Monatshefte für Chemie 122, 967–976 (1991)

Monatshefte für Chemie
Chemical Monthly

Haloaldehyde Polymers, XLIX**: Analysis of Linear Bornyl Oxide Initiated, Acetate Endcapped Chloral Oligomers by Potassium Ionization of Desorbed Species Mass Spectrometry

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Abstract. Linear chloral oligomers initiated with lithium bornyl oxide and acetate endcapped were analyzed by potassium ionization of desorbed species (K^+ IDS) mass spectrometry. Using this technique we observed ions resulting from the [unimer]K^+ with a mass of 381 daltons, to the [hexamer]K^+ with a mass of 1 119 daltons. Furthermore, analysis of the isotope pattern supported our structural assignment. The individual lower oligomers were also investigated by GC and NMR spectroscopy.

Keywords. Chloral oligomers; Bornyl oxide initiation; Mass spectrometry; Potassium ionization of desorbed species; Chlorine isotope pattern.

Haloaldehyd-Polymere, 49. Mitt.: Analyse linearer bornyloxid-initiierter Chloral-Oligomere mit Acetat-Endgruppen mittels Kaliumionisierung desorbierter Spezies

Zusammenfassung. Zur massenspektroskopischen Analyse der Chloral-Oligomere wurde die Kaliumionisierung desorbierter Spezies (K^+IDS) Massenspektrometrie eingesetzt. Mittels dieser Technik konnten wir Ionen des [Unimer]K^+ mit einer Masse von 381 Dalton bis zum [Hexamer]K^+ mit einer Masse von 1 119 Dalton beobachten. Die Strukturzuordnungen wurden zusätzlich von der Isotopenverteilung bestätigt. Die einzelnen niedrigeren Oligomere wurden auch mittels GC und ^{1}H-NMR untersucht.

Introduction

We have recently investigated the oligomerization and polymerization of trihaloacetaldehydes especially of chloral [1–6] and have used achiral initiators (tertiary

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** Previous paper in this series: Haloaldehyde Polymers XLVIII. W. J. Simonsick Jr., K. Hatada, Fu Xi, and O. Vogl [27] butoxide) [4, 7–9] or chiral initiators (bornyl oxide and others) [3, 10–15] for our syntheses. We focused on the characterization of the individual oligomeric species by mass spectrometry and NMR spectroscopy and the determination of their configuration by single crystal X-ray analysis [7–10]. Of special interest was the oligomerization of fluoral [16, 17] and chloral [3, 18, 19] with chiral initiators.

We found that the addition of chloral to the initiating chiral bornyl oxide anion resulted in an approximately equal mixture of two diastereomeric monoaddition products, the chloral terminated alkoxides of the unimer. As further additions of chloral proceeded, oligomeric alkoxides became increasingly stereospecific. *Meso* addition became significant over *racemo* addition in the dimeric alkoxides and highly specific starting with the trimer and completely specific thereafter. As the oligomer equilibria were established it was necessary to stabilize the composition of the oligomeric alkoxides by acetylation with acetic anhydride. The isomer fractions were isolated by fractional distillation; some of the individual isomers, the (*R*)-unimer, the (*R*,*R*)-dimer and the (*R*,*R*,*R*)-trimer have been isolated and crystallized. Their absolute configurations were determined by single crystal X-ray crystallography [10].

In the past we had specially studied the polymerization of chloral with chiral initiators. We had found that polychloral could be obtained in the form of transparent films with high optical rotations. The high values of the optical rotations [12–15, 20] were somewhat puzzling; however, these experiments have been repeated by several investigators over the years and were found to be completely reproducible. Our ultimate goal was then to prepare polychloral samples, whose polymer structures consisted of polymeric helices of only one screw sense [21–23] and whose optical activity was exclusively based on molecular asymmetry not consisting of the regularly obtained 50 : 50 mixture of right and left handed helices.

In our attempts to approach this goal, we carefully investigated the oligomerization of chloral with chiral initiators and selected bornyl oxide as the chiral anionic initiator. We are fully aware that the bornyl oxide anion is not very bulky and may not be the best chiral initiator for our ultimate objective. We used bornyl oxide as the initiator because the oligomerization of chloral with this initiator provided chloral oligomers that were sufficiently volatile and could easily be analyzed by GC. These chloral oligomers were also amenable to mass spectrometric characterization.

