Haloaldehdye Polymers. 47. Analysis of Linear Fluoral Oligomers by Gas Chromatography and Potassium Ionization of Desorbed Species[†,‡]

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ABSTRACT: Linear fluoral oligomers initiated with *tert*-butoxide or bornyl oxide and acetate end-capped were analyzed by potassium ionization of desorbed species (K^+IDS) combined with gas chromatography (GC). Using K^+IDS it was possible to identify fluoral diacetate and the oligomers up to the undecamer. *tert*-Butoxide initiated oligomers showed masses from the unimers of 253 daltons up to the mass of 1233 daltons, the undecamer. The individual lower oligomers were also identified by GC. Bornyl oxide terminated, acetate capped fluoral oligomers were also analyzed and characterized to masses up to 1215 daltons, the decamer, by K^+IDS; GC characterization was also carried out.

Introduction

The stereochemistry of the embryonic state of anionic perhaloaldehyde polymerization has been investigated extensively during the past few years.[1-5] The main emphasis was on designing conditions that would lead to the synthesis of the ideal helix.[6-8] Early investigations have shown that perhaloacetaldehydes containing more than two chlorine (or bromine) atoms, upon polymerization, gave rise to exclusively isotactic polymers.[9,10] As a consequence, the oligomerization of chloral has been studied by GC, NMR spectrometry, single-crystal X-ray analysis of individual chloral oligomers,[11-14] and, recently, potassium ion mass spectrometry of the desorbed species.[15,16] Bromal oligomerization has also been briefly investigated.[17]

Trifluoroacetaldehyde (fluoral) polymerization has been studied in the past.[18,19] Fluoral was shown to polymerize to a stereospecific crystalline, isotactic polymer or to a less stereospecific, amorphous polymer. It was found that fluoral has the highest ceiling temperature of all the perhaloacetaldehydes. The polymerization of other fluorine-containing perhaloacetaldehydes has also been investigated,[20-27] and rules have been established to predict when perhaloacetaldehydes will form exclusively stereospecific isotactic polymers.

It had been reasoned that anionic fluoral polymerization would not lead to stereospecific and helical polymers under polymerization conditions that gave stereospecific isotactic polychloral or polybromal. Nevertheless it was considered important to investigate the oligomerization of fluoral and to determine the stereochemistry of the fluoral oligomers.

It was expected that severe handling problems might arise from the fact that fluoral has a boiling point of −15 °C and a ceiling temperature of +85 °C, a very unfavorable condition for cryotachensic polymerization. Chloral, with a boiling temperature of +98 °C and a ceiling temperature of +15 °C, is more easily handled because it has a liquid range between the boiling point and the ceiling temperature.

Linear oligomers of chloral initiated with *tert*-butoxide or bornyl oxide anions and acetate end-capped were recently analyzed by K^+IDS.[28,29] Individual oligomeric species were characterized, and the mixtures were analyzed.

It was the objective of this work to prepare oligomers of fluoral, initiated with *tert*-butoxide or bornyl oxide, to characterize them by GC, and to subject the oligomer mixtures to mass spectrometric analysis by K^+IDS.

Experimental Section

A. Materials. [(1*S*)-*endo*](−)-Borneol (99%), $[\alpha]^{20}_D = -35.6°$ (c 5, C_2H_5OH), *n*-butyllithium (1.6 M, in hexane), methylcyclohexane (anhydrous), acetic anhydride, methyl trifluoroacetate, and lithium aluminum hydride (1.0 M, in diethyl ether) were obtained from Aldrich Chemical Co. and were used without further purification.

Lithium *tert*-butoxide (Alfa Products) was sublimed twice at 150 °C and 0.1 mmHg before use.

B. Measurements. The analysis of the fluoral oligomers was carried out on a Varian 3300 gas chromatograph (column: 50 cm × 3 mm stainless steel, packed with Chrom G.H.P. 100/200 that was coated with 5% OV 101). For the analysis of the mixture of *tert*-butoxide terminated, acetate end-capped fluoral oligomers (TBFAM), the run conditions for the GC analysis were as follows: initial column temperature, holding time at that temperature 2.5 min, and then constant temperature increase at 2.5 °C/min; the chart speed was 30 cm/h. For the analysis of the bornyl oxide terminated, acetate end-capped fluoral oligomers (BFAM), the column temperature started at 90 °C and was increased at a constant rate of 1 °C/min. The injection port temperature was 230 °C, the detector temperature was 200 °C, and the chart speed of the recorder was 20 cm/h.

