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HALOALDEHYDE POLYMERS. 63. DIACYL-TERMINATED TRIHALOACETALDEHYDE OLIGOMERS

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HALOALDEHYDE POLYMERS. 63. DIACYL-TERMINATED TRIHALOACETALDEHYDE OLIGOMERS

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Key Words: Oligomerization, Trihaloacetaldehydes, Chloral, Bromal, Tertiary Amines, Alkaloids, Acid Anhydrides

ABSTRACT

Mixtures of diacyl-terminated trichloroacetaldehyde (chloral) oligomers were synthesized using tertiary amines as initiators followed by end-capping with diacyl anhydrides. Not only were the oligomeric alkoxide molecules acyl end-capped when the

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reaction mixture was treated with the acid anhydride, but the initiator fragment that was attached to the initiated end was also replaced by an acylate group. Eight different anhydrides were used for end-capping reactions allowing us to synthesize a number of symmetric chloral oligomers diacylates. A mechanism for the oligomerization of the chloral monomer was proposed on the basis of the results obtained from these investigations. Similar oligomerizations of bromal initiated with tertiary amines, and end-capped with acetic anhydride, gave the corresponding oligomeric bromal diacetates. All the trihaloacetaldehyde oligomer mixtures were analyzed by gas chromatography and the individual components were identified by K+IDS mass spectrometry.

INTRODUCTION

The understanding of the initiation and termination of aldehyde polymerization contributes significantly to our knowledge of the polymerization of trihaloacetaldehydes [1-4]. Knowledge of the structure and end-groups allows us to understand and predict the thermal, oxidative and hydrolytic stability of these polymers. Initiation reactions play an essential role for the development of the ultimate conformational structure of the polyacetal main chain.

The polymerization of trihaloacetaldehydes, especially of chloral, is most conveniently and effectively carried out by anionic polymerization. The nucleophiles, which are able to initiate the polymerization of trihaloacetaldehyde monomers, include alkoxides, acylates, chlorides, tertiary amines, and phosphines [5-7]. Alkoxides, acylates, and chlorides initiate these polymerizations by adding to the carbonyl carbon of the monomers, forming chloral terminated alkoxides which are the carriers of the subsequent polymerization.

Tertiary phosphines behave differently. A detailed study of the initiation of chloral with triphenylphosphine revealed that the actual initiating species is triphenyl(dichloroethyleneoxy)-phosphonium chloride [8] and chloride is the initiating anion. In our continuous work on the polymerization of chloral and the mechanism of chloral initiation, we had always assumed that the initiation of this polymerization with tertiary amines would behave similarly. We expected that the initiation of chloral with tertiary amines would create an ammonium salt chloride and we believed that the polymerization of chloral was

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initiated by the addition of the chloride anion to the carbonyl atom of chloral [9]. We have now found, and presented in our recent preliminary papers, [10-12] that the chloral oligomerization with tertiary amines, is initiated by the direct addition of the tertiary amine initiator to chloral forming a zwitterion ammonium alkoxide which, after treatment with acetic anhydride gave the chloral oligomer diacylate mixture capped on both sides.

Many years ago, we investigated the chloral polymerization initiated with tertiary amines [5]. The polymerization proceeded quite rapidly but the chloral samples were quite unstable. Furthermore, when the polymerization was carried out between glass plates (to prepare films or sheets of polychloral) the polymer stuck tenaciously to the glass plates, and usually the plates had to be broken to isolate the formed polymer.

In previous studies, we also determined [13] that the polymerization of chloral initiated with a chiral alkoxide could produce optically active polymer. The optical activity was caused by macromolecular asymmetry (helicity) of the main acetal polymer chain.

We have also shown that the stability of the one-handed helices of the chloral oligomers depends on the size of the end-groups [14, 15] but also to some extent, on the degree of polymerization of the oligomers. We observed that in the cases of lower oligomers where the end-groups were small, such as in the case of methyl groups, the helix inversion in solution proceeded readily and at low temperature up to the tetramer. When the initiating end-group was as large as a tertiary butyl group, helical reversion did not take place up to quite high temperatures.

It was the objective of this work to study the oligomerization and polymerization of chloral and bromal using tertiary amines as initiators and to end-cap these oligomers with acylate anhydrides with increasing bulkiness. Furthermore, we wished to use optically active tertiary amines, such as are available as alkaloids as initiators for the oligomerization of chloral/bromal. It was hoped that a chiral chloral oligomer chain of a one-handedness could be synthesized directly and stabilized by using bulky end-capping reagents that would prevent any helix inversion which would "racemize" the individual oligomers. It was our further objective to characterize these symmetric diacyl-terminated haloaldehyde oligomers by GC and Potassium Ionization of Desorbed Species (K^+IDS) mass spectrometry [16-18].

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EXPERIMENTAL

Materials

Chloral was obtained from the Montrose Company and was purified to polymerization grade monomer as described previously [19]. The content of impurities were determined by GC and were shown to be less than 800 ppm.

Bromal (Aldrich Chemical Company) was treated first with antimony trifluoride, then with phosphorus pentoxide (both Aldrich Chemical Company) and vacuum distilled [20].

Lithium tert-butoxide (Fluka Chemical Corporation) was sublimed in vacuum at 0.5 mm Hg at 150°C.

Tertiary Amines

Triethylamine, pyridine, (R,R)-(-)- and (S,S)-(+)-2,3-dimethoxy-1,4-bis(di-methyl-amino)butane (DDAB), cinchonidine, cinchonine, quinidine, quinine, nicotine, strychnine and sparteine were all obtained from Aldrich Chemical Company, and were used without further purification.

Acid Anhydrides

Acetic anhydride, propionic anhydride, n-butyric anhydride, iso-butyric anhydride and pivalic anhydride were all purchased from the Aldrich Chemical Company, benzoic anhydride from Fluka Chemical Corporation. Diphenylacetic anhydride and adamantanecarboxylic anhydride were synthesized from the corresponding carboxylic acids.

Solvents

Methylcyclohexane, dichloromethane, benzene, tetrahydrofuran, petroleum ether, all anhydrous, were purchased from Aldrich Chemical Company.

Measurements

Oligomers of chloral and bromal were analyzed by capillary gas chromatography on a Varian 3300 Gas Chromatograph (capillary fused silica column: I. D. 0.5mm x 10 m, injector temperature 250°C, column temperature 140°C, temperature increase 5°C/min., detector temperature 250°C, helium flow rate 5 mL/min.) [21] and K+IDS mass spectrometry were performed on a Finningan 4615B quadruple GC/MS system previously described [22].

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The optical activity of chloral oligomers was measured on a Perkin-Elmer 241 Polarimeter in a glass cell with a path length of 10 cm using a sodium lamp (589 nm).

Preparations

Anhydrides

Diphenylacetic Anhydride

Diphenylacetic anhydride was prepared from diphenylacetic acid (Aldrich Chemical Company) and acetic anhydride [23]. In a 250 mL flask, diphenylacetic acid (70 g, 0.33 mol) was added to acetic anhydride (70 mL, 0.74 mol), and the mixture was heated to reflux for 2 hours. The acetic acid produced by the reaction (75 mL) was collected in a Dean-Stark adapter. The mixture was cooled to room temperature and the crude product was dissolved in anhydrous ether (30 mL) and allowed to crystallize. Thirtyseven grams of yellowish crystals (55% yield, m.p. 98-100°C) were obtained. The product was recrystallized twice from petroleum ether and yielded white crystals (11 g), m.p. 102-103°C.

Adamantanecarboxylic Anhydride

Adamantanecarboxylic anhydride was synthesized according to a procedure [24] similar to that of the preparation of diphenylacetic anhydride. In a 250 mL round bottom flask, 1-adamantane-carboxylic acid (30 g, 0.17 mol) [m.p. = 172-4°C] (Aldrich Chemical Company) was added to acetic anhydride (50 mL, 0.53 mol) and the mixture was heated to reflux for 2 hours at oil bath temperature of 175°C. During the reaction, 45 mL of acetic acid was collected in a Dean-Stark adapter. After cooling to room temperature, the crude product was diluted with 50 mL of dry ether and the clear solution was cooled to -50°C. White crystals had formed which were filtered through a fritted filter and washed with cold petroleum ether. After drying in vacuum, 19 g of 1-adamantane carboxylic acid anhydride (68 % yield) was obtained, m.p. =195-7°C.

Oligomerization of Trihaloacetaldehyde with Tertiary Amines

Oligomeric Trihaloaldehyde Diacetates

The oligomerization of chloral with tertiary amines (e.g. triethylamine or strychnine) as the initiators was typically carried out as follows: In a 250 mL three-neck flask, 20 mmol of tertiary amine was diluted with 50 mL of dry sol-

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vent (methylcyclohexane or dichloromethane) and the solution was heated to 40°C. In a separate 50 mL flask, 100 mmol of freshly distilled chloral (10 mL), (molar ratio of chloral to amine = 5:1) was diluted with 30 mL of solvent, the solution was warmed to 40°C and added to the initiator solution using a dry syringe. The content of the flask was then cooled to -5°C while stirred with a Teflon coated magnetic stirring bar. Soon, a thick white suspension had formed which we attribute to oligomeric and polymeric alkoxides of chloral.

