Macromolecules **1985,** *18,* 846–850

Novel Polyalcohols with Hydroxymethyl Side Chains from Base-Catalyzed Polycondensation of Diols

Taketoshi Kito,* Kohji Yoshinaga, Nobukadzu Hatanaka, Jiichiro Emoto,[1a] and Makoto Yamaye[1b]

Department of Material Engineering, Kyushu Institute of Technology, Sensui-cho, Tobata-ku, Kitakyushu-shi, 804 Japan. *Received February 22, 1984*

ABSTRACT: The polycondensation of a diol, $HOCH_2(CH_2)_{n-2}CH_2OH$, in the presence of potassium phenoxide or potassium 2-naphthyl oxide gave a polymer, whose average structure was determined by ^{13}C NMR as $[-CH(CH_2OH)(CH_2)_{n-2}-]$. A polymer from 1,10-decanediol was hardly soluble in ordinary solvents including pyridine and methanol. It was molded to give a rubberlike film. A polymer from 1,6-hexanediol, however, gave a stiff and brittle one. The hydroxyl groups of these polymers were readily esterified by acetic anhydride.

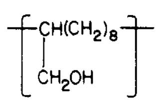
Introduction

Primary alcohols with at least one hydrogen atom at the α-carbon atom give the corresponding 2-alkyl-substituted alcohols when heated in the presence of potassium alkoxide (the Guerbet reaction, eq 1).[2] Modifications of this reaction have been conducted by many authors because a substantial amount of the corresponding carboxylic acid forms as a byproduct when potassium alkoxide is used as a base catalyst. To avoid acid formation, nickel or copper chromite was used together with various bases.[3-5]

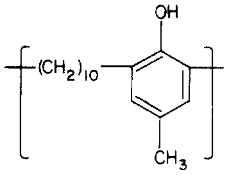
$$2RCH_2CH_2OH \xrightarrow{\text{base}} RCH_2CH_2CHRCH_2OH + H_2O \quad (1)$$

If the Guerbet reaction is applied to diols, polymers with hydroxymethyl groups on the aliphatic carbon chain are expected to form. Miller and Bennett reported the condensation of 1,4-butanediol in the presence of a mixture of tripotassium phosphate and copper chromites.[6] They obtained a higher-boiling product, but neither structural nor molecular weight determination for this product was performed. They claimed, however, the isolation of four trimers of 1,4-butanediol, namely, 3,6-, 3,8-, and 5,6-bis(hydroxymethyl)-1,10-decanediol and 5-(2-hydroxyethyl)-3-(hydroxymethyl)-1,9-nonanediol.

We have reported that a weak base such as potassium 2-naphthyl oxide or phenoxides is an effective catalyst for the Guerbet reaction.[7] When potassium 2-naphthyl oxide was heated in a primary alcohol, the corresponding 2-alkyl-substituted alcohol was obtained together with 1-alkyl-2-naphthol.[8] Similar results were obtained for potassium salts of various phenols including *p*-cresol and 2,4- and 2,6-dimethylphenols.[9] On the basis of these results, a polymer of structure **1** or **2** would be expected to form if 1,10-decanediol is heated with potassium *p*-cresolate. In fact, we could obtain only a polymer of structure **1**. We report the syntheses and properties of polyalcohols by polycondensation of diols, $HOCH_2(CH_2)_{n-2}CH_2OH$.



1



2

Experimental Section

The NMR (^1H NMR and ^{13}C NMR) spectra were obtained on a JEOL JNM-C-60 HL (60 MHz) spectrometer, with Me_4Si as internal standard, and the UV spectra on a Jasco UVI DEC-430-A. The gas and liquid chromatographies were performed with a Yanagimoto G-180 and a Toyo Soda HLC-802UR, respectively.

2-Octyl-1-dodecanol (6, X = OH) and 1,10-Decanediol (7, X = OH). Alcohol **6** (X = OH) was prepared according to the literature[7] (see also ref 10) and **7** (X = OH) is commercially available (Wako Pure Chemical Industries, Ltd., Special Grade).

Polymerizations. Representative procedures are described below.

