Polymerization of bicyclic ethers: 2. N.m.r. structure study of the polymer formed from 3-oxabicyclo[3,2,2]nonane

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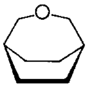
The polymerization of 3-oxabicyclo[3.2.2] nonane (I) was carried out in methylene chloride with phosphorus pentafluoride and epichlorohydrin at temperatures ranging from –25° to +25°C. Slow polymerization rates were generally observed, leading to low molecular weight amorphous polymers. By ^{13}C n.m.r. and ^{1}H n.m.r. analysis of the monomer and polymer compounds, it was possible to assign the polymer the structure of a poly(1,4-cyclohexylene-dimethylene there). By comparing the polymer n.m.r. spectra with the proton spectra of two reference compounds, it was possible to establish a microstructure for the repeating unit of the polymer in which the methylenether groups on positions 1 and 4 of the cyclohexane ring are *cis* to each other. A propagation scheme through oxonium ions is proposed in order to explain the formation of *cis* polymer.

INTRODUCTION

The n.m.r. charcterization of the adduct of 3-oxabicyclo[3.2.2]nonane (I) with phosphorus pentafluoride (PF_5) has allowed us to suggest that the observed inability of PF_5 to initiate polymerization was due to the geometry of this latter complex rather than to the lack of polymerizability of (I)[1]:



(I)

Moreover, by adding a promotor such as epichlorohydrin (ECH) to PF_5, we have found that the polymerization of (I) is actually taking place. This result, which confirms the previously expected polymerizability of (I), prompted us to investigate more in detail the polymerization of this bicyclic ether. Since the polymerization reaction of (I) is slow, we considered it more convenient to investigate the polymerization mechanism by an n.m.r. study of the polymer structure by n.m.r., rather than through direct kinetic measurements. Here, we wish to report the results of this n.m.r. investigation; the structural assignment of the polymer has been made by comparing its n.m.r. spectra with those of the monomer and of two reference compounds.

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EXPERIMENTAL

Materials

3-*Oxabicyclo*[3.2.2]*nonane* (I) was prepared, purified, and dried as previously described[1].

Phosphorus pentafluoride (PF_5) was obtained, purified, and used as reported[2].

Epichlorohydrin (ECH). The commercial product (Rudi Pont Ltd) was fractionally distilled and dried by refluxing over calcium hydride. It was distilled on a vacuum line, degassed, and stored over molecular sieves.

Solvent Methylene chloride was purified, dried, and transferred to the vacuum line as reported[2].

cis *and* trans-1,4-*cyclohexanedimethanols* (*IV*) *and* (*V*) were obtained in the form of dibenzoates by benzylation of the commercial mixture (Fluka) according to the method of Haggis and Owen[3]. The *cis* and *trans* dibenzoates were purified by fractional crystallization and their identity was checked by comparing their i.r. spectra and melting points with those reported in literature[4]. They were converted into the corresponding (IV) and (V) by hydrolysis with methanol and sodium at reflux temperature. The *trans* isomer is an easily crystallizable solid (m.p. ~66°C), whereas the *cis* isomer is a non-crystallizable oil at room temperature with an impurity consisting of the other isomer remaining.

Table 1 Polymerization of 3-oxabicyclo[3.2.2] nonane (I)[a]

Monomer (I) (mol l^{-1})	Initiator system PF$_5$ (mol l^{-1})	 ECH[b] (mol l^{-1})	Temperture (°C)	Reaction[c] time (h)	Yield (%)	$\overline{M}_n$[d]
3.90	0.080	0.080	25	144	24.9	2250
3.90	0.080	0.080	0	144	18.0	3290
3.90	0.080	0.080	−10	144	11.1	3800
3.90	0.080	0.080	−25	240	5.8	4230

