The Reaction of the Obtained Polyurethanes with Adipoyl Chloride. Recently, we have reported the reaction of spiroorthocarbonate derivatives with acid halide accompanying the ring-opening transfer reaction.[16] The reactions of the obtained polyurethanes (P_{I}, P_{II}, P_{III}, and P_{IV}) having spiroorthocarbonate groups in the main chain with adipoyl chloride are attempted.

As summarized in Table III, the large differences of reactivity between the polyurethane P_{I} and P_{III} were observed. The reaction of the polyurethane P_{I} having a five-membered spiro-ring structure underwent cleavage of the main chain, confirmed by IR analysis of the reaction mixture, and no gelled polymers were obtained. In the typical case of P_{I}-1a, the IR spectra showed absorption bands at 1780 cm^{-1} attributable to a five-membered cyclic carbonate and 1720 cm^{-1} due to on an ester group, and the obtained polymer is soluble in THF. These results may suggest that the polymers containing the five-membered cyclic carbonate structure at the terminus of the polymer are obtained by the cleavage of a spiro-ring.

On the other hand, in the reaction of P_{III} having a six-membered spiro-ring structure with adipoyl chloride, the cross-linked polymer was mainly obtained. The IR spectra of the obtained cross-linked polymer, which is insoluble in DMF, showed absorption bands at 1740 and 1720 cm^{-1} for linear carbonate and ester group, respectively (Scheme VI).

These differences of reactivity between P_{I} and P_{III} depend on the ring size of spiroorthocarbonate; that is, the mixture of poly(carbonate–ether) and polyether accompanying with elimination of ethylene carbonate is obtained in the polymerization of the five-membered spiroorthocarbonate, but six-membered spiroorthocarbonate afford exclusively the poly(carbonate–ether) without the elimination of a six-membered cyclic carbonate.[17]

Registry No. **1**, 66290-97-9; **2**, 110374-62-4; **3a**, 120600-68-2; **3b**, 120600-69-3; **4a**, 120874-02-4; **4b**, 120874-03-5; **5a**, 121441-45-0; **5b**, 121441-46-1; $\mathbf{P}_{\mathrm{I}}$**-1** (copolymer), 121425-70-5; $\mathbf{P}_{\mathrm{I}}$**-1** (SRU), 121425-80-7; $\mathbf{P}_{\mathrm{I}}$**-2** (copolymer), 121425-71-6; $\mathbf{P}_{\mathrm{I}}$**-2** (SRU), 121541-44-4; $\mathbf{P}_{\mathrm{I}}$**-3** (copolymer), 121425-72-7; $\mathbf{P}_{\mathrm{I}}$**-3** (SRU), 121425-81-8; $\mathbf{P}_{\mathrm{I}}$**-4** (copolymer), 121425-73-8; $\mathbf{P}_{\mathrm{I}}$**-4** (SRU), 121425-82-9; $\mathbf{P}_{\mathrm{II}}$**-1** (copolymer), 121425-74-9; $\mathbf{P}_{\mathrm{II}}$**-1** (SRU), 121425-83-0; $\mathbf{P}_{\mathrm{II}}$**-2** (copolymer), 121425-75-0; $\mathbf{P}_{\mathrm{II}}$**-2** (SRU), 121541-45-5; $\mathbf{P}_{\mathrm{III}}$**-1** (copolymer), 120881-09-6; $\mathbf{P}_{\mathrm{III}}$**-1** (SRU), 121425-84-1; (P_{III}-1)($ClCO(CH_2)_4COCl$) (copolymer), 121425-78-3; $\mathbf{P}_{\mathrm{III}}$**-2** (copolymer), 121425-76-1; $\mathbf{P}_{\mathrm{III}}$**-2** (SRU), 121541-46-6; $\mathbf{P}_{\mathrm{III}}$**-3** (copolymer), 120881-05-2; $\mathbf{P}_{\mathrm{III}}$**-3** (SRU), 121425-85-2; (P_{III}-3)-($ClCO(CH_2)_4COCl$) (copolymer), 120924-75-6; $\mathbf{P}_{\mathrm{III}}$**-4** (copolymer), 120881-07-4; $\mathbf{P}_{\mathrm{III}}$**-4** (SRU), 121425-86-3; $\mathbf{P}_{\mathrm{IV}}$**-1** (copolymer), 120881-06-3; $\mathbf{P}_{\mathrm{IV}}$-1 (SRU), 121425-87-4; $\mathbf{P}_{\mathrm{IV}}$**-2** (copolymer), 121425-77-2; $\mathbf{P}_{\mathrm{IV}}$**-2** (SRU), 121541-47-7; 2-mercaptoethanol, 60-24-2; 3-mercaptopropanol, 19721-22-3; phenyl isocyanate, 103-71-9.

