Short Communication

Oligo(oxytetramethylene)s and Their Derivatives: Models for Segmented Poly(ether ester)s and Polyurethanes

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Introduction

Segmented poly(ether ester)s consisting of crystallizing sequences of poly(oxytetramethyleneoxyterephthaloyl) as the so-called "hard segment" and sequences containing non-crystallizing segments of poly(oxytetramethylene) as the so-called "soft segments" have attracted commercial¹¹ as well as scientific²⁻⁵ interest.

Recently we have reported the melting and mutual compatibility behaviour of well defined and uniform oligoesters⁶⁾. This paper describes the strategy of synthesis and some of the properties of molecularly uniform α -hydro- ω -hydroxypoly(oxytetramethylene)s (1) which are suitable precursors for the soft blocks of segmented copoly(ether ester)s as well as polyurethanes with uniform block length. The crystallization behaviour of these oligoethers is of particular interest since the soft blocks with long enough sequence length are able to segregate under crystallization, influencing the properties of the block copolymers⁷).

Furtheron, from the physical properties of the pure oligoethers the understanding of the properties of pure poly(oxytetramethylene) and of mixtures which occur in the above mentioned block copolymers is improved. It is worthwhile to note that molecularly uniform oligomers 1 have not been synthesized so far despite the fact that low-molecular-weight 1 is widely used as prepolymer in the course of the synthesis of block copolymers.

Results and Discussions

Substances

The route of synthesis is described in Scheme 1. A typical example of preparation is given in the Exptl. Part. Further details will be reported elsewhere. By this method amounts of 20 to 50 g are readily prepared.

Scheme 1. Route of synthesis for molecularly uniform α -hydro- ω -hydroxypoly(oxytetramethylene)s, (1), Eq. (i) and α -hydro- ω -chloropoly(oxytetramethylene)s, (4), Eq. (ii)

The following series of oligomers were synthesized:

- a) the "etherdiols" 1 with n = 2, 3, 4, 5, 6, 7
- b) the " α -chloro- ω -hydroxyethers" 4 with n = 1, 2, 3
- c) the "N-phenyl urethanes" of the etherdiols

$$NH-CO-R_n-O-CO-NH-$$
 (5) with $n = 1, 2, 3, 4, 5, 6$

The etherdiols 1 and the chloro derivatives 4 were purified by distillation, the uncorrected boiling points are given in Tab. 1. The individual oligomers were characterized by elemental analysis, DSC, IR, ¹H NMR, and ¹³C NMR as will be reported elsewhere. The purity was checked with GPC in all cases. The GPC trace of an artificial mixture of a series of separately prepared oligomeric etherdiols is shown in Fig. 1.



Fig. 1. GPC trace of an artificial mixture of α -hydro- ω -hydroxypoly(oxytetramethylene)s H-(-O--CH₂--CH₂--CH₂--CH₂--OH (1) (1 count = 5,25 ml). R.I.D. = refractive index difference

Melting behaviour

The melting points and enthalpies of the individual oligomers as determined by DSC are summarized in Tab. 1.

According to Flory⁸⁾ the melting point of the individual oligomer with the degree of polymerization n is given by Eq. (1) where T_m^0 is the melting point of the infinitely large and perfect polymer crystal with a molar heat of melting ΔH_m^0 . R has its usual meaning.

$$\frac{1}{T_{\rm m}} = \frac{1}{T_{\rm m}^0} + \frac{2R}{\Delta H_{\rm m}^0} \cdot \frac{1}{\rm n}$$
(1)

The treatment of our data following Eq. (1) is shown in Fig. 2.

Straight lines are obtained for each set of "etherdiols" with either odd or even n. This is in accordance with the well known behaviour of alkanes. The lines extrapolate to a common intersection point on the ordinate, the reciprocal melting point of the pure crystalline phase of poly(oxytetramethylene). Thus, T_m^0 is determined as $45 \pm 2^\circ$ C, in good agreement with 43° C, given by Tadokoro⁹. Although the N-phenyl urethanes of the etherdiols do not reveal a

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n	$T_{\rm m}/^{\circ}{ m C}$	$\Delta h_{\rm m}/({ m J/g})$	b. p. in °C at 0,01 mbar
a) H+OCH	₂ CH ₂ CH ₂ CH ₂ -)- _n OH (1):		
2	2,6	87	108
3	31,3	161	151
4	18,3	127	183
5	37,0	187	226
6	31,3	153	253
7	36,0	145	
b)	NH-CO+OCH2CH2CH2CH	$I_2 \rightarrow OCO - NH - $ (5):	
1	180,2	185	
2	119,3	138	
3	73,8	121	
4	53,8	104	
5	48,2	108	
6	47,2	103	
c) H+OCH	$_{2}CH_{2}CH_{2}CH_{2}\rightarrow_{n}Cl(4):$		
1			35
2			87
3			136

Tab. 1. Melting points T_m , heats of melting Δh_m and boiling points (b. p.) of the oligoethers with various end groups described in Scheme 1

linear relationship due to the dominance of the N-phenyl urethane end groups in the crystallization behaviour, the curve, too, can be extrapolated to the same intersection point.

