Cationic oligomerization of isopropyloxirane

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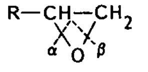
The structures of isopropyloxirane (IO) oligomer prepared with a cationic initiator and poly-IO prepared by coordination polymerization were investigated by ^{13}C n.m.r. spectroscopy. The spectra are consistent with non-rearranged polymeric structural units. This is related to the nature of the bridged propagating oxonium ion intermediate in the cationic oligomerization.

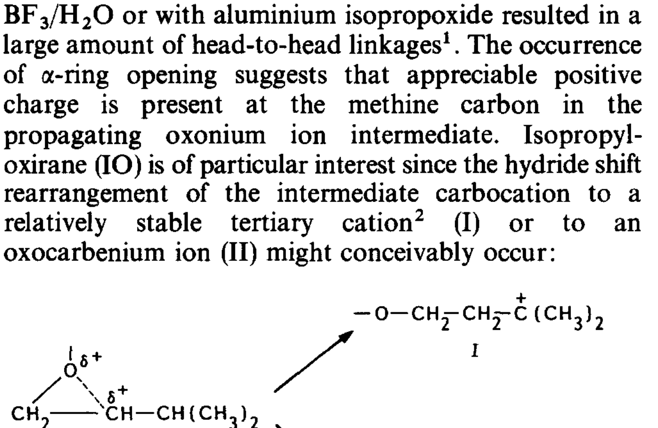
(Keywords: isopropyloxirane oligomer; poly(isopropyloxirane); ^{13}C n.m.r. spectroscopy; bridged oxonium ion intermediates)

INTRODUCTION

Cationic polymerization of unsymmetrically substituted oxiranes is known to occur in a non-regioselective manner involving both α- and β-ring opening:



For example, the polymerization of methyloxirane with BF_3/H_2O or with aluminium isopropoxide resulted in a large amount of head-to-head linkages[1]. The occurrence of α-ring opening suggests that appreciable positive charge is present at the methine carbon in the propagating oxonium ion intermediate. Isopropyloxirane (IO) is of particular interest since the hydride shift rearrangement of the intermediate carbocation to a relatively stable tertiary cation[2] (I) or to an oxocarbenium ion (II) might conceivably occur:



The possibility of rearrangement is of interest since its occurrence (or absence) will reflect the nature of the intermediate involved in the polymerization process. Strong bridging interaction between the oxygen and the electron-deficient carbon could preclude such rearrangement. On the other hand, the observation of hydride shift rearrangement in the polymerization of IO would suggest weak or no oxygen bridging to an electron-deficient secondary carbocation.

^{13}C n.m.r. is a powerful tool for investigating the structure of cationic poly-IO. This paper presents the results of a ^{13}C n.m.r. study of cationic IO oligomer and of stereoregular poly-IO prepared by coordination polymerization of IO. The spectrum of the latter polymer was of considerable use in the interpretation of the cationic oligomer spectrum.

EXPERIMENTAL

Materials

Chloromethane was passed through 3 Å molecular sieves and condensed directly into the polymerization flask. Zinc chloride (Aldrich Chemical Co., gold label) was fused, cooled and ground to a powder in a nitrogen atmosphere. Acetone was kept over 3 Å molecular sieves, filtered and distilled. Aluminium isopropoxide (AIP) was obtained from Ventron, Alfa products (98+%). Isopropyloxirane was prepared by the method of Guss and Rosenthal[3] and fractionally distilled through an annular Teflon spinning band column (b.p. 80–84°C). Gas chromatographic analysis (24′ Carbowax 20 M, 80°C) indicated 98% purity, and i.r. showed strong absorption in the vicinity of 12 μm, characteristic of oxirane ring vibrations.

Spectroscopic and other analyses

^{13}C n.m.r. spectra were taken with an IBM WP200 FTNMR spectrometer operating at 50.3 MHz. Samples of oligomer were 28% w/w in $CDCl_3$; samples of polymer from coordination polymerization were 20% w/w in a 1:1 C_6D_6–C_6H_6 mixture. All chemical shifts (δ) reported were referenced to tetramethylsilane. Gas chromatography analyses were carried out with a Hewlett-Packard 5880A instrument using a flame ionization detector. I.r. spectra were taken with a Beckman 4260 spectrophotometer.

Cationic oligomerization of isopropyloxirane

Boron trifluoride etherate (0.25 ml) was added with stirring to IO (4.93 g) dissolved in chloromethane at −80°C under nitrogen. An exothermic reaction occurred which raised the temperature of the reaction mixture to −60°C. The reaction mixture was kept at −80°C under nitrogen for 7 days, then quenched with wet methanol. The reaction mixture was added with stirring to excess chilled methanol giving a viscous oil which was dissolved in dichloromethane and dried over anhydrous $MgSO_4$. On removal of the dichloromethane and drying under vacuum, 3.01 g of a viscous oil was obtained (61% yield).