(a) Polymerization in a Flask. 1,10-Decanediol (17.4 g, 0.100 mol) and potassium phenoxide (6.61 g, 0.0500 mol) were placed in a 300-mL flask fitted with a condenser, a mechanical stirrer, and an N_2 inlet and outlet tube. The mixture was heated with stirring in an oil bath kept at 260 °C for 9 h under atmospheric pressure and at 220 °C for 1 h in vacuo (10 mmHg). The mixture was cooled down to room temperature and methanol was added to such an extent that the whole material was completely dissolved at refluxing temperature (a small amount of the contents remained insoluble). A viscous material settled down on the bottom of the flask after overnight standing and was separated by decantation. This procedure was repeated 3 times. The polymer obtained was heated to remove the solvent at 150 °C for 5 h in vacuo (no. 3 in Table I). Methanol-soluble products could be effectively separated by addition of water (e.g., no. 7). As for a polymer with lower viscosity (e.g., no. 8) the reaction mixture was heated at 250 °C in vacuo to distill unreacted diol.

(b) Polymerization in an Autoclave. In a 300-mL stainless steel autoclave with a mechanical stirrer were placed 1,10-decanediol (17.4 g, 0.100 mol) and potassium phenoxide (6.61 g, 0.0500 mol). Under nitrogen the mixture was heated with stirring at 270 °C for 10 h (no. 2 in Table I). The resulting mixture was treated as described above.

(c) Stepwise Polymerization. 1,10-Decanediol (112.0 g, 0.644 mol) was heated with potassium phenoxide (8.05 g, 0.0610 mol) in an autoclave at 300 °C for 4 h by the method as described in part b. After the mixture was transferred into a flask, the reaction under reduced pressure (less than 0.1 mmHg) was continued at 250 °C, and 28% of unreacted 1,10-decanediol was recovered. When mechanical stirring became difficult (after about 2 h), the reaction mixture was cooled and molded into film by the following method.

Film Processing. A sample polymer was sandwiched between the two metal blocks and, with application of vacuum (less than 1 mmHg) to the film-processing device (Shibayama Kagaku, SS-VP-50), pressed at 250 °C, to give a uniform film.

Preparation of a Polymer Free from the Base (PhOK or 2-$C_{10}H_7OK$). The polymer (no. 3 or no. 11 in Table I) was dissolved in methanol and the solution was acidified with aqueous HCl. Precipitates were collected, washed with water, and dried at 100 °C in vacuo for 5 days.

Acetylation of the Polymer (No. 2 in Table I). In a flask, 1.00 g of the polymer was dissolved in 5 mL of pyridine containing 2 mL of acetic anhydride and the mixture was allowed to stand at room temperature for 1 day. Pyridine and the unreacted acetic anhydride were removed under 10 mmHg at 100 °C. The ^{13}C NMR spectra of no. 2 and its acetylated product are shown in Figures 2 and 7, respectively.

Heating of 2-Ethyl-1-hexanol (EH) and 1-Butanol with Potassium Phenoxide. A mixture of EH (12.98 g, 0.0989 mol), 1-butanol (7.44 g, 0.100 mol), and potassium phenoxide (6.79 g, 0.0513 mol) was heated at 270 °C for 5 h in an autoclave. After being washed with 2% NaOH and then with water, the mixture was analyzed by gas chromatography (OV101, 2 m, 125 °C). Only

0024-9297/85/2218-0846$01.50/0

Table I
Polymers from α,ω-Alkanediols

expt no.	diol n^a	base	base/diol^b	method^c	temp, °C	time, h	yield, %	$[\eta]^d$	remarks
1	10	C_6H_5OK	0.50	F	270	24			gelation
2	10	C_6H_5OK	0.50	A	270	10		0.11	
3	10	C_6H_5OK	0.50	F	260	9	46	0.36	*e*
4	10	C_6H_5ONa	0.50	F	260	20			*f*
5	10	C_6H_5OK	0.25	F	260	10	29	0.39	
6	10	C_6H_5OK	0.125	F	260	25		0.28	
7	8	C_6H_5OK	0.50	F	260	12	87	0.20	
8	6	C_6H_5OK	0.50	F	260	10	49	0.04	
9	10	p-MeC_6H_4OK	0.50	F	280	10			gelation
10	10	p-MeC_6H_4OK	0.50	F	260–290	7	57	0.19	
11	10	2-$C_{10}H_7OK$	0.10	A	300	4	74		*g*

[a] General formula, $HO(CH_2)_nOH$. [b] mol/mol ratio. [c] Symbols F and A mean reactions run in a flask and in an autoclave, respectively. [d] At 30 °C in pyridine. [e] The mixture was further heated at 220 °C for 1 h in vacuo. Without this procedure, $[\eta]$ was 0.28. [f] Elastic product was not obtained. [g] The mixture was further heated at 250 °C for 2 h in vacuo.

