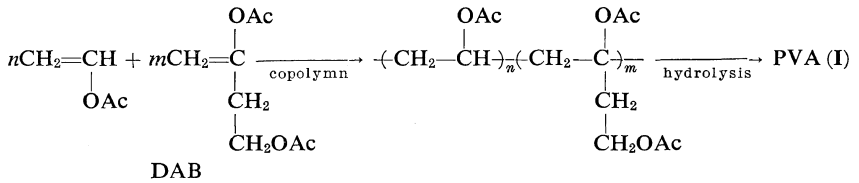


PVA (I)



PVA (II)

Models PVA(**I**) and PVA(**II**) were prepared by hydrolysis of the copolymer of vinyl acetate and 2,4-diacetoxy-1-butene(DAB) and that of vinyl acetate and 1,3,5-triacetoxy-5-hexene(TAH), respectively. Monomers DAB and TAH are new compounds.



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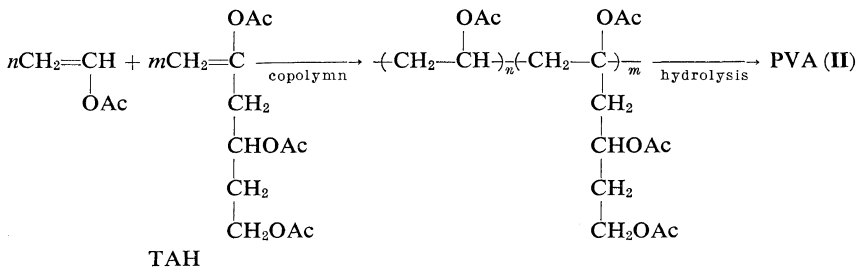

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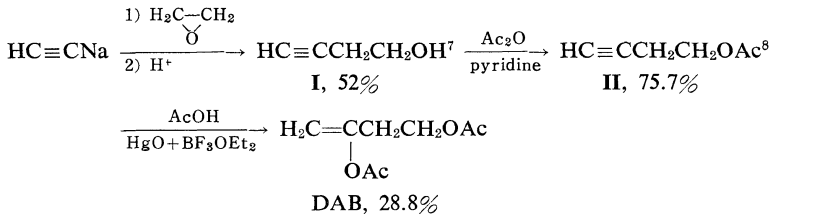
RESULTS AND DISCUSSION

Synthesis of 2,4-Diacetoxy-1-Butene

Monomer DAB was prepared according to the following series of reactions.



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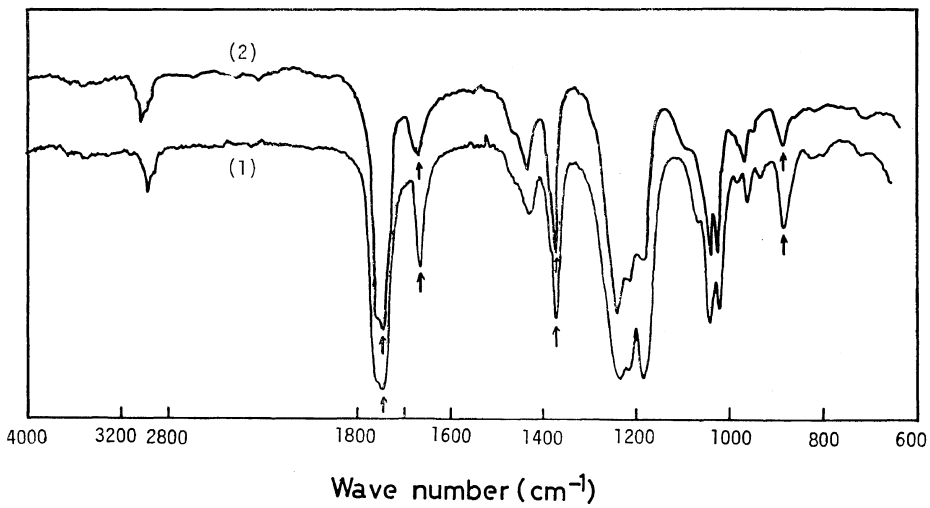


Figure 1. IR spectra of 2,4-diacetoxy-1-butene(DAB)(1) and 1,3,5-triacetoxy-5-hexene(TAH)(2).

