

## ***Liquid Crystals***

### **Liquid crystal polyethers obtained from endo- and exo-2-methyl-7-oxabicyclo[2.2.1]heptane**

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#### Summary

Polyethers prepared by ring-opening polymerization of endo- and exo-2-methyl-7-oxa[2.2.1]heptane have been found to exhibit thermotropic liquid crystal properties. The lower melting characteristics of the polyether prepared from the exo isomer are related to an irregular polymer structure compared to a very uniform structure of the polyether prepared from the endo isomer. In spite of the irregularities, liquid crystals form easily since apparently the various structural units are accommodated in the mesophases. The structural differences arise from the difference in steric hindrance from the methyl substituent of the two isomeric monomer in the chain propagation.

#### Introduction

Considerable efforts have been devoted in recent years to the synthesis of polymers having thermotropic liquid crystal properties. The work aimed at obtaining polymers with mesogenic elements in the main chains has overwhelmingly been directed towards the polyesters (1-3).

We have, however, now succeeded in observing liquid crystal behavior in polyethers obtained by ring-opening polymerization of endo- and exo-2-methyl-7-oxabicyclo[2.2.1]heptane, referred to in the following as endo- and exo-2-MOBCH.

In addition to reporting the liquid crystalline properties we wish to relate these to our recent structural investigation of these polymers by high field NMR. This has in some ways cast new light on the polymerization of these monomers compared to previously published results based on less powerful techniques (4, 5).

#### Experimental

The polymers have been prepared as previously published (4, 6) and a selected number of polymers synthesized at different temperatures were investigated. The melting transitions were observed on a Reichert-Jung polarizing microscope fitted with a Mettler FP82 Hot Stage, and photomicrographs were taken using equipment from American Optical. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded in deuteriochloroform at room temperature with TMS as internal reference on a Bruker AM 500 FT instrument operating at 500 MHz and 125 MHz.

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### Results and Discussion

We have found that poly(exo-2-MOBCH) always melts at much lower temperatures than poly(endo-2-MOBCH), and differences of 75-100°C between the two polymers were found irrespective of the polymerization conditions.

The samples of poly(exo-2-MOBCH) prepared under different conditions very easily formed liquid crystal phases showing the characteristic features of nematic melts as shown in Figure 1. The sample shown here formed an isotropic melt at 188°C. The poly(endo-2-MOBCH) did not so easily form a liquid crystalline melt. For the polymer shown in Figure 2 melting did not begin until 220°C with a tendency to form liquid crystal regions over a narrow range of 10-20°C. In this case liquid crystal regions were observed in an otherwise isotropic melt at 260°C. However, at this temperature degradation occurred as evidenced by gradual discoloration of the sample.

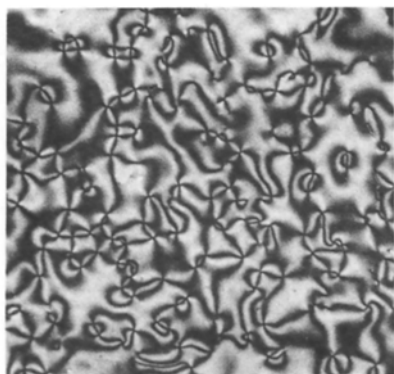


Figure 1. Poly(exo-2-MOBCH) prepared at -50°C. Typical nematic melt photographed at 149.2°C with crossed polarizers. Magnification 140X.

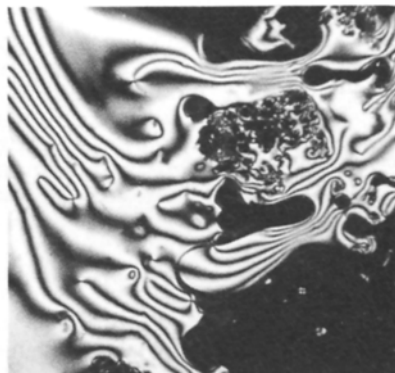


Figure 2. Poly(endo-2-MOBCH) prepared at -50°C. A region showing nematic melt features, photographed at 260.0°C with crossed polarizers. Magnification 140X.

