Haloaldehyde Polymers. X. Poly(dibromochloroacetaldehyde)*

D. W. LIPP and O. VOGL

*Polymer Science and Engineering, University of Massachusetts,
Amherst, Massachusetts 01003, U.S.A.*

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ABSTRACT: Dibromochloroacetaldehyde was synthesized in good yield from chloroacetaldehyde diethyl acetal by bromination. It was purified to give a monomer suitable for homo- and copolymerization. Polymerization could be carried out with anionic and cationic initiators; anionic polymerization gave good yields of a crystalline polymer which could be stabilized. Vacuum degradation of the polymer gave the monomer form quantitatively. The T_g of polymerization (1 *M*) was -40°C . Dibromochloroacetaldehyde copolymerized with chloral and phenyl isocyanate to insoluble and infusible polymer, but was less reactive than chloral.

KEY WORDS Poly(dibromochloroacetaldehyde) / Dibromochloroacetaldehyde / Haloaldehyde Polymers / Ceiling Temperatures / Cryotachensic Polymerization /

A number of haloacetaldehydes have recently been prepared and their polymerization behavior investigated. The most prominent of the perhalogenated acetaldehydes is chloral,¹⁻⁴ but chlorofluoroacetaldehydes have also been studied.⁵⁻⁸ These investigations were primarily carried out to determine the extent of size or bulkiness of the perhalomethyl side chain on whose upper side only isotactic polymers have been able to be prepared. The dichlorofluoromethyl group to be the smallest group whose corresponding aldehyde produces only insoluble, presumably isotactic polymer. Poly(chlorodifluoroacetaldehyde) also exists in a soluble (presumably atactic) and polyfluoral in a soluble elastomeric form.

Very recently it was demonstrated that bromodichloroacetaldehyde could be synthesized from triphenylphosphine and chloral followed by bromination of the double bond in the dichlorovinylphosphonium compound.^{9,10} Hydrolysis of the salt followed by careful purification gave polymerization-grade monomer capable of being polymerized by anionic initiators. As in the

case of chloral, alkali metal alkoxides and tertiary amines, especially the heterocyclic tertiary amines served as good initiators. Also SbCl_5 , AlCl_3 , H_2SO_4 , and trifluoromethanesulfonic acid gave the homopolymer of bromodichloroacetaldehyde. The polymer was characterized, the rate of polymerization under anionic and cationic polymerization conditions investigated, and the ceiling temperature of polymerization determined.

Copolymerization of bromodichloroacetaldehyde was accomplished with chloral and with phenyl isocyanate and primarily with anionic initiators.

The objective of this work was to synthesize the previously unknown dibromochloroacetaldehyde, to characterize and purify it, to study its homo- and copolymerization and the stability of its polymers and to determine the ceiling temperature for polymerization.

EXPERIMENTAL

Materials

Chloroacetaldehyde diethyl acetal, phenyl isocyanate and *n*-butyl isocyanate (Aldrich Chemical

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Co.), were fractionated under reduced pressure before use. Trifluoromethanesulfonic acid (Aldrich Chemical Co.), was used in the condition just as obtained.

Pyridine, acetic anhydride and nitrobenzene (Eastman Kodak Co.), were used from freshly opened bottles. Bromine and aluminum chloride (Fisher Scientific Co.), were used directly. Aluminum chloride was handled in a dry box filled with dry nitrogen.

Chloral (Montrose Chemical Co.), was used after careful fractionation.¹¹

Lithium tertiary butoxide (LTB) (Ventron Alfa Products) was sublimed at 0.1 mm and 150°C prior to its use. Toluene (Mallinckrodt Chemical Co.), was dried over sodium wire.

Triphenylphosphine (Ph_3P) (Mallinckrodt Chemical Co.), was used without further purification. Antimony pentachloride (Fisher Scientific Co.), was distilled at 75°C and 20 mm through a 30-cm Vigreux column.

Measurements

Infrared spectra were obtained on a Perkin-Elmer 727 infrared spectrometer at a "normal" scan rate or on a Beckman infrared spectrometer at a slow scan rate. Proton magnetic resonance spectra (PMR) were obtained on a Hitachi Perkin-Elmer R-24 spectrometer or on a 90-MHz Perkin-Elmer R-32 spectrometer.

DSC measurements were made under nitrogen on a Perkin-Elmer DSC-1B instrument at a scan rate of 20°C/min.

TGA data were obtained on a Perkin-Elmer TGS-1 thermobalance under nitrogen at a heating rate of 20°C/min; the heating rate was regulated by a Perkin-Elmer UU-1 temperature program control. The gas chromatograms were obtained on a Varian Associates Model 920 gas chromatograph on a 2-m column packed with 35-% diisodecyl phthalate on Chromosorb W or on a 1-m Porapak Q column.