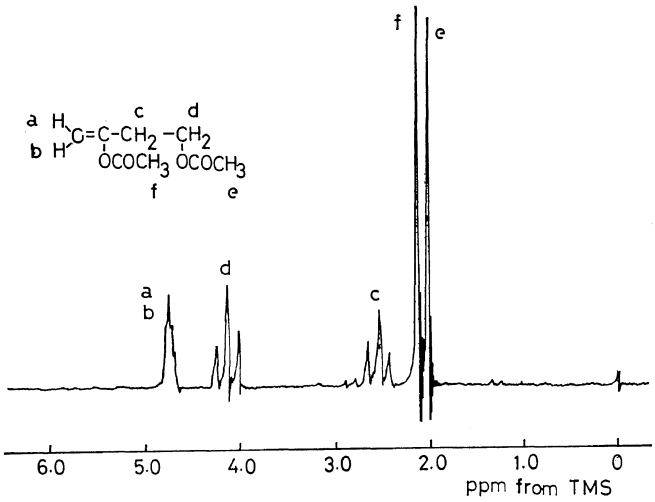


Figure 2. NMR spectrum of 2,4-diacetoxy-1-butene(DAB).

Figure 1 shows an IR spectrum of DAB. The characteristic absorption bands at 1745, 1665, 1373, and 885 cm^{-1} were assigned to $\nu C{=}O$(ester), $\nu C{=}C$(vinyl), $\delta_s CH_3$(acetyl), and $\delta CH(CH_2)$, respectively. In Figure 2 is shown an NMR spectrum of DAB together with the assignments of the resonance peaks.

In the last step of the synthesis (addition of acetic acid to 4-acetoxy-1-butyne(**II**)), 1-acetoxy-3-butanone(**III**) was formed in considerable quantity as a by-product. **III** was isolated as a lower boiling distillate in the fractional distillation of the reaction mixture. According to the suggestion of Hennion and Nieuwland[9] one of the possible route for the formation of **III** might be as follows

$$\underset{\text{DAB}}{CH_2{=}C(OAc)CH_2CH_2OAc} \xrightarrow{AcOH} \left(CH_3C(OAc)_2CH_2CH_2OAc \right) \xrightarrow[\text{heat}]{-Ac_2O} \underset{\textbf{III}}{CH_3C(=O)CH_2CH_2OAc} \qquad (4)$$

This side reaction could be responsible for the low yield of DAB.

Synthesis of 1,3,5-Triacetoxy-5-Hexene(TAH)

Four kinds of approach were attempted for the preparation of 1,3-diacetoxy-5-hexyne(**V**) which is the precurser of TAH.

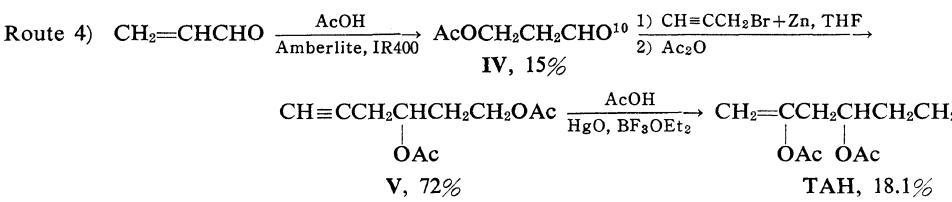
$$\text{Route 1)}\quad ClCH_2CH{=}CH_2 \xrightarrow[H_2SO_4,\ Ac_2O]{(CH_2O)_n} \underset{37\%}{ClCH_2CH(OAc)CH_2CH_2OAc}$$

$$\xrightarrow[2)\ H^+]{1)\ CH{\equiv}CNa} CH{\equiv}CCH_2CH(OH)CH_2CH_2OH \longrightarrow \underset{\textbf{V}}{CH{\equiv}CCH_2CH(OAc)CH_2CH_2OAc} \qquad (5)$$

$$\text{Route 2)}\quad BrCH_2CH{=}CH_2 \xrightarrow[H_2SO_4]{(CH_2O)_n} \underset{70\%}{BrCH_2-\langle O^{-}\rangle O} \xrightarrow[\text{or } CH{\equiv}CLi]{CH{\equiv}CNa} CH{\equiv}CCH_2-\langle O^{-}\rangle O \xrightarrow[H_2SO_4]{Ac_2O} \textbf{V} \qquad (6)$$

$$\text{Route 3)}\quad CH{\equiv}CMgBr + BrCH_2CH{=}CH_2 \xrightarrow[THF]{CuCl} \underset{32\%}{CH{\equiv}CCH_2CH{=}CH_2}$$

$$\xrightarrow[H_2SO_4]{(CH_2O)_n} CH{\equiv}CCH_2-\langle O^{-}\rangle O \longrightarrow \textbf{V} \qquad (7)$$



