

Several Reactions of Poly(vinyl alcohol)-Type Acetaldehyde Polymer

TSUTOMU MATSUBARA* and TATSUYA IMOTO, *Faculty of Engineering, Osaka City University, Osaka, Japan*

Synopsis

The preparation of the acetaldehyde polymers (PACH) having a poly(vinyl alcohol)-type structure and the thermal degradation of PACH have been reported previously. This paper will describe detailed aspects of several reactions of PACH. Copolymerization of PACH with toluene diisocyanate (TDI) was performed both thermally and catalytically. When piperidine was used as catalyst, the rate of reaction between PACH and TDI was found to depend on the concentration of both the active hydrogen of PACH and the isocyanate group of TDI. Acid and alkali treatment of PACH were carried out. On treatment with sulfuric acid, white polymers with good spinnability were obtained. The copolymerizations of acetaldehyde with *n*-butylaldehyde were performed in the presence of sodium amalgam as catalyst. The reaction products were colorless, viscous liquids and assumed from the infrared and NMR spectra, elemental analyses, molecular weights and solubility tests to be aldol condensation-type copolymers.

INTRODUCTION

In previous papers, it has been reported that an acetaldehyde polymer of poly(vinyl alcohol)-type (PACH) is obtained by the polymerization of acetaldehyde in the presence of such catalysts as alkali metal amalgam,^{1,2} alkaline earth metal amalgam,³ and evaporated sodium,⁴ and the degradation of PACH has been also studied.⁵

Meanwhile, Modena et al.⁶ reported that a polymer which is the same as polyacetaldehyde catalyzed by sodium amalgam was obtained by using potassium carbonate as catalyst, and that the structure of this polymer was not of the poly(vinyl alcohol) type in view of NMR analysis.

On the other hand, from the precise analysis of infrared and NMR spectra of PACH and its acetylated product, and the measurement of the concentration of active hydrogen of PACH, we have obtained further evidence supporting our assumption for the structure of PACH of the poly(vinyl alcohol) type.⁷

The molecular weight of PACH obtained to date is too low for the polymer to be considered for industrial use. However, PACH is an active prepolymer which has several active hydrogens and an active carbonyl group. We tried the copolymerization to increase the molecular weight and to produce a polymer having industrial utility.

* Present address: Chisso Corporation, Chiyoda-ku, Tokyo, Japan.

This paper will describe in detail several reactions of PACH: the thermal and catalytical copolymerization of PACH with toluene diisocyanate (TDI), the acid or alkaline treatment of PACH, and the copolymerization of acetaldehyde (AcH) with *n*-butylaldehyde (*n*-BA) with the use of sodium amalgam as catalyst.

Copolymerization of PACH with TDI

Many methods of synthesis of polyurethane by polymerization of diisocyanate with polyhydric alcohol have been reported⁸ and are already being used commercially. However, there are few reports of copolymerization of a polyhydric alcohol containing an aldehyde group with diisocyanate. A patent⁹ reports that mixtures of tertiary amine and some aldehydes having 1–10 carbons, for example, benzaldehyde, act as catalysts for the preparation of polyurethane. Another patent¹⁰ reports that a polymer is obtained by polymerization of organic aldehyde with isocyanate. On the other hand, there have been many reports and patents on reactions other than polymerization of isocyanate and aldehyde, especially formaldehyde. Concerning the reaction of acetaldehyde with isocyanate, Takita et al.¹¹ reported that the aldehyde double bond $>C = O$ with $-N = C <$ forms a copolymer at low temperature in presence of anionic catalyst.

Meanwhile, in this paper, copolymerizations of PACH with TDI performed both thermally and catalytically will be reported. The polymerization products were either white or slightly yellow and assumed to be of polyurethanelike in structure, both from the infrared spectral analyses and the solubility tests. By choosing suitable conditions for this copolymerization, one can prepare a reaction product whose melting point falls within the range of 50–200°C. When piperidine was used as catalyst, the rate of reaction between PACH and TDI was found to depend on the concentrations of both the active hydrogen of PACH [Act. H] and the isocyanate of TDI [NCO].

