Monatshefte für Chemie 110, 453—471 (1979)

Monatshefte für Chemie

© by Springer-Verlag 1979

Haloaldehyde Polymeres XIII.[a] Polydibromofluoroacetaldehyde

Richard W. Campbell and **Otto Vogl***

Polymer Science and Engineering Department, University of Massachusetts,
Amherst, Massachusetts, U.S.A.

(Received 18 July 1978. Accepted 25 July 1978)

Dibromofluoracetaldehyde (*DBFA*) was prepared by reducing methyl dibromofluoroacetate with lithium aluminium hydride (*LAH*) at low temperatures whereby the *LAH* was added to dibromofluoroacetate. The initially obtained *DBFA* hydrate was dehydrated to the free aldehyde. Methyl dibromofluoroacetate was synthesized together with methyl bromodifluoroacetate by air oxidation of 1,1-dibromo-2,2-difluoroethylene. The mixture of oxidation products, consisting of two acid halides, was treated with methanol and gave a mixture of the methyl esters which here separated by distillation.

DBFA was polymerized with anionic and cationic initiators to crystalline insoluble poly-*DBFA*. Poly-*DBFA* degraded quantitatively at elevated temperatures to monomeric *DBFA*. Copolymerization of *DBFA* with chloral gave copolymers with nearly the same comonomer composition as the feed. *DBFA* was also copolymerized with phenyl isocyanate to a copolymer which contained acetal and urethane linkages.

(Keywords: Haloaldehyde polymers; Dibromofluoroacetaldehyde, Polymerization; Ceiling temperature, Thermal degradation; Copolymerization)

Halogenaldehyd-Polymere XIII: Polydibromfluoracetaldehyd

Dibromfluoracetaldehyd (*DBFA*) wurde aus Dibromfluoressigsäuremethylester durch Addition des Lithiumaluminiumhydrids zum Ester hergestellt. Das zuerst erhaltene *DBFA*-Hydrat wurde zum freien Aldehyd dehydratisiert. Der Dibromfluoressigsäuremethylester wurde unter gleichzeitiger Herstellung von Bromdifluoressigsäuremethylester durch Luftoxydation von 1,1-Dibrom-2,2-difluorethen erhalten. Das Oxydationsprodukt, das die Säurehalogenide enthielt, wurde mit Methanol behandelt und gab eine Estermischung, die durch Destillation getrennt werden konnte. *DBFA* wurde mit anionischen und kationischen Initiatoren zu unlöslichen, kristallinen Poly-*DFBA* polymerisiert. Der polymere *DBFA* wurde quantitativ bei erhöhter Temperatur zu monomerem *DBFA* abgebaut. Copolymerisation von *DBFA* mit Chloral gab ein Copolymer mit der gleichen Copolymerzusammensetzung wie das ursprüngliche Verhältnis der zwei Monomeren. *DBFA* copolymerisierte auch mit Phenylisocyanat zu Copolymeren mit Acetal- und Urethangruppen in der Kette.

---

[a] Part XII: *R. W. Campbell* and *O. Vogl*, Makromolekulare Chemie, in press.

0026-9247/79/0110/0453/$ 03.80

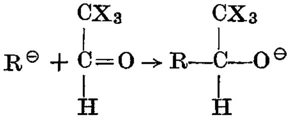
Introduction

Dibromofluoroacetaldehyde (*DBFA*) was prepared and polymerized in order to obtain further information about the polymerizability of haloacetaldehydes and how the size of the trihalomethyl group influences the polymer stereoregularity of completely halogenated acetaldehydes.

It has been found in the past that trifluoroacetaldehyde[1] and acetaldehyde[2–4] can be polymerized to rubbery atactic polymers and to crystalline insoluble presumably isotactic polymers depending on the individual polymerization conditions (Eqn. 1). Often a mixture of soluble and insoluble polymer corresponding to different degrees of "atacticity" has been observed[5]. Chlorodifluoroacetaldehyde[6] and bromodifluoroacetaldehyde[7] were also polymerized to insoluble crystalline polymers, but some polymerizations also gave soluble, amorphous, polymers of relatively low molecular weight. The tacticity of these soluble portions could not be determined by NMR because the characteristic acetal protons were not sufficiently resolved even at higher temperatures indicating possibly a stiffer polymer chain or helicity of the polymer chain in solution. Haloacetaldehyde polymers with groups larger than those indicated gave only insoluble crystalline polymers[8]; even bromal has recently been polymerized[9].

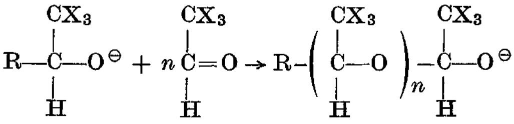
Equation 1. Anionic Polymerization Mechanism of Trihaloacetaldehydes

Initiation



$$R^{\ominus} + \underset{H}{\overset{CX_3}{C}}{=}O \rightarrow R{-}\underset{H}{\overset{CX_3}{C}}{-}O^{\ominus}$$

Propagation



$$R{-}\underset{H}{\overset{CX_3}{C}}{-}O^{\ominus} + n\,\underset{H}{\overset{CX_3}{C}}{=}O \rightarrow R{-}\left(\underset{H}{\overset{CX_3}{C}}{-}O\right)_n{-}\underset{H}{\overset{CX_3}{C}}{-}O^{\ominus}$$

It was the objective of this work to synthesize *DBFA*[10], and to attempt the polymerization with cationic and anionic initiators. The study of the copolymerization of *DBFA* with chloral, the "standard" comonomer for perhaloacetaldehyde polymerization, and with phenyl isocyanate was a further objective of this work as well as the determination of the ceiling temperature of *DBFA* polymerization.

Experimental Part

Materials

1,1-Dibromo-2,2-difluoroethylene was obtained from PCR Co. and distilled before us.

Trifluoromethyl sulfonic acid (Eastman Kodak Co.), lithium aluminium hydride (Ventron Alfa Products), sulfuric acid (Fisher Scientific Co.), PCl_5 (Stauffer Chemical Co.), and $SbCl_5$ (Allied Chemical Co.), were used as obtained.

Lithium tertiary butoxide (*LTB*) (Ventron Alfa Products), was purified by sublimation at 0.1 mm/150 °C before use.

Triphenylphosphine (Ph_3P) (Aldrich Chemical Company), was recrystallized from benzene.

Chloral (Montrose Chemical Company) was dried over P_2O_5, distilled, and used immediately[11].