Bornyl oxide initiated chloral oligomers, up to the hexamer could be identified by GC and those up to the trimer by high resolution ^{1}H NMR spectroscopy. Lower oligomers were also isolated as individual compounds, crystallized and subjected to single crystal X-ray crystal investigations which established the absolute configurations of the compounds [10].

Chemical ionization spectrometry has been known as an excellent technique for the analysis of sensitive organic compounds. One of the newest selective techniques, the potassium ionization technique, called K^+IDS, (K^+ ionization of desorbed species) uses thermionic emission of potassium ions from a matrix containing potassium [24–26]. This type of analysis gives pseudo molecular ions in the form of $[M]K^+$ with little or no fragmentation. Our instrumentation technique allows the detection of potassium molecular ions possessing masses up to 1,800 daltons. The observed ions are equal to the molar mass number plus that of the potassium ion of 39 daltons [25, 26]. It was found to be a very suitable method for examining our perhaloaldehyde oligomers [16, 27].

We have recently reported the results of our K^+IDS mass spectrometric investigations of acetate endcapped tertiary butoxide initiated fluoral and chloral oligomers [27]. Because of our basic interest in the polymerization and oligomerization of perhaloaldehydes, especially with chiral initiators, we have continued our emphasis on K^+IDS as a means of characterizing oligomers of perhaloacetaldehydes. It was therefore the objective of this work to study linear bornyl oxide terminated acetate capped chloral oligomers by K^+IDS.

Experimental Part

Chloral was obtained from the Montrose Company and was purified to polymerization grade as described previously [28]. (1*S*, 2*R*, 4*S*)-(−)-Borneol (99%), *n*-butyllithium, (1.6 *M*, in hexane) methylcyclohexane (anhydrous), and acetic anhydride were obtained from the Aldrich Chemical Company; they were used without further purification. Dichloromethane (Fisher Scientific Co.) – used for optical rotation measurements – was used as received.

The mixture of bornyl oxide initiated, acetate capped chloral oligomers (BIAC) was prepared as described previously [3, 10]. (1*S*, 2*R*, 4*S*)-(−)-Borneol (77 g, 0.5 mol) in methylcyclohexane (400 ml) was treated with *n*-butyllithium in hexane (312 ml, 0.5 mol). At about 50°C chloral (370 g, 2.5 mol, in 160 ml of methylcyclohexane) was added, the mixture was cooled to room temperature and quenched with acetic anhydride (56 g, 0.55 mol). After work-up, 233 g (48%) of product was obtained, which gave, after careful fractional distillation under reduced pressure, the unimer fraction (40 g) boiling at 108–110°/0.025 mmHg, the dimer fraction (82 g), b.p. 157–159°/0.025 mmHg, and 3 g of a relatively pure trimer, boiling range 190–195°/0.0005 mmHg was also obtained.

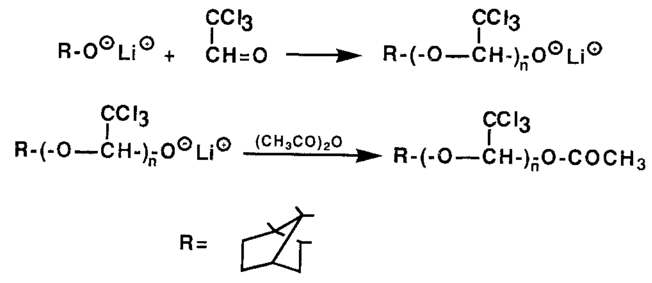
The separation of the oligomers by GC and HPLC as well as the single crystal X-ray analysis of the unimers, dimers and trimers has also been described previously [10].

A Varian 3000 Gas chromatograph (column: 50 cm × 5 mm stainless steel, packed with Chromasorb G.H.P. 100/200 which was coated with 5% OV101, or column: 1.5 m × 5 mm, packed with Chromasorb Q11, 80/100, coated with OV17) was used to analyze the oligomers and to ascertain the purity of the chloral. The column temperature was programmed for a constant temperature increase from 130° to 250°C.

The mass spectrometric experiments were performed on a Finnigan 4615B quadruple GC/MS system. An EI source configuration was used in all K^+IDS experiments. The ion source pressure (ion gauge) was $< 10^{-6}$ mmHg with a source temperature of 200°C. For a more detailed explanation of the experimental procedures involved in the K^+IDS technique consult Ref. [26].