The optical rotations were measured on a Perkin-Elmer 241 polarimeter in a macrocell (volume 1 mL, path length 10.0 cm) at the wavelength of the sodium line (589 nm) at room temperature.

The IR spectra of the oligomers were determined neat, between salt plates, and the polymer samples were measured as KBr pellets. The spectra were taken on a Perkin-Elmer Model 1320 infrared spectrometer.

All mass spectrometry experiments were performed on a Finnigan 4615B quadrupole GC/MS system. An EI source configuration was used in all K^+IDS experiments. The ion source pressure (ion gauge) was $<10^{-6}$ Torr with a source temperature of 200 °C.[28]

[†] This paper is dedicated to Professor Bengt Rånby on the occasion of his 70th birthday with our warmest wishes.

[‡] Previous paper in this series: Simonsick, W., Jr.; Hatada, K.; Xi, F.; Vogl, O. Haloaldehyde Polymers. 46. *Polymer*, in press.

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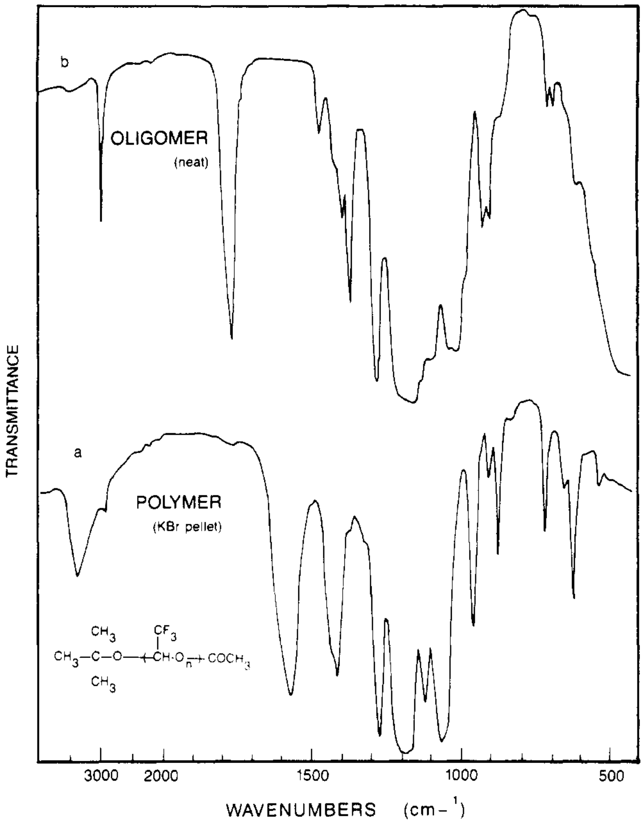


Figure 1. IR spectra of *tert*-butoxide initiated, acetate end-capped fluoral polymer and oligomers: (a) polymer; (b) oligomers.

C. Procedures. *tert*-Butoxide Terminated, Acetate End-Capped Fluoral Oligomers (TBFAM). Fluoral was prepared by reducing methyl trifluoroacetate with lithium aluminum hydride at −78 °C according to the method of Pierce.[30] The fluoral gas obtained from this reaction was trapped in a receptor that was cooled in a dry ice–acetone bath; it was used for the following reactions.

Into a 100-mL three-neck round-bottom flask equipped with a magnetic stirring bar, a Dewar condenser (dry ice–acetone), and a gas inlet and exit were placed lithium *tert*-butoxide (2.4 g, 0.03 mol) and methylcyclohexane (60 mL) under an argon atmosphere. After the lithium *tert*-butoxide was dissolved, liquid fluoral (10 mL, 0.15 mol) was slowly injected into the solution with a cold syringe. The reaction was allowed to continue at room temperature with vigorous stirring; some white polymer powder was formed immediately. The reaction mixture was stirred for 20 min; acetic anhydride (3.0 mL) was then added to end-cap the reaction mixture. After stirring for 2 h, the reaction mixture was added to water (50 mL), and the suspension was filtered; 3.3 g of polyfluoral powder was collected, yield 18% (IR spectrum in Figure 1a).