[a] Solvent, methylene chloride

[b] ECH = epichlorohydrin

[c] At the indicated reaction time the polymerization was still in progress

[d] By vapour pressure osmometry in dichloroethane at 37°C

Polymerization procedure

The polymerization of (I) was carried out in a glass apparatus sealed under high vacuum. A Pyrex phial containing a known amount of (I) was connected, via a break-seal, to the previously described[2] vacuum line. (I) was transferred by sublimation into the reaction ampoule and the required amounts of solvent, ECH and PF$_5$ were added at liquid nitrogen temperature. After rapid melting and mixing, the solution was allowed to stand at the desired temperature in a thermocryostat. After a particular time, the reaction mixture was neutralized by adding a few drops of ammoniacal methanol. In order to free the polymer from any catalyst residue, it was recovered by steam distillation of the reaction mixture, and then purified by reprecipitation into CH_3OH from CCl_4 solution. After drying at 70°C, the polymer appeared as a colourless, transparent sticky mass.

Number-average molecular weights were determined with a model 301 Hewlett-Packard vapour pressure osmometer in 1,2-dichloroethane at 37°C using benzil for calibration.

Spectra

^{13}C n.m.r. spectra were recorded on a Bruker WH 90 spectrometer operating at 22.63 MHz in $CDCl_3$+TMS solution. Data were collected in a 16K memory and Fourier transformed. ^{1}H n.m.r. spectra were obtained with a JEOL PS-100 spectrometer (100 MHz) in a $CDCl_3$ +$(CD_3)_2CO$ (3:2 v/v) solution. Chemical shifts are measured in ppm from an internal TMS standard. The i.r. spectra were recorded from 250 to 4000 cm^{-1} with a Perkin-Elmer 521, double beam, grating spectrophotometer, on samples of monomer and polymer in CCl_4 solutions.

RESULTS AND DISCUSSION

The bicyclic ether I can be considered to be a 3,6-disubstituted oxepane. The driving force of its polymerization is due to ring strain introduced by the bicyclic structure which is relieved on polymerization. In particular, the strain energy of I was estimated to be 5 kcal mol^{-1} (=21 kJ mol^{-1})[5], so it was not surprising to find that in the presence of a more suitable initiator, the polymerization of I occurred. Some of the results of polymerization under various experimental conditons are summarized in *Table* 1. It is evident from these data that the polymerization is generally quite slow, despite the sizeable concentrations of both the monomer and the initiator. A long reaction time was also required to obtain an acceptable conversion at room temperature. Higher ratios of ECH to PF$_5$ were not used, to avoid the possibility of incorporating ECH into the polymer itself. All the polymer samples were amorphous, sticky and had a low molecular weight. Furthermore, their molecular weight did not increase appreciably with decreasing temperature.

The ^{13}C n.m.r. spectra of solutions of (I) [spectrum (a)] and of the corresponding polymer [spectrum (b)] are reported in *Figure* 1. Because of the simplicity of the spectrum, the signal assignments of α-methylene, ring methylene, and methyne carbons of I were straightforwardly made by comparison with the chemical shift values obtained from direct measurements of related cyclic ethers, such as hexamethylene oxide (oxepane) and 7-oxabicyclo[2.2.1]heptane (1,4-epoxycyclohexane), taking into account the deshielding effect of the ether oxygen, as well as the signal intensity ratios. These results were also confirmed by off-resonance proton decoupling technique. The ^{13}C n.m.r. spectrum of the polymer further displays three resonances, of which only two are somewhat shifted, when compared with those of the monomer: differences among these resonances are reported in *Table* 2.

As shown in spectrum b, there is no evidence of chemical irregularities in the polymer. The shielding and the deshielding effects on C-2,4 and C-1,5, in the mo-