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Polymerization of 1,5-Dioxepan-2-one. 1. Synthesis and Characterization of the Monomer 1,5-Dioxepan-2-one and Its Cyclic Dimer 1,5,8,12-Tetraoxacyclotetradecane-2,9-dione

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ABSTRACT: A new technique for isolation of 1,5-dioxepan-2-one, resulting in a higher yield, 18% compared to 5% in an earlier reported article where acrylonitrile was used as starting material, is presented and the new compound 1,5,8,12-tetraoxacyclotetradecane-2,9-dione has been identified as the cyclic dimer. The melting point of 1,5-dioxepan-2-one has been found to be 35 °C and of its cyclic dimer 117 °C. Both compounds have been characterized by ^{1}H NMR and IR spectroscopy and their respective molecular weights have been determined by mass spectrometry.

Introduction

The synthesis of 1,5-dioxepan-2-one (DXO) was first mentioned in a patent in 1973.[1] The synthesis started from 3-(2-hydroxyethoxy)propionitrile, which was obtained from ethylene glycol and acrylonitrile and was ring closed with dry HCl (g) to form the imino ether hydrochloride salt in about 75% yield. The compound was described as white crystals: no melting or decomposition point nor chemical analysis was reported. Hydrolysis with distilled water at 50 °C for 1 h and workup resulted in a 45% yield of a viscous semicrystalline mass, which, according to elemental analysis and NMR spectroscopy, was claimed to be DXO; no molecular weight of the compound was reported. Although anticipated, no polymerization or copolymerization was described.

Copolymers of DXO with ε-caprolactone of various compositions (0–15 mol % DXO) were later prepared.[2] The new process for the preparation of DXO resulted in

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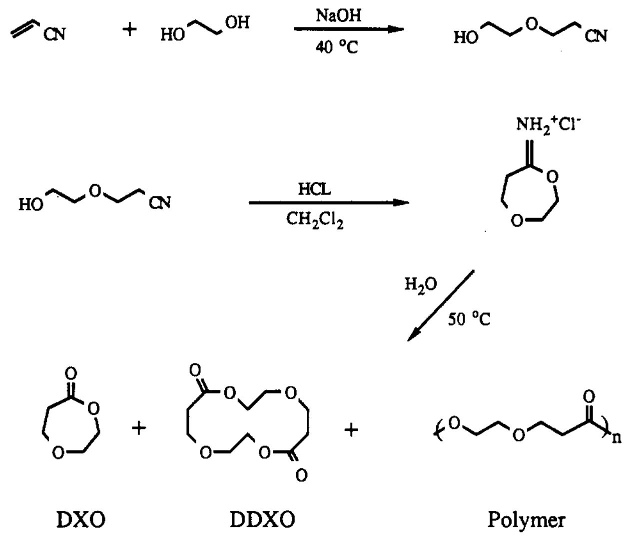

Figure 1. Synthesis of DXO according to ref 1.

colorless crystals, mp 35 °C, on recrystallization from ether. No yield nor further characterization was reported, but the compound could be copolymerized with glycolide and/or lactide to a 20–30% DXO incorporation and an intrinsic viscosity of up 1.8 dL/g.[3]

DXO was again synthesized from acrylonitrile and ethylene glycol,[4] recrystallized from acetone (mp 37 °C), and examined by ^1H NMR spectroscopy; the ring conformation was discussed.