Results and Discussion

Chloral oligomerization initiated with lithium bornyl oxide was carried out and the reaction mixture was immediately endcapped with acetic anhydride to freeze the equilibrium mixture of the oligomeric alkoxides (Scheme 1). We obtained a mixture of oligomers that, because of the chirality of the bornyl oxide anion, contained two diastereomeric unimers. Of the higher oligomers (similar to our experiments with tertiary butoxide initiation) not all the possible isomers in the oligomer fractions were present and only some of them could be identified. In this BIAC series, three dimers were identified, the result of meso and racemo addition. In addition, trimers and tetramers of increasing stereospecificity, and consequently decreasing number of individual isomers, could be also isolated.



Scheme 1

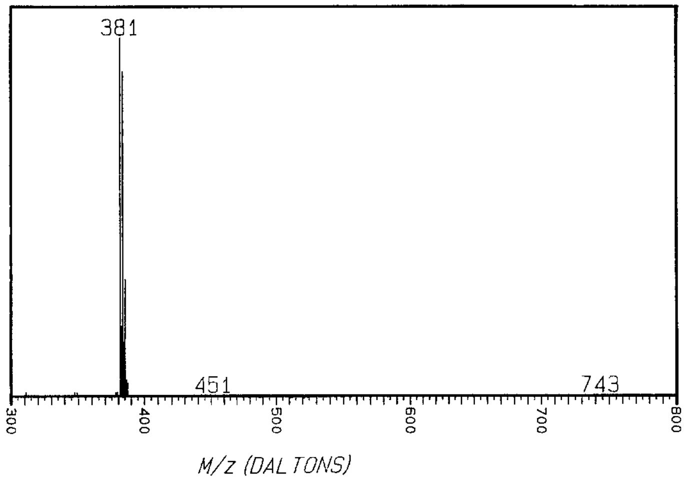


Fig. 1. Mass spectrum of bornyl oxide initiated acetate capped unimer: 381

Mass spectrometry has been shown to be a very useful technique to analyze mixtures of oligomers obtained from the careful study of the initiation process. This has been demonstrated in fluoral oligomerization and tertiary butoxide initiated chloral oligomerization. K^+IDS mass spectrometry, a relatively new mass spectrometric technique, was found to be excellent for the analysis of these oligo-

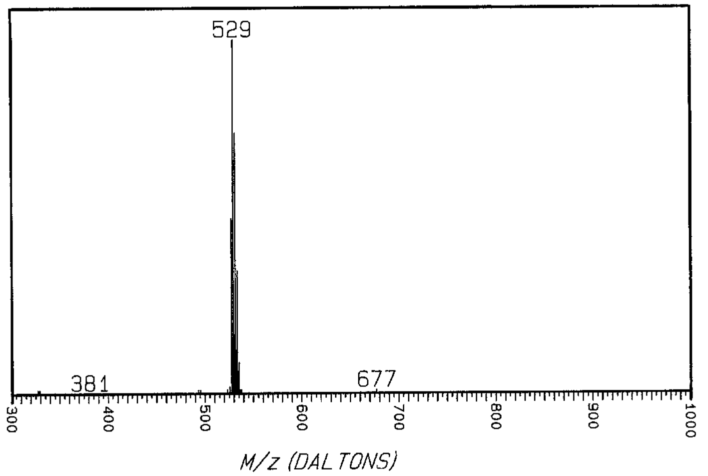


Fig. 2. Mass spectrum of bornyl oxide initiated acetate capped dimer: 529

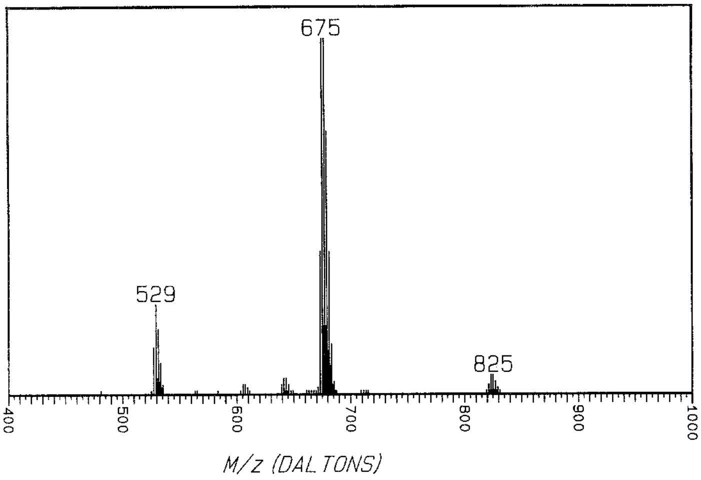


Fig. 3. Mass spectrum of bornyl oxide initiated acetate capped trimer fraction: major mass peak at 675