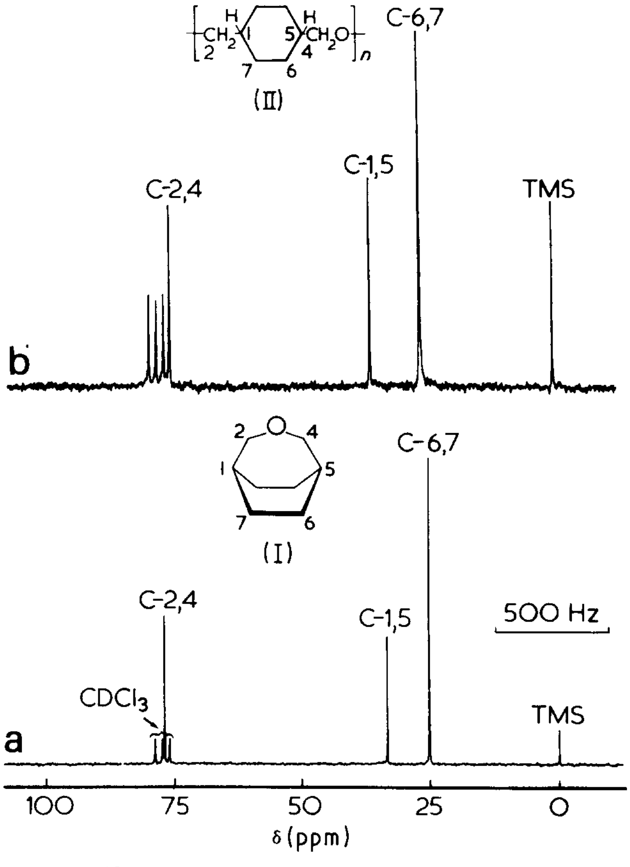


Figure 1 ^{13}C n.m.r. proton noise decoupled spectra (22.6 MHz) of (a) 3-oxabicyclo[3.2.2] nonane, and of (b) the corresponding polymer. (a) 200 mg ml^{-1} in $CDCl_3$ at 35°C; (b) 100 mg ml^{-1} in $CDCl_3$ at 35°C

Table 2 ^{13}C n.m.r. chemical shifts at 22.6 MHz of the monomer (I) and of the polymer obtained with PF_5 and ECH at 0°C (negative sign means upfield shift); $CDCl_3$ solutions; TMS internal standard

Carbons	δ monomer (ppm)	δ polymer (ppm)	Δδ (polymer–monomer) (ppm)
C–2,4	77.17	74.74	−2.43
C–1,5	33.50	35.80	+2.30
C–6,7	25.46	25.46	0.00

nomer and in the polymer respectively, may be explained in terms of a loss of sterical constraint caused by the opening of the ether linkage in the monomer. The occurrence of the ring-opening process is also confirmed by the comparison of the i.r. spectra of both monomer and polymer solutions. Indeed, the i.r. spectrum of I displays two sharp absorptions at 1145 and 1065 cm^{-1} associated with the breathing frequency of the ether ring. In the polymer spectrum these bands are replaced by a single, broad absorption at 1120 cm^{-1} due to the asymmetric C–O–C stretching, typical of linear aliphatic ethers. All these observations strongly indicate that the polymer is a poly(1,4-cyclohexylene dimethylene ether) whose structural formula (II) is reported in *Figure* 1. No differences were observed in the spectra of the polymers obtained at various temperatures.

Although ^{13}C n.m.r. spectroscopy provides a useful tool for observing and measuring geometrical isomerism in polymers[6–8], it was not possible here to deduce the true configuration of the polymer base unit from the peaks assignment of spectrum b.

The presence of the 1,4-disubstituted cyclohexane ring in the structure (II) can lead to the occurrence of *cis* and *trans* forms. Thus, we decided to have further information on the polymer structure by also taking advantage of ^1H n.m.r. spectroscopy.

The proton spectrum of the polymer solution is reported in *Figure* 2, and shows three resonances centred at 3.25 (doublet, $J_{HH} = 6.7$ Hz), 1.75, and 1.45 ppm from TMS. The integral ratio among these three signals is 2:1:4, so that the doublet at 3.25 ppm can be assigned to the methylene protons outside the cyclohexane ring (strongly deshielded by the oxygen atom), while the broad resonance at 1.75 ppm and the peak at 1.45 ppm must be respectively correlated to the methyne and to the methylene protons of the cyclohexane ring.