Doubts have accumulated concerning the composition of the semicrystalline mass presently described as DXO,[1] where the ring closure reaction used could, theoretically, lead to 1,5,8,12-tetraoxacyclotetradecane-2,9-dione (DDXO, the cyclic dimer of DXO) and also to the oligomers or polymers of these two compounds, see Figure 1. It is known that strained ring compounds with a ring size of 7–10 can readily form cyclic dimers or even larger ring cyclic oligomers (in addition to some polymers).[5] The 10-membered compound 1,4-diazocyclodecane-2,3-dione was initially isolated as the cyclic dimer, and only after careful examination, especially by mild techniques for the determination of molecular weight, could the cyclic monomer be identified and characterized.

The objective of the present work has been to investigate the synthesis of DXO and to thoroughly characterize and isolate the product or products that arise, in which we expect to find not only DXO but also the cyclic dimer DDXO. In this paper a new technique for isolation of DXO is discussed as well as the differences in interpretation of the ^1H NMR spectra given earlier.[4,6]

Experimental Section

Materials. Ethylene glycol, acrylonitrile, and tetraisopropyl orthotitanate were of analytical grade (Merck). All chemicals were used as received.

Instrumentation and Measurements. All 200-MHz ^1H NMR spectra were recorded on a Brucker WP-200 spectrometer in $CDCl_3$ solutions at room temperature with TMS as internal standard. All IR spectra were recorded on a Perkin-Elmer FTIR Model 1710 spectrometer equipped with a 3600 data station. A Finnegan GC–MS was used to determine the molecular weights, using methane as ionizing gas. The GC column used was from J & W, type DB-1. Elemental analyses were performed by Mikro Kemi AB, Uppsala.

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to determine the melting points, which were recorded with a heating rate of 10 °C/min and reported as the peak temperature of the second heating scan.

A Waters GPC system, which was run with chloroform for all measurements, consisted of a solvent delivery system (Model 6000A), an automatic injector (Wisp 710B), and a differential refractometer. A column from Waters of the type micro-styragel 100 Å and one TSK gel column from Varian, type G1000HB. were used.

3-(2-Hydroxyethoxy)propionitrile. Ethylene glycol, 1240 g (20 mol), and a solution of sodium hydroxide (30 g in 30 mL of water) were stirred together in a 2-L round-bottomed flask, and 330 mL (5 mol) of acrylonitrile was dropped into the solution at such a rate that the temperature did not exceed 40 °C. When all the acrylonitrile had been added, the temperature was maintained at 40 °C for 5 h. The mixture was then neutralized with 25% HCl solution, and the excess ethylene glycol was removed under reduced pressure. The residue was distilled twice under reduced pressure, bp (0.2 mbar) 104 °C, to give 369 g of 3-(2-hydroxyethoxy)propionitrile, yield 69%.

Anal. Calcd for $C_5H_9O_2N$: C, 52.1, H, 7.9; O, 27.8; N, 12.2. Found: C, 50.3; H, 8.0; O, 30.2; N, 11.5.

Imino Ether Hydrochloride Formation. 3-(2-Hydroxyethoxy)propionitrile, 50 g (0.44 mol), was stirred together with 4 L of dry methylene chloride while a stream of dry HCl gas was passed through the solution for 6 h. The solution was left overnight and the white crystals of the imino ether were filtered off, washed with dry methylene chloride, and vacuum dried, yield 51.8 g, 78%.

Anal. Calcd for $C_5H_{10}O_2NCl$: C, 39.6; H, 6.6; O, 21.1; N, 9.2; Cl, 23.5. Found: C, 35.7; H, 7.4; O, 25.4; N, 8.9; Cl, 22.5.

Hydrolysis of the Imino Ether Salt. The imino ether hydrochloride crystals, 50 g (0.34 mol), were added to 500 mL of water and the temperature was raised to 50 °C. After 30 min the cloudy solution had clarified, and an oily phase was observed on the surface; 15 min later the solution was extracted with 2 × 300 mL methylene chloride. The methylene chloride phase was dried over anhydrous magnesium sulfate and evaporated to leave a viscous liquid, yield 21.4 g (54%).

After a short time, crystals started to develop. They were filtered off and recrystallized twice in toluene to give 2.9 g (3.7% yield, based on acrylonitrile) of white crystals, mp 117 °C.

