Polymer Bulletin 1, 41–45 (1978)

Polymer Bulletin

Selective Preparation of a Twenty-Membered Cyclic Oligoester from 6,8-Dioxabicyclo[3.2.1]octan-7-One

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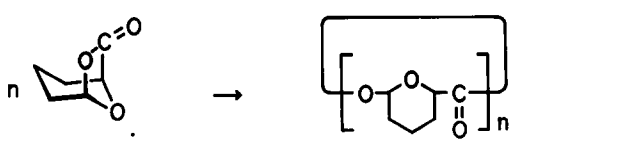
INTRODUCTION

Cationic ring-opening polymerization of cyclic monomers is often accompanied with formation of macrocyclic oligomers of various ring sizes (GOETHALS 1977). Recently we found that the cationic polymerization of 6,8-dioxabicyclo[3.2.1]octan-7-one (*1*) at low temperatures below -30°C provided exclusively ten-, twenty-, and thirty-membered macrocyclic oligoesters (*2*) consisting of alternating tetrahydropyran and ester moieties without formation of any linear polymer (OKADA *et al.* 1974 and 1977). The total yield and composition of these cyclic oligomers were markedly dependent upon the reaction conditions: The ten-membered cyclic dimer was predominantly formed in methylene chloride at -40°C except in the early stage of the reaction, whereas the thirty-membered cyclic hexamer was produced preferentially in 1-nitropropane at the same temperature. However, the twenty-membered cyclic tetramer was much less readily formed under any conditions described in the previous papers (*loc. cit.*) We wish to report herein the selective preparation of the cyclic tetramer from *1*. The cyclic tetramer having carbonyl and ether oxygens which are capable of interacting with cations is highly expected to behave as an ion carrier in a similar way as naturally occurring macrolides.



1 *2*

RESULTS AND DISCUSSION

The preparation and purification of the monomer *1*, the polymerization procedure, and the characterization of the reaction products were carried out as described in detail in the previous paper (*loc. cit.*). Some of

0170-0839/78/0001/0041/$01.00

TABLE 1

Oligomerization of 6,8-Dioxabicyclo[3.2.1]octan-7-one in chloroform[a]

Solv., ml	Temp., °C	Time, hr	Conversion, %				
			DP=2	DP=4	DP=6	DP>6[b]	total
2	-40	1	0	54	26	11	91
2	-40	24	0	91	0	0	91
4	-40	4	1	52	28	0	81
4	-40	24	1	83	0	0	84
4	-40	192	0	82	0	0	82
4	-60	4	1	35	17	28[c]	81
4	-60	24	3	61	25	3	92

[a] Monomer, 2g; BF_3OEt_2, 10 mol% to monomer.
[b] Higher oligomers.
[c] Higher oligomers and polymer.

the results of the oligomerization of *1* in chloroform solution are presented in Table 1.

The data in Table 1 clearly show the preferential formation of the cyclic tetramer in the oligomerization in chloroform solution. It was produced even nearly quantitatively, particularly when the reaction was carried out in rather concentrated solution at -40°C for 24 hours. From the variation in the product distribution with reaction time, it is noticeable that the cyclic hexamer and higher oligomers, and even polymers in the reaction at -60°C, which had been formed in a relatively short reaction time, were transformed eventually into the cyclic tetramer, although the total conversions did not alter appreciably. Such a transformation seems to indicate that the cyclic hexamer and other higher analogues were formed by a kinetically controlled process. It is to be noted that the unusually high initiator concentration (10 mol%) was used in these experiments. With the initiator concentration of 1 mol% as in the experiments in other solvents reported earlier (*loc. cit.*), the reaction took place only very sluggishly.

The cyclic tetramer was isolated by gel permeation chromatography, and crystallized in acetonitrile or chloroform. X-ray analysis of the crystals is currently

in progress. Anal.: Calcd. for $(C_6H_8O_3)_4$, C, 56.26, H, 6.31; Found, C, 56.12, H, 6.43. MW; Calcd., 512; Found (Vapor pressure Osmometry), 518. ^{13}C-NMR ($CDCl_3$, TMS): δ 168.5 (C=O), 90.9 (-OCHO-), 69.5 (-CH-CO-), 27.4 ($-CH_2CH_2CH_2-$), and 17.9 ppm ($-CH_2CH_2CH_2-$). Powdery meterials of the cyclic tetramer as isolated by gel permeation chromatography showed the ^{13}C-NMR spectrum completely identical to that of the crystals. This means that the cyclic tetramer formed in this oligomerization is not a mixture of two or more geometrical isomers but one of the isomers having a symmetrical configuration (C_4 or S_4).