To acyl cap this mixture, it was treated with an acid anhydride (130 mmol), cooled to -10°C [using a precooled (to at least -10°C) syringe]. The suspension was stirred for 1 hour at -5°C, the suspension was allowed to warm to room temperature and the liquid containing the oligomer fraction was separated from the solid polychloral by filtration through a fritted glass filter funnel. The filtrate was washed in a separatory funnel with 10% aqueous sulfuric acid solution to remove the unreacted amine.

The top layer was separated, neutralized by washing with aqueous sodium bicarbonate solution, washed with distilled water and dried over anhydrous

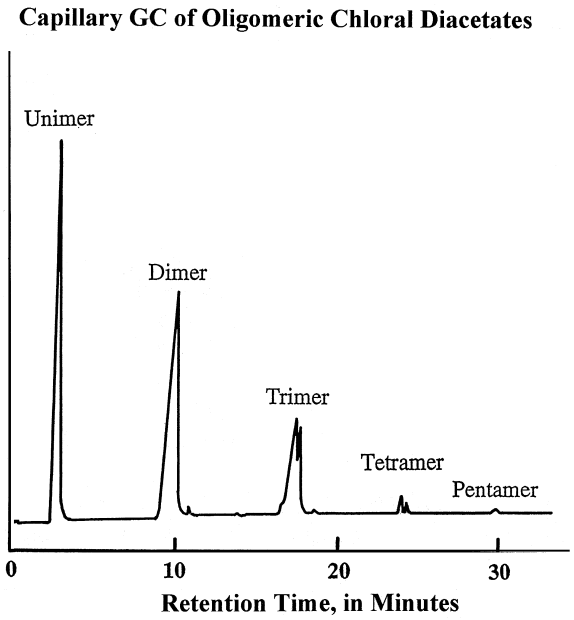

Figure 1. Capillary Gas Chromatogram of Oligomeric Chloral Diacetates.

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magnesium sulfate. The solvent was removed under reduced pressure and the oligomer mixture was obtained as a colorless oily product. The crude mixture was analyzed by GC (Figure 1) and K^+IDS mass spectrometry (Figure 2). In some cases, the lower oligomers (mostly unimers and dimers) were removed by vacuum distillation in a Kugelrohr.

In the specific example, triethylamine (1.9 g, 18 mmol), in a 100 mL flask, was diluted with methylcyclohexane (30 mL) and heated to 50°C. In another flask, 9 mL of chloral (91 mmol, mol ratio of monomer to initiator 5:1) was diluted with methylcyclohexane (10 mL) heated to 50°C and added to the amine solution. The mixture was cooled to 15°C, which resulted in the formation of a thick white suspension. After treatment with 10 mL of acetic anhydride (10 mL, 0.11 mol), the polychloral powder (3.9 g, 29% conversion) was separated from chloral oligomers (14.3 g) and the oligomers isolated as described above.

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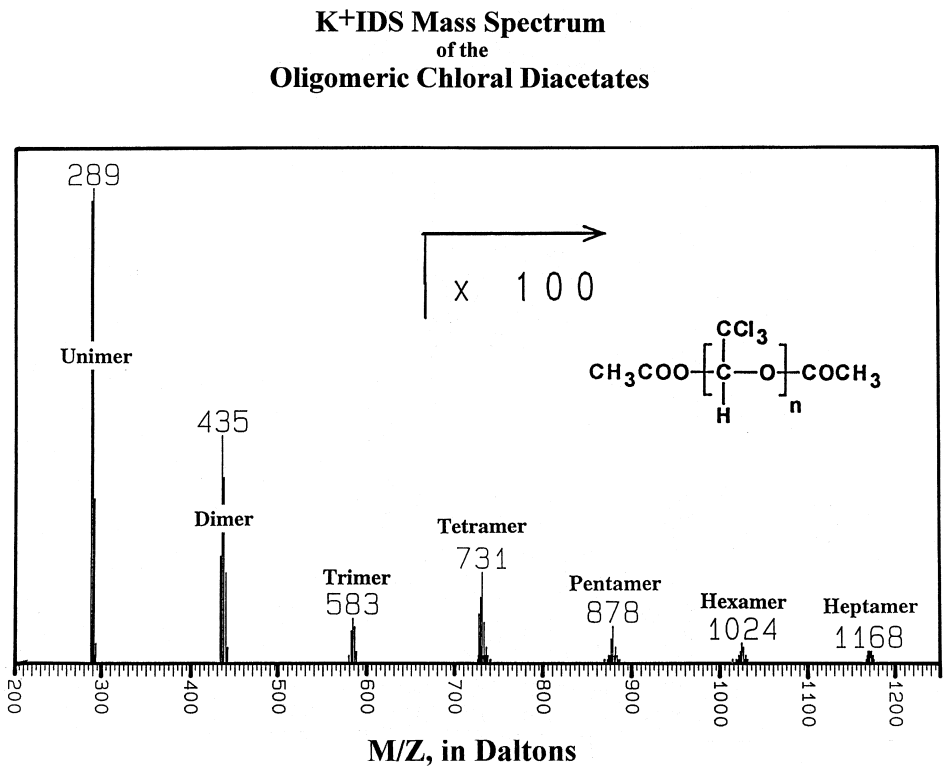

Figure 2. K^+IDS Mass Spectrum of Oligomeric Chloral Diacetates.

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A similar oligomerization of chloral was also carried out with other tertiary amines as the initiators. Pyridine (5.6 g, 15 mmol) was diluted with anhydrous methylcyclohexane or dichloromethane (60 mL) and heated to 40°C. Chloral (15 mL, 0.15 mol) was diluted with 20 mL of solvent, heated to 40°C and added to the initiator solution. The mixture was then cooled to 0°C, and after the formation of solid polychloral, it was treated with the excess of cold acetic anhydride (18 mL, 0.19 mol). The oligomers were separated from polychloral (4.9 g,) and isolated (yield 18 g).

The oligomerization of chloral with a chiral tertiary amine, (S,S)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDAB) was carried out as follows: The solutions of DDAB (0.8 g, 4 mmol) in methylcyclohexane (2 mL) and chloral (1.5 g, 10 mmol) in methylcyclohexane (2 mL) were separately heated to 50°C under a nitrogen atmosphere. The chloral solution was added to the initiator solution and the ensuing solution was stirred with the magnetic stir-

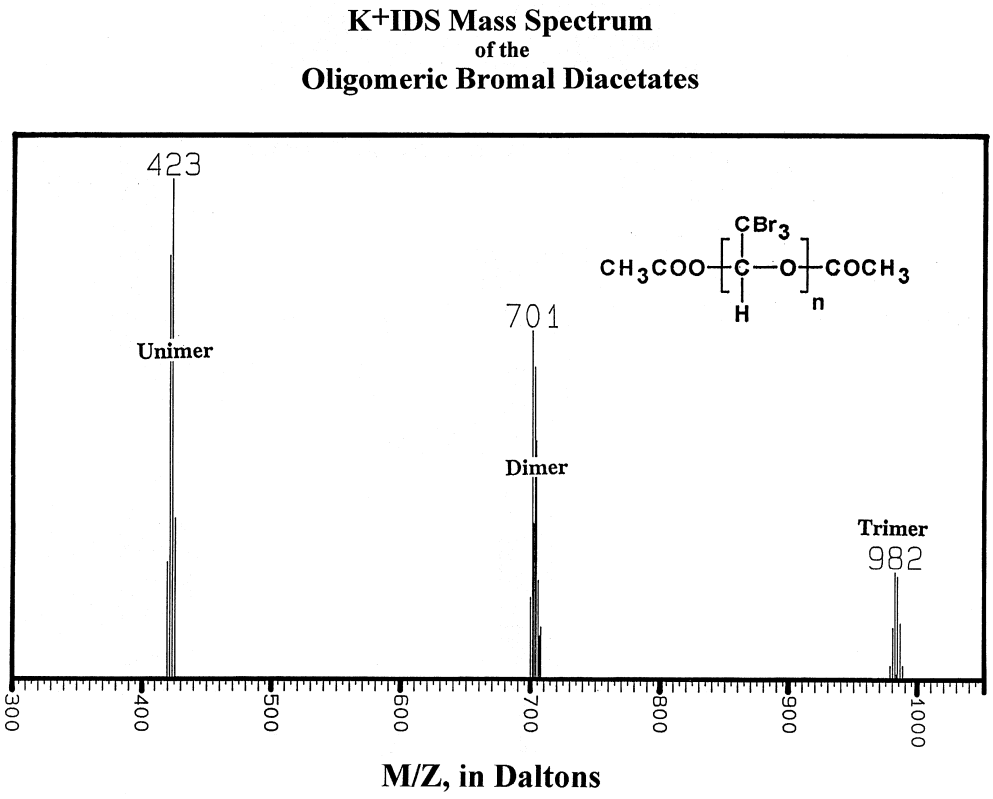

Figure 3. K^+IDS Mass Spectrum of Oligomeric Bromal Diacetates.

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ring bar while the solution was slowly cooled. When the temperature reached 25°C, a white powder of polychloral formed, acetic anhydride (2 mL, 20 mmol) was added and the suspension was allowed to undergo the end-capping reaction at 25°C for one hour. After the usual work up, 1.8 g of the oligomer mixture was obtained. The GC spectrum of all tertiary amine initiated chloral oligomers end capped with acetic anhydride is very similar to those obtained from triethylamine initiation.