In route 1, the first step is Prins reaction.[11,12] The reaction of 2,4-diacetoxybutyl chloride and sodium acetylide gave three main fractions in the fractional distillation all of which are composed of complicated mixtures. IR spectra indicated that all the fractions contain ethynyl group and alcohol groups. It appeared impracticable, however, not only to isolate but to identify the desired compound in the mixture. In route 2, 4-bromomethyl-1,3-dioxane was prepared according to the literature[12] in which the preparation of 4-chloromethyl-1,3-dioxane was described. The ethynylation of 4-bromomethyl-1,3-dioxane was unsuccessful. The starting material was recovered unreacted after the treatment with sodium acetylide or lithium acetylide in liquid ammonia. In route 3, ethynylmagnesium bromide[13] was reacted with allyl bromide in the presence of a catalytic amount of cuprous chloride to yield allylacetylene. This material was then subjected to the Prins reaction under reaction conditions according to the literature.[14] The fractional distillation of the reaction mixture gave a distillate at a boiling range of 70—75°C/2 mmHg. An IR spectrum, however, indicated that this product was not the desired compound, *i.e.*, ether and carbonyl groups were observed but not the ethynyl group. Route 4 was a successful route for the preparation of TAH. The details are described in the experimental part of this report.

Figure 1 shows an IR spectrum of TAH. All the characteristic absorption bands are completely consistent with those of DAB. An NMR spectrum of TAH is shown in Figure 3 together with the assignments of the resonance peaks. In the last step of the TAH synthesis, two types of ketones were obtained as the result of side reactions. One of those was 1,3-diacetoxy-5-hexanone(**VI**) which was isolated by fractional distillation of the reaction mixture. This compound could be obtained in a similar reaction to eq 4. Another ketone was 1-acetoxy-*trans*-3-

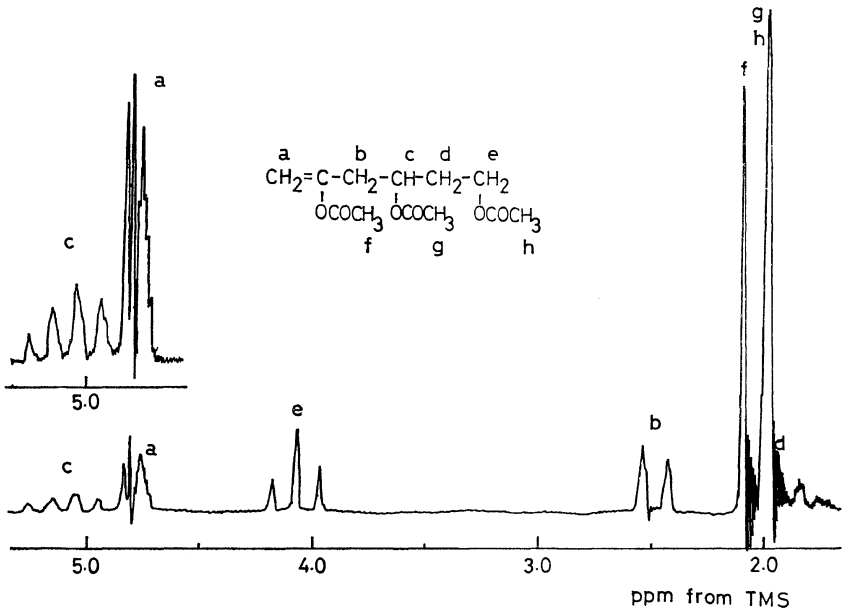
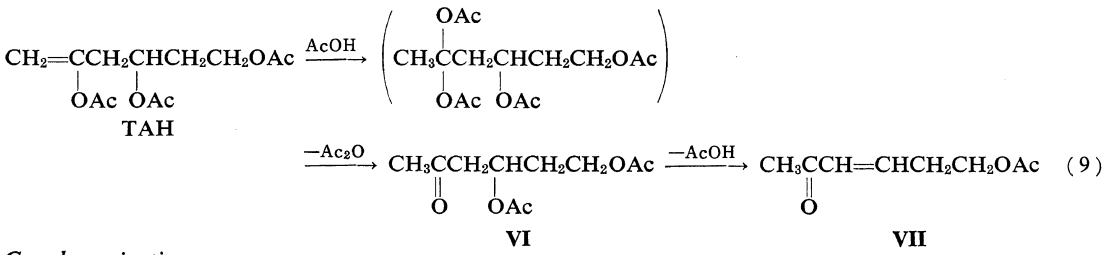