TABLE 2

Selective Preparation of Cyclic Oligomers of 6,8-Dioxabicyclo[3.2.1]octan-7-one[a]

Init., mol%	Solvent,	ml	Conversion,% DP=2	DP=4	DP=6	DP>6
1	Acetonitrile	2	92	0	0	0
10	Chloroform	2	0	91	0	0
1	1-Nitropropane	4	2	1	56	0

[a] Monomer, 2g; initiator, BF_3OEt_2; temp., -40°C; time, 24 hr.

Table 2 summarizes the most suitable reaction conditions for the selective preparation of the cyclic dimer, tetramer, and hexamer from *1*. The data obtained in 1-nitropropane requires complimental remark: Although the cyclic hexamer was produced predominantly in this solvent under the specified reaction conditions given in Table 2, it was converted, although gradually, into the cyclic dimer when the reaction mixture was allowed to stand for a very long time (*e.g.* 192 hour). It must also be pointed out here that all the reaction systems given in Table 2 become jelly or solid as the reaction proceeds. It was speculated from the apparent changes of the reaction mixtures that solubility must be one of the important factors contributing to the selective formation of the cyclic oligomer of a particular ring size. Therefore, the solubilities of the cyclic dimer, tetramer, and hexamer of *1* were determined at -40°C in four different solvents (Table 3).

The solubilities of these cyclic oligomers vary widely depending on their ring sizes and the solvents. Of the three cyclic oligomers, the cyclic dimer shows the lowest solubility in any of the solvents except

TABLE 3

Solubilities of Cyclic Oligomers of 6,8-Dioxabicyclo-[3.2.1]octan-7-one at -40°C

Solvent	Solubility, g/100ml		
	DP=2	DP=4	DP=6
Acetonitrile	0.10	0.71	1.1
Methylene chloride[a]	0.33	23	21
Chloroform	1.9	0.88	22
1-Nitropropane	0.17	5.1	1.7

[a] The cyclic dimer is predominantly formed in the oligomerization in this solvent, but sometimes accompanied with considerable amounts of other oligomers of different ring sizes.

chloroform. In chloroform, the solubility of the cyclic tetramer is lower than that of the cyclic dimer, and moreover it is surprisingly lower than that of the cyclic hexamer. It would appear that such a characteristic solubility is related to the selective formation of the cyclic tetramer in chloroform. In 1-nitropropane, on the contrary, the solubility of the cyclic tetramer is three times higher than that of the cyclic hexamer, which is in turn one order of magnitude lower than those in methylene chloride and chloroform. The preferential formation of the cyclic hexamer in 1-nitropropane under the specified conditions (Table 2) seems to be ascribable to the relatively lower solubility of the cyclic hexamer. However, the difference in the oligomerization products between in 1-nitropropane and in acetonitrile can not be interpreted fully satisfactorily in terms of solubility alone. As described above, the cyclic hexamer was predominantly formed in 1-nitropropane, but eventually it was transformed into the cyclic dimer. Such a transformation observed in 1-nitropropane bears resemblance, more or less, to that in acetonitrile or methylene chloride, except that the conversion of the cyclic hexamer to the cyclic dimer is much faster in the latter two solvents (*loc. cit.*).

Thus, the specific solvent effect on the formation of the cyclic oligomers from *1* can not be generalized, simply on the basis of the solubility data. However, it seems adequate to say, at least qualitatively, that the cyclic oligomer having the lowest solubility in a given solvent is preferentially formed in the oligomer-

ization in the solvent. The foregoing results, along with the temperature and time dependences of the reaction products as reported in the previous papers (*loc. cit.*), lead us to the conclusion that the formation of macrocyclic oligoesters from *1* is controlled primarily by solubility and kinetic factors. Therefore, by proper selection of reaction conditions such as solvent, temperature, and reaction time, one of the ten-, twenty- and thirty-membered cyclic oligoesters *2* can be obtained preferentially and, in some cases, even nearly quantitatively.

SUMMARY

A twenty-membered macrocyclic oligoester consisting of alternating tetrahydropyran and ester moieties was prepared selectively by the cationic oligomerization of 6,8-dioxabicyclo[3.2.1]octan-7-one (*1*) in chloroform at -40°C with boron trifluoride etherate as an initiator. The solubility data of ten-, twenty-, and thirty-membered cyclic oligomers of *1* in four different solvents, along with the significant time dependence of the product distribution, indicate that the formation of these cyclic oligomers is controlled primarily by solubility and kinetic factors.

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Received May 3o, 1978.