Procedures

Synthesis of Dibromochloroacetaldehyde from Chloroacetaldehyde Diethyl Acetal. A 500 ml 3-neck round-bottom flask was equipped with a pressure-equalizing addition funnel, a nitrogen inlet tube, and a reflux condenser. The flask was purged with dry nitrogen for 10 min and then chloroacetaldehyde diethyl acetal (100 ml,

0.67 mol) was added and the assembly was placed into an oil bath at 100°C. Bromine (85 ml, 1.5 mol) was added dropwise while stirring at a rate that just allowed the red color in the flask to vanish. This addition was complete after 8 hr. The addition funnel was replaced with a ground glass stopper and the reflux condenser was removed and replaced with an adapter for distillation. One end of the condenser was joined to an adapter and its other end to a 100-ml round-bottom receiving flask with a vacuum adapter, which was cooled in a dry ice-isopropanol bath. Volatile products (EtBr 95%, EtOH 5%) were collected at a pressure of 15 mm and 40°C. The receiving flask was replaced with a 200-ml round-bottom flask. Phosphorus pentoxide (5.0 g) was added and the entire apparatus was purged with dry nitrogen for 5 min. The flow of nitrogen was lessened and the flask was then heated with an oil bath at 150°C while cooling the receiving flask in a dry ice-isopropanol bath. After ethanol was collected up to a vapor temperature of 100°C, the vapor temperature rose rapidly. Distillation was continued using a dry 200-ml flask and the pressure (controlled by a manostat) was reduced to 100 mm; the second fraction was impure dibromochloroacetaldehyde.

The receiver was then removed from the cold bath and was allowed to warm to room temperature under a blanket of nitrogen. The aldehyde was then redistilled from the P_2O_5 at 100°C/30 mm under nitrogen. The first 3 ml were collected and the receiver was replaced with one that had been cooled in a dry ice-isopropanol bath at -78°C. About 30 ml of colorless liquid were collected as a middle cut. The aldehyde was redistilled from phosphorus pentoxide (3.0 g) under nitrogen at 30-mm pressure through a 6-inch Vigreux column. The first 4 ml of dibromochloroacetaldehyde were discarded and then about 25 ml of pure aldehyde were collected as a colorless liquid (25.2 ml, 38-% yield), boiling at 147–148°C (760 mm). The infrared spectrum (neat) showed major absorptions at 1750 cm^{-1} (vs) ($\text{C}=\text{O}$ stretch), 3500 cm^{-1} (w) (overtone); 2850 cm^{-1} (m), 650 cm^{-1} (s). The carbonyl stretch in hexane was 1758 cm^{-1} and in the gas phase 1768 cm^{-1} .

The PMR spectrum showed one peak at $\delta =$

8.7 ppm. *Anal.* Calcd for C_2HBr_2ClO : C, 10.17; H, 0.42; Cl, 15.01; Br, 67.66. Found: C, 10.24, H, 0.60; Cl, 14.59; Br, 67.39.

Polymerization of DBCA with Pyridine. A 12-inch long (10-mm I.D.) Pyrex tube was sealed at one end, washed, dried and flamed out. Freshly distilled DBCA (2 ml, 20 mmol) was added followed by pyridine (0.4 ml of a 1-molar solution in toluene, 0.4 mmol or 2 mol%); the tube was inserted in a liquid nitrogen bath, sealed at 0.1-mm pressure, thoroughly cooled to room temperature and then placed in a dry ice—chlorobenzene slush bath at -45°C for 72 hr. A self-supporting gel formed after 10 min. The polymerization was essentially complete after 1 hr but was allowed to proceed for 72 hr.

The tube was warmed to room temperature and was then cut into sections about 2.5-cm long with a glass file. The sections of tubing containing the polymer were soaked in an acetic anhydride (10 ml)—acetone (10 ml) mixture for 24 hr at -10°C . The polymer was isolated, washed with acetone (50 ml), soaked for 24 hr in dichloromethane (20 ml) at -10°C , filtered and dried. Poly-DBCA (2.37 g, 52-% yield) was obtained as colorless translucent chips. The infrared spectrum (KBr) showed absorptions at 2940 cm^{-1} (C—H stretching), 1370 cm^{-1} , 1338 cm^{-1} , and 1310 cm^{-1} (C—H bending), 1105 cm^{-1} , 1065 cm^{-1} , 1040 cm^{-1} , 950 cm^{-1} (vs), (C—O stretching), 802 cm^{-1} (C—C stretching or C—Cl stretching), 780 cm^{-1} , and 726 cm^{-1} (C—halogen stretching). *Anal.* Calcd for C_2HBr_2ClO : C, 10.17, H, 0.42; Cl, 15.01; Br, 67.66. Found: C, 10.38, H, 0.69; Cl, 15.00; Br, 67.28.

*Stabilization of Poly-DBCA by Treatment with PCl_5 .*¹² To a dry 125-ml flask being slowly purged with dry nitrogen were added poly-DBCA (1.0 g) and PCl_5 (15 ml of a 1-M solution in CCl_4). A reflux condenser was connected to the flask and the flask was heated to reflux with an oil bath for 2 hr. The flask was allowed to cool; the product was collected on a sintered funnel, rinsed with CCl_4 (50 ml), and dried under nitrogen (0.89 g, 89-% yield). The infrared spectrum of this product could be superimposed on spectra for unstabilized poly-DBA. A TGA of this product indicated that the thermal stability was increased substantially by this treatment.