Coordination polymerization of isopropyloxirane

IO (7.0 g, 0.081 mol) was polymerized with AIP (0.20 g, 0.0010 mol) and $ZnCl_2$ (0.13 g, 0.0010 mol) in a sealed

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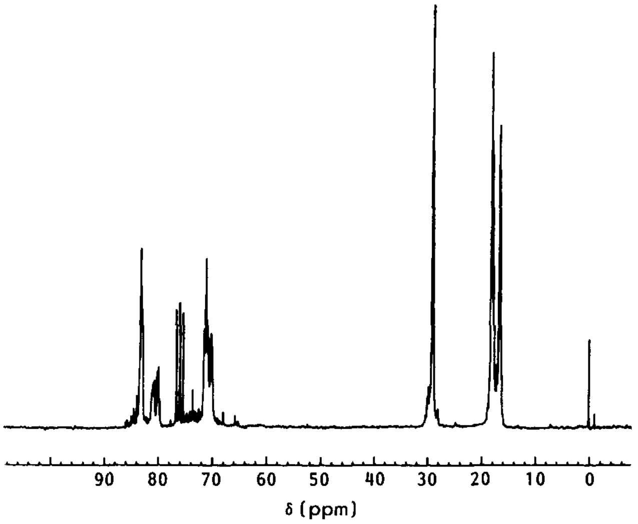


Figure 1 ^{13}C n.m.r. spectrum (50.3 MHz) of isopropyloxirane oligomer

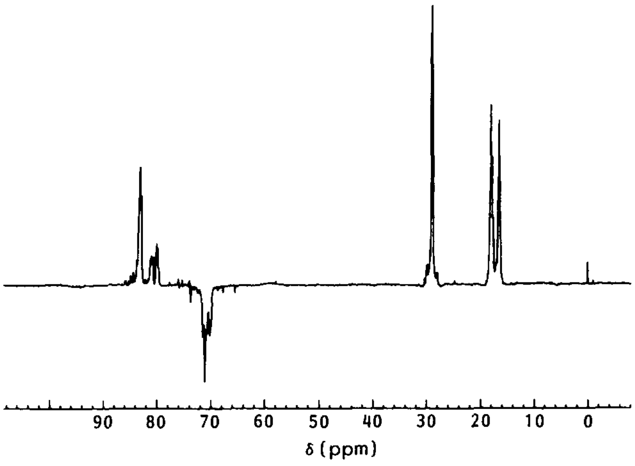
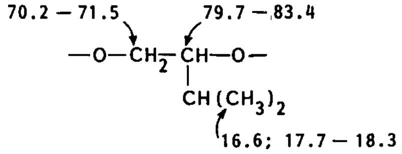


Figure 2 DEPT spectrum of isopropyloxirane oligomer

tube at 80°C. The product was dissolved in benzene and the solution was washed with 1 M HCl, water, dilute $NaHCO_3$, distilled water, and dried over anhydrous $MgSO_4$. The solvent was removed by distillation and finally by freeze-drying, giving 4.54 g (65% yield). A 1.00 g sample of the polymer was fractionated by the addition of acetone, cooling to −20°C and centrifuging at −20°C. This yielded three fractions: insoluble at room temperature (0.23 g); insoluble at −20°C (0.10 g) and soluble at −20°C (0.61 g).

RESULTS AND DISCUSSION

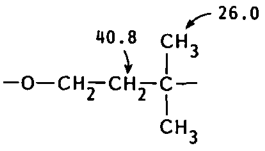
The cationic oligomerization of IO was carried out with boron trifluoride etherate at −80°C in chloromethane. Under these conditions the oligomer formed has an approximate molecular weight of 600 (vapour pressure osmometry)[4]. The ^{13}C n.m.r. spectrum of the oligomer consisted of several major groupings, each formed by several closely spaced peaks, as well as many minor peaks (*Figure 1*). This complexity is expected in view of the lack of regiospecificity of ring opening and the importance of end group effects due to low molecular weight. However, the spectrum is consistent with non-rearranged units:



