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Oligomers from Hydroxymethylfurancarboxylic Acid

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ABSTRACT

Polycondensation of 5-hydroxymethyl-2-furancarboxylic acid (1) was studied. Oligoesters of 1 were prepared by using 2-chloro-1-methylpyridinium iodide (2) as a polycondensation agent. The solution polycondensation in pyridine at a 2 / 1 molar ratio more than 1.2 at 60°C gave selectively the macrocyclic oligoesters at a total yield more than 91% : cyclic trimer (> 33%), tetramer (> 35%), pentamer (> 13%) and higher oligomers (> 9%). The polycondensation in n-hexane in place of pyridine with tri-n-butylamine as a scavenger of hydrogen halide produced selectively the linear oligoesters from trimer to hexamer. That in toluene instead of n-hexane yielded the polyester, the cyclic and linear oligoesters. A mechanism is proposed for the formation of the cyclic oligoesters.

INTRODUCTION

Native ionophores generally contain ester and amide linkages which are biodegradable. On the other hand, synthetic ionophores are mostly based on ether and aza linkages. Nonactin, a native ionophore antibiotic, is a macrocyclic oligoester, tetramer of 5-(2-hydroxypropyl)-tetrahydrofuran-2-isopropionic acid.

In general, furan derivatives are susceptible to resinifing on heating due to a side-reaction at the furan ring and a carbonyl substituent stabilizes a furan ring and a hydroxymethyl substituent

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acts conversely [1]. Moore and Kelly [2,3,4] prepared linear polyesters by the polycondensation of 2,5-furandicarboxylic acid derivatives and various diols including 2,5-di(hydroxymethyl)furan. Ogata and Simaura [5] obtained linear polyamides from 3,4-furandicarboxylic acid derivatives. However, the formation of any cyclic oligoester was not reported in these papers.

Recently, Nakamura and Morikawa [6] produced 5-hydroxymethylfurfural from D-fructose in a high yield of 90% by using a strong acidic ion-exchange resion as a catalyst. The oxidation of 5-hydroxymethylfurfural gave easily 5-hydroxymethyl-2-furancarboxylic acid using a copper catalyst [7].

In the present study, the synthesis of macrocyclic oligomers containing a furan nucleus and an ester linkage as an alternating unit was attempted by condensation of 5-hydroxymethyl-2-furancarboxylic acid under mild conditions.

MATERIALS

5-Hydroxymethyl-2-furancarboxylic acid (1) was synthesized from commercial 5-hydroxymethylfurfural according to the procedure of the patent [7].

Solvents, tri-n-butylamine, and ethandiol were purified by usual methods.

2-Chloro-1-methylpyridinium iodide (2) was synthesized from 2-chloropyridine and methyl iodide according to the literature [8] and used without further purification. Poly(ethylphosphate) (4) was synthesized from phosphorous pentaoxide and diethyl ether [9].

Commercially available antimony trioxide, calcium acetate, and imidazole were used without further purification.

METHODS

1. Analyses

High performance liquid-solid chromatograms (HPLC) were measured with a Waters model ALC/GPC 244 chromatograph having a μ-Porasil column (Φ 3.9 mm × 300 mm).

Gel permiation chromatograms (GPC) were recorded on a TOYO SODA model HLC-802 UR chromatograph equipped with a TSK-GEL 3000H column (Φ 18 mm × 610 mm) and two 2000H columns.

^{1}H-NMR and ^{13}C-NMR spectra were obtained with a JEOL model FX90Q spectrometer, IR spectra (KBr disk) with a JASCO model A-3 spectrometer, UV spectra with a Hitachi model 340 spectrophotometer in chloroform solution, and MS spectra with a Hitachi model M-52 spectrometer.

2. Solution Polycondensation

5-Hydroxymethyl-2-furancarboxylic acid (1) (250 mg), 2-chloro-1-methylpyridinium iodide (2) (540 mg), tri-n-butylamine (1 mL), and solvent (20 mL) were placed in a 50 mL glass vessel. The mixture was stirred for 5 hours at 60°C under nitrogen atmosphere. Methanol (1 mL) was added, and the reaction mixture was heated for 20 minutes. The carboxyl end groups of 1 and linear oligoesters were converted into methyl esters.