Anal. Calcd for $C_5H_5O_2$: C, 51.7; H, 6.9; O, 41.3. Found: C, 51.6; H, 6.8; O, 41.6.

1,5-Dioxepan-2-one (DXO). After removal of the crystals with a melting point of 117 °C, 25 g of the oily phase was distilled under vacuum together with 0.5 g of tetraisopropyl orthotitanate. When the temperature was maintained at 200 °C, the oil became increasingly more viscous before the monomer DXO started to distill off at low pressure. A second distillation was carried out for further purification of the DXO (62 °C and 0.4 mbar), yield 16.41 g (18% based on acrylonitrile). DXO obtained in this way may crystalline but had to be further purified by recrystallization in anhydrous ether, mp 35 °C.

Results and Discussion

Evidence for the Cyclic Dimer. The viscous liquid isolated after the hydrolysis of the imino ether hydrochloride salt was analyzed by GPC. The chromatogram, shown in Figure 2, reveals three peaks. Two of these were identified as DXO and the compound with a melting point of 117 °C by comparison with chromatograms of the pure compounds. The third peak certainly originates from oligomers, polymers, or higher cyclic compounds.

The IR spectra of DXO and of the crystals with mp 117 °C are shown in Figures 3 and 4. Due to the absence of an OH band in the latter spectrum we can therefore be certain that this compound is cyclic; it has a larger molecular weight than DXO, Figure 2, and agrees with the general formula $C_5H_5O_3$ on the basis of elemental analysis. We can assume that this is in all probability the cyclic dimer DDXO. To substantiate this further we decided to determine the molecular weight of the two compounds. These compounds will be designated DXO and DDXO in the following discussion.

Determination of Molecular Weight. The molecular weights of DXO and DDXO were determined by both electron impact ionization and chemical ionization in GC–MS. In the former case, which usually causes exten-

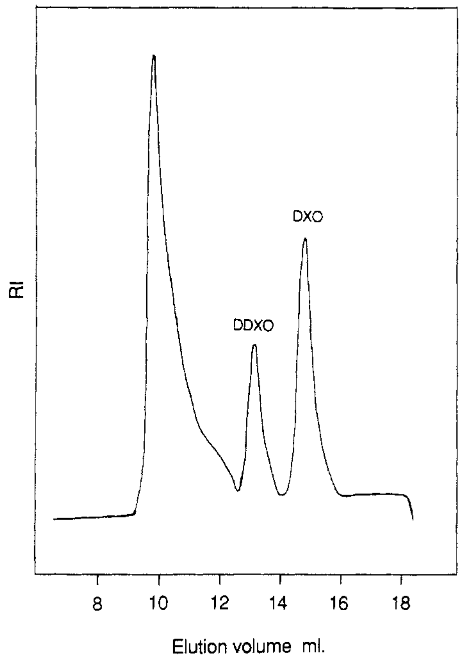

Figure 2. GPC of the viscous oil obtained after hydrolysis of the imino ether hydrochloride salt.

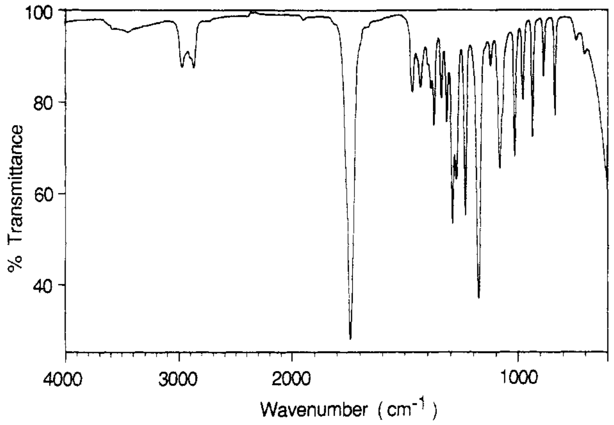

Figure 3. IR spectrum of 1,5-dioxepan-2-one (KBr tablet).