Bromal oligomerization was performed using a procedure similar to that used for the chloral oligomerization, only the oligomerization reaction had to be carried out at much lower temperatures. The mixture of bromal (5.2 g, 50 mmol) and tertiary amine (2.3 g of sparteine, 10 mmol) was prepared in dichloromethane (15 mL) at room temperature. The solution was cooled over a period of 30 minutes to -60°C, at which temperature the precipitation of insoluble polybromal started. The acetic anhydride (5 mL, 53 mmol) used for end-

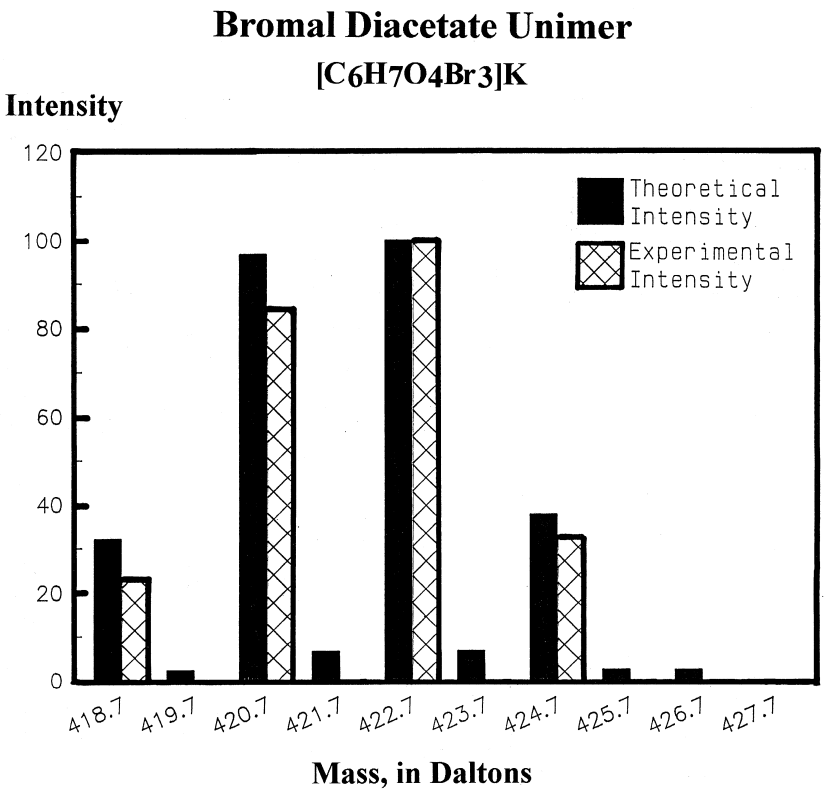

Figure 4. Isotope Distribution of the Bromal Diacetate Unimer.

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capping reaction was cooled to -70°C and added with a cooled syringe, also to -70°C. The suspension which had formed, was stirred for 5 hours at -70°C and the temperature was then allowed to raise to 20°C. After an additional hour of stirring at room temperature, the suspension was filtered through a fritted glass filter, the filtrate was concentrated as in the case of the chloral oligomers isolation and 9.5 g of a dark crystalline product was obtained. The crude oligomer mixture was analyzed by K^+IDS mass spectrometry in Figure 3. Figure 4 presents the theoretical and experimental isotope intensities for the unimer in support of our assignments.

End-Capping of Tertiary Amine Initiated Chloral Oligomers with Various Anhydrides

Propionic Anhydride

Triethylamine (2.1 g, 20 mmol) in dichloro-methane (60 mL) was used for the initiation of the oligomerization of chloral. The monomer (10 mL, 0.10

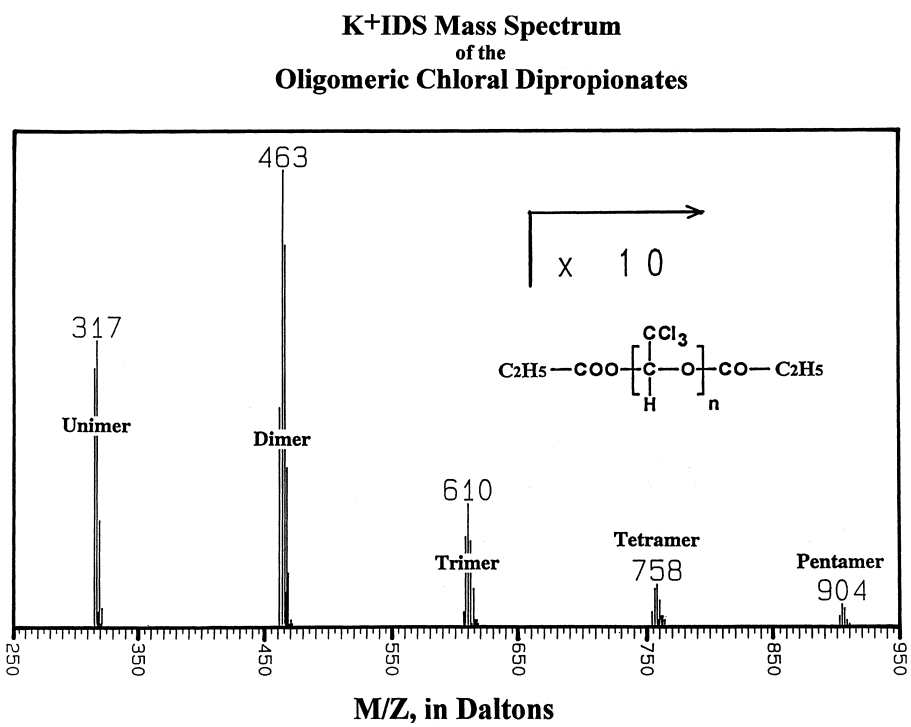

Figure 5. K^+IDS Mass Spectrum of Oligomeric Chloral Dipropionates.

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mol) was diluted with dichloromethane (40 mL) and both solutions were mixed at 40°C. The solution was gradually cooled. Polychloral started to form when the solution temperature had reached 0°C; when the reaction mixture was at -10°C propionic anhydride (13 mL, 0.10 mol) was added. After 11 days at -20°C, the suspension was worked up in the usual way and gave an oligomer mixture (18.1 g). The K^+IDS spectrum is shown in Figure 5 with the corresponding isotope comparison pattern plot for the trimer seen in Figure 6.

n-Butyric Anhydride

For the synthesis of chloral oligomers terminated with n-butyrate end groups, a similar procedure, as in the case of propionic anhydride capping was used. Triethylamine (2.1 g, 20 mmol) in dichloromethane was added to the chloral monomer (10 mL, 0.10mol). After the formation of solid polychloral, n-butyric anhydride (16 g, 0.10 mol) was added. The oligomer fraction was isolated after the reaction was allowed to proceed for 3 weeks at -20°C. The K^+IDS

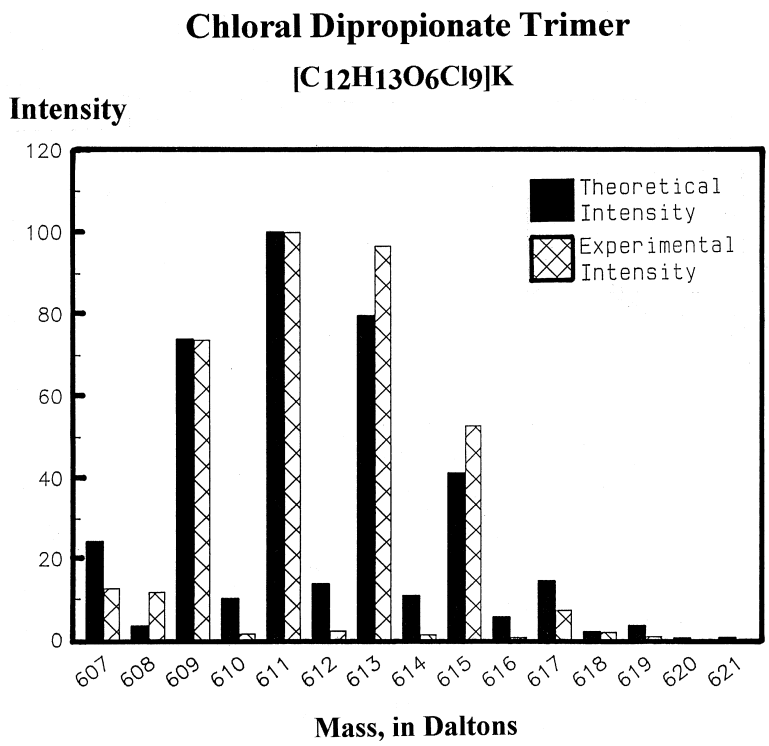

Figure 6. Isotope Distribution of the Dipropionate Chloral Trimer.

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spectrum is seen in Figure 7. Figure 8 presents the experimental and theoretical isotope patterns for the tetramer in corroborating our assignments. For the isobutyrate capped oligomer mixture, prepared in a similar way the K^+IDS spectrum is shown in Figure 9.

Pivalic Anhydride

Triethylamine (0.8 g, 7.7 mmol), diluted with dry dichloromethane (80 mL) was allowed to interact with a chloral solution (7.5 mL, 77 mmol) in dichloromethane (15 mL) at 40°C. After cooling to -10°C solid polychloral had formed and pivalic anhydride (14 mL, 70 mmol) was added. After a reaction time of 5 weeks, the reaction was worked up and the oligomer mixture (16.3 g) was isolated. The GC spectrum is shown in Figure 10 and the K^+IDS spectrum in Figure 11.