The reaction mixture was poured into 300 mL of water. A brown precipitate was filtrated, dried in vacuo, and washed with chloroform (100 mL) to give a white polyester of 1. The chloroform washings contained the oligoesters.

3. Determination of Product Yield and Distribution

Yields of oligoesters were determined by high performance liquid-solid chromatography (HPLC). Methyl 2-furoate as an internal standard was added into the chloroform solution of the oligoesters.

In determination of the product distribution during the reaction, anthracene was added as an internal standard in the reaction vessel. A small amount (1 mL) of the reaction mixture was sampled out, and added into hot methanol (20 mL). The methanol was evaporated under a reduced pressure. The residue was dried in vacuo, diluted with chloroform, and analyzed with HPLC with an ultraviolet absorption detector (at 254 nm). Absorption coefficients of three small size cyclic oligoesters at 254 nm in chloroform (ε_{254}) were determined : cyclic trimer (3a), 3.84×10^{4} ;

cyclic tetramer (3b), 5.88×10^4; cyclic pentamer (3c), 4.90×10^4 L mol^{-1} cm^{-1}. The other larger cyclic oligoesters (3d), the methyl ester of 1 (5a), and the methyl esters of the linear oligoesters (5b-e) were assumed to have the same ε_{254} with methyl 2-furoate (1.31×10^4 L mol^{-1} cm^{-1}) per a monomer unit.

RESULTS

1. Melt Polycondensation

5-Hydroxymethyl-2-furancarboxylic acid (1) (670 mg) and antimony trioxide (22 mg) placed into a pyrex glass ampoule were heated at 200°C for 5 hours under a reduced pressure ($\leq$ 0.5 torr) of nitrogen gas. As soon as 1 started to melt, its color changed into black. The product was a hard black solid wihtout showing any IR absorption bands of organic groups.

Monomer 1 is susceptible to resinifing on heating above the melting point, 168°C. No polycondensation, however, takes place below the temperature.

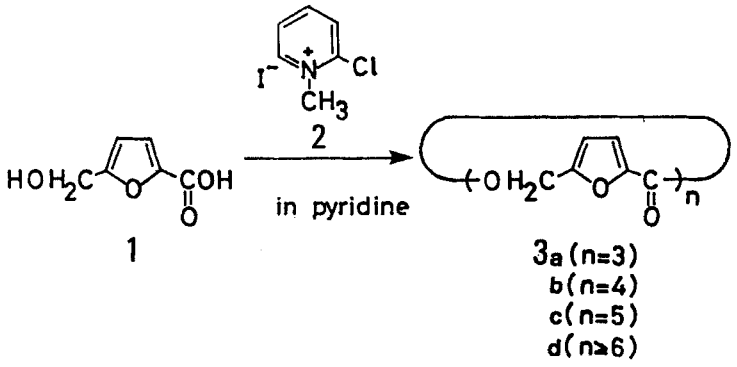
2. Transesterification Polycondensation

Monomer 1 (480 mg), ethandiol (660 mg), antimony trioxide (7 mg), and calcium acetate (5 mg) were placed into a pyrex glass ampoule. The content was stirred magnetically, and heated at 150°C for 5 hours under a reduced pressure ($\leq$ 0.02 torr). The reaction product was diluted with dimethyl sulfoxide. The solution was poured into methanol to give 40 mg of a black solid. The IR spectrum of the solid showed an absorption at 1720 cm^{-1}. On the other hand, no reaction took place at temperatures lower than 110°C.

3. Polycondensation using 2-Chloro-1-methylpyridinium Iodide

A solution polycondensation of monomer 1 was carried out in various solvent at 60°C for 5 hours by using 2-chloro-1-methylpyridinium iodide (2) as a condensation agent. Tri-n-butylamine was added as a scavenger of hydrogen halide. The product distribu-

tions were determined by using a high performance liquid-solid-chromatograph (HPLC) with an UV detector (at 254 nm).



