Professor Zambelli for many useful discussions and for allowing us to use their unpublished data.

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A. Provasoli and D. R. Ferro*
Istituto di Chimica delle Macromolecole del CNR
12-20133 Milano, Italy

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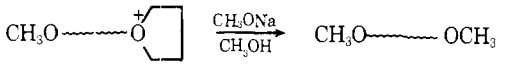
Macrocyclic Tetrahydrofuran Oligomers

Formation of macrocyclic oligomers is a well-known side reaction in the ring-opening polymerization of three- and four-membered cyclic ethers. Under certain conditions the macrocyclic ethers are the predominant products of the polymerization of ethylene oxide[2] and may account for as much as 35% by weight of the polymerization products of oxetane.[3] No corresponding macrocycles however have been found in the polymerization products of the next higher homologue tetrahydrofuran (THF).[4] We wish to report the identification of a series of macrocyclic oligomers formed during the polymerization of tetrahydrofuran.

The polymerizations were initiated with $Me_3O^+BF_4^-$ or CF_3SO_3Me in nitromethane. Samples of the polymerization mixture were quenched with MeONa/MeOH to give dimethoxy poly(tetramethylene) ether. The neutralized solutions of the polymer products were analyzed by gas chromatography and GC–mass spectrometry.



The gas chromatograph used was a Varian Aerograph Series 2700 model with flame ionization detectors. The columns were 60 cm long, packed with 10% SE-30 on Chromosorb W-HP. The injection port had exchangeable glass inserts. Column temperature was programmed at 20 °C/min from 100 to 275 °C. BHT (2,6-di-*tert*-butyl-4-methylphenol) was used as internal standard. Electron impact (EI) mass spectra were obtained with a Du Pont 21-490 GC/MS system. Chemical ionization mass spectra were obtained on a Du Pont 21-491 GC/MS system with isobutane as the reagent gas.

Computer reconstructed total ion chromatograms of the low molecular weight oligomers which are volatile under these conditions are shown in Figure 1. Electron impact mass spectra of the individual peaks indicate two homologous series of fragmentation patterns. For the series of peaks designated 2, 3, 4, etc. (Figure 1), there are two predominant fragments in the mass spectra, *m/e* 87 and 45. They are attributed to fragments containing a methoxy group:

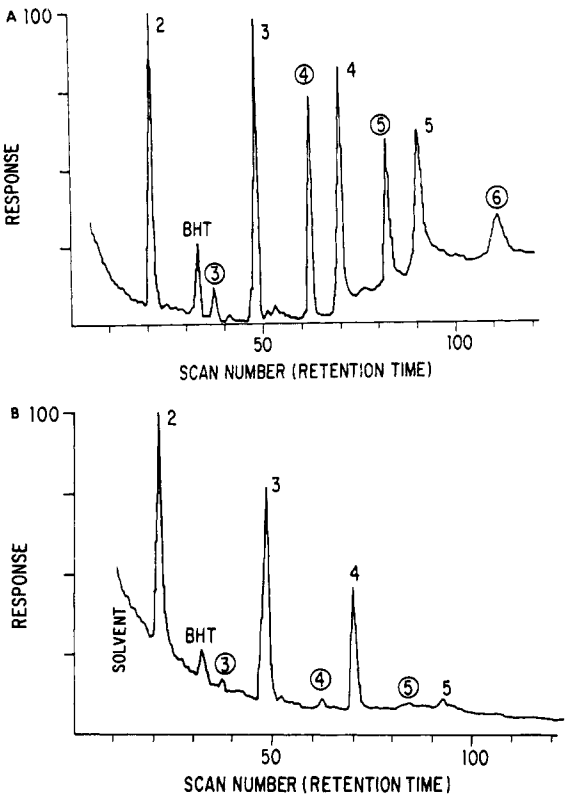
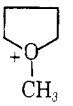


Figure 1. Total ion chromatograms of tetrahydrofuran oligomers. $THF/CH_3NO_2/Me_3OBF_4$ = 45.5/53.4/1.1 mol %; polymerization time = 24 h: (A) polymerization temperature = 25 °C; (B) polymerization temperature = 50 °C; 2, 3, etc. = linear oligomers; ③, ④, etc. = macrocyclic oligomers.

m/e 45: $CH_3OCH_2^+$

m/e 87: $CH_3OCH_2CH_2CH_2CH_2^+ \longleftrightarrow$ 

This series of peaks was therefore assigned to the linear dimethoxy oligomers (dimer, trimer, tetramer, etc.). The mass spectra of the other series of peaks designated ③, ④, etc. (Figure 1A), show five major fragments of *m/e* 71, 43, 41, 55, and 73, in order of decreasing intensity. Although much more complex, these spectra contain all the fragments of the monomeric THF ring. In contrast to the previous series, the strong peaks at *m/e* 87 and 45, corresponding to the fragments with methoxy groups, are not observed here. The absence of methoxy end groups suggests macrocyclic structures.