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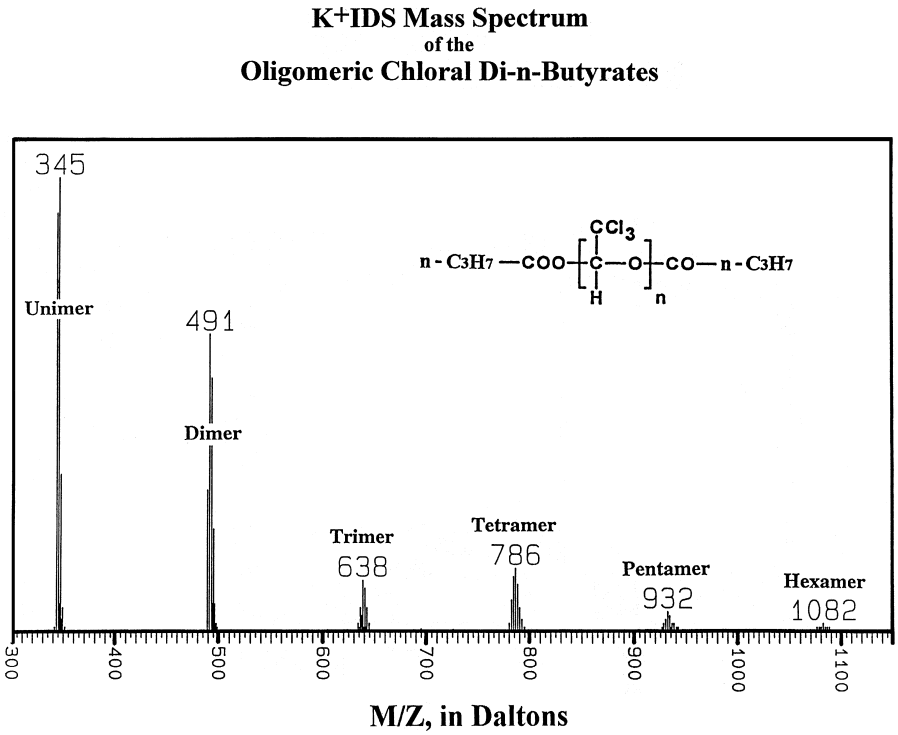

Figure 7. K^+IDS Mass Spectrum of Oligomeric Chloral Di-n-Butyrates.

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Benzoic Anhydride

In a 250 mL flask, triethylamine (2.1 g, 20 mmol) was diluted with dichloromethane (60 mL) and, at 40°C, chloral (10 mL, 0.10 mol) in dichloromethane (40 mL) was added. The solution was cooled with stirring to -10°C, a slurry was obtained to which benzoic anhydride (20 g, 88 mmol) was added. The end-capping reaction was allowed to process for 6 weeks at -20°C. The oligomer fraction (15 g) was isolated and characterized by K^+IDS (Figure 12).

Diphenylacetic Anhydride

In a 250 mL flask, triethylamine (0.5 g, 5 mmol) was dissolved in dichloromethane (30 mL) and heated to 40°C. Chloral (5 ml, 51 mmol), dissolved in dichloromethane (20 mL), was added to the initiator solution. The flask was cooled with stirring to -10°C and a solution of diphenylacetic anhydride (20 g, 48 mmol) in dichloromethane 40 mL), cooled to -30°C, was added. The flask

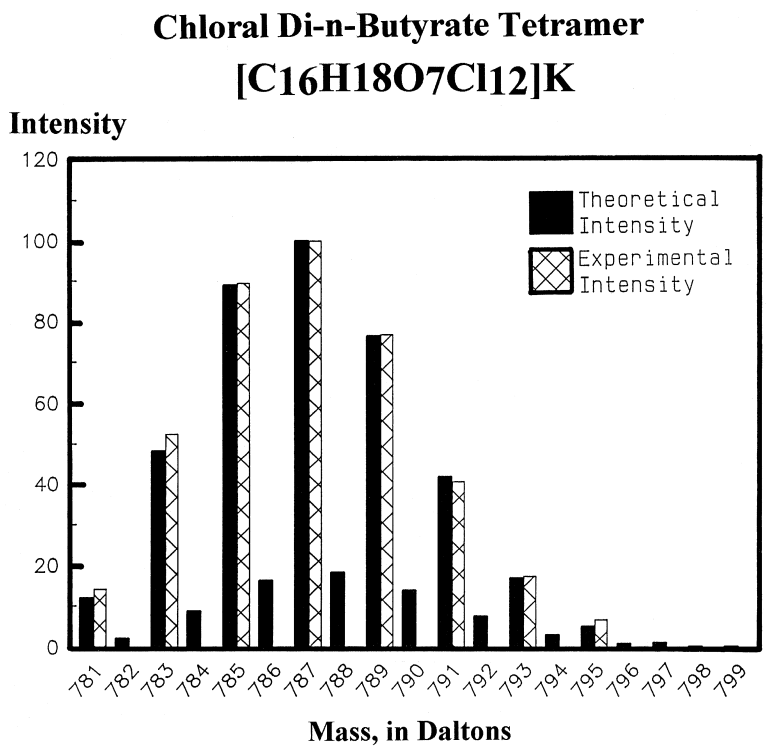

Figure 8. Isotope Distribution of the Di-n-butyrate Chloral Tetramer.

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was kept at -20°C for 8 weeks. After the usual work up, the diphenylacetate capped chloral "oligomer" were isolated, (yield, 13.7 g) consisting essentially only of the unimer. The K^+IDS spectrum is shown in Figure 13.

Adamantanecarboxylic Anhydride

Triethylamine (0.45 g, 4.5 mmol) in dichloromethane (30 mL) was used for the initiation of chloral monomer (4.4 mL, 45 mmol) in dichloromethane (20 mL). After cooling the solution from 40°C to -10°C and solid polychloral was formed, a solution of adamantanecarboxylic anhydride (13.8 g, 40 mmol) in dichloromethane 30 mL), which was cooled to -30°C was added. The flask was kept at -20°C for 7 weeks and the mixture was worked up as usual. The "oligomer" were isolated (12.8 g) and subjected to K^+IDS analysis; Figure 14 shows that once again only the unimer was obtained.

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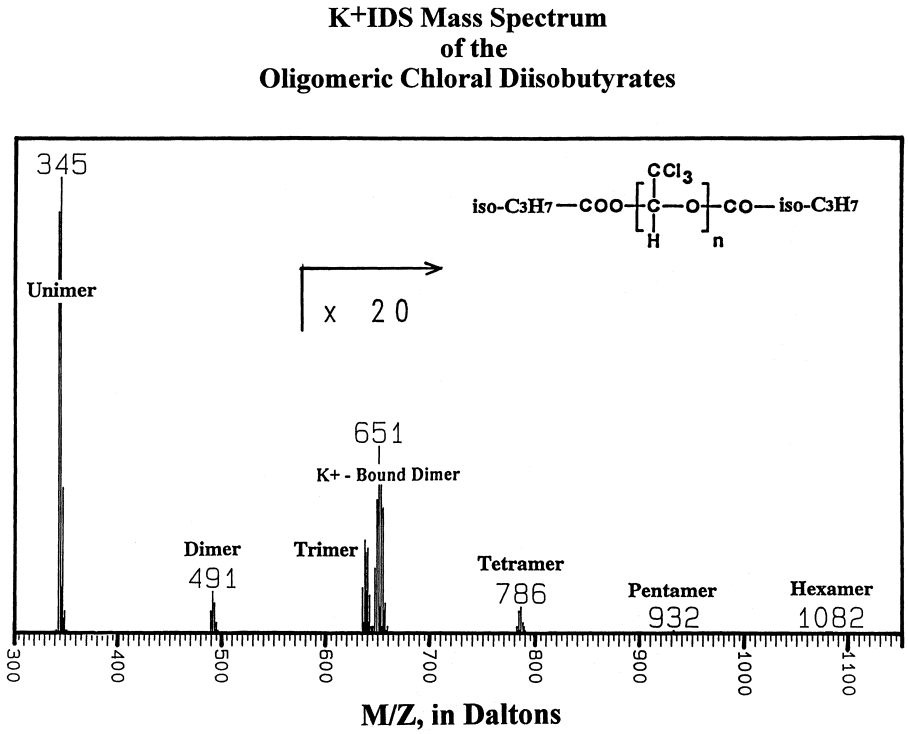

Figure 9. K^+IDS Mass Spectrum of Oligomeric Chloral Di-iso-Butyrates.

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RESULTS AND DISCUSSION

We have studied the oligomerization and polymerization of chloral and, to a limited extent, of bromal with tertiary amines as the initiators. We have also successfully used a number of diacyl anhydrides to "cap" the oligomerization and polymerization experiments and obtained, to our surprise, not just the oligomeric or polymeric acylates, but the diacylates of the chloral oligomers. We have also investigated the synthesis of chloral oligomers using chiral tertiary amines as initiators in attempts to synthesize directly chiral oligomers (chirality based on helicity). The results and implications of these experiments are discussed below.