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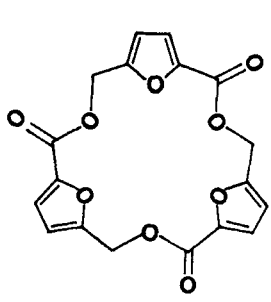
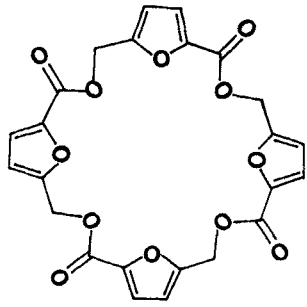


3a



3b

The results are summarized in Table 1.

Both the yields and distributions of the products are remarkably dependent on the reaction solvents. Among the solvents used, pyridine is the best for the preparation of cyclic oligoesters ; (Run 1). In n-hexane solution, linear oligoesters are selectively produced in low yields ; (Run 2). The product selectively was low in toluene solution : cyclic and linear oligoesters and chloroform-insoluble polyester are formed in low to moderate yields ; (Run 3).

TABLE 1. Polycondensation of 5-Hydroxymethyl-2-furancarboxylic Acid (1) using 2-Chloro-1-methylpyridinium Iodide (2) in Various Solvents[a)]

Run	Solvent	Tributyl amine(mL)	Yields of cyclic oligomers(wt-%)					Yields of linear oligomers(wt-%)[b)]					Yield of[c)] polymer (wt-%)
			3 mer	4	5	≥6[b)]	total	3 mer	4	5	≥6	total	
1	Pyridine	1.0	33.4	35.3	12.6	9.3	90.6	2.8	1.7	1.3	1.5	7.3	0
2	n-Hexane	1.0	0.1	1.0	0.3	0	1.4	4.9	6.1	3.9	4.7	19.6	trace
3	Toluene	1.0	2.9	11.6	6.1	1.9	23.9	2.3	1.6	2.2	4.5	10.6	24.7
4	Toluene	2.0	2.4	11.4	5.7	1.9	22.1	1.0	2.0	2.4	4.1	9.5	31.1
5	Toluene	4.0	1.1	9.1	2.0	0.6	10.9	0.9	3.4	2.7	3.4	10.4	41.2
6	Chloroform	1.0	5.2	7.6	4.0	1.1	17.9	0.5	0.5	0.4	0.4	1.8	0

a) Reaction conditions : 1, 250 mg ; 2, 540 mg (molar ratio of 2 to 1, 1.2) ; reaction time 5 h ; bath temp., 60°C ; solvent, 20 mL.

b) Determined by assuming that each monomer unit of the oligomers has an equal ε_{254} to that of methyl 2-furoate.

c) Insoluble in chloroform.

The product distribution in toluene depends on the concentration of tri-n-butylamine. With the increasing concentration of tri-n-butylamine, the yields of oligoesters decrease, while the yield of polyester increases ; (Run 4 and 5).

In dimethyl sulfoxide and N,N-dimethylformamide solutions, 2-chloro-1-methylpyridinium iodide (2) does not work as a polycondensation agent at all, yielding no oligoester, presumably because of its reaction with the solvents.

The reaction mixtures in pyridine, toluene, and n-hexane solutions were heterogeneous, while those in chloroform, dimethyl sulfoxide, and N,N-dimethylformamide were apparently homogeneous.

The solution polycondensation in pyridine was investigated in detail. The results are summerized as shown in Table 2.

When a solution of 1 in pyridine is added dropwise to a suspension of 2 in pyridine at 60°C, smaller size cyclic oligoesters are preferentially obtained ; (Run 7) : cyclic trimer (3a) in 46%, cyclic tetramer (3b) in 13%, and cyclic pentamer (3c) in 2% yield. Linear oligoesters (5a-e) are not formed under such a condition that 1 is reacted in dilute solution.