Due to extensive fragmentation of the molecular ions (M) under electron impact (EI) conditions, molecular weights cannot be determined. However, the molecular weights of the oligomers corresponding to the individual GC peaks can be obtained from the recently developed chemical ionization (CI) mass spectrometry. This technique uses a lower energy ionizing plasma to protonate the parent compounds, thus preventing complete fragmentation of the molecular ions.[5] Examples of a CI spectrum and a corresponding EI spectrum are shown in Figure 2.

Figure 2A illustrates the EI fragmentation pattern of the compound corresponding to GC peak ④, which is the strongest peak of the series without the abundant *m/e* 87 and 45 fragments. The corresponding CI spectrum is seen in Figure 2B. The highest *m/e* observed here are 289 and 290, representing $(M + 1)$ and $(M + 2)$. The molecular weight of the compound corresponding to GC peak ④ is therefore 288 and was assigned the structure of a cyclic tetramer of THF. Similarly, the molecular weights of the compounds corresponding to GC peaks ③, ⑤, and ⑥ were found to be 216, 360, and 432,

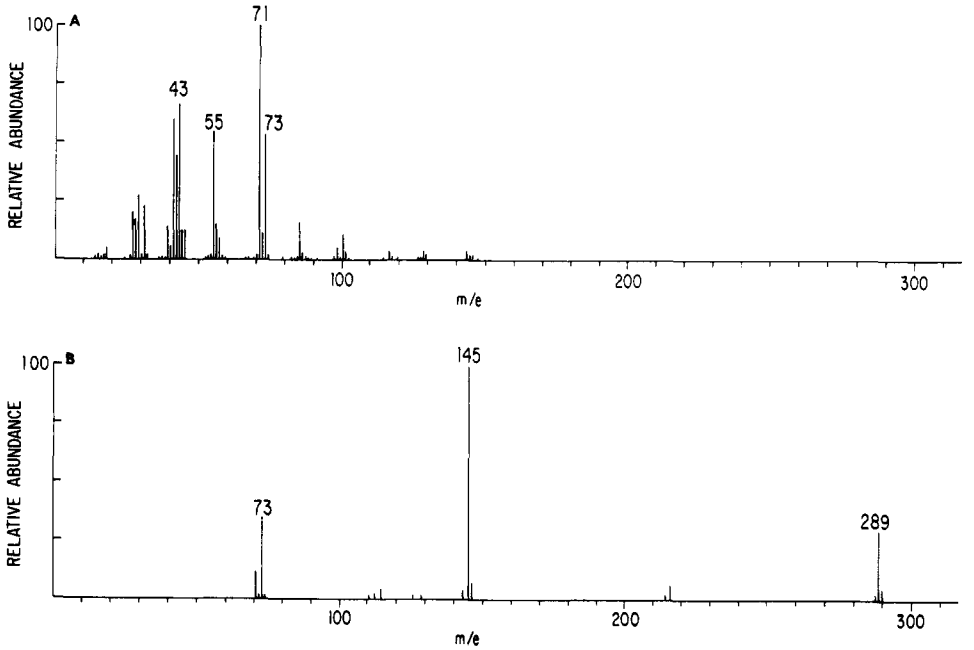
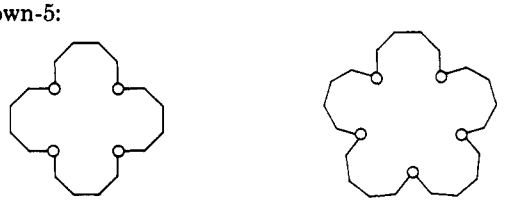


Figure 2. (A) Electron impact mass spectrum of 20-crown-4 (GC peak ④ in Figure 1A). (B) Chemical ionization mass spectrum of 20-crown-4 (GC peak ④ in Figure 1A).

respectively, corresponding to the cyclic trimer, pentamer, and hexamer of THF.

These findings confirm the presence of macrocyclic oligomers in tetrahydrofuran polymers. The concentration of these macrocycles, however, is much smaller than the concentration of the corresponding cyclic oligomers in ethylene oxide or oxetane polymerizations. The fraction of volatile macrocycles detectable under our GC conditions is generally less than 3% of the total polymer weight. The cyclic tetramer is normally present in the highest concentration, followed by cyclic pentamer, and cyclic hexamer, although the relative concentrations may vary with reaction conditions. A maximum in the ring size of cyclic oligomers may be rationalized by the low probability of formation of larger rings, as shown by theoretical calculations,[6] and the decreased tendency of formation of cyclic dimers and trimers due to possible steric interactions. Nevertheless, cyclic dimer is formed, although in very low concentrations. Cyclic octamer is the highest cyclic oligomer observed under the conditions described above.