Figure 3. NMR spectra of 1,3,5-triacetoxy-5-hexene(TAH).

hexene-5-one(**VII**), being isolated also by the fractional distillation. Compound **VII** is considered to be formed by the elimination of acetic acid from **VI** (eq 9). The methylene proton at the 4-position of **VI** might be active enough to cause the elimination.



Copolymerization

The reaction conditions and results are summarized in Table I for the bulk copolymerization of ^{14}C-labelled V*Ac(M_1) and DAB(M_2). Copolymerization was carried out at 0°C to minimize the undesired formation of branches. The copolymer composition was determined by radioactivity measurements and Figure 4 shows the copolymer composition curve. The monomer reactivity ratios determined from a Fineman—Ross plot by use of the least-squares method are $r_1=1.63\pm0.07$ and $r_2=0.52\pm0.13$. The rate of copolymerization was reduced with increasing DAB contents in comparison to the homopolymerization of vinyl acetate. The solubility of the copolymer was quite similar to that of poly(vinyl acetate).

In Table II are given the results of the copolymerization of V*Ac(M_1) and TAH(M_2) at 60°C. This copolymerization was unsuccessful at 0°C because the rate of copolymerization was extremely low compared with that of the V*Ac—

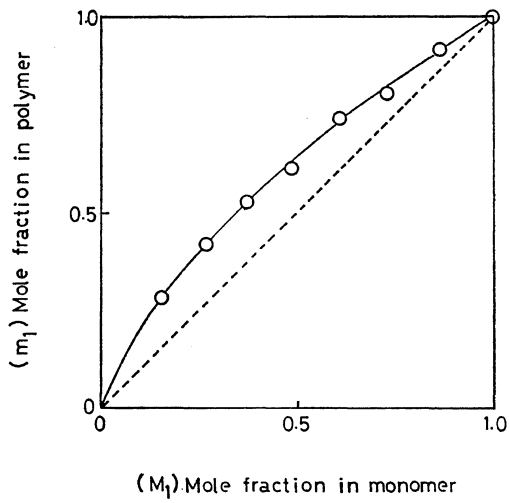


Figure 4. Copolymer composition curve for V*Ac-(M_1) and DAB(M_2); initiated by (n-Bu)$_3$B—O_2 at 0°C.

Table I. Bulk copolymerization of V*Ac(M_1) and DAB(M_2) at 0°C initiated by (n-Bu)$_3$B—O_2[a]

M_1, mmol	M_2, mmol	Conversion, %	Polymn time, hr	M_1 mol fract in copolymer
52.66	0	15.07	0.4	1.00
50.72	7.46	18.46	3.5	0.920
41.35	14.63	7.27	5.0	0.806
36.42	22.87	5.30	6.5	0.748
30.17	30.62	3.28	10	0.615
8.57	14.04	2.95[b]	28	0.530
5.86	15.50	7.51[b]	48	0.422
3.76	19.66	4.43[b]	48	0.285
0	23.51	2.91[b]	144	0

[a] (n-Bu)$_3$B, 0.2 mmol; air, 0.5 m*l*.
[b] (n-Bu)$_3$B, 0.5 mmol; air, 1.0 m*l*.