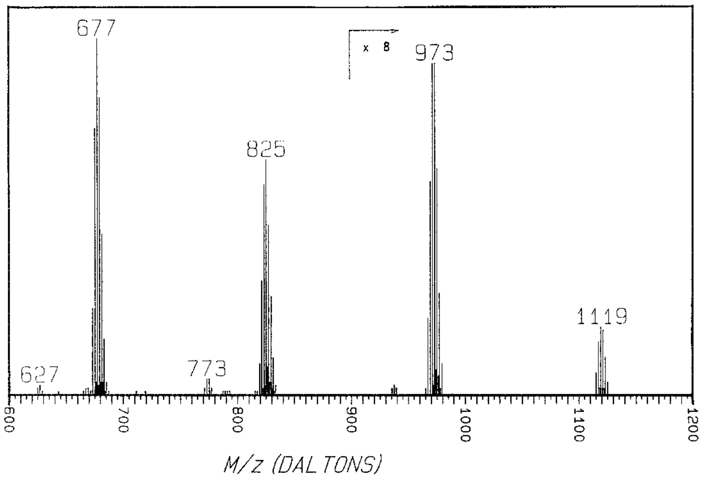


Fig. 4. Mass spectrum of bornyl oxide initiated higher oligomers

mers. It can identify individual masses of the fractions of oligomers from the oligomer mixtures but unfortunately cannot distinguish between diastereomers. The BIAC oligomer mixtures have been analyzed before by GC and NMR [3, 16].

The K^+IDS mass spectra of the oligomers BIAC have been determined. Our analysis is restricted to mass numbers of the intact oligomers plus the potassium ion $[M]K^+$. Very little, if any, fragmentation was observed under the conditions of our mass spectrometric experiments. The mass spectra showed clusters of ions centered at the mass peaks $[M]K^+$. The clusters are due to the isotopic distribution of the chlorine atoms in the molecule. The detailed analysis of the chlorine isotope distributions provided us with additional information on the identity and purity of the individual compounds.

Fig. 1 shows the K^+IDS mass spectrum of the unimer of relatively high purity ($[M]K^+ = 381$ daltons). Fig. 2 shows the mass spectrum of the BIAC dimer of

