groscopic 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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Table I
Polymerization of 1,5,8,12-Tetraoxacyclotetradecane-2,9-dione by Organotin Compounds

sample	initiator	(M), mmol	(M)/(I)	time, h	temp, °C	yield,[a] %	M_n	M_w	M_w/M_n
1	Bu_2SnO	1.95	210	20	130	85	8000	17800	2.21
2	Bu_2SnO	2.19	440	20	130	82	28400	50200	1.77
3	Bu_2SnO	2.20	475	10	180	86	16500	30100	1.81
4	Bu_2SnO	2.13	420	20	180	93	17400	30200	1.74
5	Sn-okt[b]	2.17	250	20	130	86	6700	10200	1.52
6	Sn-okt	2.19	500	20	130	83	13000	19300	1.48
7	Sb_2O_3	2.14	470	20	180	0	0	0	

[a] Measured by calibration of the dimer peak in the GPC chromatogram. [b] Stannous 2-ethylhexanoate.

Table II
Results of the Polymerization of 1,5-Dioxepan-2-one[a]

sample	initiator	(M), mmol	(M)/(I)	temp, °C	yield,[b] %	M_n	M_w	M_w/M_n
1	Bu_2SnO	10.6	285	100	84	13900	28000	2.0
2	Bu_2SnO[c]	10.7	293	100	86	12200	18900	1.6
3	Bu_2SnO	17.3	500	100	81	4200	11600	2.8
4	Bu_2SnO	17.5	1000	100	83	6600	10300	1.6
5	Sn-okt[d]	10.7	234	100	90	19600	36600	1.9
6	Sn-okt	19.1	500	100	84	7400	15200	2.1
7	Sn-okt	9.7	537	100	85	12800	23900	1.9
8	Sn-okt	17.6	1000	100	83	6300	12700	2.0
9	$(i\text{-Pr})_4Ti$[e]	21.8	1000	100	88	7300	12600	1.7
10	Teyssié	15.3	280	90	57	18100	25300	1.4

[a] Polymerization time was 6 h. [b] Measured by calibration of the dimer peak in the GPC chromatogram. [c] Dibutyltin oxide and lauryl alcohol in molar ratio 1:2. [d] Stannous 2-ethylhexanoate. [e] Tetraisopropyl orthotitanate.

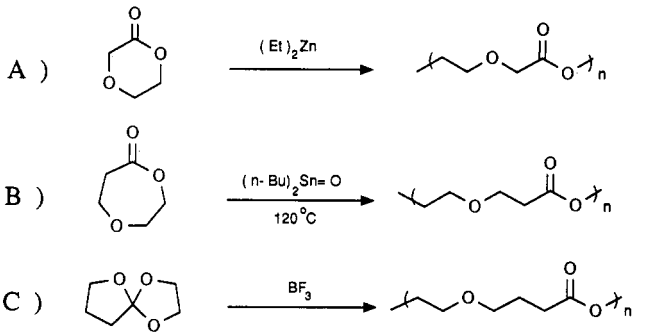

Figure 1. Aliphatic poly(ether–ester) polymerized by ring-opening polymerization of (A) 1,4-dioxan-2-one, (B) 1,5-dioxepan-2-one, and (C) 1,4,6-trioxaspiro[4.4]nonane.

(Merck) was dried to constant weight in a vacuum oven. 3-Chloroperbenzoic acid (Aldrich) was used as received. Iodometry was used to determine the active amount of peracid to 82 mol %.

3-Chloropropionyl chloride (Aldrich) was used as received. Toluene and decaline were dried over sodium and distilled in a N_2 atmosphere. Methylene chloride was distilled over P_2O_5.

1,5-Dichloropentan-3-one and tetrahydro-4*H*-pyran-4-one were synthesized by Friedel-Crafts acylation of ethylene with 3-chloropropionyl chloride followed by ring closure.[9] The synthesis of 1,5,8,12-tetraoxacyclotetradecane-2,9-dione (DDXO) was described in our first paper in this series[8] and recrystallized in methanol immediately before use.