The product selectivity, i.e. the ratio of cyclic oligoesters to linear ones are remarkably dependent on the molar ratio of 2-chloro-1-methylpyridinium iodide (2) to 5-hydroxymethyl-2-furancarboxylic acid (1) in feed. Completely selective synthesis of the cyclic oligoesters can be achieved by using more than 1.65 times of 2 to 1, as shown in Run 8.

Because pyridine works also as a scavenger of hydrogen halides, the addition of tri-n-butylamine is not necessary for the condensation in pyridine ; (Run 10).

A temperature effect is significant in the product distribution. The distribution shifts toward larger size oligoesters with the decreasing temperature ; (Run 11).

The product distributions in the reactions course were also pursured.

The total concentration of cyclic oligoesters, that of linear oligoesters, and the concentration of the monomer (1) relative to

TABLE 2. Polycondensation of 5-Hydroxymethyl-2-furancarboxylic acid (1) using 2-Chloro-1-methylpyridinium Iodide (2) in Pyridine Solvent[a)]

Run	Molar ratio of 2 to 1	Tributyl amine(mL)	Temp. of bath(°C)	Yields of cyclic oligomers(wt-%)					Yields of linear oligomers(wt-%)[c)]				
				3 mer	4	5	≥6[c)]	total	3 mer	4	5	≥6	total
1	1.2	1.0	60	33.4	35.3	12.6	9.3	90.6	2.8	1.7	1.3	1.5	7.3
7[b)]	1.2	1.0	60	46.3	13.1	2.3	0	61.7	0	0	0	0	0
8	1.65	1.0	60	34.7	35.2	16.0	10.5	96.4	0	0	0	0	0
9	0.75	1.0	60	9.9	16.9	6.4	1.3	34.5	4.4	3.2	4.0	9.5	21.1
10	1.2	none	60	33.8	35.0	17.0	15.1	100.9	3.1	1.7	1.3	0	6.1
11	1.2	1.0	20	20.6	36.6	17.9	7.3	82.4	0.5	0.4	0.5	0.3	1.7

a) Reaction conditions : 1, 250 mg ; pyridine, 20 mL ; reaction time, 5 h.

b) A solution of 1 and tributylamine in 20 mL of pyridine was added dropwise to a heated suspension of 2 in 150 mL of pyridine over a period of 4.5 h and the reaction mixture was heated for additional 2.5 h after the addition was completed.

c) Determined by assuming that each monomer unit of the oligomers has an equal ε_{254} to that of methyl 2-furoate.

the initial monomer concentration were determined by assuming that each of the monomer units in the cyclic oligoesters larger than pentamer and in the linear oligoesters, and 1 had the same molecular extinction coefficient at 254 nm.

The relative concentrations are plotted against the reaction time as shown in Figure 1. The reaction is fast at 60°C enough to finish the condensation almost completely in one hour. Linear oligoesters are main products at an early stage of the reaction at 20°C. The total concentration of the linear oligoesters reachs a maximum within 40 min, and then decreases gradually. The formation of cyclic oligoesters becomes predominant, and almost 100 %.

Figure 2 shows the plots of the concentrations of the individual cyclic and linear oligoesters against the reaction time. Figure 2 also indicates that linear oligoesters are produced before the formation of the cyclic ones. The concentrations of the linear oligoesters and monomer 1 decrease with the increase of the

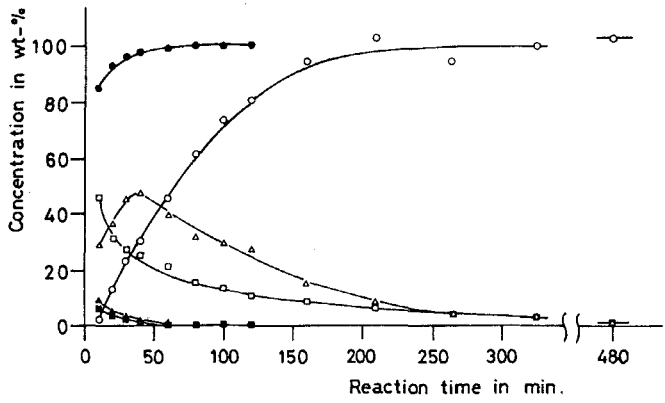


FIGURE 1. Concentration of monomer (1), total concentration of cyclic oligoesters and total concentration of linear oligoesters relative to initial monomer concentration vs. reaction time[a] : monomer (□), cyclic oligoesters (○), linear oligoesters (△) in the reaction at 20°C ; monomer (■), cyclic oligoesters (●), linear oligoesters (▲) in the reaction at 60°C.
a) Reaction conditions : 1, 250 mg; 2, 540 mg (2 / 1 molar ratio 1.2) ; pyridine, 20 mL.