$$-O-CH_2-CH(CH(CH_3)_2)-O-$$

Two groups of peaks at 16.6 and at 17.7–18.3 ppm are assigned to the isopropyl methyl groups which are chemical shift non-equivalent due to the proximity of the chiral centre in the oligomer backbone. Peaks at 79.7–83.4 ppm are assigned to the backbone methine carbon and at 28.8–29.3 ppm to isopropyl methine while the methylene carbon gives rise to a group of peaks at 70.2–71.5 ppm. This latter assignment was confirmed by a DEPT spectrum[5] (CH_2 negative; CH, CH_3 positive) in which the peaks at 70.2–71.5 ppm inverted while the other peaks remained positive (*Figure 2*). In order to confirm the non-rearranged structure, a sample of poly(isopropyloxirane) (PIO) was prepared by the coordination polymerization of IO with AIP and zinc chloride. The ^{13}C n.m.r. spectrum (*Figure 3*) of a fraction of PIO insoluble in acetone at room temperature is consistent with isotactic head-to-tail polymer and showed singlets at 17.89, 19.50 ppm (non-equivalent isopropyl CH_3); 73.07 ppm (CH_2); 84.77 ppm (CH, backbone); 30.78 ppm (CH, isopropyl). A DEPT spectrum (*Figure 4*) confirms these assignments.

Consecutive rearranged units in a PIO structure derived from cation I are identical to those in poly(2,2-dimethyloxacyclobutane)[6]. The chemical shift value reported for the CH_2 non-adjacent to oxygen in poly(2,2-dimethyloxacyclobutane)



$$-O-CH_2-CH_2-C(CH_3)_2-$$

is 40.8 ppm[6]. No peak is observed in this region of the spectrum of the IO oligomer (*Figure 1*). A rearranged IO unit followed by a non-rearranged unit is not expected to alter the value of this chemical shift significantly. The

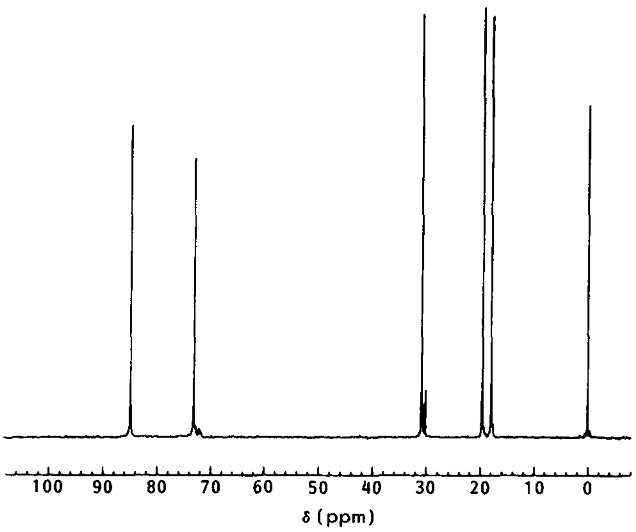


Figure 3 ^{13}C n.m.r. spectrum (50.3 MHz) of poly(isopropyloxirane) prepared with aluminium isopropoxide–zinc chloride initiator

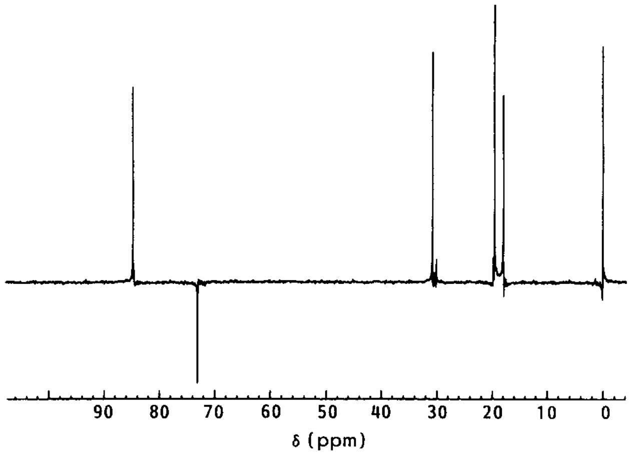


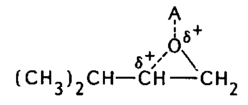
Figure 4 DEPT spectrum of poly(isopropyloxirane)

chemical shift of methyl carbons in rearranged IO is also significantly different than that observed for isopropyl methyl groups.

Rearrangement of the propagating carbocation to an oxocarbenium ion II would lead to a polyacetal structure. The ^{13}C n.m.r. chemical shifts observed for the cationic IO oligomer are very close to the analogous shifts we have observed for the insoluble fraction of poly-IO prepared by coordination polymerization and are not in agreement with a rearranged polyacetal structure.

We therefore conclude that no significant hydride shift rearrangement occurred in the cationic oligomerization of IO under the reaction conditions used in this study[4].

The propagating intermediate involved in the cationic oligomerization of IO is best represented as:



where A = polymer chain or a Lewis acid initiator.

Bridging by oxygen is sufficiently strong to stabilize the carbocationic centre and to reduce the tendency for hydride migration.

ACKNOWLEDGEMENT

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