Oligomerization and Polymerization of Chloral and Bromal with Tertiary Amines Initiators and Acetic Acid Anhydride as Capping Reagent

For the initiation of the chloral oligomerization and polymerizations with tertiary amines, we used first triethylamine as the initiator, and treated the

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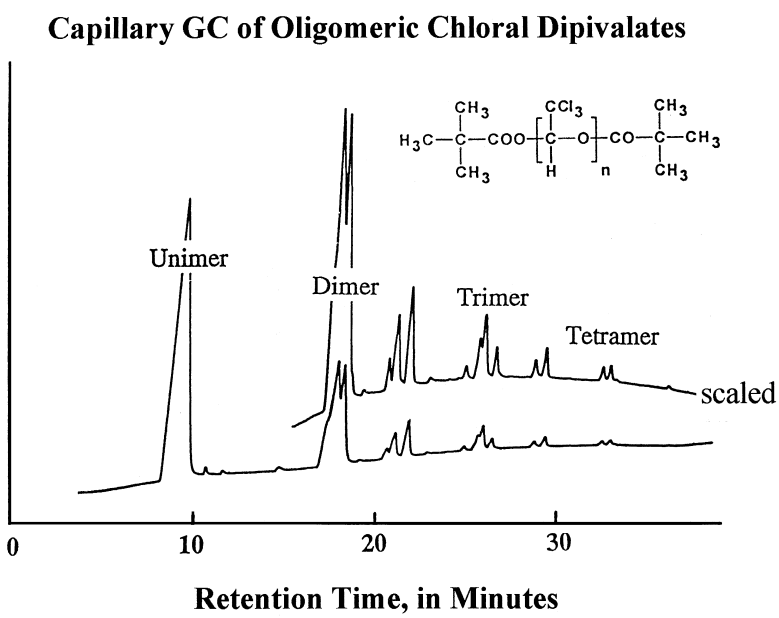

Figure 10. Capillary Gas Chromatogram of the Oligomeric Chloral Dipivalates.

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reaction mixtures with acetic anhydride [see also 10, 11]. In order to establish the composition of the soluble oligomer mixtures of chloral and the molecular weights of the individual components, we subjected this mixture first to capillary gas chromatography (Figure 1) and then to K^+IDS mass spectrometry analysis (Figure 2).

To our surprise, the $[M]K^+$ values of K^+IDS mass spectrometry revealed that the amine portion of the oligomerization experiment was no longer the end group caused by the initiating tertiary amine. The structure of the oligomers was supported by their infrared spectrum; it showed no ammonium end groups. The chloral oligomers were terminated on both ends with an acetate, $COOCH_3$, group. The mass spectral analysis and the concurrent mass calculations confirmed, that each of the individual oligomeric species had an additional molecular weight group of 102 added to the expected molecular weight of the individual oligomers. This surprising result indicated that the entire moiety of the molecule

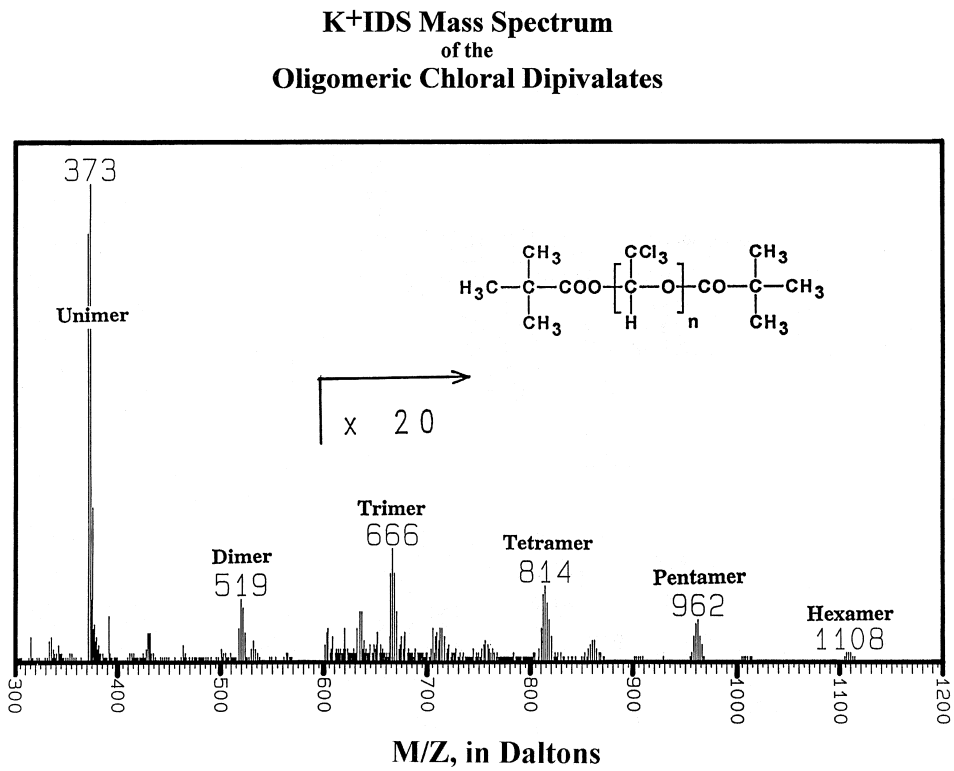

Figure 11. K^+IDS Mass Spectrum of Oligomeric Chloral Dipivalates.

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of acetic anhydride was incorporated into the oligomers by the reaction with acetic anhydride.

We came to the conclusion that the addition of the units of acetic anhydride to the reaction mixture of the oligomerization of chloral initiated with a tertiary amine could only be accommodated when, after the initiation reaction of the tertiary amine with the first molecule of chloral, acetic anhydride reacted with the mixture in the following way. It reacted first with the alkoxide end of the mixture to form a $COCH_3$ end group, and the remaining $OCOCH_3$ group displaced the teriary amine of the initiating end, the ammonium group, to form the diacetates of the oligomeric mixture releasing the tertiary amine (Scheme 1).

Figure 2 shows the K+IDS spectrum of the oligomeric chloral diacetates. We can see the unimer-chloral diacetate, which is observed at $[M]K^+ = 289$ Daltons (Da), the dimer at $[M]K^+ = 435$ Da, the trimer at $[M]K^+ = 583$ Da, the tetramer at [M]K+ = 731 Da, the pentamer at $[M]K^+ = 878$, the hexamer at $[M]K^+ = 1024$ and the heptamer at $[M]K^+ = 1168$ Da. The larger than ex-

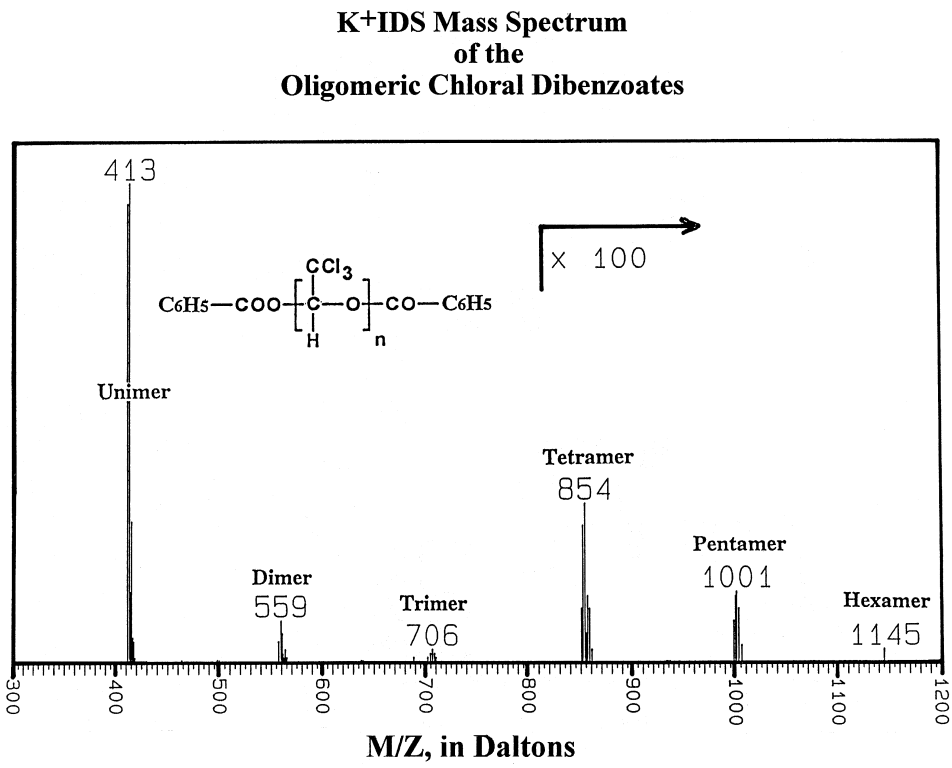

Figure 12. K^+IDS Mass Spectrum of Oligomeric Chloral Dibenzoates.

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pected amount of the unimer of the chloral diacetate might have been produced by the direct acetylation of unreacted chloral with acetic anhydride. We have shown in separate experiments in this work, that uncatalyzed acetylation of chloral in the absence of tertiary amine is very slow.

The amount of the "real" oligomers, starting form the dimer, can be semiquantitatively estimated by K^+IDS mass spectrometric analysis. But the amounts of the individual oligomers and their direct individual relationship depend on the details and exact conditions of each run.