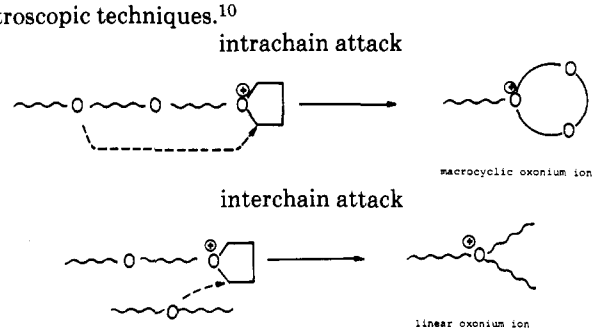
Since such a variety of different macrocyclic ethers are formed, we found it convenient to use the "crown ether" nomenclature to refer to these compounds.[7] The cyclic trimer, trioxacyclopentadecane, would then become 15-crown-3, the cyclic tetramer tetraoxacycloeicosane would become 20-crown-4, and the corresponding pentamer would become 25-crown-5:



20-CROWN-4 25-CROWN-5

It is interesting to compare our results with a report on the formation of cyclic oligomers during the polymerization of the next lower homologue, oxetane.[3a] Only cyclic trimers and tetramers were formed from oxetane, and no higher cyclic oligomers were found. In oxetane polymerization, higher temperatures favored the formation of cyclic compounds, and little cyclic oligomer was observed below 50 °C. In the THF system, on the other hand, intramolecular cyclization seems to be less favored at higher temperatures: at 50 °C mostly linear oligomers were observed and only very low concentrations of cyclic compounds (Figure 1B). In the oxetane system, cyclization appears to be a concurrent process with polymer formation and not the result of a backbiting mechanism,[3a] while in THF polymerizations the concentration of macrocycles increases with time even after the equilibrium conversion to polymer is reached. We therefore conclude that a backbiting mechanism must be responsible for the formation of THF crown ethers.

The proposed mechanism of formation of THF crown ethers involves formation of macrocyclic tertiary oxonium ions by intrachain attack. The presence of macrocyclic oxonium ions, and of linear "dormant" oxonium ions, has been discussed earlier[4,8,9] and was confirmed more recently by spectroscopic techniques.[10]



The direct spectroscopic evidence was based on the difference between the NMR signal intensities of the exo-cyclic and endo-cyclic methylenes of the tetrahydrofuranylium ion.[11] Although there is no difference in chemical shift between the endo- and exo-cyclic α-methylene protons[12] (triplet at 4.86 ppm, Figure 3), there is a considerable difference between the endo- and exo-cyclic β protons.[10,13] The endo-cyclic β protons are more deshielded (multiplet at 2.39 ppm) due to the fact that they are both β and γ to an oxonium center, as compared to the exo-cyclic (linear and macrocyclic) β protons (quintet at 2.06 ppm). The ratio between these endo- and exo-cyclic protons should be 2, as found after short polymerization times. The presence of macrocyclic or linear oxonium ions is indicated by a decrease in this ratio. This has been observed after longer polymerization times (Figure 3).[10]

THF crown ethers are formed by nucleophilic attack on the

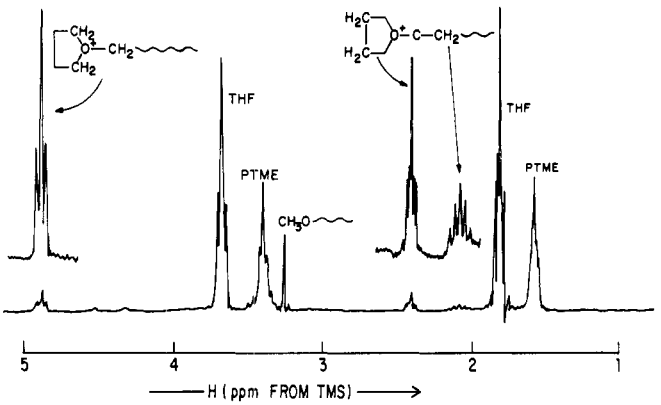
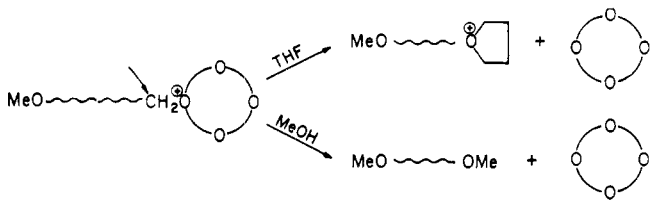


Figure 3. ^{1}H NMR spectrum (220 MHz) of THF/methyltriflate. THF/CD_3NO_2/$CF_3SO_3CH_3$ = 55.4/41.5/3.1 mol %; 30 min: endo/exo = 2; 360 min: endo/exo = 1.6 (PTME = polytetramethylene ether).

exo-cyclic α-methylene group of these macrocyclic oxonium ions:



Attack on endo-cyclic α-methylene groups will only produce linear chains. The formation of THF crown ethers is therefore rather inefficient, but since they represent "dead" polymer, they will tend to accumulate until an equilibrium concentration is reached. This is in agreement with the present finding of an increase in the concentration of crown ethers with time in living THF polymerization systems.