Preparation of the Bimetallic μ-Oxo Alkoxide Initiator. The synthesis was conducted by condensation of zinc acetate with aluminium isopropoxide in molar ratios 1:2 in decaline.[11] Isopropyl acetate started to distill of at 100 °C and the reaction was completed by successively raising the temperature to 180 °C over a 5-h period. Decaline was then removed by vacuum distillation and the residue dissolved in toluene. An insoluble fraction was removed by centrifugation of the solution kept under a N_2 atmosphere. Atomic absorption confirmed the molar ratio 1:2 between Zn and Al.

1,5-Dioxepan-2-one. Tetrahydro-4*H*-pyran-4-one, 55 g (0.55 mol), was added to a slurry of 160 g (0.75 mol) of 82% 3-chloroperbenzoic acid and 82 g (1 mol) of sodium bicarbonate in 800 mL of dry methylene chloride. The slurry was kept under constant stirring at 0 °C while THP was added and was then maintained at 20 °C for 16 h. After filtration, the methylene chloride phase was washed with sodium bisulfite and sodium bicarbonate to eliminate any remaining peracid.

The methylene chloride phase was evaporated to give a slightly yellow oil. Distillation under reduction pressure (68 °C, 1 mbar) gave 80% yield of DXO. Before polymerization DXO was recrystallized twice in anhydrous diethyl ether and dried in vacuum over P_2O_5, mp 35 °C (DSC).

Polymerization. The polymerization of both DXO and DDXO was conducted by adding the monomer and the initiator, the exact amount is found in Tables I and II, to 20-mL serum bottles containing a stirring bar. The serum bottles were purged with N_2 and sealed off. The temperature of polymerization was in the case of DXO 100 °C and for DDXO 130 and 180 °C due to the high melting point for DDXO (mp 117 °C). The polymer formed was directly analyzed by GPC and the polymerization yield was calculated from the area of the monomer peak, the area having been calibrated by injection of pure monomer. To remove the monomer residue and the metal catalyst, the polymer was dissolved in methylene chloride and washed with 2 M HCl and thereafter with water. The polymer was precipitated in methanol. A polymer free of monomer was obtained by discharging the methanol solution before all the polymer had settled.

In the solution polymerization using the bimetallic μ-oxo alkoxide as catalyst, both the catalyst and the recrystallized DXO were dissolved in toluene and transferred to a serum bottle by means of a syringe. Prior to the experiment the serum bottle had been heated to 200 °C, sealed off, and allowed to recover to room temperature while a stream of dry N_2 was passed through it. The polymerization was conducted at 90 °C for 3 h and then stopped by adding 2 M HCl. After adding 20 mL of methylene chloride, the organic phase was washed two times with water methylene chloride, the organic phase was washed two times with water and dried over $MgSO_4$ and the polymer was precipitated in heptane.

Instrumentation. 200-MHz ^1H/NMR and 25-MHz ^{13}C NMR spectra were recorded on a Brucker WP-200 spectrometer. The ^1H–^{13}C chemical shift correlation spectrum was obtained on a 400-MHz Brucker AP-400. All spectra were obtained from $CDCl_3$ solutions at room temperature with TMS as internal standard.

The IR spectra were recorded on a Perkin-Elmer FTIR Model 1710 equipped with a 3600 data station. The polymer spectra were recorded from a thin film made from CH_2Cl_2 solution on NaCl windows.

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to determine the thermal glass transition temperature of the polymer. The heating rate was 20 K/min and the scan was stopped 15 °C above the transition; the sample was cooled at 40