The oligomerization of the other trihaloacetaldehyde monomer, bromal, was equally interesting. Careful experimentation for both polymerization and "end-capping" were needed to stabilize the monomer/polymer equilibrium of bromal to obtain stable bromal oligomers (see Experimental). Bromal polymerization has one of the lowest ceiling temperatures (-75°C) of polymerization of any addition polymerizations known [20].

We found that the oligomerization/polymerization of bromal using

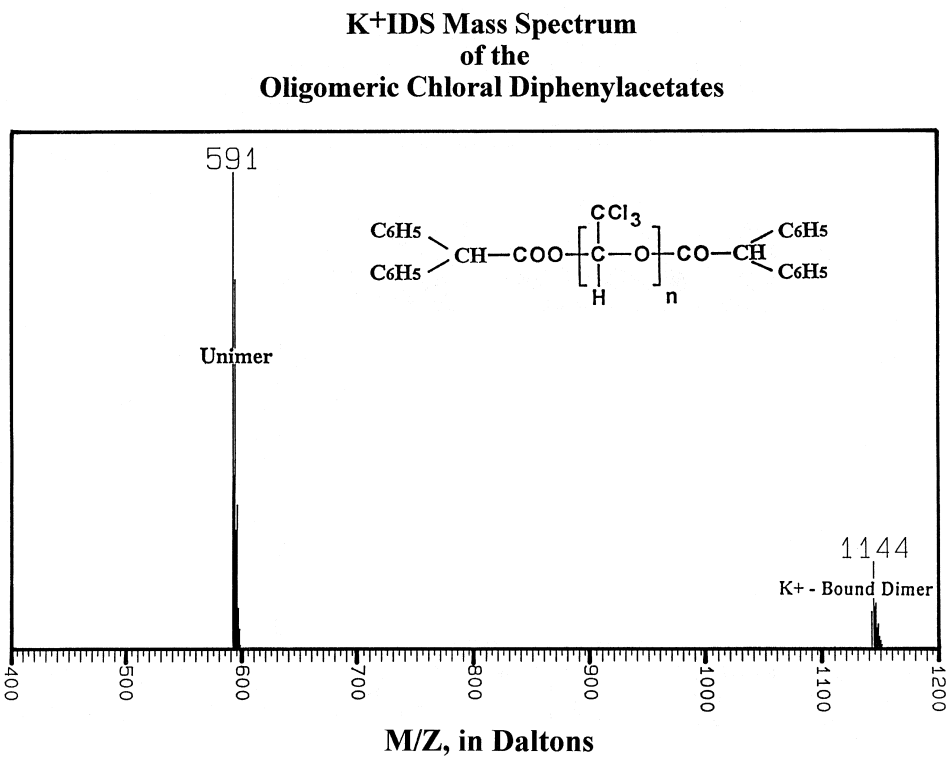

Figure 13. K^+IDS Mass Spectrum of Chloral Diphenylacetate Unimer.

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triethylamine as the initiator can be accomplished in dichloromethane at -60°C. The conditions for the successful acyl capping reaction of the oligomer mixture is very critical. The way acetic anhydride was added had an important influence on the effectiveness of the end-capping of the bromal oligomers. If the reagent was added at room temperature, the naturally established equilibrium of the oligomer mixtures (based primarily on the local temperature effects) is shifted to the direction of the bromal unimer and no higher oligomers were observed.

The optimal temperature for the addition of acetic anhydride to cap the bromal oligomer mixture was -70°C – just above the melting point – of free bromal in the mixture. This delicate balance of the temperature profile led to the formation of some end-capped polybromal which was isolated in a conversion of up to 40%.

The mixture of bromal oligomers was characterized by K^+IDS mass spectrometry. Figure 3 shows the K^+IDS mass spectra of the unimer, dimers

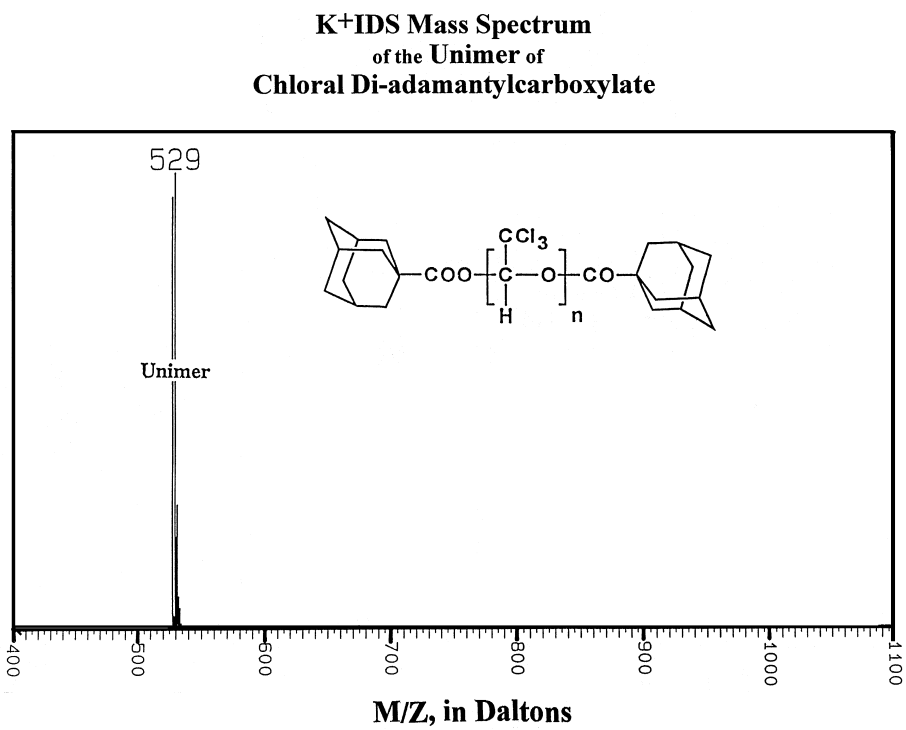

Figure 14. K^+IDS Mass Spectrum of Chloral Diadamantanecarboxylate Unimer.

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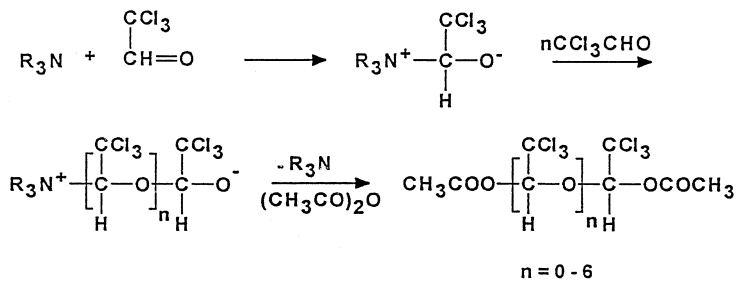

Scheme 1. Synthesis of Chloral Diacylate Oligomers

and trimers of higher bromal oligomers. Figure 4 gives the analysis of the isotope distribution of the diacetate of the bromal unimer and shows an excellent agreement between the theoretical and the experimental isotope intensities.

End-Capping of Tertiary Amines Initiated Chloral Oligomers and Polymers with Higher Acid Anhydrides

The chloral oligomerization procedures using tertiary amines as the initiators are also capable of being end-capped with other acid anhydrides. The results of oligomer compositions capped with higher diacid anhydrides differed somewhat because of the lower reactivities of the anhydrides. Acylation with higher anhydrides needed extended reaction times to acylate the oligomers/polymer equilibrium. Additional problems arose because some of the anhydrides crystallize at these lower reaction temperatures.

We have studied the end-capping of the chloral oligomerization mixtures with "higher acid anhydrides" such as propionic anhydride, n-butyric, isobutyric, benzoic, diphenylacetic and adamantane carboxylic anhydride.

For the preparation of chloral oligomers, satisfactory results of this oligomerization/capping were obtained after reacting the oligomer mixture for 10 days at -20°C. The K^+IDS analysis of the dipropionate endcapped chloral oligomers showed oligomers up to the pentamer. We can see the unimer-chloral diproprionate, which is at $[M]K^+ = 317$ Da, the dimer at $[M]K^+ = 463$ Da, the trimer at $[M]K^+ = 610$ Da, the tetramer at $[M]K^+ = 758$ Da, and the pentamer at $[M]K^+ = 904$, (for the actual values see Figure 5 and Table 1). A detailed isotope analysis of the trimer was carried out and showed a most satisfactory agreement between the theoretical and experimental intensities for the individual isotope compositions (Figure 6).

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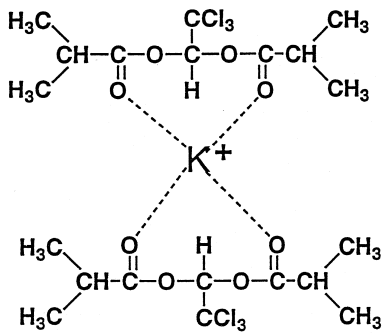

Scheme 2. Potassium-Bound Chloral Di-isobutyrate Dimer

For the synthesis of chloral oligomers terminated with two n-butyrate end groups, a reaction time of the oligomer mixture of 3 weeks at -20°C with n-butyric anhydride was found necessary. The oligomer mixture was analyzed by GC and showed the presence of higher oligomers. K^+IDS analysis confirmed the presence of oligomers up to the hexamer; the unimer - chloral di-n-butyrate at $[M]K^+$ = 345 Da, the dimer at $[M]K^+$ = 491 Da, the trimer at $[M]K^+$ = 638 Da, the tetramer at $[M]K^+$ = 786 Da, the pentamer at $[M]K^+$ = 932 and the hexamer at $[M]K^+$ = 1082 (Figure 7). The detailed study of the di-n-butyrate tetramer by isotope analysis, is displayed in Figure 8.