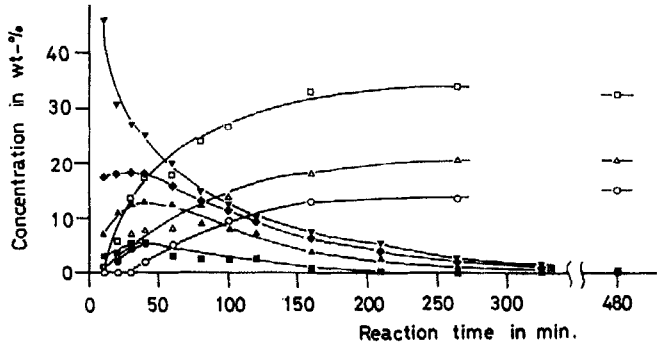


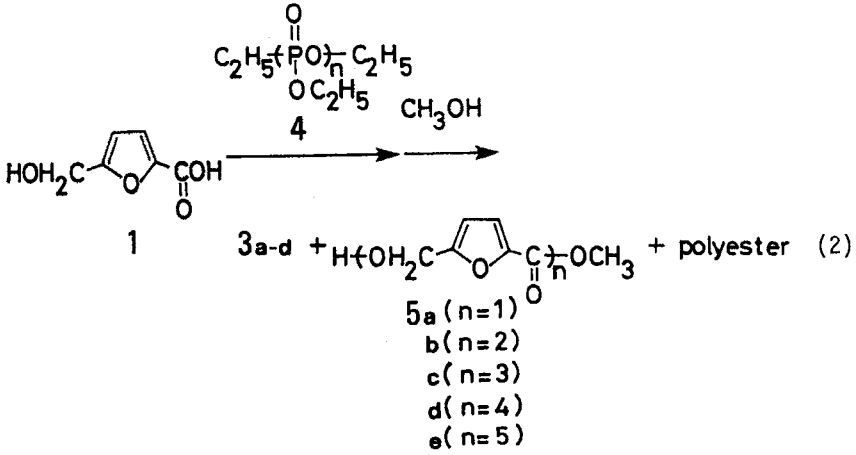
FIGURE 2. Concentrations of monomer (1), cyclic oligoesters, and linear oligoesters relative to initial monomer concentration vs. reaction time[a] : monomer (▼), cyclic trimer (△), cyclic tetramer (□), cyclic pentamer (○), linear dimer (◆), linear trimer (▲), linear tetramer (■), linear pentamer (●).
a) Reaction conditions : 1, 250 mg, 2, 540 mg (2 / 1 molar ratio 1.2) ; pyridine, 20 mL ; at 20°C.

molecular size. On the other hand, among the cyclic oligoesters, tetramer has the highest concentration over all the reaction time.

4. Polycondensation using Poly(ethylphosphate)

Monomer 1 (502 mg), poly(ethylphosphate) 4 (3 mL), imidazole (959 mg), and 1-methyl-2-pyrrolidone (25 mL) were placed in a oven-dried, 50 mL round-bottom glass flack. The mixture was stirred for 23 hours at 60°C under nitrogen atmosphere. The reaction system was homogeneous, and colorless throughout. The solvent was removed under a reduced pressure until the volume of the reaction mixture decreased to about 5 mL. Projecting the mixture into 500 mL of methanol gave a white precipitate immediately. Washing it with chloroform gave polyester of 1 (28 mg, yield 6 %). The methanol and chloroform solution were collected, and concentrated to about 5 mL by distillation. The residue was then poured into 300 mL of water to give a white precipitate. 101 mg of oligoesters were filtrated, and dried in vacuo (yield 23 %). 35 % of them was linear oligoesters in 8.0 % yield :

linear monomer (5a) in 1.4 %, dimer (5b) in 1.8 %, trimer (5c) in 1.6 %, tetramer (5d) in 1.8 %, pentamer (5e) in 0.5 % yields. The residual part was cyclic oligoesters in 15 % yield.