Acid or Alkali Treatment of PACH

Acid or alkali treatments of PACH were carried out. With sulfuric acid treatment of PACH, a white, spinnable polymer (softening point = 50–62°C) was obtained.

Copolymerization of Acetaldehyde and *n*-Butylaldehyde

Copolymerizations of AcH with *n*-BA were carried out by using sodium amalgam as catalyst for the purpose of comparison with PACH. Tanaka et al.^{12–15} reported the effect of monomer mole ratio and the equilibrium of polymerization system in the copolymerization of AcH with *n*-BA at low temperature (–55 to –78°C) using Et_2AlNPh_2 as catalyst. Besides, there are several reports, including a patent on copolymerization,¹⁶ the polymerization of AcH with glyoxal,¹⁷ the equilibrium between butylalde-

hyde and polybutylaldehyde,¹⁸ and polymerization of butylaldehyde;¹⁹ all of them describe a polyester-type polymer.²⁰

On the other hand, Imoto and Aotani²¹ studied the polyaldol condensation-type polymer of *n*-BA using sodium amalgam as catalyst. At temperatures higher than -30°C , a polyaldol condensation-type polymer of *n*-BA was obtained; at temperatures less than -30°C , a polyether-type polymer was obtained.

In this investigation, copolymerizations of AcH with *n*-BA were carried out in the temperature range of -30 to 5°C with sodium amalgam as catalyst; the reaction products were assumed to be of the polyaldol condensation-type copolymer, in view of the infrared and NMR spectral analyses, and the results of elemental analyses, measurements of molecular weight, and solubility tests.

EXPERIMENTAL

Preparation of Reagents

AcH and sodium amalgam used here were prepared by the previous described method.^{2,3} *n*-BA was prepared by the method of Walling.¹⁹ *n*-BA of commercial first grade was washed with acid sodium carbonate and dried with magnesium carbonate and then purified by distillation two times under dry nitrogen gas.

TDI was purified by distillation under reduced pressure ($105\text{--}108^{\circ}\text{C}/8$ mm Hg).

Piperidine, ethylenediamine, methyl alcohol, ethyl alcohol, benzene, dimethylformamide (DMF), tetrahydrofuran (THF), and anisole of commercial first grade were purified by usual method, respectively.

Preparation of PACH Samples

As shown in Table I, PACH samples were prepared by bulk polymerization of acetaldehyde at 0°C for 20 hr with the use of sodium amalgam or calcium amalgam as catalyst by the previously described method.^{2,3}

TABLE I
PACH samples

	Catalyst	Molecular weight
Copolymerization with TDI	Na-Hg	288 ^a
		300 ^a
Acid or alkali treatment	Na-Hg	358 ^a
	Ca-Hg	462 ^b
Sulfuric acid treatment	Na-Hg	480 ^b
	Ca-Hg	428 ^b
		450 ^b

^a Measured by Takara ebulliometer (benzene as solvent).

^b Measured by cryoscopic method in benzene.

Copolymerization of PACH with TDI

Thermal Copolymerization. The copolymerizations were carried out in a three-necked 100-ml flask fitted with a stirrer, condenser, and dropping funnel. After a fixed amount of PACH (MW = 300) dissolved in anisole as solvent was kept at 100–140°C, a fixed amount of TDI also dissolved in anisole as solvent was dropped through the dropping funnel into the flask. Then the temperature of the copolymerization system was raised slowly to the boiling point of anisole. The mixture suddenly reacted at about the boiling point of anisole, and the reaction system becomes hard. After the reaction product, which was yellow or dark yellow was washed several times with boiling ethyl alcohol and dried under reduced pressure, infrared spectral analysis and measurements of solubility, melting point, and intrinsic viscosity of the polymer were carried out.

Catalytic Copolymerization. Using two PACH samples whose molecular weights were 300 and 358, the efficiency of piperidine and ethylenediamine as catalyst on the copolymerization with TDI was studied. The apparatus used here was the same as that used in the thermal copolymerization. After a slight amount of catalyst (about 0.03 mole/l.) was added to a fixed amount of PACH dissolved in anisole, the system was kept at the desired reaction temperature. Then, a fixed amount of TDI, also dissolved in anisole, was added to this reaction system. The reaction product was added to ethyl alcohol or water, and the polymer was precipitated. The polymer was reprecipitated from the DMF–water system and dried under reduced pressure.