Using similar oligomerization conditions and capping with iso-butyric anhydride, gave, after one month at -20°C the di-iso-butyrate endcapped oligomer mixture. K^+IDS analysis confirmed the presence of chloral di-iso-butyrate oligomers up to hexamer, the unimer - chloral diisobutyrate at $[M]K^+$+ = 345 Da, the dimer at $[M]K^+$ = 491 Da, the trimer at $[M]K^+$ = 638 Da, the tetramer at $[M]K^+$ = 786 Da, the pentamer at $[M]K^+$ = 932 and the hexamer at $[M]K^+$+ = 1082 (Figure 9).

The detailed K^+IDS study also revealed that one significant extra peak at $[M]K^+$ = 651 Da was present. This peak should be assigned to a dimer consisting of two di-iso-butyrate unimer units is associated with one potassium cation (Scheme 2). Such species are sometimes formed under mass spectrometric conditions when there are locally not enough potassium ions to form the associate with each single chemical individual present in the system and the structure of the chemical species is appropriate for a formation of such a species. We have seen such "potassium-bound dimers" in the past. They seem to require chemical structures, like acyl groups.

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Anhydrides with larger, and more hindered (bulkier) acyl groups were less reactive (or less soluble under the reaction conditions). In addition, the extended reaction times required for the acylation reaction allowed side reactions. Figure 10 shows the gas chromatogram of an oligomeric chloral mixture that was end-capped with pivalic anhydride over a period of 5 weeks at -20°C. It shows the presence of chloral dipivalate oligomers up to the tetramer in addition to some as yet unidentified side-products. The K^+IDS analysis confirmed the presence of the oligomers up to the hexamer, the unimer - chloral dipivalate at $[M]K^+$ = 373 Da, the dimer at $[M]K^+$ = 519 Da, the trimer at $[M]K^+$ = 666 Da, the tetramer at $[M]K^+$ = 814 Da, the pentamer at $[M]K^+$ = 962 and the hexamer at $[M]K^+$ = 1108 (Figure 11). Other, as yet unidentified, species were also observed.

The results presented until now were obtained using aliphatic acid anhydrides for the end-capping of chloral oligomer mixtures. Slightly different results were expected when aromatic acid anhydrides were used. First we used benzoic anhydride. After end-capping the oligomer mixture at -20°C for 6 weeks, a dibenzoate chloral oligomer mixture was obtained which showed oligomers up to the hexamer by K^+IDS mass spectral analysis; the unimer - chloral dibenzoate at $[M]K^+$ = 413 Da, the dimer at $[M]K^+$ = 559 Da, the trimer at $[M]K^+$ = 706 Da, the tetramer at $[M]K^+$ = 854Da, the pentamer at $[M]K^+$ = 1001 and the hexamer at $[M]K^+$ = 1145 (Figure 12).

Table 1 summarizes the $[M]K^+$ and [M] mass spectral data of the masses of diacyl chloral oligomers terminated with acetic, propionic, n-butyric, isobutyric, pivalic and benzoic anhydrides. Higher oligomers were also produced in minute amounts; they have been fleetingly observed in the K^+IDS analysis, but have not been consistently identified beyond any reasonable doubt.

The success of the synthesis of benzoate terminated chloral oligomers encouraged us to use also another aromatic, even bulkier, more highly hindered acid anhydrides. Diphenylacetic acid anhydride required a capping time of 8 weeks at -20°C. K^+IDS mass spectral analysis showed only the diphenylacetate terminated unimer of chloral, but no higher oligomers (Figure 13). In addition to the unimer peak at $[M]K^+$ = 591 Da, a peak at 1144 Da was observed. We attribute the peak to the "potassium-bound dimer" of the choral di-diphenylacetate unimers where one potassium ion is attached to two unimer molecules (Scheme 2).

In another attempt to prepare diacyl capped chloral oligomers with even bulkier end-groups, we chose as the end-capping reagent adamantanecarboxylic

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TABLE 1. Calculated Nominal $[M]K^+$ and [M] Values for Diacyl Chloral Oligomers (DAO)

DCO $[M]K^+/[M]$	Acetic	Propionic	Anhydride n-Butyric iso-Butyric	Pivalic	Benzoic
Unimer	289/250	316/277	345/306	373/334	413/374
Dimer	435/396	464/425	492/453	520/481	560/521
Trimer	583/544	611/572	639/600	667/628	707/668
Tetramer	731/692	759/720	787/748	815/776	855/816
Pentamer	877/838	906/867	934/895	962/923	1002/963
Hexamer	1025/986	1053/1014	1082/1043	1110/1071	1150/1111
Heptamer	1173/1134	1200/1161	1129/1190	1257/1218	1297/1258

anhydride. After a period of 50 days at -20°C, the capped reaction mixture was analyzed by K^+IDS mass spectrometry. It showed only one mass peak of the adamantanecarboxylate terminated chloral unimer with a $[M]K^+$ = 529 Da (Figure 14).

To achieve oligomerization of chloral and successful endcapping with anhydrides it was important to balance the temperatures of oligomerization and capping. This is easily achieved with the relative reactive acetic anhydride. Higher dianhydrides are sterically hindered, cannot approach the reactive site, and are consequently less reactive In these cases, the reaction time had to be increased. On the other hand, higher dianhydrides are crystalline solids that are not very soluble under reaction conditions. If capping does not occur under the reaction conditions, as the reaction mixture is warmed to room temperature de-polymerization to the monomer takes place and ultimately the monomer is capped, yielding the monomer diacylate, as is seen in the capping experiments with diphenylacetic acid anhydride and adamantanecarboxylic anhydride.

Oligomerization and Polymerization of Chloral with Chiral Tertiary Amines Initiators

The polymerization of chloral with tertiary amine as initiators was also carried out with a number of selected tertiary amines in addition to triethyl-amine. They included pyridine, and seven additional tertiary amines that were chiral, optically active [10, 11]. We had selected as chiral tertiary amines the alkaloids nicotine, strychnine, sparteine, cinchonine, cinchonidine, quinine and

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quinidine. We expected that the chiral tertiary amines caused the composition of the polymers/oligomers of chloral initiated with these initiators, to be similar to those obtained from triethylamine initiation but hoped that they might be optically active. First of all, we found that the chloral oligomeric mixtures obtained from these polymerizations had indeed approximately the same oligomer composition as those that where initiated with triethylamine as the initiator.

The individual mixtures of the chloral oligomers, (the diacetates) initiated with the chiral tertiary amines showed no optical rotation. In some cases a very small value was noticed. We have, however concluded, that this small rotation could be attributed to a trace amount of the chiral tertiary amine (alkaloids) that had not been completely removed from the oligomer mixture by acid washing during the work up. The chiral tertiary amines had relatively high optical rotation as compared to the rotation that might have been expected from any chiral chloral oligomers.

We had established earlier [14, 15] that pure, acetate end-capped chloral pentamer prepared by initiation with lithium tertiary butoxide and isolated by HPLC on a chiral column has a specific rotation of -23.7°. We have shown that tertiary butoxide initiated, acetate endcapped chloral oligomers are rigid-helical in solution at room temperature according to NMR evidence.

Helical inversion of chloral oligomers with small end groups, methoxy end groups, had been found to exist at room temperature up to the tetramer. We had concluded that the possibility of helical inversion for chloral oligomers with such relatively small end groups as acetate end groups could exist. Based on earlier observations, only oligomers with more than five monomer units, pentamers, were stable to helical inversion for chloral oligomers up to 200°C and for the trimer to above room temperature.

In our previous experiments to establish the development of the stereospecificity of oligomerization in our systems, [25-28] we used lithium tertiary butoxide (LTB) as the anionic initiator for the polymerization of trihaloacetaldehydes. We studied extensively the formation of chloral oligomers and that of higher molecular polymers. This achiral initiator forms first a racemate of $(CH_3)_3COCHCCl_3O$-. Further propagation led to oligomers and polymers with helical conformations which consist of equal amounts of left- and right-handed polymer helices.

When chiral tertiary amines were used as initiators we had hoped that these initiators might induce chirality in the oligomeric structures and we expected to find at least some optical activity of the oligomer mixture. Measure-

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ments of the optical activity of the oligomer mixture showed that the mixture was inactive even though the measurement were made on the neat product mixture (no solvent) in cells with a path length of 10 cm. We have concluded that either no optical activity had been introduced into the oligomer mixtures, that helix inversion had occurred during the capping procedure or that the amount of higher oligomers, the tertamer and pentamer which would most likely carry the optical activity because of their possible resistance to helix inversion providing the source of the rigid helical structure with optical activity were present in amounts too small to measure.