1-butanol (0.0655 mol) and EH (0.115 mol) were detected. In the chromatogram from another run of 270 °C for 10 h, three additional small peaks (relative intensity to EH of 0.9%, 1.3%, and 1.5%) with retention time longer than that of EH were present; none of these peaks were assigned to 2,4-diethyl-1-octanol or 2-butyl-2-ethyl-1-hexanol (condensation products from EH and 1-butanol) by GC-MS analysis.

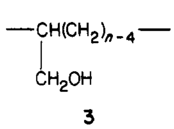
Stress–Strain Curve. A sample film (width, 5.0 mm; length, 30 mm; thickness, 0.98 mm; cross-sectional area, 4.9 mm^2) of no. 5 in Table III was subjected to a stress–strain test (Shimadzu Autograph IS-5000). Elongation speed was 50 mm/min.

Thermal Analysis. A sample polymer (5.40 mg) was subjected to thermal gravimetric and thermal differential analyses (ULVAC IGD-5000; heating rate, 10 °C/min) under nitrogen.

Results and Discussion

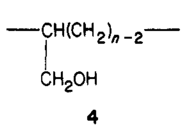
α,ω-Alkanediol was heated in the presence of a base such as potassium salt of phenol, p-cresol, or 2-naphthol in a flask or in an autoclave to form an elastic product. The results are summarized in Table I.

Structural Analysis. In the polymerization of diols, if two types of reactions (the Guerbet reaction shown in eq 1 and the alkylation of phenol) occur competitively, the resulting polymers will be composed of structures 1 and 2. These elastic products free from base were dissolved in pyridine-d_5 and analyzed by ^{1}H NMR. No appreciable signals were detected above 5 ppm (δ value) except the signals derived from the solvent. Thus, if only the Guerbet reaction occurs in the present polymerization, the polymer structure can be shown by the combination of structural units 3–5 in the case of diol, $HOCH_2(CH_2)_{n-2}CH_2OH$, because the α-carbon atom should be combined with the β-carbon atom of another diol molecule. The possibility of containing such a long-chain branching structure as reported by Miller and Bennett[6] was ruled out because a model reaction of 2-ethyl-1-hexanol and 1-butanol with potassium phenoxide gave no appreciable amount of such condensation alcohols as 2,4-diethyl-1-octanol and 2-butyl-2-ethyl-1-hexanol; this indicates that β-branching alcohols are much less reactive under the conditions used. If any hydroxymethyl groups in the polymer reacted, a hardly soluble polymer with network structure might be obtained. Polymers that we used for NMR analyses were completely soluble in pyridine.



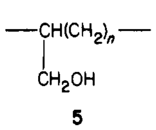
$-\underset{\displaystyle CH_2OH}{\underset{|}{C}H}(CH_2)_{n-4}-$

3



$-\underset{\displaystyle CH_2OH}{\underset{|}{C}H}(CH_2)_{n-2}-$

4



$-\underset{\displaystyle CH_2OH}{\underset{|}{C}H}(CH_2)_{n}-$

5

To determine polymer structures, ^{13}C chemical shift values (^{13}C CS values) for various alkanes were calculated by means of an additivity relationship. If a hydrogen atom in an alkane is substituted by the hydroxyl group, the values for the α-, β-, and γ-carbons shift downfield.[11] Compounds 6 and 7, where X = OH, were chosen as model compounds because of their partial structures similar to the polymers, 6 (X = OH) for structural units 3–5, and 7 (X = OH) for the end groups of polymers. All the CS values for 6 (X = OH) were 65.0, 41.6, 32.1, 32.0, 31.0, 30.5, 30.2, 27.8, 23.4, and 14.7 ppm, and those for 7 (X = OH) were 62.0, 33.6, 29.8, and 26.4 ppm. The ^{13}C NMR spectrum of 6 (X = OH) is shown in Figure 1. The CS values of 7 (X = OH) were determined on the basis of the signals of 1-decanol already assigned:[11] 62.0, 33.6, and 26.4 ppm for C_1, C_2, and C_3, respectively (for numbering, see 8). An assignment of the signals of 6 (X = OH) was made as follows. On the basis of the calculated values of 6 (X = H) (19.6, 32.5, and 36.9 ppm for C_1, C_2, and C_3, respectively), the CS values of C_1, C_2, and C_3 were obtained as 68.6, 42.9, and 33.4 ppm by the use of parameters reported (49, 10.4, and −3.5 ppm for α-, β-, and γ-carbons, respectively[12,13]). The observed values of 65.0 and 41.6 ppm are close to the first two calculated ones and, in addition, these two signals became split into triplet and doublet, respectively, by the off-resonance method. Therefore, the CS values of 65.0 and 41.6 ppm were assigned to C_1 and C_2, respectively. The value of 32.0 ppm was tentatively assigned to the C_3 signal because there were two observed