Table II. Bulk copolymerization of V*Ac(M_1) and TAH(M_2) at 60°C initiated by AIBN[a]

M_1, mmol	M_2, mmol	Conversion, %	Polymn time, hr	M_2 mol fract in copolymer
20.76	0	17.2[b]	0.25	1.00
18.58	1.22	39.4	6.5	0.959
18.49	2.38	70.6	25.5	0.902
16.94	3.32	36.0	29	0.866
16.51	4.38	40.4	35.5	0.852
16.69	5.87	32.3	78	0.815
14.77	6.41	23.0	73	0.761
13.07	8.88	11.2	94.5	0.696
11.91	8.86	33.0	113	0.682
8.59	10.89	12.2	113	0.554

[a] [AIBN], 0.5 mol%.
[b] [AIBN], 0.25 mol%.

DAB system even at low concentrations of TAH. The bulk homopolymerization of TAH at 60°C using 0.5 mol% of AIBN did not give any detectable amount of polymer. It seems that TAH is lower in reactivity than DAB as shown in the rate of copolymerization mentioned above and also in the fact that DAB gave a low yield of homopolymer (Table I) even at 0°C. Monomer reactivity ratios of TAH, as will be shown below, are essentially the same as those of DAB. Therefore, the low homopolymerizability of TAH might be due to the lower reactivity of the propagating TAH radical presumably because of steric hindrance. Figure 5 is a copolymer composition curve. Figure 5 shows that the monomer composition in the copolymer is close to that in the monomer feed. A Fineman—Ross plot can be applied even to high conversion data. The monomer reactivity ratios thus determined by use of the least-squares method are $r_1=1.49\pm0.03$ and $r_2=0.67\pm0.14$. All the copolymers are soluble in the same solvents as PVAc.

PVA(I) and PVA(II)

Figure 6 shows the IR spectra of PVA(I) and

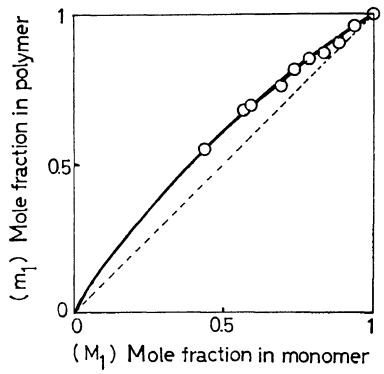


Figure 5. Copolymer composition curve for V*Ac-(M_1) and TAH(M_2); initiated by AIBN at 60°C.

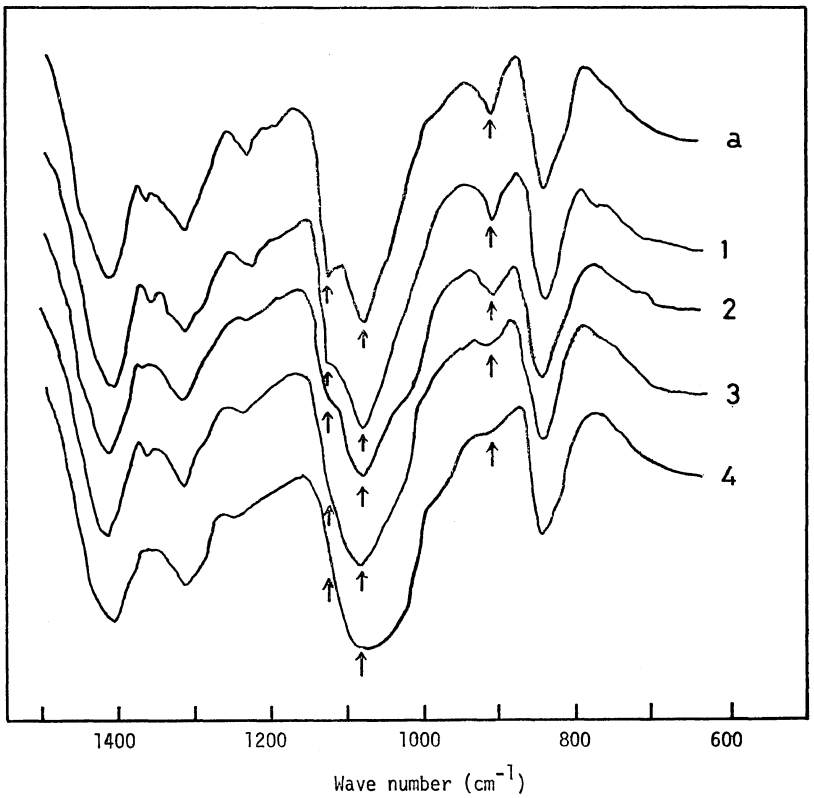


Figure 6. IR spectra of PVA derived from the copolymers of V*Ac—DAB and V*Ac—TAH: a, PVA; 1, PVA(I), DAB mol fract 0.055; 2, PVA(I), DAB mol fract 0.130; 3, PVA(II), TAH mol fract 0.065; 4, PVA(II), TAH mol fract 0.129.