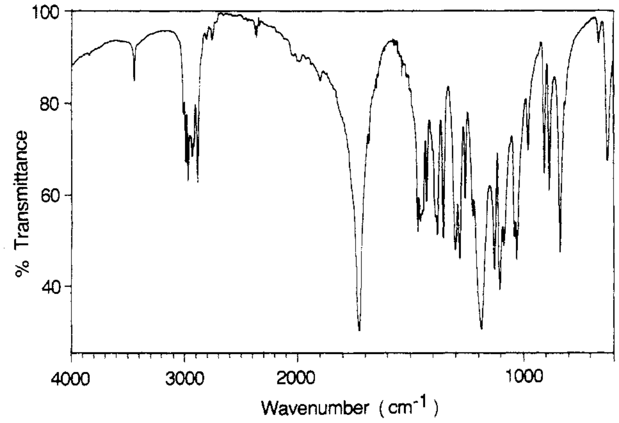

Figure 4. IR spectrum of the crystals with mp 117 °C (KBr tablet).

sive fragmentation, no molecular weight peak is found for the cyclic dimer. The mass spectrum of DDXO in Figure 5 shows peaks at m/z = 116 and higher and also a very small peak at m/z = 232, which is too weak to be taken as a molecular weight peak. DXO shows a peak at m/z = 116 but no peaks beyond as shown in Figure 6.

In the case of the milder technique of chemical ionization, using methane as ionizing gas, the compounds show hardly any fragmentation. On the other hand, the peak of the quasi-molecular ion $(M + H)^+$ is very intense. Even the $(M + C_2H_5)^+$ can be seen for both compounds, which makes the molecular weight determination more reliable. The two peaks mentioned above were found in the CI mass spectrum of DDXO, corresponding to $(DDXO + H)^+$ at m/z = 233 and $(DDXO + C_2H_5)^+$ at m/x = 261. The integer part of the molecular weights is 232, exactly double the molecular weight of DXO.

The two peaks $(DXO + H)^+$ and $(DXO + C_2H_5)^+$ at m/z = 117 and 145, respectively, for DXO give a molecular weight of 116. In the same spectrum, another peak was found at m/z = 233, which could belong to the quasi-molecular ion $(DDXO + H)^+$, which indicates that the sample could be contaminated with DDXO. However, due

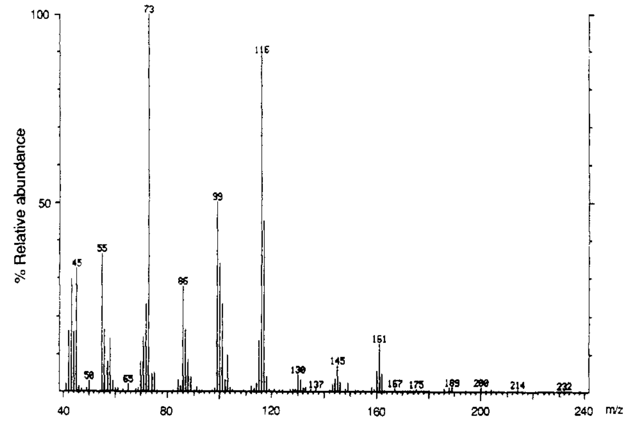

Figure 5. Mass spectrum of DDXO with electron impact ionization (70 eV). Elution temperature from GC column: 168 °C.

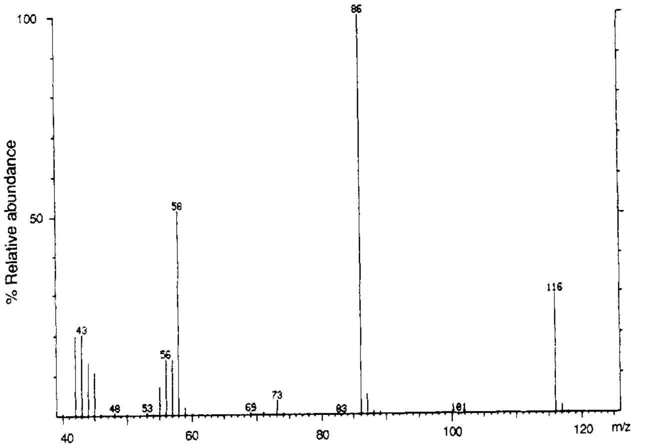

Figure 6. Mass spectrum of DXO with electron impact ionization (70 eV). Elution temperature from GC column: 125 °C.