The melting temperature at which a mobile melt pool is formed as well as the isotropization temperature varied with the preparative conditions and tended for poly(exo-2-MOBCH) to be significantly higher with lower polymerization temperature as shown in Figure 3. The molecular weight (and intrinsic viscosity) also increased with this temperature as shown in our previous publication (4)). The nematic range varied from 40-60°C according to the way of preparation. The variations in melting ranges for poly(endo-2-MOBCH) with polymerization temperature were only marginal as also shown in Figure 3 and melt down occurred at 240-245°C, while isotropization mostly occurred before the temperature exceeded 260°C.

It is, therefore obvious that the melting behavior of the two types of polymers is significantly different. In the previous investigation (4) we had noted the marked difference in solubility of the polymers since the samples of poly(exo-2-MOBCH) were always completely soluble in THF and chloroform,

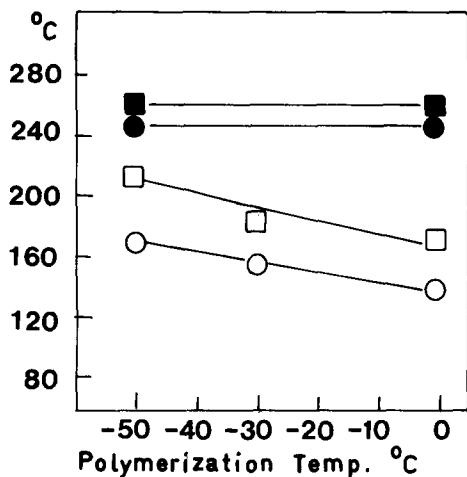


Figure 3. Variation in melt temperature  $T_m$  (o) and isotropization temperature  $T_i$  (□) for poly(exo-2-MOBCH) prepared at different temperatures. Corresponding values for poly(endo-2-MOBCH) indicated with filled symbols.

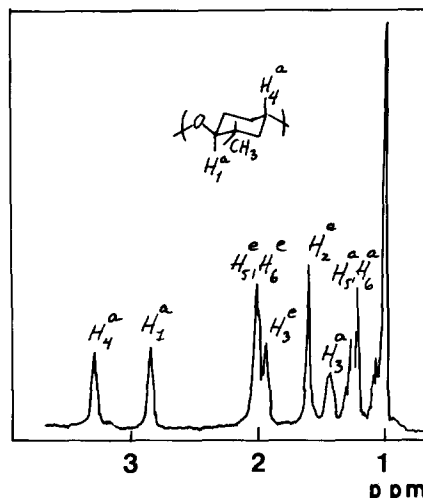
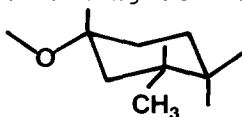


Figure 4. 500 MHz  $^1\text{H}$  NMR spectrum of poly(endo-2-MOBCH), chloroform soluble fraction.

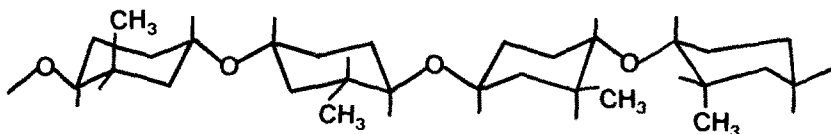
while the poly(endo-2-MOBCH) was insoluble in common solvents, although it could be dissolved in *m*-cresol. This distinct difference in solubility behavior was thought to be governed by whether the methyl group had an axial or an equatorially position in the most stable conformation, thus influencing the packing and interaction of the chains. In case of poly(exo-2-MOBCH) one also ascribed a possible interconversion between the two chair conformations, resulting in some mobility, as a possible contribution to a higher solubility. Such conformational equilibria have been observed (5), however, later studies have also indicated that the rings of polymers of this type appear to move as stiff units (7).