The latter narrow band is characteristic of the cyclohexane at room temperature[9] as well as of those compounds which exhibit axial and equatorial protons that are equivalent because of the rapid chair–chair interconversion process of the cyclohexane ring[10,11]. These ^1H n.m.r. observations support strongly a *cis* configuration for the homo-1,4-disubstituted cyclohexane ring of the repeating unit of the polymer. This latter can be better represented by the structure (III) in which equally favoured forms are rapidly interconverting.

Low temperature spectra were obtained at −80°C, working as far away as possible from viscosity and solubility problems. They showed only a broadening of the peaks and did not give any further information.

In order to confirm conclusively the configuration of the polymer unit, the ^1H n.m.r. spectra (c) and (d) of reference compounds, *trans* and *cis* 1,4-cyclohexanedimethanol (IV) and (V), were examined; these spectra are reported in *Figure* 3. Integral ratios 1:1:1 and deshielding effects for the *trans* isomer allowed us to assign the doublet at 3.40 ppm to the methylene protons external to the ring, while the two multiplets at 1.85 and 1.02 ppm pertain respectively to the equatorial and axial protons of the methylene ring. The fact that the resonance of the protons of the cyclohexane ring consists of two separate signals strongly suggests a stable conformation (IV) without a rapid ring flipping[10]. The broad peak at 1.45 ppm is due to the methyne protons. The resonance due to the hydroxyl groups at 3.23 ppm was confirmed by D_2O exchange. A low temperature spectrum (−40°C) also showed a slitting of the doublet centred at 3.40 ppm into an apparent triplet due to the lowering of the hydroxyl proton exchange rate.

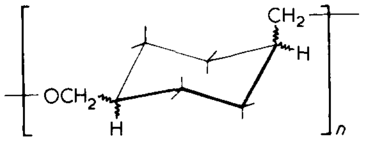
Similar perusal of the spectrum of the *cis* isomer (d) led us to assign the doublet at 3.47 ppm ($J_{HH} = 6.7$ Hz) to the methylene protons of the hydroxymethyl groups and the broad peak at 3.15 ppm to the hydroxyl protons. The resonance of the methylene ring protons centered at 1.46 ppm appears as a narrow band partly superimposed to the resonance of methylene protons. This pattern is well explained by assuming a rapid conformational interconversion of the cyclohexane ring. Chair interconversion in the *cis* form of 1,4-homo disubstituted cyclohexane derivatives is favoured because it occurs between equivalent conformations (Va, Vb)[4,10,11], i.e.:

$$\text{axial–equatorial} \rightleftarrows \text{equatorial–axial}$$

whereas in the *trans* configuration, interconversion occurs between conformers of different energy:

$$\text{axial–axial} \rightleftarrows \text{equatorial–equatorial}$$

From this ^1H n.m.r. structure analysis it follows that the polyether of I consists of repeating units in which the two



(III)

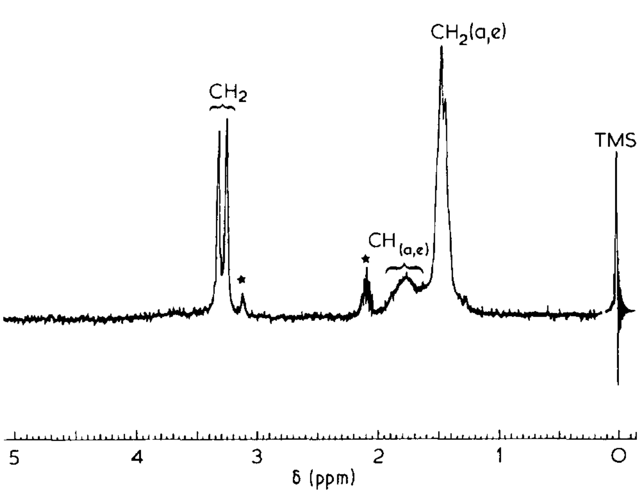


Figure 2 ^1H n.m.r. spectrum (100 MHz) of the polymer from 3-oxabicyclo[3.2.2] nonane. 30 mg ml^{-1} in $CDCl_3/(CD_3)_2CO$ (3/2 v/v). (a, e) are for axial and equatorial protons. Starred peaks are due to solvent impurities