Synthesis of Dibromofluoroacetaldehyde (DBFA)

Synthesis of Dibromofluoroacetyl Fluoride and Bromodifluoroacetyl Bromide by Oxidation of 1,1-Dibromo-2,2-difluoroethylene[12]: A dried 100 ml 3-neck flask was fitted with a rubber septum, an oxygen inlet tube and a condenser vented to a trap which in turn was equipped with a drying tube and cooled in Dry Ice/acetone. Into the flask was placed a magnetic stirring bar, and 1,1-dibromo-2,2-difluoroethylene (33.5 g, 0.15 mol) and the flask was placed in an ice/water bath. Oxygen was introduced at the rate of 2 ccm per minute under the surface of the stirred liquid. The progress of the oxidation was followed by periodically removing samples and analyzing them by gas chromatography [(using a 6′ × 1,4″ column of Apiezon N on Chromosorb W (100/120) with the injection port temperature of 70 °C, column temperature of 55 °C, detector temperature of 240 °C and a helium flow of 50 ccm/min]. Peaks were found at 6.0 and 6.9 minutes. The first corresponded to the mixture of oxidation products dibromofluoroacetyl fluoride and bromodifluoroacetyl bromide. The latter peak was the starting material. When no more olefin was detected by G.C., (after about 6.5 h), the reaction was stopped, and a plae yellow liquid product was obtained.

Preparation of Methyl Bomodifluoroacetate and Methyl Dibromofluoroacetate: The reaction mixture was slowly distilled, the mixed halides codistilled over the range of 65–80 °C, under nitrogen, directly into a receiver flask which was cooled to 0 °C, and contained a suspension of 20 g KF in 40 g dry methanol. The reaction with methanol was instantaneous and gave a mixture of methyl dibromofluoroacetate and methyl bromodifluoroacetate. The methanol solution was washed three times with a 10 % sodium bicarbonate solution and then with water, and dried overnight over magnesium sulfate. The products were separated by fractional distillation to give methyl bromodifluoroaxcetate (b.p. 96–98 °C, lit. b.p. 96 °C[12] and methyl dibromofluoroacetate (b.p. 83 °C (71 mm), lit. b.p. 85 °C (80 mm)[12]. The yields of the two compounds were 7.1 g and 8,0 g (molar ratio 1.0:0.85), respectively, for an overall combined yield of 50 % from the olefin. The purity of the individual products was checked by G.C. using a 6′ × 1,4″ Carbowax 20M on Chromosorb W column with temperatures as follows: injection port 140 °C; column 75 °C; detector 240 °C. Using a helium flow of 50 ccm/min the compounds were eluted at 2.25 and 25.5 minutes, respectively, each having impurities of less than 0.5 %. The major impurity in each compound was the other compound.

The infrared spectrum of the neat film of methyl dibromofluoroacetate had IR peaks at (in cm^{-1}) 2970 (vs) (C—H stretching), 1780 (vs) (C=O stretching). 1445 (vs) (C—H bending), 1310 (ms) (C—O stretching), 1182 (vs) (C—F stretching), 1130 (ms), 988 (ms), 915 (ms), 875 (ms), 815 (vs), and 722 (ms)[13]. The PMR spectrum showed a singlet at 3.98 ppm (*TMS*) (5% in $CDCl_3$). The F^{19} signal was also a singlet located at 20.35 ppm downfield from trifluoroacetic acid.

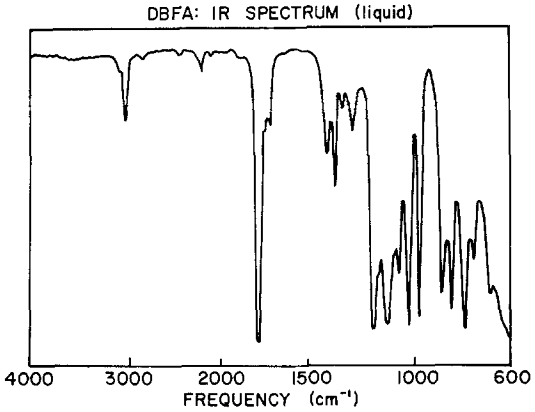


Fig. 1. Infrared spectrum of *DBFA* (liquid)

Reduction of Methyl Dibromofluoroacetate to the Hydrate $[CBr_2FCH(OH)_2]$: Methyl dibromofluoroacetate was reduced in a manner as described previously[6].

Methyl dibromofluoroacetate (10.0 g, 40 mmol in 15 ml anhydrous ethyl ether was charged into a 100 ml 3-neck flask which had been equipped with a magnetic stirring bar, a 25 ml pressure equalizing addition funnel and a reflux condenser topped with a $CaCl_2$ filled drying tube; the flask was cooled to —78 °C. In a separate operation, powdered lithium aluminium hydride (0.40 g, 11 mmol) was slurried in 50 ml anhydrous ether in a 250 ml flask equipped with a stirring bar and reflux condenser and maintained under a slight positive pressure of nitrogen. The $LiAlH_4$ sludge was added dropwise to the methyl dibromofluoroacetate solution in one hour. After stirring for an additional 30 minutes, the Dry Ice/acetone bath was removed, the mixture was allowed to slowly warm to room temperature and was poured into a stirred mixture of 200 g crushed ice and 2 ml conc. H_2SO_4 to dissolve the aluminium salts. The aqueous layer was removed using a separatory funnel and extracted twice with ether. The ether portions were combined and the ether removed under reduced pressure (25 mm) at room temperature. Crude *DBFA* hydrate was distilled at 120 °C and 0.1 mm and was obtained in good yield (9.3 g, 97% yield).

Preparation of DBFA: Crude *DBFA* hydrate (6 ml) was mixed with conc. H_2SO_4 (6 ml) in a 25 ml distillation flask equipped with a magnetic stirring bar and a 15 cm *Vigreux* distillation head. The pressure was reduced prior to heating by means of a vacuum pump and *Cartesian* diver type manostat. The clear liquid was obtained in good yield and distilled with a b. p. 66 °C at 105 mm (6.6 g, 75% yield from the ester).

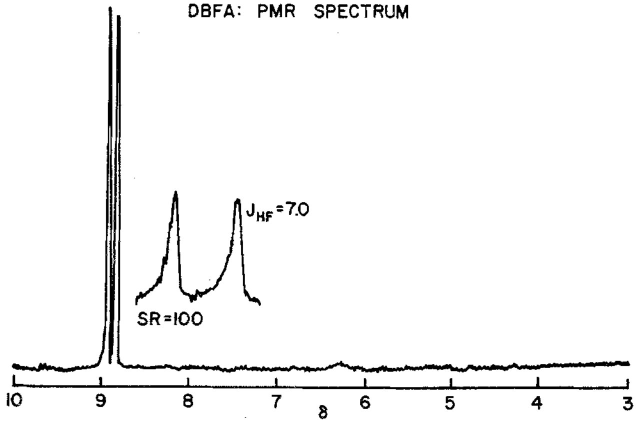


Fig. 2. ^{1}H NMR spectrum of *DBFA*

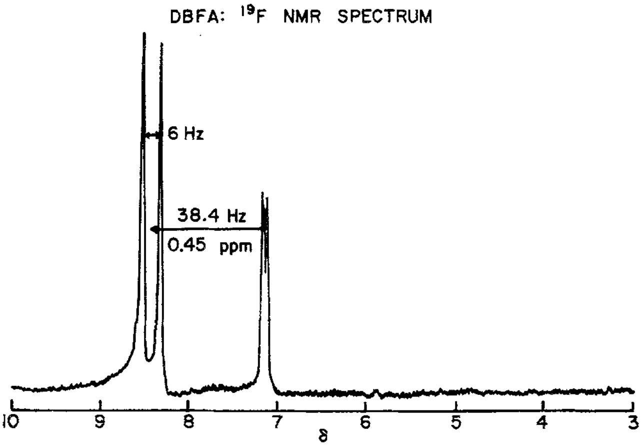


Fig. 3. ^{19}F NMR spectrum of *DBFA*

The purity of the *DBFA* was checked using GC. A one microliter sample was injected onto a column containing 33% diisodecyl phthalate on Chromosorb W at 115 °C. The only peak eluted other than the monomer (16.5 minutes) was present in less than 25 ppm level and was assigned to *BDFA* based on retention time (6.9 minutes).