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J. M. McKenna,[1a] T. K. Wu,[1b] and G. Pruckmayr*[1c]
Elastomer Chemicals Department, Plastic Products and Resins Department, and Industrial Chemicals Departments, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19898

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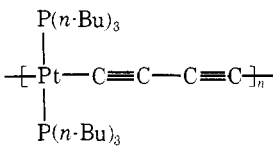
A New Extended Chain Polymer. Poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl]

Recently, a large variety of polymers containing ferrocene or related transition metal complexes have been prepared. However, polymers containing σ-bonded transition metal atoms in the main chain have not yet been reported. The interest in functional polymeric materials is growing rapidly. We expected that the polymers having the backbone composed of conjugated poly-yne and platinum metal atoms might have straight rodlike structures and particular properties in solution or in catalysis. In the previous paper[1] we reported the



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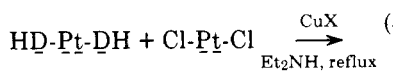
syntheses of oligomers composed of such repeat units and here we wish to report on the synthesis and characterization of high molecular weight poly[*trans*-bis(tri-*n*-butylphosphine)-platinum 1,4-butadiynediyl] (1) prepared by the following method.



Pt and D represent *trans*-$(n\text{-}Bu_3P)_2Pt$– and –C≡C–C≡C–, respectively.

Preparation and Characterization of Polymer. Cuprous iodide (7 mg, 0.037 mmol) was added to a stirred deoxygenated solution of Pt(DH)$_2$ (1.3968 g, 2.0 mmol) and $PtCl_2$ (1.3404 g, 2.0 mmol) in 50 mL of diethylamine under a nitrogen atmosphere. The reaction mixture was heated to a gentle reflux for 1 day and then evaporated to dryness under reduced pressure. The residue was dissolved in methylene chloride and the resulting solution was filtered by alumina column chromatography. After evaporation of the filtrate, a pale yellow product was collected and purified by repeated precipitation from methylene chloride into methanol. Finally, a benzene solution of the product was frozen and then freeze-dried under reduced pressure to afford a pale yellow polymer **1**, yield 2.5 g (96%). The elemental analyses were in good agreement with calculated values. Anal. Calcd for $C_{28}H_{54}P_2Pt$: H, 8.40; C, 51.92; P, 9.56, Found: H, 8.63; C, 51.89; P, 9.81. The IR spectrum of polymer **1** shows a peak at 1999 cm^{-1} attributed to $\nu_{C\equiv C}$ and no trace of the 3307 cm^{-1} acetylenic hydrogen band of the monomer HD-Pt-DH. The UV spectrum of polymer **1** is very similar to that of the model compound Cl-Pt-D-Pt-D-Pt-Cl. The λ_{max} have shifted to slightly longer wavelengths in the polymer. These facts indicate that the polymerization proceeds through the expected route without any side reactions. Polymer **1** was easily dissolved in methylene chloride, diethylamine, THF, benzene, toluene, and even in *n*-hexane at a reflux condition, but not in methanol. The high solubility of polymer **1** is thought to be attributed to butyl substituents on phosphorus which would protect the polymer backbone and decrease intermolecular interaction. Intrinsic viscosity measurement in THF varied from 0.9 to 1.3 dL/g for a series of polymers made using this technique. A sample of polymer **1** ($[\eta]$ = 1.20 dL/g) was fractionated from a methylene chloride solution using methanol as the precipitant to afford a fraction having $[\eta]$ of 2.11 dL/g (yield 60%). Sedimentation equilibrium of the fraction in toluene provided a weight-average molecular weight ($\bar{M}_w$) of 119000–122000 ($\bar{n}_w$ = 184–188).[2] Thermogravimetric analysis at a heating rate of 5 °C/min of polymer **1** showed a rapid decomposition in air at 270 °C and 42% weight loss in vacuo at 325–400 °C.

^{31}P Nuclear Magnetic Resonance Spectra of the Polymer. In structural studies of the Pt-diyne polymer, configurational analysis of platinum moiety in polymer using ^{31}P NMR provides a method which proves the rodlike structure of the polymer. Previously we have reported that the spectra of several monomers and model compounds illustrated