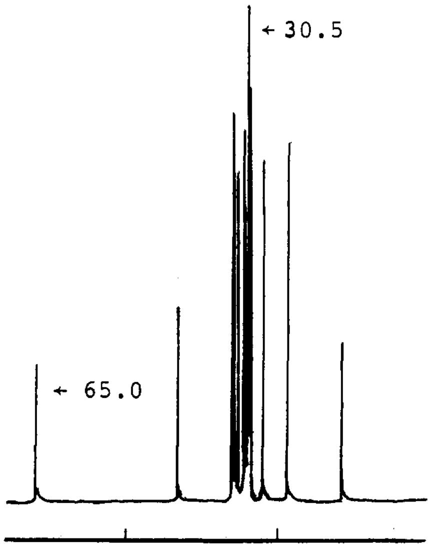


Figure 1. ^{13}C NMR spectrum of 2-octyl-1-dodecanol (46% in pyridine-d_5).

$CH_3(CH_2)_9CH(n\text{-}C_8H_{17})CH_2X$ $XCH_2(CH_2)_8CH_2X$
6 7

Table II
^{13}C Chemical Shift Values of a Polymer from 1,10-Decanediol[a] and 1,8-Octanediol[b]

	chem shift,[d] ppm		
	obsd		
position[c]	no. 2[a]	no. 7[b]	calcd
1[e]	64.9	65.0	65.0
2[e]	41.4	41.4	41.6
3[e]	31.8	31.9	32.0
4	27.5	27.6	27.3
		28.1	27.5
5	30.6	30.7	30.2
6	30.1	30.2	30.0
7			30.0
1′[e]	62.1	62.3	62.0
2′[e]	33.7	33.7	33.6
3′[e]	26.5	26.6	26.4
4′			29.7
5′			30.0

[a] No. 2 in Table I. [b] No. 7 in Table I. [c] Position 1 or 1′ (end group) stands for that of the carbon atom carrying OH group. [d] Solvent: pyridine-d_5. [e] For positions 1–3, the calculated values were taken from 6 (X = OH); for 1′–3′, they were taken from 7 (X = OH).

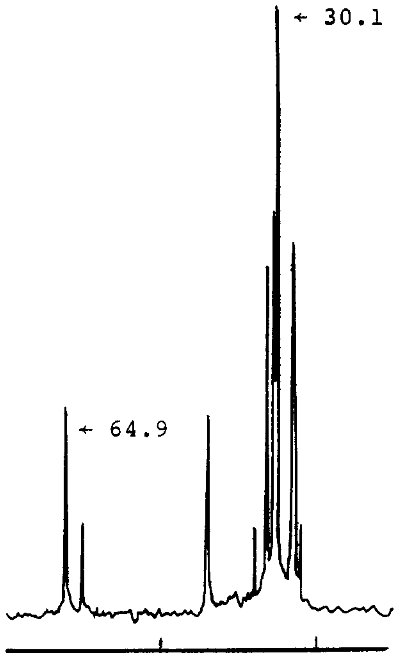
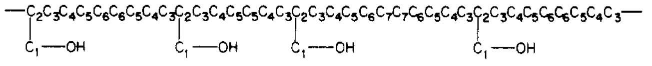


Figure 2. ^{13}C NMR spectrum of polymer no. 2 in Table I (10% in pyridine-d_5).

signals equally possible of being assigned, 32.1 and 32.0 ppm, but no appropriate means of distinguishing between them are currently available. If the repeating units of the polymer obtained are shown as **3**–**5**, each ^{13}C CS value in the polymer can be calculated. In Table II, these values are listed together with the observed ones of the polymers from 1,10-decanediol and 1,8-octanediol. In Figures 2 and 3, NMR spectra of these polymers are shown. Values for C_1'–C_5' in Table II were assigned to the end group. All the CS values of the signals observed in ^{13}C NMR spectra were in good agreement with the calculated ones.