The *DBFA* was characterized by its elemental analysis, infrared, PMR and F^{19} NMR spectra.

The infrared spectra were obtained from a film of the neat liquid on NaCl plates (Fig. 1), in the gaseous state and in 2% solutions in $CHCl_3$ and in n-hexane.

The neat liquid sample had bands at 3497 (s) (overtone), 2861 (s) (C—H stretching), 1751 (vs) (C=O stretching), 1395 (m), 1358 (s) (C—H bending in plane), 1319 (w), 1268 (m), 1165 (s), 1092 (s), 1031 (m), 983 (vs), 930 (vs), 813 (m), 766 (s), 700 (s), and 651 (m).

The NMR spectra were measured on a 2 % solution of the *DBFA* in $CDCl_3$. The PMR showed a doublet centered at 8.86 ppm ($J_{H\text{-}F}$ = 7.0 Hz) (Fig. 2). The F^{19} spectrum was also a doublet, 0.60 ppm downfield from trifluoroacetic acid (external); $J_{H\text{-}F}$ = 7.0 Hz (Fig. 2).

Anal. Calcd. for C_2HBr_2FO: C 10.93, H 0.46. Found: C 10.98, H 0.48.

Preparation of DBFA Hydrate [$CBr_2FCH(OH)_2$]: Water was added in 4 microliter increments to a solution of *DBFA* (5 % in $CDCl_3$) in a 5 mm NMR tube and the changes in chemical shifts observed by PMR. The initially present aldehyde proton doublet at 8.86 ppm was replaced by two new peaks which appeared as a doublet at 5.10 ppm and a singlet at approximately 4 ppm with an integrated intensity of 1:2. The position of the latter peak, which can be assigned to the hydroxyl protons, was concentration dependent due to hydrogen bonding. The position of the former peak, the acetal proton, was not affected by concentration.

When this experiment was repeated using D_2O instead of water the doublet due to the acetal proton was still observed to have a chemical shift of 5.10 ppm, but no peak appeared at 4 ppm due to the isotopic replacement in the hydroxyl protons.

Polymerization of DBFA

The general procedure employed in the sealed ampule polymerization of *DBFA* has already been fully described in the polymerization of *DBFA*[7].

Polymerization of DBFA with LTB at —78 °C: A solution of *LTB* (0.3*M* in *MCH*)(0.61 mole %) was used to initiative *DBFA* (1.07 g, 4.9 mmol) at 60 °C. The tube was quickly cooled by placing it into a Dry Ice/acetone bath. A gel was formed within 30 seconds at —78 °C. After 10 days the tube was cut open and still contained some liquid *DBFA*. The polymer was slurried in acetone (50 ml) overnight, the entire polymer dissolved and 0.17 g (16 % conversion) of insoluble polymer was isolated after precipitation in water.

The thermal stability of the polymer was measured by *DTG* and decomposition maxima were observed at 223 °C and 340 °C for the polymer before and after treatment with PCl_5, respectively (Fig. 5*A*).

Polymerization of DBFA with Pyridine at Room Temperature: DBFA (0.84 g, 3.80 mmol) and a break tube containing pyridine in toluene (0.125 mmol, 3.3 mole %) was sealed and the tube heated to 60 °C, the inner tube broken by shaking whereby the contents mixed rapidly. The tube was immersed in a room temperature water bath and after less than one minute the contents of the tube solidified to an opaque white mass. After 24 hours the tube was broken gave 0.05 g of a white brittle material which was insoluble in acetone (6 % conversion). No acetone soluble polymer was precipitated on mixing the filtrate with cold water.

The thermal stability of the poly *DBFA* was measured by *DTG* before and after PCl_5 stabilization. In each case two maxima of the rate of degradation were observed. The raw polymer had peaks at 153 °C and 222 °C; after stabilization the peak temperatures were increased to 230 °C and 341 °C (Fig. 5*B*).

The infrared spectrum of the raw polymer in a KBr pellet was recorded (Fig. 4) and characteristic peaks (in cm^{-1}) are at 3380 (b) (OH), 2945 (m) (C—H stretching), 1387 (m) (C—H bending), 1358 (m) (C—H bending), 133 (m) (C—H bending), 1155 (m) (C—O stretch), 1110 (m), 1059 (s) (C—O stretch), 1029 (w), 1004 (w), 960 (s), 830 (vs) and 800 (w).

Polymerization of DBFA with Sulfuric Acid at 25 °C: DBFA (0.95 g, 4.33 mmol) and concentrated sulfuric acid (0.022 mmol, 0.51 mole %) were sealed in an ampule and the monomer was initiated and maintained at room temperature. The mixture had gelled after one hour; after 24 hours the tube was opened, the contents were soaked with acetone and 0.76 g (80 % conversion) of an acetone insoluble polymer were obatined. No soluble polymer was recovered on pouring the filtrate into cold water.

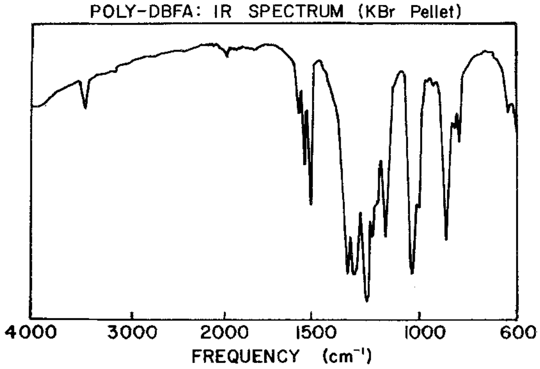


Fig. 4. Infrared spectrum of poly-*DBFA* (KBr pellet)

Thermal characterization by *DTG* showed the raw and PCl_5 stabilized polymers had maximum rates of thermal decomposition at 259 °C and 363 °C, respectively (Fig. 6*A*).

Anal. Calcd. for C_2HBr_2FO: C 10.93, H 0.46. Found: C 11.29, H 0.55.