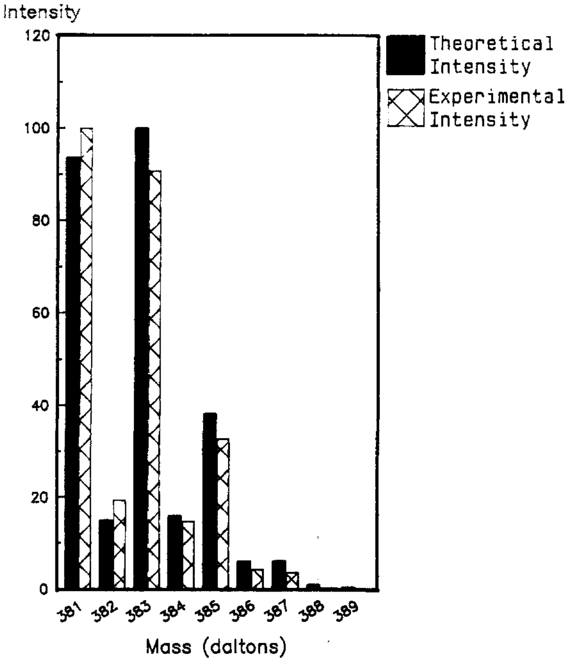


Fig. 5. Isotope analysis of bornyl oxide initiated acetate capped unimer: 381

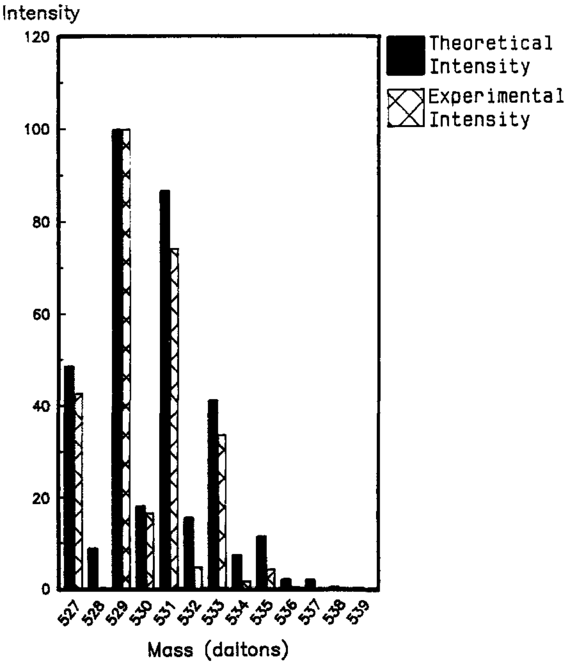


Fig. 6. Isotope analysis of bornyl oxide initiated acetate capped dimer: 529

chloral ($[M]K^+ = 529$ daltons). The small peak at 435 daltons which is also present in some of the mass spectra corresponds to the mass of the potassium ion plus the dimer of chloral diacetate. Traces of the unimer $[M]K^+$ are still present. The mass spectrum of the crystalline sample of the BIAC dimer, m.p. = 52–54°C, shows a $[M]K^+$ value of 529 daltons. This is the typical mass spectrum of a highly purified compound of this series. This particular sample has been used for single crystal analysis of the dimer of chloral and is the (R, R)-dimer (Fig. 2).

The mass spectra (K^+IDS) of higher BIAC oligomers are shown in the next two figures. In Fig. 3 the trimer fraction is clearly evident with the mass maximum centered at its base peak: $[M]K^+$ at 675 daltons. It is accompanied by the dimer peak ($[M]K^+ = 529$ daltons); a considerable amount of tetramer ($[M]K^+ = 825$ daltons) can also be seen. Even higher molecular weight BIAC oligomers have been observed as seen in Fig. 4. In addition to the trimer ($[M]K^+ = 677$ daltons), a tetramer ($[M]K^+ = 825$ daltons) several higher molecular weight peaks can be identified. In the presentation of the molecular peaks in Fig. 4, the intensity of the higher mass peaks, starting from the [pentamer]K^+ at 973 daltons and the [hexamer]K^+ at 1 119 daltons, is increased by a factor of 8.

The trichloromethyl groups of the chloral units of the oligomers contribute to a predictable characteristic isotope pattern of chlorine. We have analyzed the unimer $[M]K^+$ to the hexamer $[M]K^+$ of the BIAC oligomers. In Figs. 5 and 6 we show the isotope pattern for the linear unimer and dimer. As a by-product of the chloral oligomerization we obtained also the acetylation product of the unchanged monomer chloral, chloral diacetate $[M]K^+ = 288$ (Fig. 7). An expanded display in the form of a bar chart is shown for the calculated and experimental values of the masses of the [hexamer]K^+ which demonstrates the powerful capabilities of the analysis of the isotope analysis of multichlorine containing organic compounds (Fig. 8).

The isotope distributions of the theoretical intensities have also been calculated for the heptamer $[M]K^+$, the octamer $[M]K^+$, and the nonamer $[M]K^+$. The [decamer]K^+ is shown in Fig. 9.

Table 1. Theoretical isotope distribution of the BIAC dimer $[M]$ K^+ for the composition $C_{16}H_{22}O_4Cl_6$ K^+

Mass	Calculated abundance
527	48.82548
528	9.00881
529	100
530	18.34898
531	86.79273
532	15.80651
533	41.29556
534	7.44086
535	11.61075
536	2.05841
537	1.93006
538	0.33299
539	0.17815