For example, as for the polymer from 1,10-decanediol the structural units of **3**–**5** (n = 10) will appear in the ratio of 1:2:1. Then, one of the possible partial structures of the polymer can be written as **8**, in which hydrogen atoms on each carbon atom are omitted. Structure **8** clearly suggests that each carbon atom (from C_1 through C_7) should appear in the ratio of 2:2:4:4:4:3:1. A signal of 30.1 ppm in Table II was assigned to C_6 and C_7 atoms, whose CS values were both 30.0 ppm by calculation. Therefore, the ratio should be 1:1:2:2:2:2. In addition it was deduced that the CS values for C_4' and C_5' (end-group carbons) happened to appear at 30.1 ppm and the intensity of this signal was increased (see Figure 2).



$$-\underset{\substack{|\\ C_1-OH}}{C_2}C_3C_4C_5C_6C_6C_5C_4C_3\underset{\substack{|\\ C_1-OH}}{C_2}C_3C_4C_5C_5C_4C_3\underset{\substack{|\\ C_1-OH}}{C_2}C_3C_4C_5C_6C_7C_7C_6C_5C_4C_3\underset{\substack{|\\ C_1-OH}}{C_2}C_3C_4C_5C_6C_6C_5C_4C_3-$$

8

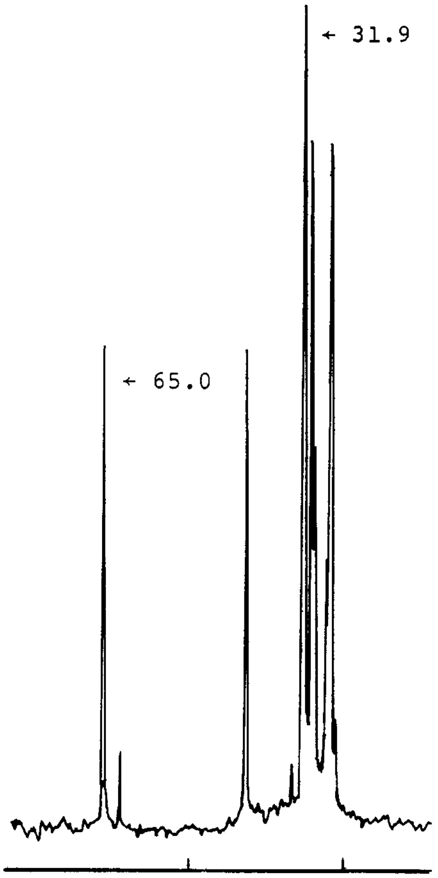


Figure 3. ^{13}C NMR spectrum of polymer no. 7 in Table I (10% in pyridine-d_5).

On the other hand, there is another feature in the structural analysis of a polymer from 1,8-octanediol. Each carbon atom (from C_1 through C_6) will appear in the ratio of 2:2:4:4:3:1. On calculation, two different values are obtained for C_4 because there are only four methylene units in structure **3**, where n is 8 (the number of carbon atom at δ-position affects the CS value). The ratio of two carbons at 27.6 and 28.1 ppm was calculated as 3:1. The CS value for C_3 was itensified by overlapping with the signals of C_4' and C_5' (end-group carbons). The magnitude of the intensity for each carbon of the polymers from 1,10-decanediol and 1,8-octanediol in Figures 2 and 3 may be consistent with the above discussion.

In addition, the signals assigned for C_1 and C_2 were split into triplet and doublet, respectively, by the off-resonance method. These results support the assumption that the polymer structure obtained here can be represented by the combination of three repeating units of **3**–**5**.

1,6-Hexanediol also gave an elastic polymer as shown in Table I. Its ^{13}C NMR spectrum consisted of about 25 signals (Figure 4) in which the first four and the fifth signals were assigned to the hydroxymethyl and the end groups, respectively.

Potassium 2-naphthyl oxide was a better catalyst for the condensation of primary alcohols (Guerbet reaction) compared with potassium phenoxide as reported earlier.[7] With

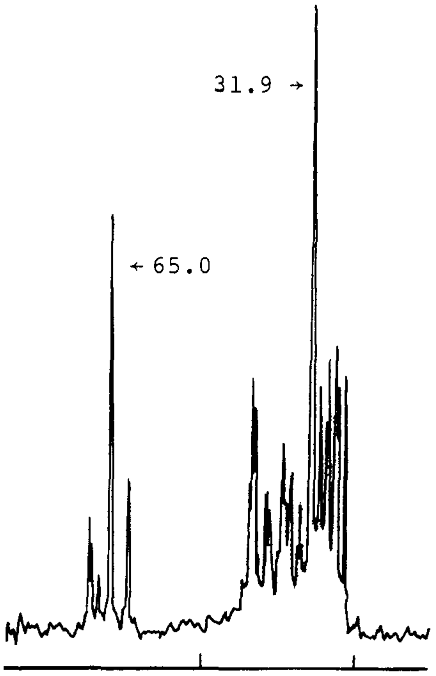


Figure 4. ^{13}C NMR spectrum of polymer no. 8 in Table I (10% in pyridine-d_5).