Measurement of Reaction Rate. The copolymerization rate of PACH with TDI was studied with the use of a PACH sample of molecular weight of 288. The reaction was carried out in a three-necked 500 ml. flask fitted with a stirrer and cooler, and THF was used by solvent. The system in which a fixed concentration of PACH and catalyst (piperidine) was dissolved in THF as solvent was kept at 30°C. After a fixed concentration of TDI dissolved in THF at 30°C was quickly added to this system, 15-ml aliquots of the mixture were pipetted out at regular intervals and added to 200 ml of 0.5% aqueous NaCl. After the precipitated polymer was washed with water and dried under reduced pressure, its yield was measured. Because, in this case, excess TDI caused the polymer by-product to react with water, the yield values were corrected against blank tests with water at the same initial concentration of TDI and the same conditions.

Acid and Alkali Treatment of PACH

Before the procedure of concentrating product under reduced pressure (the last step in the preparation of PACH) was carried out, the reaction product was divided into four or five parts and was used in the following experiment. One part was concentrated under reduced pressure by the previous method,² and the value of yield was measured. To the other parts, the aqueous solutions of 1*N* H₂SO₄, 1*N* HCl, or 1*N* NaOH was

added, respectively, and the reaction was continued for 20 min at 15°C. After the reactions, the polymers were extracted by diethyl ether and concentrated under reduced pressure (45°C/5 mm Hg) and the yield measured. When the polymer obtained here was reprecipitated by the methyl alcohol-water system, a white, powderlike reprecipitant was obtained from only the product of sulfuric acid treatment. It was dried under reduced pressure. Measurements of molecular weight and melting point and the infrared spectral analysis were carried out on this product.

Also, sulfuric acid treatments at 70°C and varying reaction times were performed. The yield and molecular weight of the polymer obtained were measured, and infrared spectral and elemental analysis were carried out.

Copolymerization of Acetaldehyde with *n*-Butylaldehyde

In the apparatus previously described,² a fixed amount of prepurified *n*-butylaldehyde was added to a 500-ml reaction vessel previously flushed with dry nitrogen gas and cooled to -30°C. Then, purified AcH monomer was added. After the previously weighed sodium amalgam was quickly added as catalyst, the temperature of the reaction system was raised slowly until the desired reaction temperature was attained, at which the system was then left for 20 hr. The reaction mixture was treated as described previously. The polymer obtained here was a colorless and viscous liquid. Infrared and NMR spectral analyses were carried out, the molecular weight and solubility in several solvents measured.

RESULTS AND DISCUSSION

Copolymerization of PACH with TDI

Thermal Copolymerization. The results of thermal copolymerization are shown in Table II.

TABLE II
Thermal Copolymerization of PACH with TDI^a

No.	PACH		TDI, g	Yield, g	[η] (in DMF, 30°C), dl/g	Appearance
	MW	Amount, g				
TDI-1	300	8.6	22.0	30		Dark yellow powder
TDI-2	300	15.0	22.0	37	0.11	Dark yellow powder
TDI-3	300	15.0	22.0	22		Dark yellow powder
TDI-4	300	15.0	22.0	15	0.09	Dark yellow powder

^a At 154°C, in anisole.

TABLE III
Catalytic Copolymerization of PACH with TDI

	PACH		TDI, g	Catalyst	Solvent	Temp, °C	Time, hr	Yield, g	[η] (DMF, 30°C dl/g	Mp, °C
	MW	Amount, g								
TDI-5	300	7.5	15.0	Ethylene- diamine	Toluene	35	3	1		
TDI-6	300	6.0	12.0	Piperidine	Toluene	35	3	3	0.05	62-64
TDI-7	300	5.0	8.0	Piperidine	THF	35	3	10		74-77
TDI-8	358	3.2	4.2	Piperidine	THF	30	1	7	0.08	>153
TDI-9	358	4.0	4.5	Piperidine	THF	30	1	8		>145