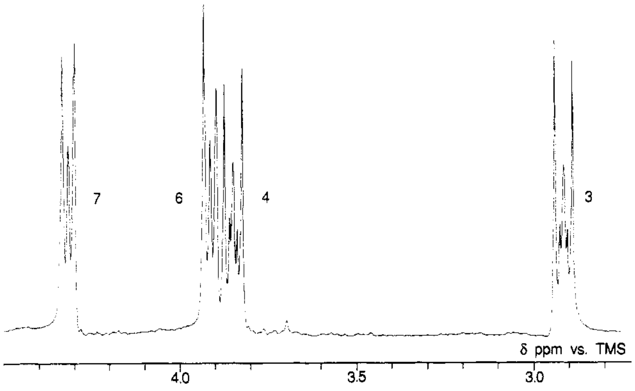

Figure 7. 200-MHz ^1H NMR spectrum of DXO in $CDCl_3$. The numbers correspond to the position of the protons; see Table I.

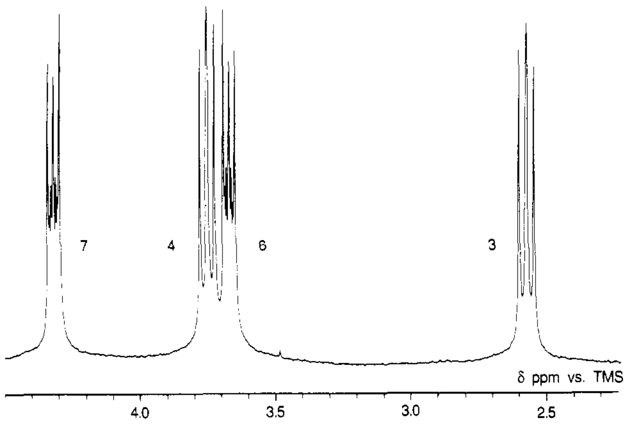

Figure 8. 200-MHz ^1H NMR spectrum of DDXO in $CDCl_3$. The numbers correspond to the position of the protons; see Table I.

Table I
^1H NMR of 1,5-Dioxepan-2-one and Its Cyclic Dimer[a]

position	DXO	DXO[b]	DXO[c]	DDXO
3	2.92	2.86	2.49	2.57
4	3.85	3.77	3.68	3.75
6	3.92	3.84	3.60	3.67
7	4.32	4.30	4.21	4.32

[a] Shifts in ppm relative to TMS. [b] Values taken from ref 6, obtained in acetone-d_6 using TMS as internal standard. [c] Values taken from ref 4, same conditions as above.

to the large difference in retention time on the GC column, this cannot be the case. It is more likely that the peak at $m/z = 233$ originates from a dimerization product formed in the mass spectrograph.

NMR. Both DXO, Figure 7, and its cyclic dimer, Figure 8, show second-order ^1H NMR spectra corresponding to AA′BB′, as expected for such compounds.[8] Since methylene protons next to an ester function have a resonance frequency at a lower field than methylene protons next to a carbonyl group,[9] the peaks for the protons in positions 7 and 3 could be assigned without any doubts. To assign the methylene protons that exist on each side of the ether function, a decoupling of the ^1H NMR spectra was done, by irradiating the protons in position 3. This shows that the protons in positions 4 and 6 in DXO have a shift relative to TMS of 3.85 and 3.92 ppm, respectively, whereas in DDXO they have changed places with each other corresponding to 3.67 and 3.75 ppm′, see Table I.

An earlier assignment for DXO, obtained from measurements in acetone-d_6, reported a shift relative to TMS of the protons in positions 3 and 4 to be 2.49 and 3.68 ppm, respectively.[4] The assignments made in that reference are assumed to be wrong. They agree much better with DDXO.

This statement is further supported by ref 6, where the shifts of the same protons are reported to be 2.86 and 3.77 ppm in acetone-d_6. This agrees very closely with our results. The differences may depend on the solvent used.

Isolation of DXO and DDXO. Table II shows the proportions in which DXO, DDXO, and the polymer/oligomer are formed, see Figure 1, using difference dilution ratios and temperatures in the imino ether hydrochloride formation step. These results were obtained with GPF by calibrating the peak areas against pure DXO and DDXO and ^1H NMR analysis.