hopes of increasing the degree of polymerization of diols, 1,10-decanediol was heated in the presence of potassium 2-naphthyl oxide (no. 11 in Table I). After the base was removed (see the Experimental Section), the polymer was analyzed by liquid chromatography, as well as by IR and UV spectroscopies. In the chromatogram a strong peak with retention time of 6776 s appeared, that of 2-naphthol being 1570 s under the same conditions. In its IR spectrum there was no significant absorption around 840 cm^{-1}, an absorption characteristic of 2-naphthol. UV spectra of both the polymer and 1-hexyl-2-naphthol had a maximum at the same absorption of 230 nm ($E^{1\%}{}_{1\text{cm}}$ = 389 for the former and $E^{1\%}{}_{1\text{cm}}$ = 3068 for the latter; solvent, MeOH), indicating the former has the structure of the 2-hydroxy-1-naphthyl moiety. In the ^{13}C NMR spectrum a new signal with low intensity (relative intensity, 5.6%) appeared at 25.8 ppm. These observations may suggest that the 2-hydroxy-1-naphthyl group was introduced into polymer chains, mainly into end groups. If this group was introduced into both the side chains and end groups of the polymer, at least two additional signals should have been found due to the carbon atoms attaching to the naphthyl group.

Solubility of Polymers in Organic Solvents. When the intrinsic viscosity was low (e.g., no. 2 in Table I), a polymer from 1,10-decanediol was soluble in methanol, pyridine (Py), tetrahydrofuran, acetone, and dimethyl sulfoxide, slightly soluble in dimethylformamide, and insoluble in chloroform. It was soluble in hot methanol but sparingly soluble in cold methanol when the viscosity was high (e.g., no. 3) and insoluble even in Py when the polymerization was continued until the mechanical stirring became difficult or impossible (e.g., no. 1 and 9). Therefore, in the latter case, the determination of intrinsic viscosity was very difficult. Occasionally, the polymers obtained were only partially soluble in Py. In such cases, the intrinsic viscosity of the soluble part was determined as shown in Table I (no. 3).

The present polymers have a large number of hydroxymethyl groups. Accordingly, individual polymer molecule chains might be associating through intermolecular hydrogen bonds. The solubility should decrease with increasing degree of polymerization.

Table III
Film-Processing Conditions[a]

expt no.	starting diol[b]	temp, °C	heating time,[c] h	film[d]	remarks
1	B	250	4	–	
2	H	250	4	+	stiff and brittle
3	D	200	4	–	
4	D	250	0.25	–	
5	D	250	0.5	+	soft rubber
6	D	250	1	+	soft rubber
7	D	250	4	+	stiff rubber
8	D	250	8	–	prepolymer free from PhOK was used

[a] Polymerization conditions: See the Experimental Section (stepwise polymerization and preparation of a polymer free from the base). [b] B = 1,4-butanediol; H = 1,6-hexanediol; D = 1,10-decanediol. [c] Under 1 mmHg. [d] +: Uniform film was obtained. –: Film was not obtained.

The present polymer is analogous to poly(vinyl alcohol) in terms of the hydroxyl group contents, but different in that the former is less soluble in water than the latter, because of a much lower hydroxyl/carbon atom ratio for the former. However, the polymer with a low degree of polymerization from 1,6-hexanediol was soluble in hot water.

Stepwise Polymerization. A long period of heating was required to get a polymer with a fiber-forming property when the polymerization was carried out in a flask. In an autoclave, on the other hand, only a viscous product was obtained because the water formed might retard the Guerbet reaction. Therefore, the polymerization was performed in the following three steps; heating of a diol with potassium phenoxide in an autoclave, in a flask, and, finally, in the film-processing device (see the Experimental Section and Table III). The polymer from 1,10-decanediol with potassium phenoxide as the base had a fiber-forming property and was insoluble in pyridine if the polymerization was interrupted at the second step. If the heating period was short in the final step (e.g., 15 min), the molded film was adhesive. With a long period of heating in the device (e.g., 4 h), the molded film was stiff, elastic, and strain resistant. A rise of stiffness and strength of the film may principally be due to a progress of the Guerbet reaction in the device. However, when the viscous polymer, free from potassium phenoxide, was heated in the device, the plasticity was lost. This might suggest that partial formation of ether linkages occurred by dehydration. (The Guerbet reaction does not proceed in the absence of base.)