At low PACH/TDI ratios (TDI-1, TDI-2), the product is obtained almost quantitatively; however, in the case of runs TDI-3 and TDI-4, this is not so. The polymer obtained is a yellow or dark yellow, and easily soluble in DMF, but slightly soluble in hot *m*-cresol and insoluble in hot water, benzene, chlorobenzene, dichlorobenzene, a 2:1 mixture of chlorobenzene and dichlorobenzene, nitrobenzene, MEK, THF, carbon tetrachloride, carbon bisulfide, alcohols and other organic solvents. Moreover, the polymer is not changed on boiling with aqueous 1*N* NaOH; however, it is discolored on boiling with aqueous 1*N* H₂SO₄.

In the infrared spectra of these copolymers, absorption bands at 3300, 1725 and 1550 cm⁻¹ appear which are attributed to -NH-, >C = O, and -C-N-groups, respectively. Although the copolymers obtained by thermal copolymerization do not have a boiling point, they decompose and discolor above 200-210°C. They can be assumed to be copolymers having a three-dimensional structure. Their intrinsic viscosity values [η], however, were about 0.1 dl/g in DMF at 30°C. It is considered that this copolymer dissolves completely in DMF in spite of its three-dimensional structure.

Catalytic Copolymerization. The results are shown in Table III.

When the catalyst was used for the reaction of PACH and TDI, copolymer could be obtained at lower temperature than in thermal copolymerization.

In this case, piperidine, for example, is a secondary amine, so it has an active hydrogen itself. The catalyst used for the reaction of alcohol and isocyanate is usually a tertiary amine,^{8b} however, in these experiments, the catalytic activity of piperidine and ethylenediamine is sufficient. Thus, in all experiments, the catalyst concentration is low (less than 0.01 mole-%) relative to PACH, so it would not be considered that the active hydrogen of the catalyst has any appreciable effect on the copolymerization reaction itself. Moreover, the yield of copolymerization can be also obtained quantitatively by using the catalyst (TDI-8 and TDI-9).

The solubility of these catalytic copolymers is better than that of thermal copolymer. It is considered that the structure of catalytic copolymer is essentially identical with that of thermal copolymer, based on the infrared spectral analysis. By choosing suitable conditions for this copolymerization, however, a copolymer which is white or slightly yellow in color and having a lower degree of three-dimensional formation, and which has some film-forming ability (but brittleness), could be obtained. These copolymers have a melting point or softening point in the range of about 60-200°C. This fact is remarkably different from the case of the thermal copolymer. However, their intrinsic viscosity [η] falls to about 0.05-0.08 dl/g in DMF at 30°C; these values are smaller than that of usual polyurethane.

Effect on the Reaction Rate of PACH and TDI. Many investigations²² have been reported already on the theory of rate in the formation of polyurethane. There was also a paper on the thermal degradation of poly-

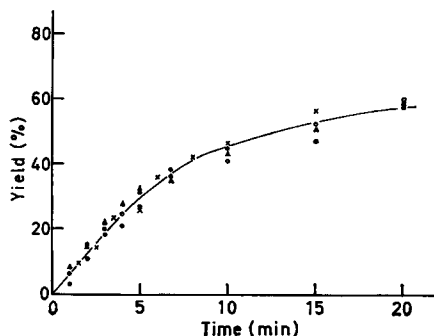


Fig. 1. Plot of yield vs. time.

urethane.²³ Recently, Robins²⁴ reported the catalytical reaction mechanism of metal ion.

In this investigation, the copolymerization of PACH having molecular weight of 288 with TDI was carried out at 30°C using piperidine as catalyst to determine the reaction order of PACH and TDI. The results are given in Figures 1–6.

On this reaction system, as the measurement of reaction rate by quantitative analysis of residual isocyanate group was very troublesome, the procedure described above of removing aliquots of reactive mixture of regular intervals and precipitating polymer was carried out.