5. Characterization of Oligoesters

The solution polycondensation were carried out by using monomer 1 (4.61 g, 32.4 mmol), 2 (13.68 g, 53.5 mmol) and pyridine (268 mL). The oligoesters of 1 was obtained in 85.4 % yield (3.44 g). Each oligoester was separated with GPC, and analyzed.

Cyclic trimer (3a) :

IR (KBr) : 3136 (aromatic C-H), 1718 (vs; C=O), 1600 (C=C), 1298 (vs; C-O-C), 1141 (s; C-O-C), and 756 cm^{-1} (aromatic C-H).

^{1}H-NMR (DMSO-d_6) : δ = 7.44 (d; aromatic H^1), 6.82 (d; aromatic H^2), and 5.43 (s; -CH_2-) ; $J_{1,2}$ = 3.5 Hz; Intensity ratio : 10 : 10 : 20.

^{13}C-NMR (DMSO-d_6) : δ = 157.0 (C=O), 153.0, 143.8, 120.0, 112.0, and 58.7 (-CH_2-) ; Intensity ratio : 16 : 47 : 22 : 100 : 92 : 81.

UV (chloroform) : λ_{max} / nm (ε / (L mol^{-1} cm^{-1}) = 254.5 (39000).

Cyclic tetramer (3b) :

IR (KBr) : 3136 (aromatic C-H), 1718 (vs; C=O), 1598 (C=C), 1300 (vs; C-O-C), 1135 (s; C-O-C), and 759 cm^{-1} (aromatic C-H).

^{1}H-NMR (DMSO-d_6) : δ = 7.44 (d; aromatic H^1), 6.90 (d; aromatic H^2), and 5.36 (s; -CH_2-) ; $J_{1,2}$ = 3.5 Hz; Intensity ratio : 10 : 10 : 20.

^{13}C-NMR (DMSO-d_6) : δ = 157.2 (C=O), 152.9, 144.2, 120.3, 114.5, and 58.1 (-CH_2-) ; Intensity ratio : 37 : 100 : 54 : 89 : 84 : 62.
UV (chloroform) : λ_{max} / nm (ε / (L mol^{-1} cm^{-1}) = 256.2 (63000)
MS : m / e 500 ± 40.
$(C_6H_4O_2)_4$ $(124.1)_4$: Calc. C 58.1 H 3.3 ; Found C 58.2 H 3.0.

Cyclic pentamer (3c) :
IR(KBr) : 3140 (aromatic C-H), 1723 (vs; C=O), 1598 (C=C), 1297 (vs; C-O-C), 1132 (s; C-O-C), and 759 cm^{-1} (aromatic C-H).
^{1}H-NMR (DMSO-d_6) : δ = 7.38 (d; aromatic H^1), 6.85 (d; aromatic H^2), and 5.37 (s; -CH_2-) ; $J_{1,2}$ = 3.5 Hz ; Intensity ratio : 10 : 10 : 20.
UV(chloroform) : λ_{max} / nm (ε / (L mol^{-1} cm^{-1}) = 258.0 (54000).
MS : m / e 600 ± 20.

The linear oligoesters were obtained by the polycondensation using poly(ethylphosphate). Each oligomer was isolated by HPLC, and characterized by ^{1}H-NMR spectra ($CDCl_3$) and GPC.

Linear monomer (5a) :
δ = 2.29 (s; masked by H_2O), 3.90 (s; 3H), 4.69 (s; 2H), 6.44 (d; 1H), and 7.12 (d; 1H).