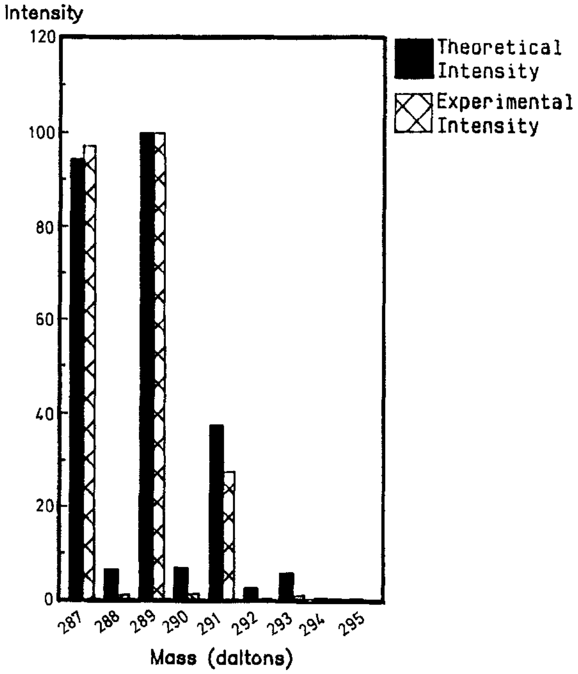


Fig. 7. Isotope analysis of chloral diacetate: 288

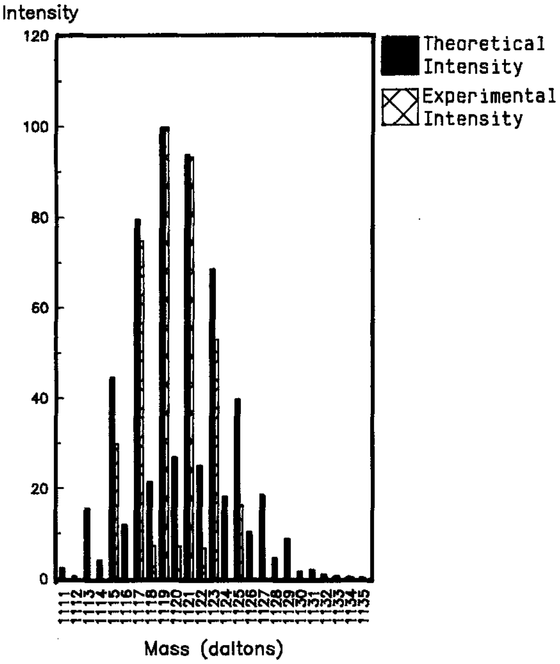


Fig. 8. Isotope analysis of bornyl oxide initiated acetate endcapped hexamer: 1119

The molecular formula of the BIAC [dimer]K^+ is $C_{16}H_{12}O_4Cl_6K$. The predicted pattern resulting from the six chlorine atoms can be calculated from the binomial expansion described in our earlier paper [27, 29]. The theoretical isotope distribution of the BIAC dimer $[M]K^+$ of 529 daltons is presented in Table 1.

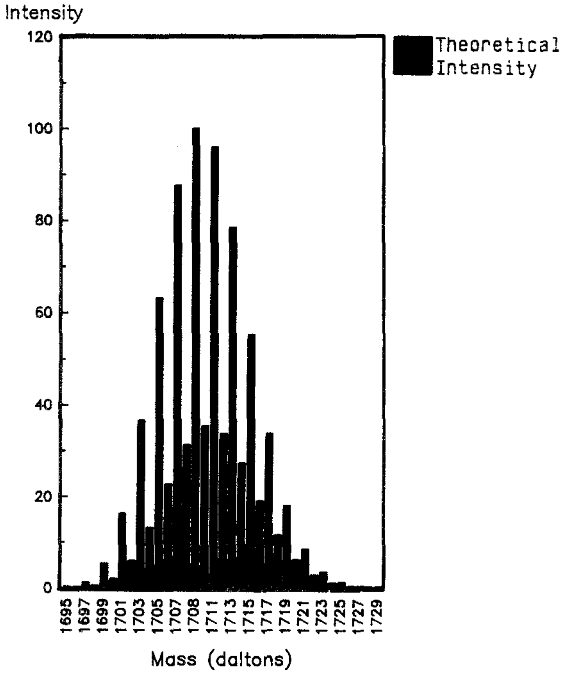


Fig. 9. Isotope analysis of bornyl oxide initiated acetate capped decamer: 1711

Fig. 5 presents in bar chart form the comparison between the theoretical and the experimental results which are in excellent agreement. We have found in all cases of our isotope analysis very good agreements between the theoretical isotope distributions and our experimental results, thus corroborating our proposed structures for the individual BIAC oligomers.

For the analysis in this work we did not use exact masses but only integer masses. This approximation affects very slightly the specific positioning of the mass axis not the profiles of the patterns. This shift is significant only for compounds with more than 20 chlorine atoms.

Acknowledgement

This work was supported by the Herman F. Mark Chair of the Polytechnic University, the National Science Foundation grant No. DMR 8617788 and the ACS PRF grant No. 18065-AC7. Karl Blom (E.I. du Pont de Nemours and Co., Wilmington Delaware) wrote the program which was used to calculate the theoretical isotope distribution. We also appreciate the cooperation of Maryann Fulginiti in the determination of the mass spectra; we are grateful to Gary D. Jaycox and F. W. H. Kruger for their many suggestions and to P. Zarras for their help during the preparation of this manuscript.

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Received January 18, 1991. Accepted February 14, 1991