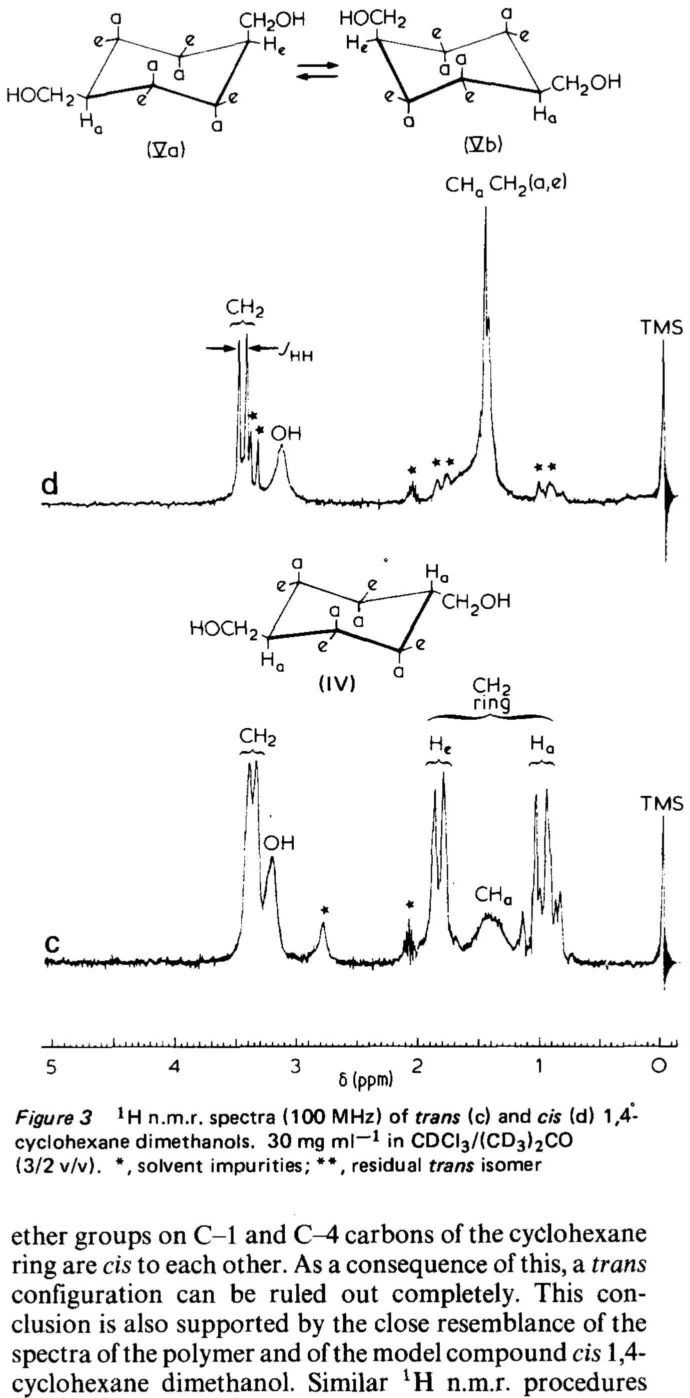
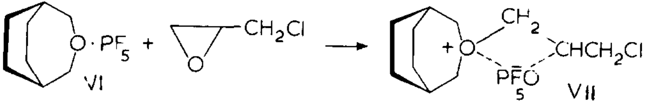


Figure 3 ^{1}H n.m.r. spectra (100 MHz) of *trans* (c) and *cis* (d) 1,4-cyclohexane dimethanols. 30 mg ml^{-1} in $CDCl_3/(CD_3)_2CO$ (3/2 v/v). *, solvent impurities; **, residual *trans* isomer

ether groups on C–1 and C–4 carbons of the cyclohexane ring are *cis* to each other. As a consequence of this, a *trans* configuration can be ruled out completely. This conclusion is also supported by the close resemblance of the spectra of the polymer and of the model compound *cis* 1,4-cyclohexane dimethanol. Similar ^{1}H n.m.r. procedures have been also applied successfully[12,13] in the study of the polymerization of different cyclic ethers.

