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Polymerization of β-Ethoxypropionaldehyde

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Vogl[1] reported that 3-methoxypropionaldehyde was anionically polymerized with potassium triphenylmethoxide in propylene at −75°C. Takida and Noro[2] attempted the cationic polymerization of methoxybutyraldehyde with use of a magnesium sulfate-sulfuric acid complex at −78°C to give a sticky elastomeric product with a low yield.

The purpose of the present work is to obtain a high molecular weight crystalline polymer from β-alkoxypropionaldehyde.

β-Ethoxypropionaldehyde was prepared by refluxing the mixture of acrolein and ethyl alcohol in the presence of triethylamine and formic acid as catalyst at 65—75°C. Bp 66.0—66.5°C/67 mmHg.

Tetrahydrofuran (THF), methylene chloride, toluene and *n*-hexane used as solvents were purified in the usual way prior to use. Purification of triethylaluminum, diethylaluminum chloride, ethylaluminum dichloride (all of them, from Ethyl Corp.), aluminum trichloride, and titanium tetrachloride was previously described.[3,4] *n*-Butyllithium was prepared by the reaction of *n*-butyl chloride and lithium in a stream of nitrogen.

Polymerization was conducted by the same method as previously described.[3,4] Resulting polymer was isolated by precipitation by pouring the reaction mixture into a large amount of water after adding a mixture of acetic anhydride and pyridine. Waring Blendor was used, when necessary, for crushing and washing the product in water.

In Table 1 are shown the results of polymerization of β-ethoxypropionaldehyde initiated by triethylaluminum at −78°C. It should be noticed that the viscosity numbers, η_{sp}/c, of resulting polymers

Table 1. Polymerization of β-ethoxypropionaldehyde initiated by triethylaluminum at −78°C*

Solv.	Initiator, mol% to monomer	Convn. %	Mp °C	η_{sp}/c**
Methylene chloride	5	62.2	143—152	11.7
Methylene chloride	1	17.4	145—149	—
n-Hexane	5	63.6	137—144	10.5
n-Hexane	1	21.0	155—165	11.1
Toluene	5	78.7	153—160	13.9
Toluene	1	25.6	158—170	12.9

* Monomer, 5 g; solv., 10 g; for 1 day.
** In *o*-cresol; c, 0.2 g/100 m*l*; at 25°C.

Table 2. Polymerization with diethylaluminum chloride*

Solv.	Temp. °C	Time day	Convn. %	η_{sp}/c**
THF	−78	7	0	—
Methylene chloride	−78	7	trace	—
n-Hexane	−78	1	19.4	—
Toluene	−78	1	71.1	12.6
Toluene	−21	5	0	—
Toluene	0	5	0	—

* Monomer, 5 g; initiator, diethylaluminum chloride, 1 mol% to monomer; solv., 10 g;
** In *o*-cresol; c, 0.2 g/100 m*l*; at 25°C.

1) O. Vogl, *J. Polym. Sci. A*, **2**, 4607 (1964).
2) H. Takida and K. Noro, *Kobunshi Kagaku*, **20**, 705 (1963).
3) H. Sumitomo and K. Kobayashi, *J. Polym. Sci. A-1*, **4**, 907 (1966).
4) H. Sumitomo and K. Kobayashi, *ibid.*, **5**, 2247 (1967) and the following papers.

measured at the concentration of 0.2g/100 m*l* in *o*-cresol at 25°C are all extremely high.

The results of polymerization with diethylaluminum chloride are given in Table 2. The rate of polymerization is found to decrease in the order, toluene>*n*-hexane>methylene chloride. No polymer was obtained in THF at −78°C and even in toluene at −21 and 0°C.

Ethylalminum dichloride gave no polymer in all these solvents at −78°C.

Table 3 summarizes the effects of aluminum compounds with different acid strength on the polymerization of *β*-ethoxypropionaldehyde at −78°C. It was found that diethylaluminum chloride with a moderate acid strength is the most active, whereas aluminum chloride and ethylaluminum dichloride with a high acid strength are inactive in the present system.

Besides these cationic initiators, *n*-butyllithium also induces the polymerization of *β*-ethoxypropionaldehyde in toluene at −78°C (for example: 1 day; 10.8% convn.; η_{sp}/c, 8.6).