Isothermal Pyrolysis of Poly DBFA: A sample of the raw polymer (0.108 g) was placed in the sample part of an L-shaped pyrolysis tube whose other end was cooled in a liquid nitrogen bath and sealed under a vacuum of 0.05 mm. The sample end was heated slowly in a sand bath to 250 °C. It was maintained at this temperature for four hours while volatile decomposition products were collected in the cooled side arm. At the end of this period no solid residue remained in the sample chamber. The collection tube was sealed off, was warmed to room temperature and contained a clear liquid. The tube was broken and the liquid was identified by NMR and GC as being exclusively *DBFA*; 96 % conversion, 1.04 g.

Copolymerization of DBFA

A. *With Chloral and Sulfuric Acid:* Freshly distilled monomers, *DBFA* (0.82 g, 3.75 mmol) and chloral (0.55 g, 3.70 mmol), were injected into a polymerization tube. The polymerization of the warm tube (80 °C) was initiated by vigorous shaking of the tube to break the inner ampule of H_2SO_4 (0.075 mmol, 2.0 %). The initiated solution was clear, but within 5 minutes at 25 °C it became a translucent gel. After 24 hours the tube was opened, washed with acetone and gave a white solid. Yield: 0.22 g, 16 %.

Poly *DBFA* was characterized by *DTG*; maxima at 246 °C and 380 °C, before and after PCl_5 treatment, but the percentage of the polymer that decomposed at these varied substantially.

Anal. Found: F 4.31% which corresponds to 40 mole % *DBFA*.

B *With Chloral and Pyridine: DBFA* (1.31 g, 5.96 mmol) and chloral (0.9 g, 6.17 mmol) were mixed in a polymerization tube and initiated with pyridine (0.36 mmol, 3 mole %) by breaking a pyridine ampule inside the sealed tube. Initiation at 85 °C was followed by cooling the clear solution to 25 °C where the contents of the ampule became opaque within one minute. After 24 hours the tube was cut open and a white solid copolymer, wholly insoluble in acetone, was obtained. Yield: 0.22 g, 10%.

The copolymer was found to decompose at the maximum degradation rates of 210 °C and 320 °C for the raw and PCl_5 treated copolymers, respectively.

Anal. Found: F 5.56%. This corresponds to 56% of *DBFA* in the copolymer.

C. *With Ph*NCO *and Pyridine: DBFA* (1.68 g, 7.66 mmol), *Ph*NCO (0.90 g, 7.5 mmol) and pyridine (4.55 mmol, 3.0 mole %) were charged into a dried polymerization tube and sealed at 0.1 mm. The solution was warmed to 85 °C and shaken until the ampule broke releasing the initiator. The sample was then placed in a bath at 25 °C where the mixture solidified within 10 minutes to a clear gel. After 24 hours the tube was opened and the copolymer was found to be completely insoluble in acetone. Yield: 0.33 g, 13%.

The *DTG* spectra showed maxima at 230 °C and 350 °C for the raw and PCl_5 treated copolymer, respectively.

Anal. Found: N 0.11%. This corresponds to 1.4 mole % *Ph*NCO incorporated into the copolymer.

Measurements

Proton and fluorine nuclear magnetic resonance spectra were obtained on a Perkin-Elmer R-32 90 MHz variable temperature NMR spectrometer. Spectra were recorded in the locked mode using internal TMS for ^{1}H-NMR spectra at normal temperature (35 °C). Hexamethyldisiloxane (*HMDS*) was used as an internal lock signal for those spectra recorded at high temperatures. ^{19}F NMR spectra were measured using trifluoroacetic acid in an external (coaxial) tube as the locking resonance signal.

Infrared spectra were obtained on either a Perkin-Elmer 257 or 727 Infrarot (4.000–600 cm^{-1}) or a 283 (4,000–250 cm^{-1}) spectrometer.Solid samples were measured as KBr pellets and liquid samples between sodium chloride plates. Gaseous samples were measured in closed cells with sodium chloride windows with a 10 cm path length. The vapors were diluted with nitrogen.

Thermal degradation was measured with a Perkin-Elmer TGS-1 thermobalance using a sample size of about 10 mg in a nitrogen atmosphere and a heating rate of 10 °C/min. The heating rate was controlled by a Perkin-Elmer UU 1 Temperature Program Control. Most data were collected using the differential mode (*DTG*), but the normal mode (*TGA*) was also utilized.

Normal melting points were measured on a Mel-Temp capillary melting point apparatus and are corrected.

Gas chromatograms were obtained on a Varian Associates Modell 920 gas chromatograph. Specific columns and conditions are described in the experimental details.

Wide angle X-ray scattering studies were carried out on an in-house made instrument with a Norelco power supply. The radiation was from Cu-K_α source having a wavelength of 1.5418 Å.

The powdered sample was placed in a 7 mm diameter hole in a 1.5 mm thick lead plate and secured with a layer of cellophane tape on each side. The sample was placed about 1 cm from the radiation port and photographic film plate positioned about 8 cm behind the sample. All distances were carefully measured before and after each exposure. The exposure time was controlled by an automatic timer and was about 8 hours for each sample.

Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Results and Discussion

DBFA was prepared by oxidation of 1,1-dibromo-2,2-difluoroethylene with oxygen to give a mixture of the bromodifluoroacetic acid bromide and the dibromofluoroacetic acid fluorides of acid, respectively[13,14]. The mixture of the acid halides was treated with methanol and gave the methyl esters. Methyl dibromofluoroacetate was separated by distillation from bromofluoroacetate and was reduced with lithium aluminium hydride to *DBFA* which was polymerized and copolymerized.

The synthesis of *DBFA* was accomplished in an overall yield of about 15-20% (Eqn. 1). Initially, 1,1-dibromo-2,2-difluoroethylene was air oxidized at 0 °C[15,16,17]. The oxidation apparently goes through the unstable 1,1-dibromo-2,2-difluoroethylene oxide which could not be isolated but rearranged directly to a mixture of dibromofluoroacetyl fluoride and bromodifluoroacetyl bromide. These products were not separated but were immediately treated with methanol at 0 °C and gave an approximately 50:50 molar mixture of methyl dibromofluoroacetate and methyl bromodifluoroacetate. The boiling points of these two compounds were far enough apart that they could easily be separated by fractional distillation. The methyl bromodifluoroacetate boiled much lower and could be isolated as the foreshot. The residual methyl dibromofluoroacetate was rectified and then reduced with lithium aluminum hydride at 0 °C. Aluminium compounds formed and were decomposed with water to the crude hydrate of *DBFA* and then dehydrated with sulfuric acid to *DBFA*. The crude *DBFA* hydrate actually contains not only the hydrate but also the methyl hemiacetal as the crude hydrate showed several peaks in the ^1H NMR spectrum which were not assignable to pure *DBFA* hydrate but to the hemiacetal. The overall yield for this preparation was nearly 20%; *DBFA* was purified by careful distillation and showed, by GC analysis, only one impurity which was found at a 25 ppm level and was identified as *BDFA*. The physical properties of *DBFA* are described in Table 1.