Figure 1 shows the reaction time–polymer yield curve for each isocyanate concentration $[\text{NCO}]$ and the excess active hydrogen $[\text{Act. H}]$. Although the polymer yield given as $(\text{weight of polymer obtained})/(\text{weight of initial monomer}) = x/a_0$, the weight of polymer obtained x does not give the value of monomer $[\text{NCO}]$ actually consumed; its value contains the added active hydrogen $[\text{Act. H}]$. Then, if it is assumed that the proportion of PACH added to TDI is constant for all times (in fact, for the reaction of NCO with active hydrogen, 1:1) and if the proportional value is assumed to be b , the value of monomer actually consumed $[\text{NCO}]$ is given by bx . Thus, the rate equation of the pseudo first-order reaction of the isocyanate is given by eq. (1):

$$dx/dt = k(a_0 - bx) \quad (1)$$

For the initial concentration, when $t = 0$, $x = 0$, the integration of eq. (1) gives

$$bkt = k't = -\ln\{(a_0 - bx)/a_0\} \quad (2)$$

Then, fixing $b = 1$, the plots of $\log(1 - x/a_0)$ against time t are shown in Figure 2. It is apparent that, for each isocyanate concentration, there is a linear relation at the early stage of reaction. Thus, it is considered that, for the reaction between PACH and TDI, the reaction rate depends by a pseudo first-order reaction on the isocyanate concentration of TDI at early stage.

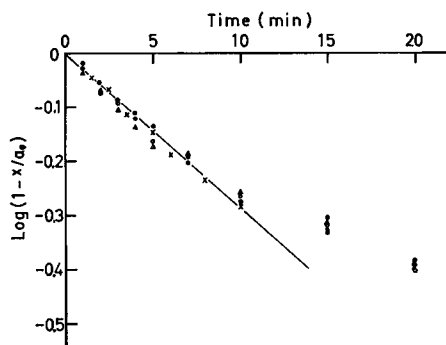


Fig. 2. Plot of $\log [(1 - x)/a_0]$ vs. time.

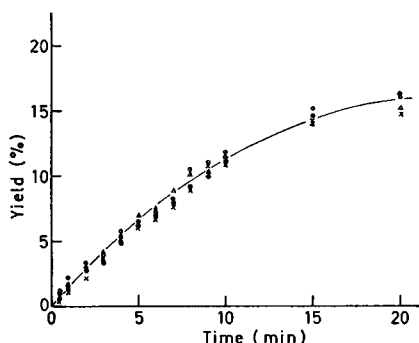


Fig. 3. Plot of yield vs. time.

On the other hand, Figures 3 and 4 show the results for active hydrogen [Act. H] of PACH, as found by the same procedure as above. Since at an early stage, linearity between $\log(1 - x/a_0)$ and time t is found, so it is considered that this reaction also would proceed as a pseudo first-order reaction relative to the concentration of active hydrogen of PACH in the early stage.

Meanwhile, the second-order reaction between PACH and TDI was studied. Figure 5 shows the relation of reaction time and polymer yield, where polymer yield is given by

$$\frac{(\text{weight of polymer obtained})}{(\text{total weight of initial monomer})} = x/a_0$$

Then, from x , the amount of monomer consumed was determined by eqs. (3) and (4). Thus, as this copolymerization is carried out at nearly equimolar conditions, the proportion of polymer obtained is equal to the ratio of monomer components PACH and TDI.