The organic layer that separated from the filtrate was washed twice with aqueous sodium bicarbonate and dried overnight with anhydrous sodium sulfate. After the solvent was removed, 9 g of crude oligomer mixture was obtained, yield 49% (IR spectrum in Figure 1b). According to the gas chromatogram, the oligomer mixture consisted of 25.5% unimer, 42.1% dimer, 19.2% trimer, 8.4% tetramer, 2.5% pentamer, 1.3% hexamer, 0.5% heptamer, 0.25% octamer, and 0.15% nonamer.

The TBFAM mixture was analyzed by GC (Figure 2) and showed the unimer as a single peak at 7.4 min, the Tishchenko product (trifluoroethyl trifluoroacetate) at 10.2 min, and the dimer fraction as two peaks of a ratio 55 (retention time 12.8 min):45 (retention time 13.5 min). The trimer fraction consists of two peaks in a ratio of 30 (retention time 15.2 min):70 (retention time 16.9 min). The gas chromatogram of TBFAM shows also the tetramer fraction with four peaks in a ratio of 30 (retention time 18.2 min):30 (retention time 19.1 min):5 (retention time 19.4 min): 45 (retention time 20.8 min). The peak at 19.4 min actually has a shoulder that is estimated to consist of a component that is 5% of the entire tetramer fraction. The pentamer fraction consists of three peaks in a ratio 20 (retention time 21.9 min): 20 (retention time 22.7 min):60 (retention time 23.9 min). The hexamer fraction has two peaks in a ratio 35 (retention time 25.6 min):65 (retention time 26.8 min) with a shoulder on the first peak (retention time 26.4 min). The heptamer shows only two GC peaks; the two isomers are present in a ratio of 30 (retention time 28.5 min):70 (retention time 29.9 min). Other peaks of the higher oligomers are noticeable, the possible octamer at 31.5 and 32.9 min and the nonamer at 35.6 min, but they could not be identified with any certainty by GC.

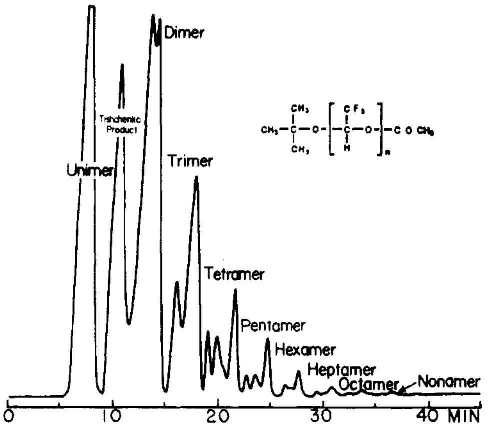


Figure 2. Gas chromatogram of *tert*-butoxide initiated, acetate end-capped fluoral oligomers.

Bornyl Oxide Terminated, Acetate End-Capped Fluoral Oligomers (BFAM). Into a 100-mL three-neck round-bottom flask equipped with a magnetic stirring bar, a Dewar condenser, and a gas inlet and exit were added borneol (4.6 g, 0.03 mol) and methylcyclohexane (50 mL). When the borneol was dissolved, *n*-butyllithium (19 mL, 0.03 mol) was slowly injected into the solution. The suspension of lithium bornyl oxide that formed was warmed to 50 °C with an oil bath. Liquid fluoral (10 mL, 0.15 mol) at −40 °C was added slowly with a cold syringe. The reaction mixture was stirred for 15 min during which time some polymer formed. Acetic anhydride (3.0 mL) was added to quench and acetate cap the reaction mixture, which was then allowed to come to room temperature. After stirring for 2 h, the mixture was added to water, and the suspension that formed was filtered; 3.5 g of polyfluoral was collected, yield 17% (IR spectrum in Figure 3a). The organic layer that had separated from the filtrate was washed with aqueous sodium bicarbonate and twice with water and then dried overnight with anhydrous sodium sulfate. After removal of the solvent, 13.5 g of the crude oligomer mixture of bornyl oxide terminated, acetate capped fluoral was obtained, yield 64% (IR spectrum in Figure 3b). The ratio of the individual components of the oligomer mixture according to our GC analysis was 2.1% unimer, 42.9% dimer, 27.8% trimer, 14.8% tetramer, 6.7% pentamer, 3.0% hexamer, 1.7% heptamer, and 0.9% octamer.