A film made of the polymer from 1,6-hexanediol was stiff and brittle and had no elasticity. In addition, it was very hygroscopic when allowed to stand in air, and became soft and less strain resistant.

Appearance and Properties. The polymer from 1,10-decanediol with potassium phenoxide became pale yellow during polymerization but turned brown on exposure to air for several weeks, probably because of the presence of residual base. The polymer free from the base was stable to discoloration. The molded film was at first transparent but became cloudy after several weeks. The polymers from 1,6-hexanediol as well as from 1,4-butanediol colored greenish and gradually dark brown under the same polymerization conditions as applied for 1,10-decanediol.

Mechanical and Thermal Properties of the Polymer from 1,10-Decanediol. The stress–strain curve for the film of no. 5 (Table III) is shown in Figure 5 and the thermal analysis in Figure 6. This film resembles elastomers in having a large elongation at break but differs

Table IV
^{13}C Chemical Shift Values (ppm) of the Acetylated Product of No. 2 (Table I) and Their Assignment

chem shift, ppm			chem shift, ppm		
obsd	calcd	assignment	obsd	calcd	assignment
170.8	170.0[a]	$\mathrm{CH_3}\mathit{C}\mathrm{OO}$	29.9	30.0	C_6, C_7, C_5'
67.2	71.6	$\mathrm{AcO}\mathit{C}\mathrm{H_2CH}$	29.9[b]	30.1	$\mathrm{AcOCH_2}\mathit{C}\mathrm{H_2CH_2}$
64.5	65.9	$\mathrm{AcO}\mathit{C}\mathrm{H_2CH_2CH_2}$	27.0	27.3	C_4
37.7	39.9	$\mathrm{AcOCH_2}\mathit{C}\mathrm{H}$	26.2	28.9	$\mathrm{AcOCH_2CH_2}\mathit{C}\mathrm{H_2}$
31.6	33.4	$\mathrm{AcOCH_2CH}\mathit{C}\mathrm{H_2}$	20.9	20.0[a]	$\mathit{C}\mathrm{H_3COO}$
30.2	30.2	C_5	28.9	29.7	$\mathrm{AcOCH_2CH_2CH_2}\mathit{C}\mathrm{H_2}$

[a] For the acetoxyl group, the corresponding chemical shift values for ethyl acetate were used (ref 11). [b] Not detected as a single signal.

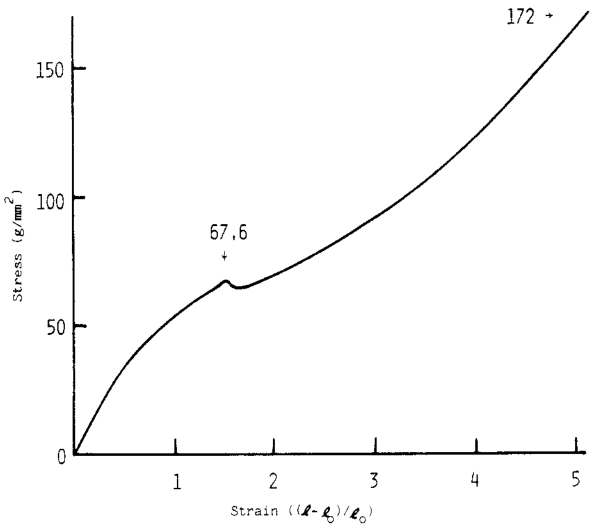


Figure 5. Stress–strain curve of the film of no. 5 in Table III.

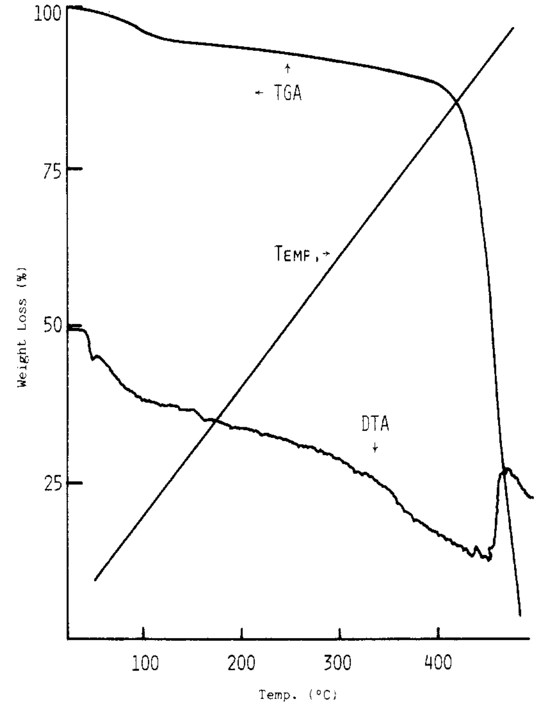


Figure 6. Thermal analysis of the film of no. 5 in Table III.