Mechanism of Oligomerization and Polymerization of Trihaloacetaldehydes with Tertiary Amines Initiators

Our mechanism for the formation of chloral oligomers based on tertiary amine initiation is shown in Scheme 1. The oligomerization of chloral with tertiary amine as initiators is started with the nucleophilic attack of the tertiary amino nitrogen to the carbonyl group of the chloral molecule [10, 11]. A zwitterion ammonium alkoxide is formed that is capable of anionic propagation on the alkoxide. Addition of this alkoxide to another chloral monomer molecules gives the dimer and further addition of chloral monomer leads to the growing oligomeric chloral chain. The problem of any zwitterion propagation mechanism is always disputed, because it requires a close proximity of the growing anion with a cationic species. Zwitterion polymerization mechanisms are often proposed without the proper considerations of charge separation. This case is no exception.

For those of us who are reluctant to accept a "zwitterion" propagation mechanism in polymerization reactions because of the necessity of charge separation, such a mechanism still seems to be compelling, even though it is not entirely satisfactory. The growth of zwitterions, oligomeric or polymeric, must occur in two different directions in order to prevent the separation of the ion pairs during the propagation step. At this time, we have not yet satisfactorily addressed this problem.

The addition of excess of acetic (or other) anhydride to the reaction mixture of oligomeric chloral alkoxides is causing first the acylation of the free alkoxide oxygen. The remaining acetate anion is capable of attacking the N-C bond of the initiating ammonium end of the oligomeric (or polymeric) species and replacing the tertiary amine from the ammonium "initiating end" of the

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oligomer/polymer to the more stable -$OCOCH_3$ end group. We have not attempted to experimentally proof that the first acetylation occurs on the free alkoxide oxygen, nor that the acetate anion species is responsible for attacking the $=N^+$-C bond to replace the initiating ammonium end of the oligomeric species with acetate.

The chloral oligomers, now as diacetates or acylates, are stable and can be isolated and purified in traditional ways of distillation or HPLC separation without decomposition. In the past it has been shown that the diacylates (diacetates) of high polymers of chloral are stable at temperatures above 250°C.

CONCLUSION

We investigated the oligomerization of chloral and bromal initiated by tertiary amines and found that tertiary amines are capable of forming oligomeric and polymeric trihaloacetaldehyde alkoxides under the appropriate conditions of stoichiometry of monomers and initiators. The "growing" alkoxide ends can be replaced and "terminated" by acetylation with acetic anhydride and the carboxylate anion remaining from the end-capping reaction can replace the tertiary amine entity of the initiating ammonium species to form another acetate end. The end-capping reactions of chloral oligomer equilibria initiated with triethylamine were performed with eight aliphatic and aromatic acid anhydrides, a reaction sequence which allowed us to synthesize oligomeric chloral mixtures with different diacyl end-groups of varying bulk size.

A number of alkaloids, chiral tertiary amines, were found to be capable of functioning as tertiary amines for the initiation of chloral oligomerization or polymerization. As far as we have found to date, they did not provide oligomers with optical activity. Optical activity was expected in some oligomers which would have been based exclusively on macromolecular asymmetry of the helical acetal main chain.

All the oligomeric products were characterized by capillary gas chromatography and K+IDS mass spectrometry. The proposed mechanism explains the formation of intermediates and final product—diacyl-terminated trihaloacetalde-hyde oligomers.

The mechanism proposed for the initiation and polymerization of chloral initiated with tertiary amines also explains the abnormal behavior of polychloral samples obtained by tertiary amine initiation.

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Polychloral samples when prepared between glass plates, initiated with tertiary amines had been known to be attached strongly to glass surfaces. We believe that amine initiated polychloral samples when prepared between glass plates, are actually grafted onto the glass surface. We think that the trialkylamine portion of the initial ammonium end group can be readily replaced by a nucleophile (such as the acetate portion of the acetic anhydride in anhydride capping) or by a nucleophilic from the ≡Si-O- part of the glass surface of a glass plate. This reaction sequence would give the following grafted structure =Si-O-$CH(CCl_3O)CHCCl_3$-O^- which can continue to grow to form a high molecular chlor-al polymer chain on the glass surface.

A somewhat different and equally plausible mechanism for grafting polychloral onto glass surfaces is shown below.

$$= Si\text{-}OH + R_3N \rightarrow = Si\text{-}O^- \; N^+R_3 \; H$$

$$= Si\text{-}O^- \; N^+R_3 \; H + CH(CCl_3)O \rightarrow = Si\text{-}O\text{-}CH(CCl_3)\text{-}O^- \; N^+R_3 \; H$$

$$\rightarrow = Si\text{-}O\text{-}[CH(CCl_3)O]_nCH(CCl_3)\text{-}O^- \; N^+R_3 \; H$$

From the very early days of polychloral investigation, polychloral was considered a very suitable form for the release of chloral and consequently chloral hydrate for drug applications. Chloral hydrate is still considered by many, as one of the most effective and harmless sleep inducing drugs. Drug release of chloral from polychloral requires a "controlled instability" of the polychloral samples. It is well known that when chloral hydrate is taken orally it has an unpleasant taste and is repugnant for regular application [29].

This problem could be eliminated when chloral hydrate could be taken in a form that slowly releases it, chloral hydrate. "Controlled unstable" polychloral is this possibility. When chloral is released from a source of chloral, such as an unstable form, for example polychloral, it is almost instantaneously hydrated in an aqueous environment to chloral hydrate. Normal (acetate) end-capped polychloral is too insoluble and also too stable to be used as a useful release agent for drugs and the uncapped polychloral alkoxide is too erratic and also of too low stability. Tertiary amine initiated polychloral when properly formulated might just have the right stability/instability to release chloral (and chloralhydrate) at the right dose rate.

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REFERENCES

[1] O. Vogl and W. M. D. Bryant, *J. Polym. Sci., A2*, 4633 (1964).
[2] O. Vogl, *Adv. Chem. Ser., 52*, 67 (1966).
[3] O. Vogl, G. D. Jaycox, C. Kratky, W. J. Simonsick, Jr., and K. Hatada, *Acc. Chem. Res., 25*, 408 (1992).
[4] C. Kratky, U. Wagner, K. Ute, K. Hatada, W. J. Simonsick, Jr., F. W. H. Kruger, F. Xi, and O. Vogl, *Macromolecules, 25*, 2319 (1992).
[5] O. Vogl, U.S. Patent 3,454,527 (1969).
[6] P. Kubisa and O. Vogl, *Polymer J., 7*, 186 (1975).
[7] K. Hatada, L. S. Corley, S. S. Vezirov, and O. Vogl, *Vysokomol Soedin., A19*, 1987 (1977); *Chem. Abstr., 87*, 152 621n, (1977).
[8] O. Vogl, *J. Macromol. Sci., Pure & Appl. Chem., A29*, 1085 (1992).
[9] L. S. Corley and O. Vogl, *J. Macromol Sci.-Chem., A14*, 1105 (1980).
[10] J. Bartus, W. J. Simonsick, Jr., K. Hatada, and O. Vogl, *Polymer Preprints*, A*CS Division of Polymer Chemistry, 33(2)*, 114 (1992).
[11] J. Bartus, K. Hatada, and O. Vogl, *Heterocycles, 35(1)*, 181 (1993).
[12] F. W. H. Kruger, J. Bartus, W. J. Simonsick, Jr., K. Hatada, and O. Vogl, *Polymer Science (Russia), 35(1)*, 19 (1993).
[13] L. S. Corley and O. Vogl, *Polymer Bulletin, 3*, 211 (1980).
[14] O. Vogl, F. Xi, F. Vass, K. Ute, T. Nishimura, and K. Hatada, *Macromolecules, 22*, 4658 (1989).
[15] K. Ute, T. Nishimura, K. Hatada, F. Xi, F. Vass, and O. Vogl, *Makromol. Chem., 191*, 557 (1990).
[16] W. J. Simonsick, Jr., *J. Appl. Polym. Sci.: Appl. Polym. Symp., 43*, 257 (1989).
[17] W. J. Simonsick, Jr., M. A. Fulginiti, F. Xi, and O. Vogl, *Pacific Polymer Preprints, 1*, 269 (1989).

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[18] W. J. Simonsick, Jr., K. Hatada, F. Xi, and O. Vogl, *Macromolecules, 24(6)*, 1720 (1991).

[19] P. Kubisa and O. Vogl, *Macromol. Synth. 6*, 49 (1977).

[20] D. W. Lipp and O. Vogl, *Polymer, 18*, 1051 (1977).

[21] C. M. Garner, Y. Ma, and J. Bartus, *Polymer Preprints, ACS Division of Polymer Chemistry, 33(1)*, 1010 (1992).

[22] W. J. Simonsick, Jr., *J. Appl. Polym. Sci.: Appl. Polym. Symp. 43*, 257 (1989).

[23] C. D. Hurd, R. Crist, and C. L. Thomas, *J. Am. Chem. Soc., 55*, 2589 (1933).

[24] H. T. Clarke and J. Rahs, *Org. Synth. Col.*, Vol. 1, 1941, p. 41.

[25] J. Zhang, G. D. Jaycox, and O. Vogl, *Polymer, 29*, 707 (1988).

[26] J. Zhang, G. D. Jaycox, and O. Vogl, *Polymer Preprints, ACS Division of Polymer Chemistry, 26(1)*, 156 (1985).

[27] K. Ute, K. Oka, Y. Okamoto, K. Hatada, F. Xi, and O. Vogl, *Polymer J., 23,* 1419 (1991).

[28] K. Ute, K. Hirose, H. Kashimoto, H. Nakayama, K. Hatada, and O. Vogl, *Polymer J., 25*, 1175 (1993).

[29] G. Donaruma, personal communication.

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