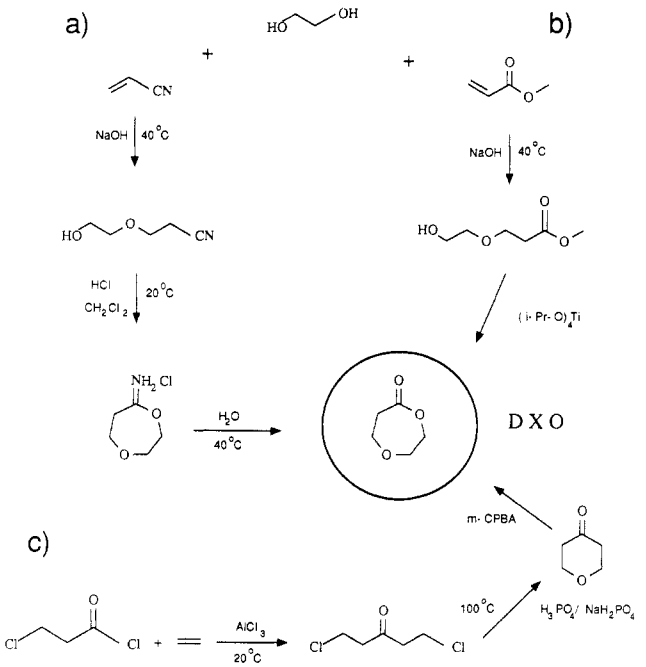

Figure 2. Synthetic paths to 1,5-dioxepan-2-one, (a) and (b), have previously been described in the literature. Path (c) is a new approach presented in this paper.

K/min. T_g was reported from the second scan. The temperature calibration was done with cyclohexane.

A Waters GPC system, which was run with chloroform in all measurements, consisted of a solvent delivery system (Model 6000A), automatic injector (Wisp 710B), and a differential refractometer. Microstyragel columns from Shodex (3 × AC-80M S and 1 × AC-802 S) were calibrated with narrow molecular weight distribution polystyrene standards and maintained at 28 °C during all measurements.

Atomic absorption, Varian 1975, was used to determine the molar relation between Al and Zn in the coordination complex.

Results and Discussion

Synthesis of 1,5-Dioxepan-2-one. The two known synthetic pathways a and b are shown in Figure 2 together with our new approach for the synthesis of DXO. Both the paths a and b give very poor yields, 5 and 17%, respectively, calculated from the starting materials.[12] This can be related to the possible formation of different oligomeric products. In the first paper in this series it is shown that the formation of the cyclic imino ether was favored by a high dilution.

Using the new and more specific path presented in Figure 2c, the problems related to the formation of oligomeric products can be avoided. The synthesis is based on the well-known technique of converting cyclic ketones into lactones using the relatively stable oxidizing compound 3-chloroperbenzoic acid. The yield of DXO based on THP was 80% at best, which must be considered normal for this type of oxidation.[13] The synthesis of THP is the limiting step in this path due to the low yield sometimes obtained in the cyclization reaction of 1,5-dichloropentan-3-one. This compound is extremely sensitive and easily loses HCl by elimination upon standing. It is therefore necessary to perform the first two steps in the synthesis consecutively in order to obtain the best result. The overall yield of DXO obtained in this way is about 48%, which is a clear improvement over other known synthetic paths.

Polymerization. Table I shows the results of the bulk polymerization of DDXO using a common transesterification catalysts, which have been shown to act as coordination initiators.[14] The propagation is believed to proceed by insertion of the lactone, via cleavage of the acyl–oxygen bond, into the metal–oxygen bond.

The catalysts were chosen due to their well-documented power of initiating the polymerization of various lactones into high molecular weight polymers.[15] Since DDXO and the polymer have very similar solubility and due to the small amount of monomers used in each experiment, the yield was calculated from the precalibrated area of monomer peak in the GPC chromatogram.

No direct connection can be seen between the monomer/initiator [(M)/(I)] ratio and the molecular weight of the polymer. The number-average molecular weight obtained by GPC is lower than what to expect theoretically, using the relationship M_n = (M)/(I) × yield, if we assume only one growing chain from each catalyst molecule. A contributory cause for the low M_n may possibly be found in the long polymerization times used, which may cause transesterifications between the polymer chains. At 180 °C the polymer became yellow, apparently due to some degradation. The molecular weights of samples 3 and 4 which were held at this temperature for 10 and 20 h, respectively, did not, however, indicate any extensive degradation.

Sb_2O_3, which is often used as a catalyst in the polymerization of glycolide and lactide,[16] was not able to start any polymerization of DDXO. An explanation for this can be that Sb_2O_3 was not soluble in DDXO at 180 °C. The dimer was recovered in nearly 100% yield. That DDXO is a very stable compound was confirmed by heating the pure dimer for 20 h at 180 °C, after which no polymer could be detected.