PVA(**II**), derived from the copolymers of V*Ac—DAB and V*Ac—TAH, respectively, together with that of PVA derived from PVAc. All the spectra were measured with films. It is clearly observed that the 1093-cm^{-1} band, which is assigned to the C—O stretching vibration of the secondary alcohol, becomes broader with increasing comonomer content. This is ascribable to the mixing of the C—O stretching bands of the primary and tertiary alcohols which result from the incorporation of short branching units in PVA. The intensity of the 916- and 1141-cm^{-1} band, which are very sensitive to crystallinity,[15-18] showed a decrease as the comonomer content increased in both the cases of PVA(**I**) and PVA(**II**). This fact suggests that the incorporation of a minor amount of short branching units into PVA decreases its crystallinity and these facts are consistent with the melting point data. In Table III are listed the melting point of PVA(**I**) and PVA(**II**) measured with DSC. It is obvious that the melting point falls remarkably with the incorporation of increasing short branching units. This tendency is more noticeable in the case of PVA(**II**), that is, the DSC peak due to the melting point was not observed when the mole fraction of short branching unit is more than 0.065. Further study of the chemical structure and the characterization of PVA(**I**) and PVA(**II**) will be described in a subsequent paper.

Table III. Melting point of PVA(**I**) and PVA(**II**)

PVA(**I**)[a]		PVA(**II**)[b]	
DAB mol fract	mp, °C	TAH mol fract	mp, °C
0	232	0	232
0.055	221	0.041	202
0.075	219	0.065	nil
0.130	nil	0.085	nil
		0.129	nil

[a] Polymerization condition of parent polymer; bulk, $(n\text{-Bu})_3B—O_2$, at 0°C.
[b] Bulk, AIBN, at 60°C.

EXPERIMENTAL

Synthesis of DAB

1-Butyne-4-ol(**I**) was prepared according to a literature.[7] From 45 g (2 mol) of sodium metal in 500 m*l* of liquid ammonia and 115 g (2.6 mol) of ethylene oxide, 72.8 g (52%) of the product was obtained: bp 60°C (37 mm).

4-Acetoxy-1-butyne(**II**) was obtained from the acetylation of I.[8] I(92.8 g) was acetylated with a mixture of acetic anhydride (150 m*l*) and pyridine (135 m*l*) at 100°C for 5 hr. The yield was 112.4 g (75.7%): bp 50°C (16 mm).

DAB was obtained by the addition of acetic acid to the ethynyl group of **II**. This reaction was carried out in accordance with the method used in the preparation of 2-acetoxy-1-hexene.[9] A mixture of 3 g of red mercuric oxide, 2 m*l* of BF_3OEt_2, and 2 m*l* of absolute methanol was warmed at 30°C to partially dissolve the mercuric oxide. To this catalyst was added 35 g (0.85 mol) of acetic acid with vigorous stirring, and then 80 g (0.72 mol) of **II** was added dropwise through a dropping funnel. The addition of **II** required about 1 hr. Stirring was continued for another 2 hr at room temperature. After stirring, the reaction mixture was poured into ice water, neutralized by adding K_2CO_3, and extracted with ether. The extract was dried over anhydrous $MgSO_4$, the ether removed by distillation, and the residue distilled under reduced pressure. The yield of DAB was 28.5 g (28.8%): bp 95°C (11 mm).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.81%; H, 7.03%
Found: C, 55.92%; H, 7.04%

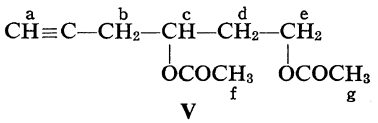
1-Acetoxy-3-butanone(**III**), formed as a by-product, was isolated as a lower boiling fraction in the fractional distillation of the reaction mixture: IR 1720(ketone $\nu C{=}O$), 1745 cm^{-1}(ester $\nu C{=}C$); NMR δ 2.0(s, 3), 2.2(s, 3), 2.8(t, 2), 4.3 ppm(t, 2).