The infrared spectrum of *DBFA* showed a typical >CO stretching frequency at 1,751 cm^{-1} and a CH bend between 1,400 cm^{-1}, and

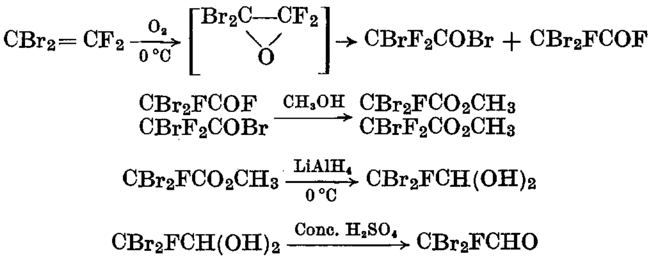
Table 1. *Physical Properties of* $CBr_2F—CHO$

B.P. [°C (mm)]	66 (105)
Infrared Carbonyl Absorption (n-hexane), (cm^{-1})	1,755
^1H NMR Chemical Shift Relative to TMS, (ppm)	8.86
$J_{H\text{-}F}$, (Hz)	7.0
^{19}F NMR Chemical Shift Relative to CF_3COOH, (ppm)	0.60
Ceiling Temperature of Polymerization, (°C),—7	—7

1,350 cm^{-1}. The 2,861 cm^{-1} band was assigned to C—H stretching. A number of additional bands were present at lower frequencies and are typical for C—Br and C—F absorption frequencies.

The ^1H NMR spectrum showed a doublet centered at 8.86 ppm with a $J_{H\text{-}F}$ of 7.0 Hz. The ^{19}F spectrum showed a doublet at 0.60 ppm downfield from trifluoroacetic acid with the same coupling constant. *DBFA* hydrate was regenerated from *DBFA* by adding water to a solution of *DBFA* in $CDCl_3$. The initially present aldehyde proton doublet at 8.86 ppm was replaced by two new peaks which appeared as a doublet at 5.10 ppm and a singlet at approximately 4 ppm. The first chemical shift peak was clearly identified as the CH frequency of the hydrate while the other peak was, according to its integration intensity ratio of 1:2, identified as the protons of the hydroxyl groups. The latter peak did not exist if the hydration was carried out with D_2O instead of H_2O.

Equation 2. Synthesis of CBr_2FCHO



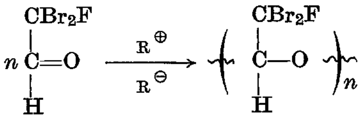
$$CBr_2{=}CF_2 \xrightarrow[0\,°C]{O_2} \left[\begin{array}{c} Br_2C—CF_2 \\ \diagdown\diagup \\ O \end{array}\right] \rightarrow CBrF_2COBr + CBr_2FCOF$$

$$\begin{array}{c} CBr_2FCOF \\ CBrF_2COBr \end{array} \xrightarrow{CH_3OH} \begin{array}{c} CBr_2FCO_2CH_3 \\ CBrF_2CO_2CH_3 \end{array}$$

$$CBr_2FCO_2CH_3 \xrightarrow[0\,°C]{LiAlH_4} CBr_2FCH(OH)_2$$

$$CBr_2FCH(OH)_2 \xrightarrow{Conc.\ H_2SO_4} CBr_2FCHO$$

Equation 3. Polymerization of DBFA



$$n\,\begin{array}{c} CBr_2F \\ | \\ C{=}O \\ | \\ H \end{array} \xrightarrow[R^{\ominus}]{R^{\oplus}} \left(\begin{array}{c} CBr_2F \\ | \\ C—O \\ | \\ H \end{array} \right)_n$$

Polymerization of *DBFA* was carried out with compounds that have been known to initiate perhaloaldehyde polymerizations by anionic (Eqn. 2, 3) or cationic mechanisms (Tab. 2). Interestingly enough, and in contrast to other perhaloaldehyde polymerizations, in terms of overall yield, cationic initiation appeared to be the more effective way of initiating *DBFA* polymerization. Sulfuric acid at 0.5 mole % initiator concentration and 25 °C gave an 80 % conversion to poly-*DBFA* which was completely insoluble in acetone. The insolubility of *DBFA* polymer is very typical as none of the initiators which we have studied produced any soluble fraction of poly-*DBFA*. At —25 °C with 0,7 mole % of H_2SO_4, a 35 % conversion of polymer was obtained after 1 week. The initiation of the polymerization was very slow especially at lower temperatures and it appeared that after 12 hours none or very little polymerization had occurred, quite different from the room temperature polymerization of *DBFA*.

Table 2. *Polymerization of* CBr_2F—CHO (Polymerization Time 1 Day)

Initiator Type	Amount (Mole %)	Polymerization Bath Temp. (°C)	Conversion[a] (%)
LTB[b]	0.24	25	0
LTB	4.9	—78	16
Ph_3P	0.26	—25	0
Ph_3P	0.32	—78	0
Pyridine	3.3	25	6
H_2SO_4	0.51	25	80
H_2SO_4	0.73	—25	35
AlEt_3	0.38	—78	10
AlEt_3	0.30	25	7
TFMSA[c]	2.9	25	27

[a] Entire Product was Acetone Insoluble.
[b] *LTB* = Lithium Tertiary Butoxide.
[c] *TFMSA* = Trifluoromethane Sulfonic Acid.

TFMSA was also an effective initiator for the *DBFA* polymerization. The initiator was used at 2.9 mole % concentration and the mixing of initiator and monomer was carried out at 60 °C. Although the two liquids (*TFMSA* and *DBFA*) were initially immiscible they became homogeneous after a few minutes of shaking. Already after 5 minutes of reaction the mixture gelled and after 1 day a 27 % conversion of poly-*DBFA* was obtained.

AlEt_3 has been used in the past for epoxide and cyclic ether polymerization; it was also used effectively for aldehyde polymerizations either unmodified or modified with water or alcohols[17]. As it is known, AlEt_3 can act as an anionic or cationic initiator depending on the modifier and is often called a coordinative initiator.

We have tested AlEt_3 to see if this compound initiated *DBFA* polymerization. In our hands, AlEt_3 is a moderately active initiator for the polymerization of *DBFA*. At 0.3 mole % of initiator at 25 °C and at —78 °C an approximately 10 % conversion of *DBFA* to the polymer was obtained.

Pyridine is a common initiator for perhaloacetaldehyde polymerization and for most of our rate studies of the haloaldehyde polymerizations it was used as the standard anionic initiator[8]. As initiator for bromal polymerization, pyridine had to be used under very carefully controlled conditions, otherwise, bromal did not polymerize. It was consequently believed that a similar problem might arise for the *DBFA* polymerization which was indeed observed. With 3 mole % of pyridine at room temperature a low conversion of 6 % of *DBFA* to poly-*DBFA* was obtained.