The polymerization of DXO is rapid compared with that of DDXO with the same initiators; see Table II. The polymerization shows again great irregularities in the molecular weight with respect to the ratio (M)/(I). The DXO used was, in spite of effort, probably not water free and this may be the reason for the low molecular weights obtained. Both dibutyltin oxide and stannous 2-ethylhexanoate are usually used together with an alcohol, which acts as the initiator, but a comparison of the results for samples 1 and 2 in Table II shows that sample 2, which contains both dibutyltin and lauryl alcohol, gave a lower molecular weight than sample 1 under the same conditions. With water present in the system, the initiator may well be the water molecule in the hydrolyzed form of the organotin compound. Addition of alcohol if water is present would cause an excess of OH groups compared to the organotin compound and would then lead to chain-transfer reactions, which lower the molecular weight.

In the case of dibutyltin oxide we have detected a strong absorption band at 1630 cm^{-1} in the IR spectrum of the product obtained after refluxing equimolar masses of dibutiltin oxide and DXO in toluene. This absorption band is most likely the carbonyl stretching of the tin carboxylate formed by the insertion of dibutyltin oxide into the lactone ring. This would be the reverse of the formation of lactones from dibutyltin oxide and ω-hydroxy acids.[17] This idea is further supported by the strong reduction of the carbonyl stretching band at 1738 cm^{-1} in the IR spectrum belonging to DXO and by the reduction in the ^1H NMR signals of the protons belonging to the ester methylene group at δ 4.33 (chemical shift relative to TMS). Further studies are, however, necessary in order to prove this mechanism, which theoretically could lead to a cyclic polymer.

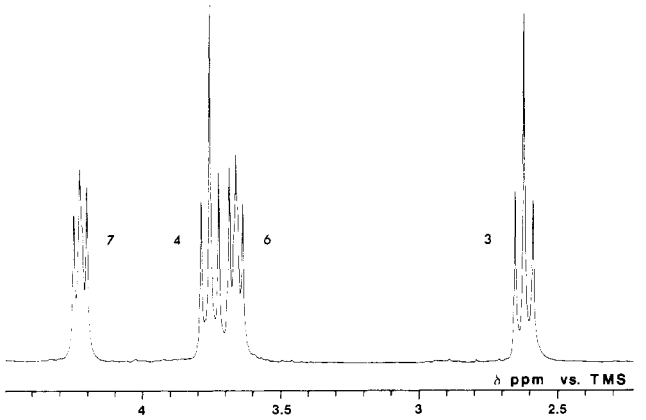

Figure 3. 200-MHz ^1H NMR spectrum of poly(1,5-dioxepan-2-one) in $CDCl_3$.

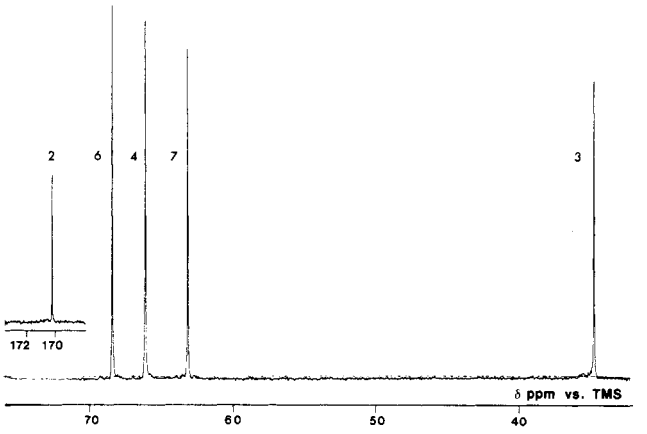

Figure 4. 25-MHz ^{13}C NMR spectrum of poly(1,5-dioxepan-2-one) in $CDCl_3$.