Synthesis of TAH

β-Acetoxypropionaldehyde(**IV**) was prepared according to Asao's method.[10] From 110 g of acrolein and 240 g of acetic acid was obtained 34 g (15%) of **IV**: bp 56.5°C (6 mm); mp 128—130°C(2,4-dinitrophenylhydrazone).

1,3-Diacetoxy-5-hexyne(**V**) was prepared by the reaction of **IV** and propargyl bromide in the presence of zinc followed by acetylation with acetic anhydride. Prior to the reaction, the zinc dust was activated by treating with 2-% hydrochloric acid for a few minutes, washed succes-

sively with water, methanol and ether, and dried under reduced pressure. A solution of 130 g of propargyl bromide and 100 g of **IV** in 200 m*l* of dried ether was added dropwise with stirring at room temperature to the mixture of 70 g of activated zinc and 130 m*l* of dried tetrahydrofuran. The addition required 4 hr. Stirring was continued for another 2 hr, the reaction temperature being kept between 15 and 25°C. Acetic anhydride (110 g) was then added dropwise at the temperature below 30°C to the reaction mixture with stirring over a period of 2 hr. When the addition of acetic anhydride was complete, the reaction mixture was diluted with ether, washed several times with water, dried over anhydrous $MgSO_4$, then distilled under reduced pressure, giving 122 g (72%) of **V**: bp 103—107°C (0.25 mm); n_D^{25} 1.444; d_4^{25} 1.066; IR 3280 (ester νC—H), 2970, 2130 (ethynyl νC≡C), 1742 cm^{-1} (ester νC=O); NMR δ, 2.17(d, 1, C$\underline{H}^a$), 2.49(q, 2, C$\underline{H}_2^b$), 4.98(m, 1, C$\underline{H}^c$), 2.00(q, 2, C$\underline{H}_2^d$), 4.12(t, 2, C$\underline{H}_2^e$), and 1.99, 2.02 ppm (s, 6, C$\underline{H}_3^f$, C$\underline{H}_3^g$).



V

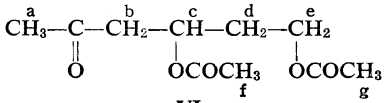
Anal. Calcd for $C_{10}H_{12}O_4$: C, 60.59%; H, 7.12%.
Found: C, 60.45%; H, 7.00%.

TAH was prepared by the addition reaction of acetic acid to the ethynyl group of **V** in accordance with the method of Hennion and Nieuwland.[9] The mixture of 3 g of red mercuric oxide, 2 m*l* of BF_3OEt_2, and 3 g of absolute methanol was warmed at 40°C to partially dissolve the mercuric oxide. To this catalyst was added 35 g of acetic acid with stirring over a period of 50 min. After addition of the acetic acid, 19 m*l* of this reaction mixture was added to 50 g of **V** at the rate of 0.5 m*l*/min to maintain the reaction temperature at 55°C. The reaction mixture was stirred at the same temperature for another 3 hr after the addition was complete, then poured into water and extracted with chloroform. 1,3-Diacetoxy-5-hexanone(**VI**) was produced as a by-product whose boiling point is very close to that of TAH. Treatment with aqueous $NaHSO_3$ was found to be the best method for the removal of **VI**. The chloroform extract was dissolved into ether after the chloroform was evaporated. The ethereal solution was shaken successively with an aqueous 15-% $NaHSO_3$ solution and water, dried over $MgSO_4$, and then distilled. After simple distillation under reduced pressure, the distillate was subjected to rectification through a fractionating column packed with a 40-cm length of glass helices. The yield of TAH was 9.1 g (18.1%): bp 87°C (0.1 mm); n_D^{25} 1.4453; d_4^{25} 1.1081.

Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.81%; H, 7.03%
Found: C, 55.90%; H, 7.04%

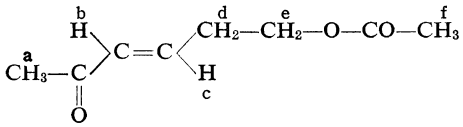
When the reaction mixture was not treated with aqueous $NaHSO_3$, **VI** was isolated as a slightly lower boiling distillate than TAH by the repeated fractional distillation of the reaction mixtures: bp 93°C (0.3 mm); IR 1745 (ester νC=O), 1725 (ketone νC=O), and 1430, 1375 cm^{-1} (methyl δ_sC—H); NMR δ 2.12(s, 3, C$\underline{H}_3^a$), 2.70(d, 2, C$\underline{H}_2^b$), 5.23(m, 1, C$\underline{H}^c$), 1.88(q, 2, C$\underline{H}_2^d$), 4.08(t, 2, C$\underline{H}_2^e$), and 1.96, 1.98 ppm (s, 6, C$\underline{H}_3^f$, C$\underline{H}_3^g$).

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54%; H, 7.46%
Found: C, 55.26%; H, 7.53%



VI

1-Acetoxy-*trans*-3-hexene-5-one(**VII**) was also isolated as a lower boiling distillate: bp 62—70°C (0.3 mm); IR 1735 (ester νC=O), 1675(vinylene νC=C), 1630(ketone νC=O), 1375, 1430 (methyl δ_sC—H), and 965 cm^{-1} (*trans*-vinylene δC—H); NMR δ 1.8(s, 3, C$\underline{H}_3^a$), 5.9(d, 1, C$\underline{H}^b$), 6.6(m, 1, C$\underline{H}^c$), 2.4(q, 2, C$\underline{H}_2^d$), 4.0(t, 2, C$\underline{H}_2^e$), and 2.0 ppm (s, 3, C$\underline{H}_3^f$).



VII

Copolymerization

Radioactive vinyl-1,2-^{14}C acetate (V*Ac) was used as a comonomer for the sake of accurate determination of the copolymer composition. The V*Ac obtained from England Nuclear Corp. was washed several times with an aqueous 5-% $NaHSO_3$ solution, washed with water, dried with $CaCl_2$, and then distilled through a Widmer

column three times; bp 72.5°C. The specific radioactivity of V*Ac used for this experiment was 0.05 μCi/g. Copolymerization of V*Ac and DAB was carried out at 0°C in the presence of $(n\text{-Bu})_3\text{B—O}_2$ as an initiating system using a Schlenk tube. After the polymerization, the contents of the tube were poured into a large excess of *n*-hexane to precipitate the polymer. The separated polymer was purified by reprecipitation into *n*-hexane from an acetone solution, dried, dissolved in benzene, and recovered by a freeze-drying technique.

Copolymerization of V*Ac and TAH was performed as follows. An ampoule containing known amounts of V*Ac, TAH and 2,2′-azobisisobutyronitrile was degassed several times in a vacuum system ($<10^{-3}$ mmHg) and sealed. Polymerizations were carried out in a thermostat at 60°C. After the required time of polymerization, the ampoule was opened, and the contents diluted with acetone and poured into a large excess of a mixture of ether and petroleum ether (1 : 1, v/v) with stirring to precipitate the polymer. The separated polymer was purified three times by reprecipitation into the mixture of ether and petroleum ether from an acetone solution, dried, dissolved in benzene, and recovered by a freeze-drying technique.

Hydrolysis of Copolymer

Ten grams of copolymer were dissolved in a mixture of 200 m*l* of acetone and 500 m*l* of methanol, then 10 m*l* of an aqueous 25-% NaOH solution was added. The reaction mixture was held at room temperature overnight until the precipitation of PVA was completed. The PVA was separated, washed by methanol, dissolved into water, and recovered by a freeze-drying technique.

Measurements

IR spectra were measured on a HITACHI EPI-2 spectrometer. NMR spectra were measured in a 10-% CCl_4 solution using a VARIAN A-60 spectrometer. The radioactivity of the copolymer was measured by using a PACKARD MODEL 3002 scintillation spectrometer. For the preparation of the sample solution for the radioactive counting, about 0.1 g of copolymer was dissolved into 10 m*l* of toluene containing scintillators (5 g of PPO and 0.3 g of dimethyl POPOP per liter toluene). The melting point of the PVA(**I**) and PVA(II) was measured with a RIGAKU DENKI YDS-TYPE differencial scanning calorimeter, using 8 mg of samples at the program rate of 20°C/min.

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