in having a yield point. An ultimate strength of no. 5 was 0.17 kg/mm^2. The film of no. 7 was torn on elongation although this film appeared the strongest of all listed in Table III. Our attempt to obtain a strong film by carrying out a polymerization for a longer period failed because a rise of melt viscosity made mechanical stirring difficult. The film was thermally stable below 380 °C.

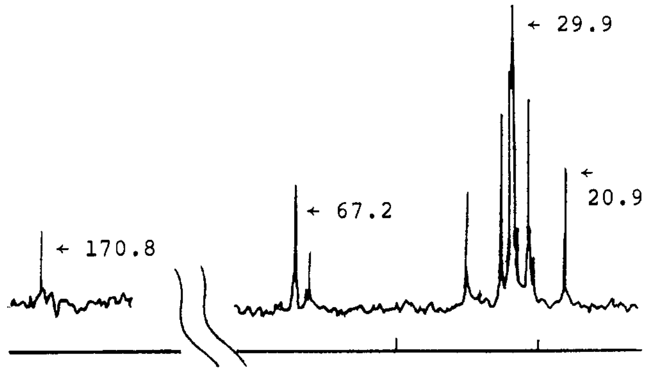


Figure 7. ^{13}C NMR spectrum of acetylated product of no. 2 in Table I (5% in pyridine-d_5).

Chemical Reactivity. Hydroxymethyl groups in the polymers were readily subjected to esterification. For example, a polymer from 1,10-decanediol (no. 2 in Table I) was esterified with acetic anhydride in pyridine, and its ^{13}C NMR spectrum is shown in Figure 7. If a hydrogen atom in alkanes is substituted by the acetoxyl group, the values for the α-, β-, and γ-carbons shift +52, +7.4, and −3.5, respectively.[12,13] The observed CS values and their assignment of the acetylated product are in Table IV. Each signal was assigned by comparing Figure 7 with Figure 2 on the basis that the acetoxyl group does not affect the CS values of carbons other than α-, β-, and γ-carbons. The IR spectrum of the acetylated product showed a strong absorption at 1740 cm^{-1}.

Acknowledgment. We express our appreciation to Mr. Shiro Konotsune, Manager of Corporative Development, Chisso Corp., for his valuable help during this work.

References and Notes

(1) (a) Chisso Corp. (b) Kyushu Kyoritsu University.
(2) Guerbet, M. *C. R. Acad. Sci.* **1917**, *165*, 559 and earlier papers.
(3) Pratt, E. F.; Kubler, D. G. *J. Am. Chem. Soc.* **1954**, *76*, 52.
(4) Dvornikoff, M. N.; Farrar, M. W. *J. Org. Chem.* **1957**, *22*, 540.
(5) Miller, R. E.; Bennett, G. E. *Ind. Eng. Chem.* **1961**, *53*, 33.
(6) Miller, R. E.; Bennett, G. E. U.S. Patent 2 875 241, 1959.
(7) Kito, T.; Ota, K. *Nippon Kagaku Kaishi* **1979**, 911.
(8) Kito, T.; Ota, K. *J. Org. Chem.* **1977**, *42*, 2020.
(9) Kito, T.; Yamaye, M.; Miyazaki, T. *Rep. Asahi Glass Found. Ind. Technol.* **1979**, *35*, 35.
(10) No. 63796K and 36619M from: "Catalogs of ^{1}H NMR and IR"; Sadtler Research Laboratories: Philadelphia, PA 19104, 1983.
(11) Breitermaier, E.; Voelter, W. "^{13}C NMR-Spectroscopy Monographs in Modern Chemistry"; Verlag Chemie Weinheim: New York, 1978; pp 150–4. Another method for calculating ^{13}C NMR chemical shifts was reported: Cheng, H. N. *Ind. Chem. News* **May 1984**, 58.
(12) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemist"; Wiley-Interscience: New York, 1972; p 47.
(13) These values are obtained by adding 9.1, 9.4, and −2.5 ppm to the values for α-, β-, and γ-carbons reported by Levy and Nelson (ref 12): Kosugi, Y.; Konishi, H. *Bunseki Kagaku* **1984**, *33*, E47.