Table III
^1H and ^{13}C NMR Chemical Shift (ppm, TMS) of the Polymer Obtained by Polymerization of 1,5-Dioxepan-2-one or Its Cyclic Dimer

	γ			γ	
position	^1H NMR	^{13}C NMR	position	^1H NMR	^{13}C NMR
2		170.2	6	3.66	66.14
3	2.62	34.80	7	4.22	68.46
4	3.77	63.18			

The water present during polymerization is also assumed to be the reason for the sometimes unsuccessful attempts to initiate polymerization of DXO by the Teyssié type of catalyst. DXO is especially interesting in combination with this catalyst, which has proved to be very efficient for the purpose of making copolymers of the ABA type using different lactones.[18,19] DDXO showed no tendency toward polymer formation together with this initiator at 90 °C in toluene.

Characterization. The polymers of DXO and DDXO are clearly of the same type according to spectroscopic analysis. Both the ^1H and ^{13}C NMR spectra, Figures 3 and 4, showed ^1H and ^{13}C chemical shift values characteristic for aliphatic polyesters that contain both ester and ether functionalities in the backbone of the chain. The AA'BB' type secondary ^1H NMR spectra found for DXO and the cyclic dimer have disappeared after polymerization due to free rotation around the bonds in the open-chain polymer. Table III shows the chemical shifts for the polymer.

The infrared spectra of the polymer, Figure 5, showed the expected carbonyl stretching band at 1738 cm^{-1} and

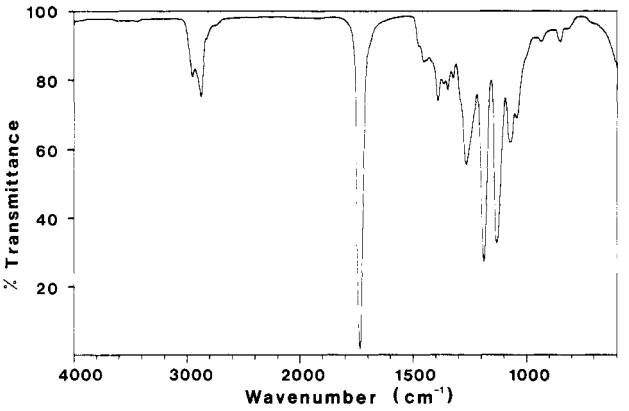

Figure 5. IR spectrum of poly(1,5-dioxepan-2-one) obtained from a thin film on a NaCl mirror.

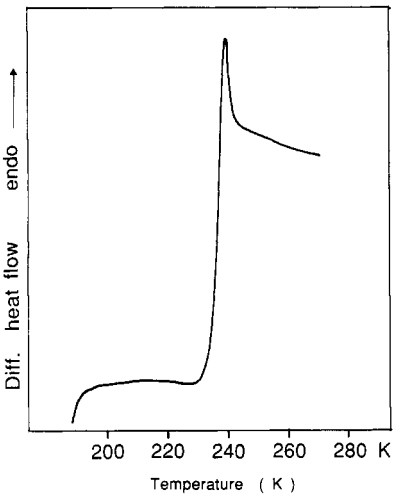

Figure 6. DSC scan of poly(1,5-dioxepan-2-one). Heating rate 40 K/min. The temperature was calibrated with cyclohexane.

the C–O stretching band at 1185 cm^{-1} of the ester group. The C–O–C stretching band of the ether group is found at 1126 cm^{-1}.

The polymer was also characterized by differential scanning calorimetry (DSC), the results of which are shown in Figure 6. The homopolymer was completely amorphous and showed no tendency to crystallize. The T_g of the polymer was found to be −39 °C. This implies that the polymer should be an excellent choice for the amorphous block in a copolymer (of the type ABA) possessing elastic properties.

Conclusion

The method of synthesizing lactones by oxidation of cyclic ketones seems also to be the best way of making DXO. The oxidation of THP has been shown to give an excellent yield of DXO compared with the methods described in the literature. The monomer is, however, difficult to purify, which causes problem when polymerization is attempted in the presence of sensitive coordination catalysts of the Teyssié type. The polymerization in bulk by ordinary transesterification catalysts easily gives high molecular weight polymers. The amorphous polymer is highly viscous and the T_g has been found to be −39 °C. The cyclic dimer of DXO is easier to purify and handle and can be polymerized to high molecular weight polymers that in thermal and spectroscopic characterization showed no differences from the polymers of DXO.