The gas chromatogram of the BFAM mixture (Figure 4) shows that the two unimer diastereoisomers are present in a ratio of 50 (retention time 6.6 min):50 (retention time 7.3 min). Two dimeric isomers were found to be present in a ratio of 65 (retention time 14.5 min):35 (retention time 16.1 min), with a shoulder at 16.8 min. There is also a small shoulder in the gas chromatogram between the dimer fraction and the trimer fraction.

The trimer fraction was identified in a ratio of 60 (retention time 17.7 min):15 (retention time min):25 (retention time 20.5 min), the tetramer fraction in a ratio of 40 (retention time 22.9 min):50 (retention time 25.9 min):10 (retention time 27.9 min), the pentamer fraction in a ratio of 30 (retention time 27.9 min): 35 (retention time 29.4 min):35 (retention time 30.9 min), and the hexamer fraction in a ratio of 60 (retention time 34.8 min): 40 (retention time 36.4 min). Some heptamer isomers at 40.3- and 41.7-min retention times were also found. It is most likely that some of the peaks that are broad have additional isomers present under the broad peaks. It should be pointed out that for the BFAM we could expect 2 diastereomeric unimers, 4 dimers, 8 trimers, and 16 tetramers, etc.

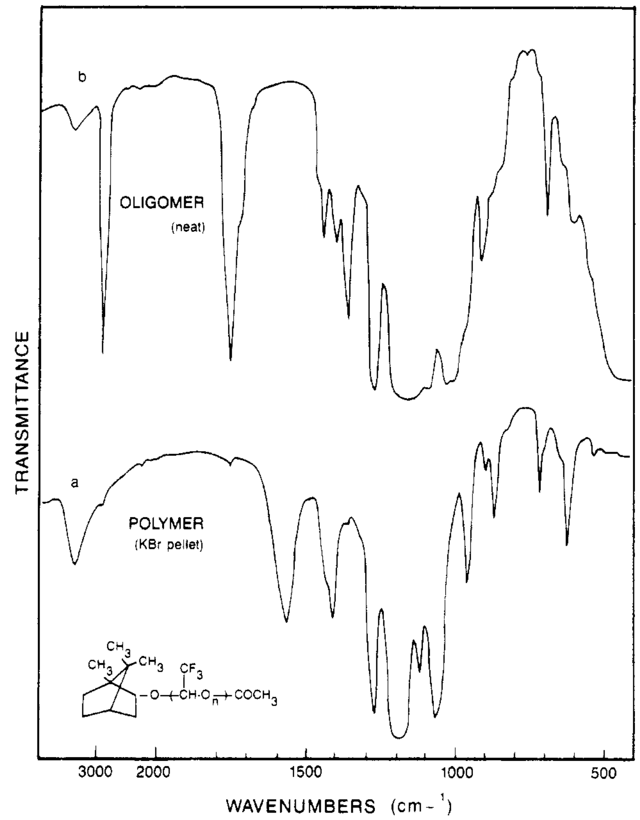


Figure 3. IR spectra of bornyl oxide initiated, acetate end-capped fluoral polymer and oligomers: (a) polymer; (b) oligomers.

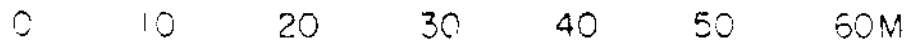


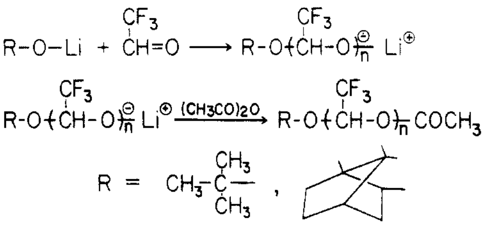
Figure 4. Gas chromatogram of bornyl oxide initiated, acetate end-capped fluoral oligomers.

The optical rotation of the bornyl oxide terminated, acetate end-capped fluoral oligomer sample (BFAM) was measured in a dichloromethane solution and found to have an optical rotation of $[\alpha]^{22}_D = -18.1 \pm 0.2°$; the optical rotation of the fluoral polymer was measured in DMAc solution and gave $[\alpha]^{22}_D = -0.8 \pm 0.2°$.

No optical rotation was detected (and none was expected) in the *tert*-butoxide terminated, acetate end-capped fluoral oligomer mixture (TBFA) or its polymer.