Linear dimer (5b) :
δ = 2.29 (s; masked by H_2O), 3.90 (s; 3H), 4.67 (s; 2H), 5.31 (s; 2H), 6.42 (d; 1H), 6.59 (d; 1H), and 7.15 (d; 2H).

Linear trimer (5c) :
δ = 2.29 (s; masked by H_2O), 3.93 (s; 3H), 4.70 (s; 2H), 5.35 (s; 4H), 6.46 (d; 1H), 6.65 (d; 2H), and 7.22 (d; masked by $CHCl_3$).

Linear tetramer (5d) and pentamer (5e) were determined from their elution volumes in GPC.

DISCUSSION

1. Reactivity of 5-Hydroxymethyl-2-furancarboxylic Acid

The furan rings in 2,5-furandicarboxylic acid, its chloride, and diesters are stable during the polycondensation reaction at

temperatures even above 250°C [2]. The furan ring in 2,5-di(hydroxymethyl)furan reacted with 2,5-furandicarbonyl chloride to give a charcoal even at a temperature as low as 80°C [1]. The stability of 5-hydroxymethyl-2-furancarboxylic acid (1) should be intermediate between those of the furan derivatives.

Further, furan derivatives are susceptible to acid, but relatively inert to base. Actually, 1 was resinified in the presence of an acid at temperatures above 150°C, but is was unchanged below that temperature.

Consequently, it was necessary for the polycondensation of 1 to use a specific polycondensation agent which could work in a basic medium at a temperature below 150°C. 2-Chloro-1-methylpyridium iodide (2) was used in macrolide syntheses [10], i.e. intramolecular condensation between a carboxyl group and a hydroxy one connected each other by a long chain. 2 was also used as a coupling reagent for esterification [8], but had not been used in polycondensation to our best knowledge. In the present study, 2 was found to be the best polycondensation agent for the cyclic oligomerization of 1. The poly(ethylphosphate) (4) with imidazole was used as a polycondensation agent for the polymerization of hydroxybenzoic acid [9]. Application of 4 with imidazole to monomer 1 gave the cyclic and linear oligoesters, and polyester in rather low yields because a side-reaction may occure between the aliphatic hydroxymethyl group of 1 and 4.

2. Cyclic Oligomerization

Figures 1 and 2 indicate that the cyclic oligoester are produced by irreversible cyclization of the linear oligoesters. Thus, the reaction is obviously controlled by the rate of intramolecular reaction (cyclization) relative to that of intermolecular reaction (linear oligoester propagation).

A nucleophilic attack of the carboxylate ion of 1 on 2 would form rapidly 2-acyloxy-1-methylpyridium iodide, an active acylating intermediate. The intermediate is converted rapidly into the carboxylic ester, 1-methyl-2-pyridone and ammonium salt by the

nucleophilic attack of the hydroxyl group of another molecule of 1 to carbonyl carbon of the intermediate in the presence of amine.

The linear oligoester propagation proceeds by repetition of the intermolecular reaction. After the linear oligoester grows to trimer, the intramolecular reaction becomes possible. An examination using CPK molecular models indicated that the cyclization of the linear trimer was slightly hindered from stereochemical viewpoint.

Another effect of 2 for the cyclization may be associated with its positive charge. In a basic solvent such as pyridine, the oxygen atom of the hydroxyl group of 1 has slightly negative charge. In the reaction mixture, the pyridinium ion of 2 probably may form a triple ion with an iodide anion and the slightly charged hydroxy group of the linear oligoesters.

Thus all the reacting species may be in the proximity of the pyridinium salt to make the intramolecular reaction advantageous.

In a nonpolar solvent such as n-hexane, the electrostatic interaction between the terminal groups of a linear oligomer molecule may not operate effectively, resulting in the formation of linear oligoesters predominantly.

CONCLUSIONS

The solution polycondensation of 5-hydroxymethyl-2-furancarboxylic acid gives the macrocyclic and linear oligoesters with the aid of 2-chloro-1-methylpyridinium iodide and poly(ethylphosphate as polycondensation agents. That using 2-chloro-1-methylpyridinium iodide in pyridine can produce selectively the macrocyclic oligoesters in high yield.

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