$$[\text{Act. H}]: xM_A/(M_A + M_B) \quad (3)$$

$$[\text{NCO}]: xM_B/(M_A + M_B) \quad (4)$$

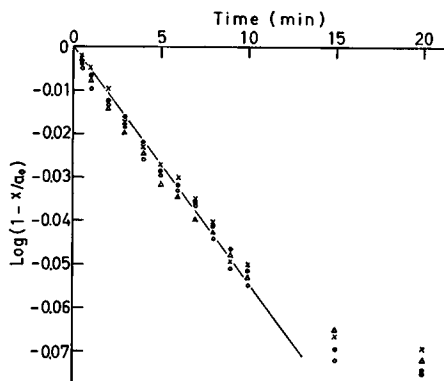
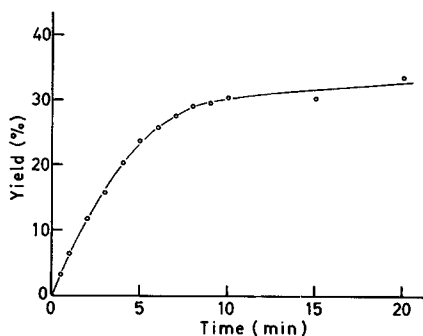
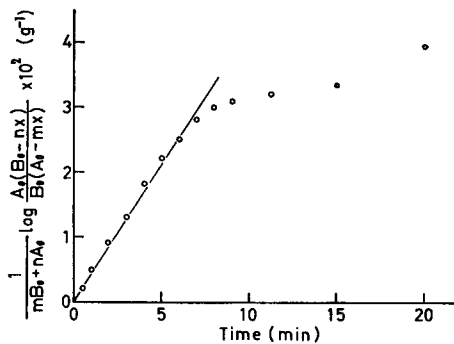
Fig. 4. Plot of $\log [(1 - x)/a_0]$ vs. time.

Fig. 5. Plot of yield vs. time.

Fig. 6. Plot of $[1/(mB_0 + nA_0)] \log [A_0(B_0 - nx)/B_0(A_0 - mx)]$ vs. time.

where M_A and M_B are the molecular weights of PACH and TDI, respectively. Now, initial weights of active hydrogen and NCO are A_0 and B_0 , respectively, so the rate equation is given by eq. (5):

$$\frac{dx}{dt} = k \left(A_0 - \frac{M_A}{M_A + M_B} x \right) \left(B_0 - \frac{M_B}{M_A + M_B} x \right) \quad (5)$$

where, as $M_A/(M_A + M_B)$ and $M_B/(M_A + M_B)$ are constant, they are replaced by m and n , respectively. At initial conditions ($t = 0, x = 0$), integration of eq. (5) gives

$$kt = \frac{1}{mB_0 + nA_0} \ln \frac{A_0(B_0 - nx)}{B_0(A_0 - mx)} \quad (6)$$

A plot of $[1/(mB_0 + nA_0)] \log [A_0(B_0 - nx)/B_0(A_0 - mx)]$ against time t is shown in Figure 6. Thus, it is observed that the relation is linear at the early stage.

It is assumed that, in the early stage, the reaction rate of PACH and TDI with piperidine as catalyst depends on the first order of the concentration of both the active hydrogen of PACH [Act. H] and the isocyanate of TDI [NCO], respectively.

Acid or Alkali Treatment of PACH

Results of the acid or alkali treatment of PACH are given in Tables IV and V, and the results of the elemental analysis of sulfuric acid-treated PACH are given in Table VI.

TABLE IV
Acid or Alkali Treatment of PACH^a

No.	PACH		Treatment	Yield, %	MW ^b	Mp, °C	Note
	Catalyst	MW ^b					
1	Ca-Hg	480	None	14.5	480		
2			1N HCl	21.1	670		
3			1N H ₂ SO ₄	22.0	1750	50-55	White powder, spinnable
4			1N NaOH	1.0	346		
5	Na-Hg	462	None	11.6	462		
6			1N HCl	19.1	577		
7			1N H ₂ SO ₄	18.3	2560	55-62	White powder, spinnable
8			1N NaOH	12.6	405		

^a Temp, 15°C; 20 min.

^b Molecular weight was measured by the cryoscopic method with benzene.

On sulfuric acid treatment of PACH, the yield and molecular weight increase markedly. The polymers obtained by treatment with sulfuric acid are white, powderlike polymers having a melting point (or softening point) and spinnability, even if PACH before treatment is a viscous liquid.

On hydrochloric acid treatment of PACH, the yield increases to some extent, but the molecular weight does not increase so much as in the case of sulfuric acid treatment. On the other hand, both the yield and molecular weight decrease on alkali treatment.

TABLE V
 Sulfuric Acid Treatment of PACH (at 70°C)

No.	Catalyst	PACH MW ^a	Treat- ing time, min	Yield, %	Final MW ^a	
9	Ca-Hg	450	0	6.0	450	White powder, spinnable
10	"	"	5	11.4	837	
11	"	"	10	16.3	961	
12	"	"	20	17.9	1218	White powder, spinnable
13	"	"	30	18.0	1305	White powder, spinnable
14	Na-Hg	428	0	8.0	428	White powder, spinnable
15	"	"	5	14.5	911	
16	"	"	10	19.5	1130	White powder, spinnable
17	"	"	20	21.9	1467	White powder, spinnable
18	"	"	30	20.2	1518	White powder, spinnable

^a Molecular weight was measured by the cryoscopic method with benzene.