Fluoral Diacetate. Acetic anhydride (3 mL) and 1 drop of concentrated sulfuric acid were placed in a 10-mL glass tube and cooled to −78 °C, cold fluoral (2.5 mL) was added, and the tube was sealed. The tube was carefully warmed to room temperature, and a strongly exothermic reaction started which was controlled by cooling the tube in an ice/water bath. After the reaction tube was kept at room temperature overnight, the tube was cooled and opened. The reaction mixture was diluted with ether (50 mL), washed with aqueous sodium carbonate and twice with water, and then dried over anhydrous magnesium sulfate. The solvent was removed at 25 mmHg and the residue distilled; 4 g of fluoral diacetate, bp 146–147 °C, was obtained. The ^1H NMR spectrum showed δ 2.16 ($COCH_3$) and 7.18 (center of peaks, ($OCH(CF_3)O$)).

Scheme I



$$R-O-Li + \overset{CF_3}{CH}=O \longrightarrow R-O\{\overset{CF_3}{CH}-O\}_n^{\ominus} Li^{\oplus}$$

$$R-O\{\overset{CF_3}{CH}-O\}_n^{\ominus} Li^{\oplus} \xrightarrow{(CH_3CO)_2O} R-O\{\overset{CF_3}{CH}-O\}_n COCH_3$$

$$R = CH_3-\underset{CH_3}{\overset{CH_3}{C}}- \; ,$$

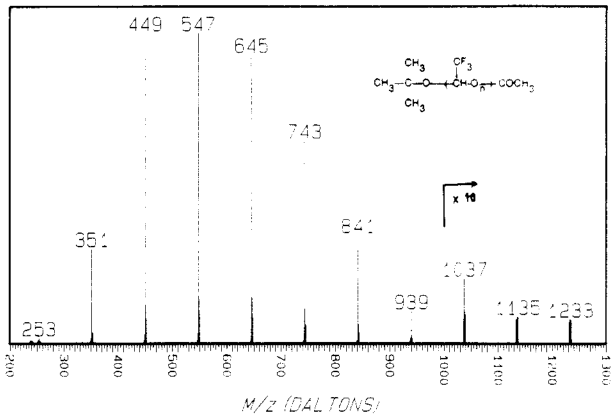


Figure 5. K⁺IDS mass spectrum of *tert*-butoxide initiated, acetate end-capped fluoral oligomers.

Results and Discussion

The oligomerization of *tert*-butoxide or bornyl oxide initiated, acetate end-capped fluoral was evaluated by GC and K⁺IDS (Scheme I).

From this analysis of the *tert*-butoxide (TBFAM) and bornyl oxide (BFAM) initiated oligomerization products by GC, it becomes clear that our earlier predictions of how the stereospecificity develops in haloaldehyde polymerization (based on side-group bulk) are correct. The side groups need to be sufficiently large to force the development of stereospecificity, namely, the isotactic helix.

As we analyze the gas chromatogram of the higher oligomers in more detail, it appears that we can see some stereospecificity developing even with the small trifluoromethyl group as the side group, as in our case, fluoral. The peak in each oligomer fraction with highest retention time seems to increase and become constant at about a 60–70% level, presumably the mm isomer.

K⁺IDS mass spectrometry is a unique way of identifying individual compounds of the same mass in a mild and selective way. Unlike GC, especially GC on chiral columns which can distinguish between diastereomers, mass spectrometry can only identify the molecular masses of individual compounds. As a consequence, it is easy to identify the individual mass fractions by K⁺IDS mass spectrometry.

TBFAM K⁺IDS spectrometry gave very clear and easily interpretable mass spectra (Figure 5). Before discussing the characterization of these oligomers, we point out that fluorocarbon compounds have a relatively high volatility in relation to their molecular weight. As a consequence, the mass spectrometry of the mixture of the linear oligomers is not quantitative in the lower molecular weight region. From the tetramer or pentamer on (the oligomers with higher molecular weights), the analysis of the compounds became semiquantitative to quantitative because of the low volatility of the compounds with masses higher than 500 daltons. We can find in the next paragraph the masses which all represent the calculated and expected mass number and their relative intensity in parentheses