LTB has also been a very active initiator for many aldehyde polymerizations, although it was not very effective for bromal polymerization when *LTB* was allowed to react with monomer for more than one minute[9]. Apparently a side reaction occurred which interfered with the initiation. It is clear that *LTB* not only can add to the carbon of the carbonyl group an aldehyde, especially perhaloaldehyde, to form an alkoxide which can initiate the polymerization but for bromoperhaloaldehydes can displace a bromide ion from the aldehyde which is ineffective to initiate polymerization. Partial success of initiation only means that the bromide displacement which would normally occur is a slower process. Consequently initiation actually occurred.

In separate experiments it was shown that bromide ion was not an initiator for bromal polymerization and indeed not for any other perhaloacetaldehyde polymerization. As a consequence, it was not excepted that *DBFA* polymerization initiated with bromide or a nucleophile of lesser activity would initiate *DBFA* polymerization.

When *LTB* was used at 0.24 mole % and the polymerization was carried out at 25 °C bath temperature, no poly-*DBFA* was obtained; with a large amount (4.50 mole %), of *LTB* and a polymerization bath temperature of —78 °C, a yield of 16 % was obtained. This reaction yield was very low if one considers that under normal conditions *LTB* produced 85 % of perhaloaldehyde polymers when the substituent *X* of the —CX_3 groups was chlorine and fluorine. As in the case of bromal, Ph_3P at —25 °C or at —78 °C did not give polymer when it was used as an initiator for the *DBFA* polymerization. This is not surprising if one realizes that Ph_3P reacts with bromal to give I and presumably with *DBFA* to give II[9].

$$Ph_3P + CBr_3CHO \longrightarrow Ph_3\overset{\oplus}{P}\text{—O—}\underset{Br^{\ominus}}{CH}=CBr_3 \qquad \text{(I)}$$

$$Ph_3P + CBr_2FCHO \longrightarrow Ph_3\overset{\oplus}{P}\text{—O—}\underset{Br^{\ominus}}{CH}=CFBr \qquad \text{(II)}$$

The polymerization experiments of *DBFA* produced poly-*DBFA* in various physical forms. In many cases a gelatinous mass was obtained which was isolated by stirring the gel in acetone whereby it coagulated, was broken up, and was easy to filter. On some occasions, poly-*DBFA* was also obtained in a powdery from, but in all cases the polymer was infusible and insoluble in all the solvents tried; no soluble fraction of *DBFA* has ever been isolated.

Because of the relatively small amount *DBFA* available as compared to the polymerization studies using commercially available chloral and bromal, the experiments were done and the polymer yields determined with limited sample sizes. The morphology of the precipitating polymer determined the availability of the growing ends during the polymerization reactions and consequently the yield of polymer. When the endgroups become occluded the dormant but active polymer chain ends were no longer available for further polymerization because poly-*DBFA* even in the gel form is insoluble.

Poly-*DBFA* showed characteristic peaks in the infrared spectrum (KBr pellet) at 2,945 cm^{-1} (C—H stretching), at 1,387 cm^{-1} and 1,358 cm^{-1} (C—H bending) and the C—O stretching at 1,155 cm^{-1} and 1,110 cm^{-1} and 1,057 cm^{-1}. Further peaks, more characteristics for the carbon-halogen stretching frequencies, were at lower frequencies. Another characteristically broad peak at 3,380 cm^{-1} was caused by the OH frequency which was observed as an endgroup of these polymers in a number of preparations particularly those when pyridine and H_2SO_4 were used as the initiator (Fig. 4).

Since poly-*DBFA* was insoluble in any solvent tried, few of the normal polymer characterization techniques could be used to describe the polymer. X-ray *Debye-Scherrer* diagrams were taken and it was found that the polymer was of medium crystallinity and had d-spacings similar to those of polychloral but with a difference in the intensity of the lines.

Poly-*DBFA* prepared with H_2SO_4 at room temperature was pyrolyzed. This pyrolysis was carried out in an A-shaped apparatus at

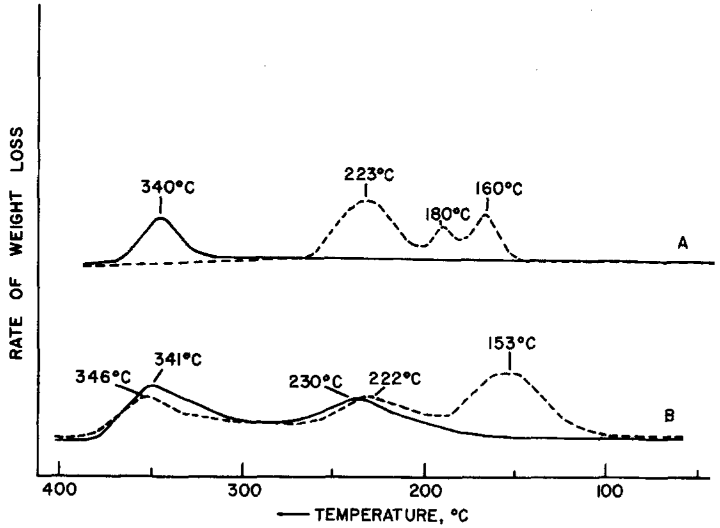


Fig. 5. *DTG* curves of poly-*DBFA* prepared with anionic initiators. *A* Initiator: *LTB*, polymerization temperature: —78 °C; polymer: insoluble. --- raw polymer, — PCl_5 treated polymer. *B* Initiator: pyridine, polymerization temperature: —25 °C; polymer: insoluble. --- raw polymer, — PCl_5 treated polymer

Table 3. *Maximum degradation rate temperature*[a] *of poly-DBFA* (Temperature in °C, Heating Rate programmed to 10 °C/min under Nitrogen Atmosphere)

Initiator Type	Raw Polymer[b]	PCl_5 Treated Polymer[b]
LTB[c]	160 (40), 223 (60)	340
Pyridine	153 (70), 222 (15), 346 (15)	230 (50), 341 (50)
H_2SO_4	199 (50), 259 (50)	363
	262	260
$\mathrm{Al}Et_3$	279	311 (60), 360 (40)
	292 (60), 355 (40)	299 (60), 365 (35)
TFMSA[d]	220	358

---

[a] These Values Vary Depending on Polymerization Temperature.

[b] In ( ) Approximate Amount of the Polymer Fractions of Respective Stability.

[c] *LTB* Lithium Tertiary Butoxide.

[d] *TFMSA* — Trifluoromethanesulfonic Acid.