 TABLE VI
 Elemental Analysis of Sulfuric Acid Treated PACH

No.	Found			C:H:O
	C, %	H, %	O, % ^a	
PACH	54.55	9.17	36.31	2:4:1
9	54.28	9.20	36.52	2:4.03:1.00
12	59.68	8.93	31.39	2:3.56:0.78 (-0.44)(-0.22)
13	59.76	8.96	31.28	2:3.58:0.79 (-0.42)(-0.21)
14	54.44	9.24	36.32	2:4.04:1.00
17	59.71	9.03	31.26	2:3.60:0.78 (-0.40)(-0.22)
18	59.66	9.00	31.34	2:3.60:0.78 (-0.40)(-0.22)

^a Calculated by difference from C and H.

The increase in molecular weight of acid-treated PACH is attributed formation of acetal or ether bonds in dehydration of PACH molecules. The acetal reaction can usually occur with either acid catalyst or alkali

catalyst;²⁵ however, it is apparent that, in the case of PACH, the alkali treatment somehow causes a decrease in molecular weight rather than an increase.

As treatment with sulfuric acid was most effective, several experiments with varying treating times were performed. The results are given in Table V, and the results of elemental analysis are shown in Table VI.

Table V shows that the increase in yield and molecular weight by sulfuric acid treatment of PACH reaches equilibrium in about 20 min. In the elemental analysis, the value of samples 9 and 14 which did not receive the sulfuric acid treatment are identical to the theoretical values for PACH. However, it is observed that the contents of hydrogen and oxygen relative to carbon in runs 12, 13, 17, and 18 which were treated with sulfuric acid, decrease in a 2:1 ratio (i.e., proportional to H₂O). Thus, this indicates that dehydration occurs on treatment with sulfuric acid. This dehydration reaction is also confirmed by the fact that, in infrared spectral analysis, the absorption band at 3300 cm⁻¹ attributed to the OH group decreases with the sulfuric acid treatment.

These facts indicate that the increase in yield and molecular weight on treatment with sulfuric acid is attributed to formation of acetal or ether bonds between molecules. However, more research will be necessary to make clear the essential difference between acid treatment and alkali treatment, and the effect of alkali treatment.

Copolymerization of Acetaldehyde and *n*-Butylaldehyde

The results of copolymerization and the elemental analysis are given in Tables VII and VIII, respectively. The infrared and NMR spectra of the copolymer are given in Figures 7 and 8, respectively.

The copolymers obtained are colorless, viscous liquids. Although the acetaldehyde homopolymer C-1 is very soluble in water and most organic solvents, and the *n*-butylaldehyde homopolymer C-2 is insoluble in water and *n*-hexane, the solubility of copolymers C-3 and C-4 is comparatively good for water but poor for *n*-hexane.

Tables VII and VIII, indicate that yield, molecular weight, and value of elemental analysis of copolymer are intermediate between those for

TABLE VII
Copolymerization of Acetaldehyde and *n*-Butylaldehyde

No.	CH ₃ CHO, g	<i>n</i> - C ₃ H ₇ CHO, g	0.3% <i>n</i> NaHg, g	Temp, °C	Time, hr	Yield, %	MW ^a
C-1	240	0	10	-30~5	20	27	391
C-2	0	245	"	"	"	58	230
C-3	225	65	"	"	"	46	343
C-4	197	90	"	"	"	55	307

^a MW was measured by a Takara-type ebulliometer (benzene as solvent).