The relatively large difference between DXO and DDXO in chemical shift of the protons for the methylene group in position 3, shown in Table I, makes it possible to separate the integrals of these two triplets. In the polymer, this methylene group has a shift (2.62 ppm) very close to that in DDXO, so the NMR integral can only be used to give the ratio of DXO relative to DDXO and the polymer. These results are in accordance with GPC measurements for DXO, suggesting that the values obtained from GPC are correct for DDXO and the polymer. As expected, the results in Table II indicate that the formation of DXO is favored by high dilution.

Table II
Ratios of DXO, DDXO, and Oligomer Polymer Based on GPC and ^1H NMR Analyses of Hydrolyzed Imino Ether Hydrochloride Salt (50 g) Obtained at Different Temperatures and Dilutions

sample	vol of CH_2Cl_2, L	temp, °C	yield, %	composition[a]		
				DXO	DDXO	polymer
1	2	0	47	21 (20)[b]	21	58
2	1	20	64	37 (37)	16	53
3	2	20	44	30 (28)	19	51
4	4	20	54	52 (51)	19	29

[a] The ratios are expressed as weight percentages. [b] Yields within parentheses are based on ^1H NMR, recalculated from mole percent to weight percent assuming that all products contain the unit $C_5H_8O_3$.

Isolation of DDXO from the viscous product obtained after hydrolysis of the imino ether hydrochloride was achieved most easily by letting it stand at room temperature for 2 days. Within this time period almost all DDXO that was able to crystallize had separated from the mother liquid. By adding toluene, in which DXO and the polymer will dissolve, the crystals are easily removed by filtration. Toluene is also a good medium for recrystallization, but methanol has also been used satisfactorily.

Isolation of DXO has been found troublesome. Vacuum distillation gives a very poor yield, due to polymerization. It seems that the best way so far is to add a small amount of reesterification catalyst and to keep the pot temperature at around 150–200 °C under high vacuum. This technique of producing monomers from a low molecular weight polyester is also used in the synthesis of glycolide and lactide.[7] DXO obtained in this manner can be further purified by distillation and recrystallization in anhydrous ether. The low melting point of DXO (35 °C) is a problem during the isolation procedure, but at the same time it gives a good indication of its purity. At room temperature the crystals first become sticky and then melt down to a liquid, due to their hygroscopic properties.[6] The polymer of DXO can also be found in this liquid and discovered by NMR.

Conclusions

In this work we have shown that the product from the synthesis described in ref 1 is composed not only of DXO but also of its cyclic dimer and the polymer/oligomer of these two compounds.

On the basis of the data obtained by the different analytical methods used to characterize the compound with mp 117 °C, the conclusion can be drawn that this is the cyclic dimer of DXO.

A contributory cause for the poor yield of DXO reported in earlier articles using recrystallization[4,6] is that the cyclization reaction gives a high amount of DDXO and polymers. We proved that a higher yield for DXO was obtained by depolymerization, using a small amount of catalyst.

The ^1H NMR spectrum shown and discussed in ref 4 does not agree with our own results for DXO. It shows more similarities to the spectrum of DDXO although the melting point is correct for DXO.

The stability of DXO is poor at room temperature compared with that of the cyclic diemr because of its hygroscopic properties and also because it can easily self-polymerize, which means that extreme care must be taken when storing and using this compound. The polymerization of these two compounds will be discussed in a later paper.

Acknowledgment. This work was supported by the National Swedish Board for Technical Development (STU). We express our deepest gratitude to Prof. O. Vogl at Polytechnic University, Brooklyn, for valuable discussions and Pierre Ljungquist at STFI, who performed the GC-MS analysis.

Registry No. DXO, 35438-57-4; DDXO, 121425-67-0; $HO(CH_2)_2O(CH_2)_2CN$, 24298-26-8; $HO(CH_2)_2OH$, 107-21-1; $H_2C{=}CH{-}CN$, 107-13-1; 1,5-dioxepan-2-iminohydrochloride (homopolymer), 35438-56-3.