Acknowledgment. This work was supported by the National Swedish Board for Technical Development (ST-

U). We thank Ulla Jacobsson, Department of Organic Chemistry, for running the NMR shift correlation spectrum and Lars Göran Danielsson, Department of Analytical Chemistry, who performed the atomic absorption analysis.

Registry No. DXO, 35438-57-4; DXO (homopolymer), 121425-66-9; DXO (SRU), 121425-79-4; DDXO (homopolymer), 121425-68-1; Bu_2SnO, 818-08-6; Sn-OKt, 301-10-0; $(i\text{-}PrO)_4Ti$, 546-68-9; zinc acetate, 557-34-6; aluminum isopropoxide, 555-31-7; tetrahydro-4*H*-pyran-4-one, 29943-42-8.

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Synthesis and Characterization of a Thermotropic, Liquid-Crystalline Polyester Comprising Phenyl Benzoate Groups Connected via a Tris(ethylene oxide) Spacer

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Received October 11, 1988; Revised Manuscript Received January 24, 1989

ABSTRACT: A new, thermotropic, liquid-crystalline dimer and high molecular weight polymer in which the rigid, mesogenic unit is connected via a tris(ethylene oxide) spacer have been synthesized. The polymer was fully characterized by IR, NMR, GPC, and dilute solution light scattering and viscometry. Experimental data indicate $\bar{M}_w \approx 100\,000$ and $\bar{M}_w/\bar{M}_n = 1.9$. The dimer revealed monotropic behavior with a nematic → isotropic transition temperature of 125.6 °C and an associated enthalpy of 0.45 kcal/mru, whereas the polymer exhibited a nematic range of approximately 3 °C, with a corresponding nematic → isotropic transition temperature of 141 °C and an associated enthalpy of 0.51 kcal/mru. Comparison of these values with the ones for the corresponding polymer with an even-numbered decamethylene spacer group indicates not only a lower nematic-to-isotropic transition temperature but, more importantly, a much lower (ca. one-third) enthalpy and entropy of the nematic-to-isotropic transition. These findings are consistent with the model of highly extended chain conformations for main-chain, thermotropic polymers with alkylene spacers and indicate little tendency for conformational order and lower orientational order in the polymer with the more flexible ethylene oxide based spacer.

Introduction

Main-chain, liquid-crystalline polymers comprising rigid units connected via flexible spacers have been studied in great detail in recent years. For this class of polymers it is now well established that the spacer groups play critical roles in determining the stability of the liquid-crystalline state over the isotropic state.[1-4] Furthermore, the spacer groups are not merely playing the role of solvent but rather participate actively in the ordering process in the nematic state. Previous studies have shown that the stability and molecular order of nematic states in semiflexible, thermotropic polymers are dominated primarily by the characteristics of highly extended conformers, which are favored due to steric packing considerations.[5-7] In addition, conformational ordering in the nematic state is found to be the most significant feature differentiating polymer liquid crystals from their monomeric analogues. Hence, the nature of molecular order in nematic polymers and its dependence on chemical structure are of utmost importance. In this context, we felt it would be of great interest to alter the nature of the spacer group by substituting the alkylene-type spacer with a more flexible ethylene oxide based spacer.

Although main-chain, liquid-crystalline (LC) polymers incorporating flexible spacers based on ethylene oxide have been previously reported in the literature,[8-12] many of these incorporate relatively long, rigid mesogens, which exhibit both smectic and nematic mesophases and yield relatively high isotropic transition temperatures (>250 °C). A model dimer and high molecular weight polymer in which the rigid mesogenic unit is short enough to yield a nematic phase in a temperature regime well below the onset of thermal decomposition would be desirable (see structures below). Furthermore, these structures would permit direct comparison with the previously studied alkylene-based spacer systems with an identical mesogenic group.

Results and Discussion

The chemical composition of the homopolymer was confirmed both by IR and ^1H NMR. The IR spectrum of the homopolymer exhibits the characteristic absorption bands one would expect for a polymer composed of aro-

0024-9297/89/2222-3846$01.50/0