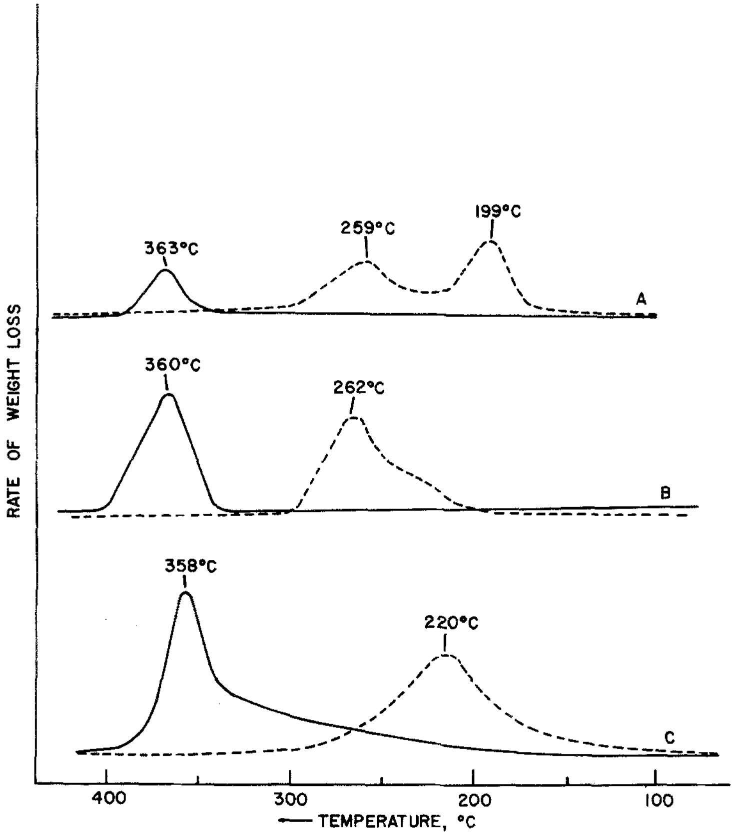


Fig. 6. *DTG* curves of poly-*DBFA* prepared with H_2SO_4 and *TFMSA* initiators. *A* Initiator: H_2SO_4, polymerization temperature: +25 °C; polymer: insoluble. --- raw polymer, — PCl_5 treated polymer. *B* Initiator: H_2SO_4, polymerization temperature: −30 °C, polymer: insoluble. --- raw polymer, — PCl_5 treated polymer. *C* Initiator: *TFMSA*, polymerization temperature: +25 °C, polymer: insoluble. --- raw polymer, — PCl_5 treated polymer

0.05 mm; one end of the tube was heated in a bath at 250 °C; the other end was cooled in liquid nitrogen. After 4 hours no solid polymer remained; the collection tube was sealed and analyzed and showed that 96 % of the weight of the polymer was pure monomer as identified by GC and NMR spectroscopy.

Poly-*DBFA*, as obtained, particularly by anionic polymerization, was relatively unstable similar to other perhaloacetaldehyde polymers but could be stabilized by treatment with PCl_5[19] (Table 3). It is believed that this treatment caused the introduction of the thermally more stable

C—Cl terminal group. While it is not known which type of endgroups of the poly-*DBFA* reacted with PCl_5, it is most likely that —OH endgroups or groups of reactivities toward PCl_5 similar to —OH groups transformed the raw polymer into a material of much higher stability. The thermal degradation spectrum of poly-*DBFA* prepared with H_2SO_4 at —25 °C showed a maximum of the degradation rate at 265 °C, after treatment with PCl_5 the maximum was at 365 °C (Fig. 5*A*). The H_2SO_4 initiated poly-*DBFA*, polymerized at —25 °C, showed a maximum rate of thermal decomposition of 259 °C for the raw polymer and 363 °C for the material treated with PCl_5 (Fig. 6*B*). Two samples of poly-*DBFA* were prepared with pyridine as the initiator. The raw polymers showed maximum temperatures of degradation of 153 °C and 225 °C and after stabilization the thermal stability was increased to 230 °C and 341 °C respectively (Fig. 5*B*).

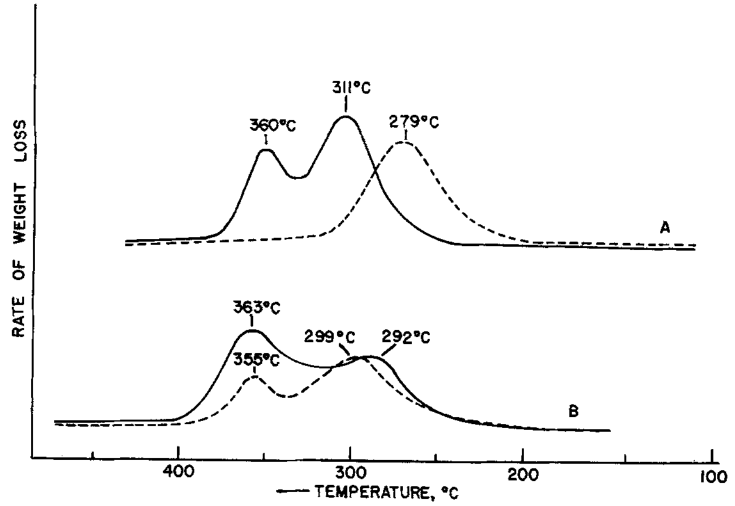
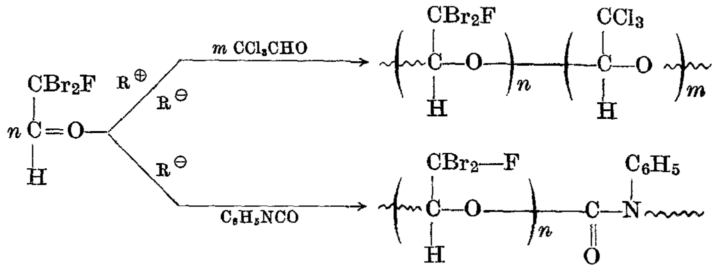


Fig. 7. *DTG* curves of poly-*DBFA* prepared with Al*Et*$_3$ initiator. *A* Polymerization temperature: +25 °C; polymer: insoluble. --- raw polymer — PCl_5 treated polymer. *B* Polymerization temperature: —78 °C; polymer: insoluble. --- raw polymer, — PCl_5 treated polymer

It has been known that aldehyde polymers initiated with Al*Et*$_3$ have an initially higher thermal stability[20]. This has also been found to be the case with a polymer of *DBFA* initiated with Al*Et*$_3$. The polymer initiated at 25 °C initially showed a maximum thermal degradation rate at 279 °C and after PCl_5 treatment maximum degradation rates at 311 °C and 360 °C (Fig. 7*A*). The polymer initiated at —78 °C showed a decomposition maxima at 299 °C for the raw polymer and 360 °C for the stabilized material (Fig. 7*B*). Polymer initiated with *LTB* at —78 °C showed a maximum rate of degradation at 223 °C and after stabilization with PCl_5, the maximum degradation rate temperature was 340 °C (Fig. 5*A*).