We have recently reinvestigated the structures of the polymers using high resolution NMR (8), and we wish here to relate these studies to the properties of the polymers. In case of poly(endo-2-MOBCH) we have performed the analysis on a chloroform soluble fraction obtained by extracting the polymers which were otherwise insoluble in this solvent. The 500 MHz  $^1\text{H}$  spectrum shown in Figure 4 was in accordance with a very uniform structure of the polymer having the repeat unit:



The deshielded axial protons in the 1 and 4 positions were found at 2,79 and 3,29 ppm in a 1:1 ratio. The other axial protons appeared at 1,22-1,59 and in the proper ratios and the equatorial protons at the 3, 5 and 6 positions at 1,90 and 2,05 ppm in 1:2 ratio. Finally the methyl protons were found at 0.99 ppm. The 125 MHz  $^{13}\text{C}$  spectrum also had the expected signals and at positions in accordance with predictions from model compounds (9). The fact that the otherwise single methyl carbon was split into a narrow triplet at 18,81, 18,84 and 18,87 ppm in a 1:2:1 ratio is indicative of the shown structure with random configuration of the triads. This very uniform structure is in accordance with the rather high melting ranges for this polymer.

In case of poly(exo-2-MOBCH) the NMR studies has revealed a more irregular structure which contains some of the following structural elements:



According to the originally proposed mechanism (4, 5) for polymerization of exo-2-MOBCH, ring-opening occurring by attack of monomer only at the unhindered neighboring position to the propagating oxonium ion should lead to a single type of repeat unit in which the methyl groups is axial in the most stable conformational form. The 500 MHz  $^1\text{H}$  spectrum showed clearly the presence of repeat units corresponding to those of poly(endo-2-MOBCH) since signals from axial protons at 2,79 and 3,29 ppm were found in addition to other deshielded axial protons arising from repeat units having the methyl groups positioned axially in the most stable conformation. Correspondingly, different signals were seen from the other axial and the equatorial protons arising from the two types of repeat units as well as different methyl protons. On this basis we proposed that ring opening may occur by attack at either of the two neighboring positions to the oxonium ion. By area integration of the proton signals it was found that the units corresponding to those of poly(endo-2-MOBCH) constitute about 30% of the sample.

The 125 MHz  $^{13}\text{C}$  spectrum yielded some additional information. The spectrum was rather complicated, however, and it was obvious that different methyl carbon signals from axial as well as from equatorial substituents could be identified. Referring to the illustrated chain element of poly(exo-2-MOBCH) it is seen that the possibility for ring opening also from the hindered side of the propagating monomer yields head-to-head and tail-to-tail structural elements. In the head-to-head configuration the methyl carbons will be deshielded compared to the methyl in the head-to-tail configuration. An area integration again indicated that roughly 30% of the units of the polymer are formed by ring opening at the sterically hindered neighboring position to the oxonium ion.

This irregular structure accounts for the lower melting temperature of the poly(exo-2-MOBCH). The clear tendency to form liquid crystalline melts is perhaps a little surprising in view of the irregularity of the structure. However, we propose it is possible that various and slightly deviating structural elements based on the cyclohexyl oxide structure may be accommodated in the mesophases.

In conclusion, the structure of the polymers and their properties is seen to be governed by whether or not the ring-opening occurs in a uniform manner. With the methyl substituent in endo position in the monomer the steric hindrance to back-side attack at C-1 of the propagating oxonium ion is so severe that ring-opening occurs only at the unhindered end of the molecule and a high melting uniform polymer is formed. With the substituent in the exo position less steric hindrance is present and a mixed structure is obtained which accounts for both lower melting temperature and higher solubility, however, it allows the formation of stable liquid crystalline phases.

#### Acknowledgements

The Danish Council for Technical and Scientific Research is gratefully acknowledged. Dr. Klaus Bock of the Institute of Organic Chemistry, Technical University of Denmark has been helpful in obtaining the NMR spectra.

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