In Fig. 1 are shown the IR spectra of *β*-ethoxypropionaldehyde and its polymer. The fact that

Table 3. Polymerization with various aluminum compounds*

Initiator	Time day	Convn. %	η_{sp}/c**
$AlCl_3$	7	0	—
$Al(C_2H_5)Cl_2$	7	0	—
$Al(C_2H_5)_2Cl$	1	71.1	12.6
$Al(C_2H_5)_3$	1	25.6	12.9

* Monomer, 5 g; initiator, 1 mol% to monomer; solv., toluene, 10 g; at −78°C.
** In *o*-cresol; c, 0.2 g/100 m*l*; at 25°C.

no carbonyl absorption at 1725 cm^{-1} but four new absorption peaks due to ether linkages appear in the range from 946 to 1100 cm^{-1} in the spectrum of the polymer, suggests that the polymer has the structure of poly(ethoxyethyl)oxymethylene.

$$n CH_3CH_2OCH_2CH_2CHO \longrightarrow -\left(-CH(CH_2CH_2OCH_2CH_3)-O-\right)_n-$$

The result of elementary analysis of the polymer is as follows: Obsd: C, 58.31; H, 9.59%. Calcd for $C_5H_{10}O_2$: C, 58.80; 9.87%.

The monomer is soluble in all common organic solvents. The solubility of the polymer at room temperature is listed in Table 4. It is almost unchanged even at elevated temperature.

A strong birefringence was observed on a polymer film through a polarizing microscope. X-Ray diffraction diagram and data of the polymer are presented in Fig. 2 and Table 5 respectively.

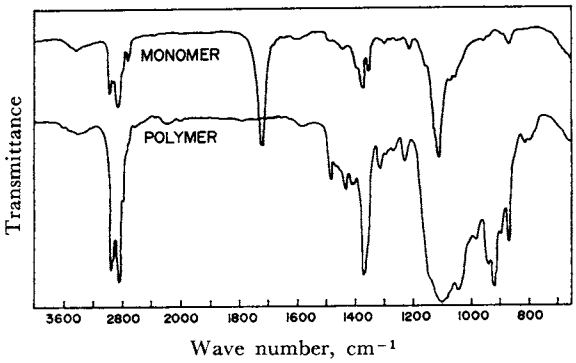

Fig. 1. Infrared absorption spectra of *β*-ethoxypropionaldehyde and its polymer.

Table 4. Solubility of poly(ethoxyethyl)-oxymethylene at room temperature

Soluble in :
phenol, *o*-cresol, and *p*-cresol.

Swelled in :
chloroform, carbon tetrachloride, methylene chloride, ethyl acetate, dimethylformamide, dimethyl sulphoxide, benzene, toluene, xylene, cyclohexane, tetralin, tetrahydrofuran, dioxane, and pyridine.

Insoluble in :
water, methyl alcohol, ethyl alcohol, acetone, methyl ethyl ketone, petroleum ether, *n*-hexane, acetonitrile, ethylene glycol monomethyl ether, and *γ*-butyrolactone.

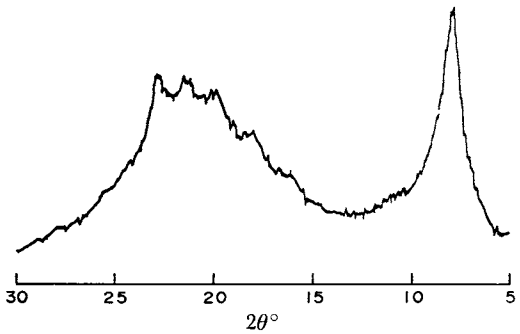

Fig. 2. X-Ray diffraction diagram of poly(ethoxyethyl)oxymethylene (Cu*Kα*, Ni filter).

Table 5. X-Ray diffraction data of poly-(ethoxyethyl)oxymethylene

Peak	Diffraction angle, 2*θ* degree	Relative intensity	Spacing *d*, Å
I	8.2	100	10.6
II	20.3	65.4	4.4
III	21.7	70.9	4.1
IV	23.0	71.7	3.9