Copolymerization of *DBFA* with chloral was carried out at room temperature with pyridine or H_2SO_4 as the initiators (Eqn. 4). With pyridine, with a mixing temperature of 85 °C and a polymerization bath temperature of 25 °C, a white crystalline copolymer was obtained in 10 % yield, after 24 hours, which was completely insoluble in acetone. The monomer feed ratio was 1 : 1 molar and the initiator concentration was 3 mole %. According to fluorine analysis, the *DBFA* content of the copolymer was 56 % indicating the *DBFA* in the pyridine initiated copolymerization was slightly more reactive than chloral. The decomposition of these copolymers was also studied and it was found that the maximum rate of degradation was at 210 °C for the raw polymers and 320 °C for the treated material.

Equation 4. Copolymerization of DBFA



The copolymer of *DBFA* with chloral and H_2SO_4 (2 mole %) as the initiator at 25 °C gave a 10 % yield of insoluble polymer after 24 hours of reaction. The copolymer contained 40 mole % *DBFA* indicating that in this copolymerization *DBFA* was less reactive than chloral. The maximum degradation temperature was 240 °C for the raw polymer and 380 °C for the treated material.

A 1 : 1 molar mixture of *DBFA* and *Ph*NCO was initiated at 85 °C with 3 mole % of pyridine and allowed to polymerize at 25 °C for 24 hours (Eqn. 4). The copolymer which was obtained in 13 % yield was completely insoluble[21] in acetone and contained only 1.4 mole % of

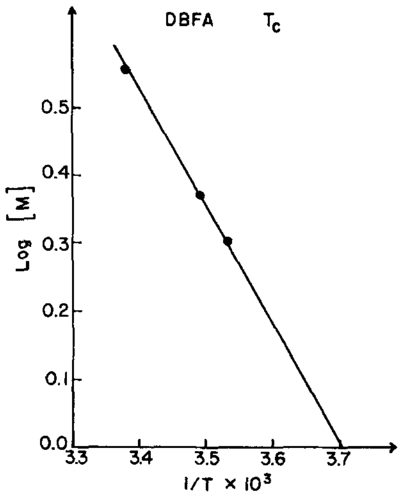


Fig. 8. Ceiling temperature determination of *DBFA* polymerization

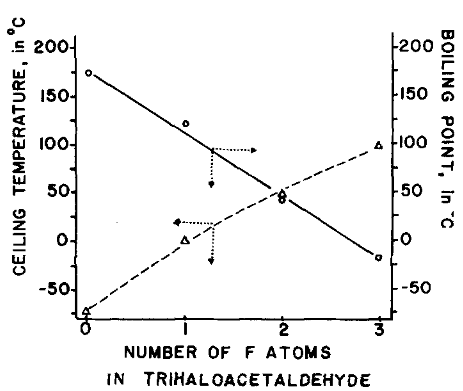


Fig. 9. Ceiling temperatures and boiling points of bromofluoroacetaldehydes

*Ph*NCO by nitrogen analysis. This value agreed with the intensity of the urethane group in the 1,740 cm^{-1} region in the copolymer indicating that very little of the phenyl isocyanate incorporated in the copolymer. The *DTG* spectrum of the copolymer showed a maximum thermal degradation temperature of 230 °C for the raw polymer and 350 °C for the PCl_5 treated copolymer.

The ceiling temperature of the *DBFA* polymerization was determined by measuring the onset of polymerization of three concentrations and it was found that the ceiling temperature was —7 °C (Fig. 8). The threshold temperature of polymerization at various concentrations was estimated measuring the first opacity of polymer formation and then extrapolating the polymerization temperatures as a function of monomer concentration in an *Arrhenius* plot to a one molar monomer concentration. This method has been found very useful in other cases of the determination of the ceiling temperatures of perhaloaldehyde polymers[22]. A relationship of the boiling points and ceiling temperatures for all bromofluoroacetaldehydes is given in Fig. 9.

Acknowledgements

This work was supported in part by the National Science Foundation Grant to the Materials Research Laboratory of the University of Massachusetts. We are also indebted to *L. S. Corley* for his assistance in the preparation of this manuscript.

References

[1] *S. Temple* and *R. L. Thornton*, J. Polym. Sci. **A 1**, **10**, 709 (1972).
[2] *O. Vogl*, J. Polym. Sci. **A 2**, 4591 (1964).
[3] *E. G. Brame*, *R. S. Sudol*, and *O. Vogl*, J. Polym. Sci. **A 2**, 5337 (1964).
[4] *E. G. Brame* and *O. Vogl*, J. Macromol. Sci. (Chem.) **A 1** (**2**), 277 (1967).
[5] *O. Vogl*, Advances in Chemistry Series **52**, 67 (1966).
[6] *B. Yamada*, *R. W. Campbell*, and *O. Vogl*, J. Polym. Sci., Polym. Chem. Ed. **15**, 1123 (1977).
[7] *R. W. Campbell* and *O. Vogl*, Makromolekulare Chemie, in press.
[8] *D. W. Lipp* and *O. Vogl*, in: Ring-Opening Polymerization (*T. Saegusa* and *E. Goethals*, eds.). ACS Symposium Series **59**, 111 (1977).
[9] *D. W. Lipp* and *O. Vogl*, Polymer (London) **18**, 1051 (1977).
[10] *P. Kubisa*, *I. Negulescu*, *K. Hatada*, *D. W. Lipp*, *J. Starr*, *B. Yamada*, and *O. Vogl*, Pure & Appl. Chem. **48**, 275 (1976).
[11] *P. Kubisa* and *O. Vogl*, Macromol. Synth. **6**, 49 (1977).
[12] *D. W. Lipp*, *R. W. Campbell*, and *O. Vogl*, Preprints, ACS Polym. Div. **18** (**1**), 40 (1977).
[13] *H. Cohn* and *E. D. Bergmann*, Israel J. Chem. **2**, 355 (1964).
[14] *R. W. Campbell* and *O. Vogl*, J. Macromol. Sci (Chem.) **A 11**(**3**), 515 (1977).
[15] *R. W. Campbell* and *O. Vogl*, Abstr. of Papers, 7th. NERM, No. 312, Albany (1976).
[16] *O. Peleta*, *F. Liska*, and *A. Posta*, Coll. Czech. Chem. Comm. **35**, 1302 (1970).
[17] *R. W. Campbell*, Ph.D. Thesis, Univ. of Massachusetts, 1978.
[18] *J. Furukawa* and *T. Saegusa*, Polymerization of Aldehydes and Oxides. New York: Wiley-Intersciene. 1963.
[19] *A. L. Barney*, U.S.-Patent 3,067,173 (1962); CA. **59**, 10310 B (1962).
[20] *W. P. Langsdorf* and *G. S. Stamatoff*, Brit.-Patent 766,629 (1957).
[21] *O. Vogl*, U.S.-Patent 3,668,184 (1972).
[22] *D. W. Lipp*, Ph.D. Thesis, Univ. of Massachusetts, 1974.