As regards the polymerization mechanisms, the lack of detailed studies concerning the chemical behaviour of the PF_5/ECH system does not yet allow formulation of a precise scheme for the initiation reaction. However, it is not unreasonable to suppose the formation of equimolecular adducts of PF_5 with (I) and ECH, in the early polymerization mixture. The complex of PF_5 with (I) has been reported to be unable by itself to initiate the polymerization of (I)[1]. Using the previous suggestion concerning the polymerization of the tetrahydrofuran initiated by PF_5 and ECH[14], we may write, for the initiation step:

Scheme 1



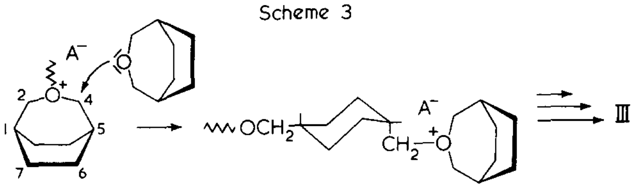
Alternatively, the formation of the inner oxonium ion (VII) may occur through reaction of the presumed PF_5/ECH complex with (I). Intermediates such as (VII) are believed to be reactive and one of the possibilities is that (VII) reacts further in order to form a propagating trialkyl oxonium salt:

Scheme 2

Considering one ECH unit per macromolecule the concentration of ECH in the polymer would exceed the limit of detectability under the n.m.r. analytical conditions used. However, the polymer spectra showed no resonance assignable to ECH. It is probable that only a small amount of initial ECH reacts according to the schemes 1 and 2. Furthermore, due to the long reaction time, chain transfer might be noticeable in this system.

The cationic polymerization of cyclic ethers has been studied extensively, and an S_N2 mechanism, involving propagation through oxonium ions, is now generally accepted[15,16]. If such a mechanism is assumed, the propagation in the polymerization of (I) can then be represented as follows:

Scheme 3



At present, *Scheme* 3 must be regarded only as a formal description. A^- is a generic counterion derived from the initiator and, in particular, it is irrespective of either ion pair or free ion.

Returning now to the propagation reaction, it is worth pointing out that the nucleophilic attack by the monomer oxygen takes place on one of the carbons (C–2 and C–4) lying α to the positive oxygen of the oxonium ion in a random manner, because of the chemical equivalence of both these sites. As a consequence of this, the ring opening of I should always give rise to the same enchainment of the polymer units. Furthermore, the methylene carbons are external to the cyclohexane ring. Therefore, the *cis* configuration of the positions 1 and 5, assumed by the cyclohexane ring in the boat–chair conversion, remains unchanged.

If carbenium ions (derived by the ring opening of the oxonium ions of I) were present, it would be expected that the polymer chain would contain structural irregularities (e.g. methyl branches). These would result from the rearrangement of the unstable primary carbenium ion into the more stable tertiary carbenium ion. However, no spectroscopic evidence for such irregularities has been obtained.

On the basis of the above results, we can conclude that under the adopted experimental conditions, (I) undergoes cationic ring-opening polymerization leading to a linear polyether, having a *cis* structure, which is formed by a growing oxonium centre rather than a carbenium ion.

As regards the nucleophilic attack, the oxonium ion of (I) appears to have a structure much less sterically hindered than the previously reported[1] octahedral structure of the PF_5/(I) complex. This observation agrees with our previous conclusion about the observed inability of both PF_5 and PF_5/(I) to initiate the polymerization of (I)[1]. Indeed, it had been implicitly suggested that once the steric hindrance were reduced the polymerization of (I) would have occurred.

It is expected that alkyl substitution at the C-2 carbon (or C-4) of (I) would lead both to more complex stereochemistry and polymer structure, due to possible head-to-tail, head-to-head and tail-to-tail polymerization. This problem and the application of ^{13}C n.m.r. spectroscopy to elucidate the polymer structure will be the subject of further research.

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