TABLE VIII
Elemental Analysis of Acetaldehyde-*n*-Butylaldehyde Copolymer

No.	Initial monomer ratio		C, %	H, %	O, % ^a
	CH ₃ CHO	<i>n</i> -C ₃ H ₇ CHO			
C-1	1	0	54.52	36.31	9.17
C-2	0	1	66.63	11.18	22.19
C-3	0.84	0.16	56.48	33.91	9.61
C-4	0.78	0.22	58.50	31.25	10.25

^a By difference from C and H.

acetaldehyde and *n*-butylaldehyde homopolymers under the same polymerization conditions.

Figures 7 and 8 show the infrared and NMR spectra of the acetaldehyde homopolymer and the acetaldehyde-*n*-butylaldehyde copolymer, respectively. Figure 7 shows that the absorption of C=C double bond at about 1650 cm⁻¹ region increases with increasing the initial mole ratio of AcH/*n*-BA. This fact can be understood by considering that this is attributed to formation of a double bond by dehydration.

In the NMR spectra (Fig. 8), the peak at 4.4–4.8 ppm attributed to the OH proton shifts with decreasing initial mole ratio of AcH/*n*-BA. Moreover, it appears that, with decreasing initial mole ratio of AcH/*n*-BA, i.e., with increasing CH₂ unit in copolymer, the peaks at about 1.3 ppm of CH₃ protons and 1.7 ppm of CH₂ protons overlap.⁷

These facts and the facts that aldol condensation-type homopolymers are obtained by homopolymerization of acetaldehyde and *n*-butylaldehyde with sodium amalgam at temperatures above -30°C, indicate that the copolymer obtained under similar conditions is also of the aldol condensation type.

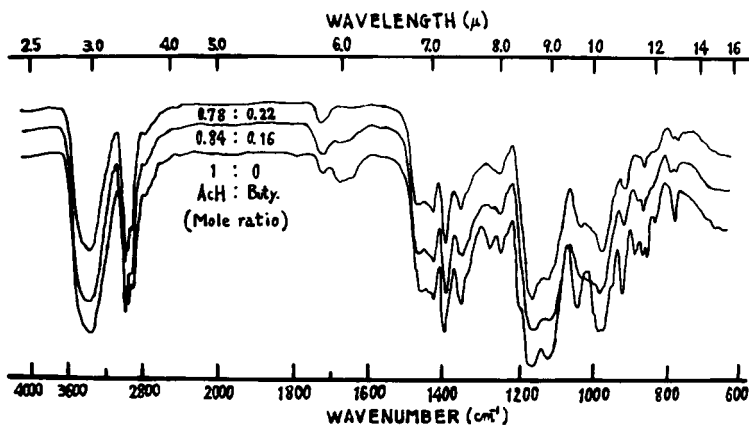


Fig. 7. Infrared spectra of acetaldehyde homopolymer and acetaldehyde-*n*-butylaldehyde copolymer.

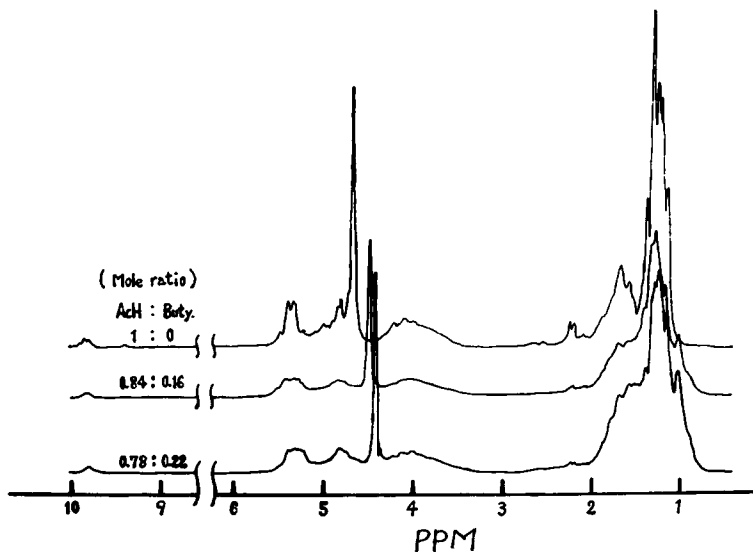


Fig. 8. NMR spectra of acetaldehyde homopolymer and acetaldehyde-*n*-butylaldehyde copolymer.

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