Obviously the slopes of the lines in Fig. 2 are strongly dependent on the structure of the oligomers. Therefore, ΔH_m^0 cannot be easily determined as suggested by Eq. (1). However,



Fig. 2. Reciprocal melting point T_m as a function of the number of oxytetramethylene units in the oligomers and the type of end group:

 $H+OCH_2CH_2CH_2CH_2\rightarrow_nOH: n \text{ even } (\circ); n \text{ odd } (\triangle)$

$$\square$$
 NH-CO+OCH₂CH₂CH₂CH₂ $-h_0$ OCO-NH- \square : (□)

from the line, representing the even number etherdiols, a value of 16,6 kJ/mol is obtained, in good agreement with 14,4 kJ/mol given in the literature¹⁰.

Experimental Part

Syntheses

As a typical example the synthesis of 5,10,15-trioxanonadecane-1,19-diol (1, n=4) is described in detail. It is based on methods published by Kruse et al.¹¹⁾ and Eliel et al.¹²⁾.

 $108 \text{ g}(0,8 \text{ mol}) \text{ SO}_2 \text{Cl}_2$ are dissolved in 800 ml freshly distilled THF. After cooling to room temperature the mixture is added in two parts to a solution of 32,4 g(0,2 mol), 5-oxanonane-1,9-diol¹³ and 182 g (1,8 mol) triethylamine in 400 ml THF. After stirring for two hours the precipitated triethylamine monohydrochloride is removed by filtration, followed by evaporation of the filtrate which is always kept alkaline.

The residue is extracted three times with 200 ml diethyl ether. The solution is washed several times with 5 wt.-% KOH and dried over KHCO₃ before the ether is evaporated. 55,8 g (0,185 mol) of bis[4-(2-tetra-hydrofuryloxy)butyl]ether 2, n = 4 are obtained.

106,4 g (0,8 mol) AlCl₃ are dissolved under cooling in 400 ml of dry diethyl ether. The mixture is added to a solution of 10g (0,25 mol) LiAlH₄ in 200 ml diethyl ether and stirred for 30 minutes. Then, 60,5 g (0,2 mol) of 2, n=2 in 400 ml diethyl ether are added under cooling. After stirring for 2 hours at room temperature 1 litre of 10 wt.-% sulfuric acid are added, dropwise at first. The layers are separated, the aqueous layer is three times extracted with 200 ml diethyl ether. The combined ether layers are dried and concentrated. The residue (49 g) contains a mixture of H-R₄-OH, H-R₃-OH, and H-R₂-OH which is fractionated by distillation; 21,5 g (0,07 mol) 2, n=4 are obtained.

The α -chloro- ω -hydroxyethers 4 are synthesized in a similar approach, e.g. 9-chloro-5-oxanonanol (4, n = 2): 44 g (0,4 mol) 4-chlorobutanol¹⁴) (4, n = 1) give 64 g (0,36 mol) 1-chloro-4-(2-tetrahydrofuryloxy)-butane (3, n = 2). 71,5 g (0,4 mol) 3, n = 2 results in 60 g of a mixture of 4, n = 1 and 4, n = 2. After distillation, 34 g (0,19 mol) 4, n = 2 are obtained.

Gel permeation chromatography (GPC)

The column (length 2 m, diameter 1 cm) was packed with Fractogel PVA 2000 (230-430 mesh ASTM) (Merck Corp.); toluene (p. a. Merck Corp.) was used as solvent under hydrostatic pressure at room temperature. The polymer was detected by a thermo-controlled refractometer R 403 (Waters Corp.), the count time was 15 minutes.

Differential scanning calorimetry (DSC)

DSC-traces were recorded using a DSC-2 (Perkin-Elmer Corp.). The data on T_m , recorded in Tab. 1 were obtained by extrapolation of the experimentally measured maxima of the endotherms to zero heating rate. The half width of the peaks at zero heating rate was of the order of 1 deg. All data were corrected for gallium, indium, and azobenzene.

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