Synthesis and characterization of new polycrown ether (schiff base)

Pradip Kumar Dutta*
Department of Applied Chemistry, Shri G. S. Institute of Technology & Science, Indore 452 003, India

Received 27 December 2000; revised 25 May 2001; accepted 12 June 2001

A semirigid 32-membered ring dialdehyde crown ether, bis (5-aldoxy-1,3-phenylene)-32-crown-10 (3), has been synthesized in one step using 3,5-dihydroxy benzaldehyde (1) and tetra (ethylene glycol) dichloride (2) in the presence of sodium hydride in DMF. A direct polycondensation reaction of bis (5-aldoxy-1,3-phenylene)-32-crown-10(3) and diamines (5) in DMF formed a high molecular weight poly crown ether (schiff base). The polymers are characterized by viscometry, elemental analysis, IR and NMR spectroscopies. The polymers are soluble in common organic solvents. The thermal characteristics of the polymers have been studied by TGA and DTA.

The role of crown ether in the area of complexation and host-guest chemistry is unique\(^1\). The study on versatility of polymeric crown in comparison with their monomeric counterparts have been focussed by various workers during the last 2 decades\(^2\). In these polymeric crown the macrocycles are mostly in the range of 15-18 membered rings. The report on macrocycles larger than 30-membered rings is limited. Crown ethers in the range of 30-membered rings and higher have the ability to bind two metal ions per cavity and also the complex with large organic cations\(^3\). A number of polymeric schiff bases are reported by polycondensation of dialdehydes with suitably placed diamino compounds. They are reported as useful catenation ligands, good absorbers for solid phase gas chromatography. Some of these are also interesting because of their semiconductor properties\(^4\). Polymeric schiff base with crown ether moiety is a unique combination in coordination polymer chemistry. This paper reports the synthesis and characteristic of a new series of poly (schiff base) which contains a semi rigid large (32-membered) macrocycle in the main chain.

---

*For correspondence (E-mail: 37 @ Yahoo.com)
Measurements
IR spectra (in KBr) were recorded with a Perkin-Elmer 837 model spectrophotometer. $^1$H-NMR spectra were run on a Varian EM390 spectrometer at 90 MHz with CDCl$_3$ as solvent using tetramethyl silane (TMS) as the internal reference. The inherent viscosity of the polymer solutions (0.5% w/v) in DMF was determined at 30°C in a Ubbelohde suspended level viscometer. Elemental analysis was made by a Heraeus Erba 1108 elemental analyzer. Thermogravimetric (TGA) and differential thermal analysis (DTA) were done with a Shimadzu DT-40 instrument at a heating rate of 10°C/min.

Results and Discussion
Monomer synthesis and characterization
Bis(5-aldoxy-1,3-phenylene)-32-crown-10 (3) was synthesized by the reaction of 3,5-dihydroxy benzaldehyde (1) with tetra (ethylene glycol) dichloride (2). The reaction is represented in Scheme 1.

The desired macrocycle as well as a second new compound, 5-aldoxy-1,3-phenylene-16-crown-5 (4) was obtained.

The $^1$H-NMR spectra were used to distinguish between 3 and 4. The $\alpha$-5-OCH$_2$ products of crown 4 appeared at 3.62-4.13 ppm whereas the $\alpha$-5-OCH$_2$ protons of product 3 appeared 3.5-4.32 ppm. The $\alpha$-OCH$_2$ protons of crown 4 appeared at lower field than those in the larger macrocycle 3 ($\Delta$δ=0.19). The methylene protons of the tetra (ethylene glycol) chain of the large macrocycle were magnetically more equivalent than in the smaller macrocycle.

The calculated results for C, H in elemental analysis of the products were in good agreement with the experimental results. The presence of ether linkages in the products was confirmed by the characteristics stretching absorption at about 1129 cm$^{-1}$ in the spectra.

Polymer synthesis and characterization
Polyazomethine crowns (6 a-c) were synthesized by the reaction of bis(5-aldoxy-1,3-phenylene)-32-crown (3) with three different aromatic diamines (5a-c). The polymerization reaction is shown in Scheme 2.

Aromatic polyazomethines are an important class of polymers for high performance fibres. The reaction of aromatic diamines with aromatic dialdehydes generally produces low molecular weight azomethine polymers by conventional polycondensation methods due to the insoluble nature of resulting polymers in organic solvents. The resulting polymers (6a-c) showed higher molecular weight with better solubility in most common organic solvents such as THF, chloroform, pyridine, DMF, DMSO, DMAC. Polyazomethine crown polymers (6a-c) were yellow, with ~ 95% yield, and $\eta_{inh}$ values between 0.30 and 0.40.

The chemical structure of polymer 6 was determined on the basis of elemental analysis, IR and NMR studies. Elemental analysis of the polymer from the chemical analysis agrees well with the theoretical values of the chemical structure.

The IR spectra of all the polymers are similar and exhibit characteristic absorptions around 1737 (C=O), 1505(C=C aromatics), 1600 (CH=N) and 1139 cm$^{-1}$ (C-O-C).

The $^1$H-NMR spectra of the polymers show a singlet at about 8.5 ppm which corresponds to -CH=N-protons of the polymer repeat limit. Besides
these, α,β and γδ-OCH₂ peaks are found at 4.15, 3.87 and 3.72 ppm respectively. The aromatic protons of polymers 6a-c appear as a broad multiplet in the region 6.4-8 ppm. Polymer 6c shows an additional sharp singlet at 4 ppm due to CH₂ protons of 4,4' diamino diphenyl methane moiety.

**Thermal behaviour of polymers**

All the polymers are found to lose weight (12-14%) around 350°C in both nitrogen and air. The high thermal stability of the polymers is mainly due to the presence of rigid azomethine linkages and aromatic moieties lies in the macro chain. All the polymers exhibit Tgs in the range of 102-78°C. The polymer 6a shows the highest Tg of 102°C. This is consistent with the rigid structure of polymer 6a compared to polymers 6b and 6c where flexible -O- and -CH₂- linkages are present in the macro chain. The reason for lowering of Tgs in the polycrown ether schiff bases (6a-c) is due to the plasticizing effect of the C-O-C linkages.

The first member of a new class of polyschiff base containing large macrocycles in the backbone has been synthesized by the direct polycondensation of a dialdoxy macrocycle (3) and diamines (5a-c). The reaction gives rise to high polymerization (96%) yield and high molecular weight polymer.

**Acknowledgement**

The author wishes to thank Dr. P. K. Chande, Director and Dr. J.K. Agrawal, Head of Chemistry of this Institute for kind permission to publish the work.

**References**