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Polymerization of 1,5-Dioxepan-2-one. 2. Polymerization of 1,5-Dioxepan-2-one and Its Cyclic Dimer, Including a New Procedure for the Synthesis of 1,5-Dioxepan-2-one

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ABSTRACT: A new method for the synthesis of 1,5-dioxepan-2-one is presented involving Baeyer–Villiger oxidation of tetrahydro-4*H*-pyran-4-one. This method is superior to other known methods with regard to both yield, 48% instead of traditional methods, which give a yield of 5–18%, and lack of side reactions, which facilitate the isolation of 1,5-dioxepan-2-one. The homopolymerizations of both 1,5-dioxepan-2-one and its cyclic dimer 1,5,8,12-tetraoxacyclotetradecane-2,9-dione have been studied by use of different transesterification catalysts in bulk and by using bimetallic μ-oxo alkoxide as catalyst in solution. The polymers obtained had molecular weights in the range 10 000–50 000 and a glass transition temperature T_g of −39 °C. The polymers were completely amorphous and have been characterized by IR, ^1H and ^{13}C NMR, DSC, and GPC.

Introduction

The polymerization of 1,5-dioxepan-2-one (DXO) together with ε-caprolactone, lactide, and glycolide have been studied in the literature.[1,2] The homopolymerization of DXO has, to our knowledge, not been studied, but the polymer has been mentioned as a side product during the synthesis of DXO.[3] This polymer could be of great interest due to its known hydrolytic degradation and in vivo absorption, which has been examined in the form of copolymers of glycolide and DXO.[4] The homopolymer of DXO can be seen as a poly(ether–ester) chain built up of two alternating species (i.e., ethylene glycol and β-hydroxypropionic acid); see Figure 1. It is therefore of interest to compare the properties of this polymer with those of the two known aliphatic poly(ether–ester) chains of ethylene glycol with α-hydroxyacetic acid and γ-hydroxybutanoic acid, shown in Figure 1. The polymer seen in Figure 1A can easily be obtained from 1,4-dioxan-2-one with diethylzinc as initiator.[5] The polymer, known as poly(*p*-dioxanone), is partly crystalline (38%) with a melting temperature T_m of 110 °C and a glass transition temperature T_g of −16 °C. The polymer has been well characterized due to its commercial use as a degradable suture filament in surgery.[6] The polymer seen in Figure 1C has been obtained from 1,4,6-trioxaspiro[4.4]nonane by using BF_3 as initiator.[7] The polymer obtained in this way had a molecular weight of 25 000 and appeared to be a viscous liquid at room temperature.

In a recent article, we have discussed the formation of DXO and its cyclic dimer, 1,5,8,12-tetraoxacyclotetradecane-2,9-dione (DDXO), by a synthetic method based on the ring closure of 3-(2-hydroxyethoxy)propionitrile with dry HCl to form the imino ether hydrochloride salt followed by hydrolysis.[8]

The low yield of DXO obtained is due partly to the formation of DDXO and oligomeric materials, which also complicates the isolation, and this calls for a more specific synthetic route that is free from side products.

Such a synthesis of DXO can presumably be achieved by using Baeyer-Villiger oxidation of tetrahydro-4*H*-pyran-4-one (THP). This compound has been synthesized in about 60% yield from the starting materials 3-chloropropionyl chloride and ethylene.[9] This type of oxidation of ketones has proved to be a most efficient way of synthesizing lactones from cyclic ketones[10] under different conditions.

The object of this work has been first to find a specific way to synthesize DXO in order to make this monomer more accessible for polymerization experiments and second to polymerize the monomer. The polymerization of both DXO and its cyclic dimer have been performed in order to characterize this new aliphatic poly(ether–ester).

Experimental Section

Materials. Dibutyltin oxide (Aldrich) was dried in vacuum at 120 °C for 24 h prior to use. Tetraisopropyl orthotitanate (Merck) was distilled under reduced pressure and stored in septum bottles under a N_2 atmosphere. Stannous 2-ethylhexanoate (Sigma) and antimony trioxide (Merck) were used as received. Aluminium isopropoxide (Aldrich) was distilled under reduced pressure and stored under a N_2 atmosphere. Zinc acetate–$2H_2O$

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