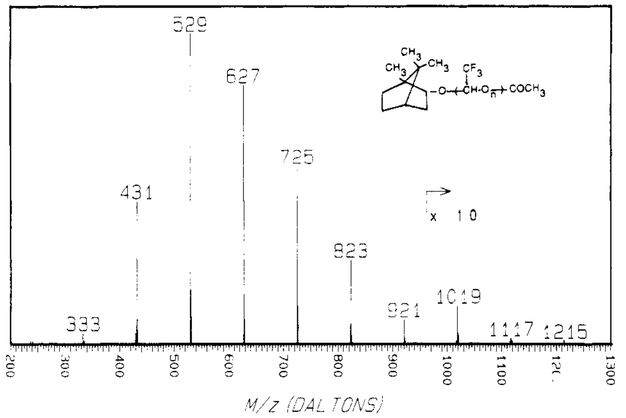


Figure 6. K⁺IDS mass spectrum of bornyl oxide initiated, acetate end-capped fluoral oligomers.

after the mass numbers. The whole mass spectrum is considered as 100%.

The mass spectrum (Figure 5) of TBFAM shows a very small amount of fluoral diacetate (1%) at $[M]K^+ = 239$ daltons, the unimer (1%) at $[M]K^+ = 253$ daltons, the dimer (6.8%) at $[M]K^+ = 351$ daltons, the trimer (21.0%) at $[M]K^+ = 449$ daltons, and the tetramer (22.0%) at $[M]K^+ = 547$ daltons. As indicated earlier, the intensity of the individual mass peaks of the spectra are lower than expected. From the pentamer, the mass spectra seem to reflect accurately the percentage of the individual fractions. The percentage decreases from the pentamer (20.3%) ($[M]K^+$ at 645 daltons) to the hexamer (14.4%) ($[M]K^+$ at 743 daltons) to the heptamer (8.0%) ($[M]K^+$ at 841 daltons). The octamer (2.9%) ($[M]K^+$ and the nonamer (1.0%) ($[M]K^+$ at 1037 daltons) are also significantly represented. The decamer (0.7%) ($[M]K^+$ at 1135 daltons) and the undecamer (0.6%) ($[M]K^+$ at 1233 daltons) can still be clearly distinguished. It is remarkable that compounds present in such low amounts can still be seen and clearly identified by K^+IDS mass spectrometry. All observed peaks are exactly at the position expected from their molecular weight.

The K^+IDS mass spectrum of BFAM shows a similar picture (Figure 6). First we see a trace amount of fluoral diacetate (5.4%) ($[M]K^+$ at 239 daltons) as in the case of the TBFAM spectrum; then we find with rather low intensities the unimer (12.7%) ($[M]K^+$ at 333 daltons), the dimers (14.3%) ($[M]K^+$ at 431 daltons), the trimer (29.6%) ($[M]K^+$ at 529 daltons), and the tetramer (25.0%) ($[M]K^+$ at 627 daltons). The lower intensities of the lower members of the series again reflect the high volatility of the lower linear fluoral oligomers. Some of the material has been lost during the procedure for the preparation of the mixture for K^+IDS analysis. The intensity of the compounds starting with the pentamer now shows the expected decreasing values. The pentamer (17.6%) ($[M]K^+$ at 725 daltons), the hexamer (8.5%) ($[M]K^+$ at 823 daltons), and the heptamer (2.5%) ($[M]K^+$ at 921 daltons) can be seen. In our spectrum the intensity of the individual oligomer peaks is expanded 10-fold above mass 1000 daltons. The octamer $[M]K^+$ is found at 1019 daltons (0.47%) and the nonamer $[M]K^+$ at 1117 daltons (0.10%). Much less prominent but clearly identifiable is the peak at 1215 daltons (0.065%), representing the decamer $[M]K^+$.

A combination of GC with K^+IDS mass spectrometry allows the analysis of linear fluoral oligomers. We have shown that both TBFAM and BFAM can be analyzed in a facile manner, and oligomers up to the undecamer can be identified.

GC analysis shows the stereochemistry of oligomerization of fluoral on the way to the formation of high polymer. The results are similar to those for the formation of chloral oligomers, which have been demonstrated earlier,[29] with one major exception: Chloral oligomerization becomes stereospecific after the formation of trimer, and only meso addition is possible for steric reasons, giving exclusively the isotactic helix for chloral high polymers. No stereospecificity develops during the fluoral oligomerization, and ultimately only atactic (less stereospecific isotactic) polyfluoral is formed.

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