Copolymerization of DBCA and Chloral with $AlCl_3$. A 12-inch long (10-mm I.D.) Pyrex tube was sealed at one end and flamed out. Freshly distilled chloral (2 ml, 20 mmol), DBCA (2 ml, 20 mmol) and 0.1 mg of $AlCl_3$ in nitrobenzene (1-M solution of $AlCl_3$ in nitrobenzene, 0.1 mmol, 0.5 mol%) were added with dry syringes. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm, shaken at room temperature and then placed in a dry ice—chlorobenzene slush bath at -45°C for 24 hr; a gel formed after 1 hr. The tube was warmed to room temperature, cut into several sections, soaked in acetone (30 ml) for 24 hr and dried. Chloral—DBCA copolymer was obtained as translucent, tough cylinders in the shape of the polymerization tube (4.93 g, 66-% yield). The infrared spectrum showed absorptions at 2940 cm^{-1} (m) (C—H stretching); 1370 cm^{-1} (w); 1344 cm^{-1} (m), 1320 cm^{-1} (s) (C—H bending); 1105 cm^{-1} (vs, b) 947 cm^{-1} (vs, b) (C—O stretching); $828\text{--}805\text{ cm}^{-1}$ (s, b), 800 cm^{-1} (s), (C—Cl stretching); 787 cm^{-1} (m); 750 cm^{-1} (s, b), 672 cm^{-1} (m) (C—Br stretching).

Copolymerization of DBCA and Phenyl Isocyanate (10-% Isocyanate in Feed). A 12-inch long (10-mm I.D.) Pyrex tube was sealed on one end. Freshly distilled DBCA (2.0 ml, 20 mmol) and phenyl isocyanate (0.2 ml, 2 mmol, 10 mol%) were added with a dry syringe, the tube was then shaken briefly and pyridine (0.4 ml of a 1-M solution in toluene, 0.4 mmol, 2 mol%) was added carefully. The tube was inserted in a liquid nitrogen bath, sealed at 0.1-mm pressure and shaken at room temperature to mix the reactants thoroughly. It was then placed in a dry ice—acetone bath at -78°C , and allowed to remain undisturbed 72 hr. After warming to room temperature, the polymerization tube was cut into several sections, soaked in acetone (25 ml) for 8 hr and dried. DBCA—phenyl isocyanate copolymer was obtained as small white granules (2.51 g, 54-% yield). An infrared spectrum (KBr) showed absorptions at 2950 cm^{-1} (m), 2885 cm^{-1} (w) (C—H stretching); 1745 cm^{-1} (vs) (C=O stretching, urethane); 1601 cm^{-1} (m), 1550 cm^{-1} (w), 1528 cm^{-1} (w), 1497 cm^{-1} (m), 1430 cm^{-1} (w) (aromatic); 1373 cm^{-1} (w), 1355 cm^{-1} (m), 1318 cm^{-1} (s) (C—H bending, acetal carbon); 1109 cm^{-1} (vs), 1068 cm^{-1} (vs), 1050 cm^{-1} (vs), 950

cm^{-1} (vs) (C—O stretching); 810 cm^{-1} (s), 789 cm^{-1} (s), 752 cm^{-1} (s), 747 cm^{-1} (s), 705 cm^{-1} (w). *Anal.* for N: 0.79% (12% of isocyanate in the copolymer).

Vacuum Degradation of Poly-DBCA Obtained from DBCA and Pyridine. A 16-inch long Pyrex tube (12-mm I.D.) was bent into a U shape and one end was sealed. DBCA powder (1.0 g) was placed in the closed end of the U-tube, and the tube was sealed at 0.1-mm pressure. The empty end of the U-tube was placed in a liquid nitrogen bath and the other end, containing the polymer, in a silicone-oil bath at 180°C . After 30 min a colorless solid had collected in the cold end of the U-tube. No residue was detected in the hot end in the oil bath. The tube was warmed to room temperature, the colorless solid was melted and the tube was cut open. A sample of the colorless liquid was drawn out with a $10\text{-}\mu\text{l}$ syringe and immediately injected into a gas chromatograph. The remainder of the colorless liquid was poured into a tared screw-cap bottle (0.97 g or 97%). The analysis by gas chromatography (35-% diisodecyl phthalate on Chromosorb W) indicated that the colorless liquid was 98-% dibromochloroacetaldehyde. An infrared spectrum was nearly superimposable on a spectrum of pure DBCA.

Polymerization Rate of DBCA at -78°C by NMR. NMR tubes and a 15-mm test tube were prepared for the experiment according to a consistent cleaning procedure¹⁰ and finally dried at 120°C for 72 hr. The test tube was clamped in a vertical position and the nitrogen flow was started through a syringe needle. The tube was purged for 5 min, heated with an air gun, allowed to cool to room temperature while a flow of nitrogen was maintained, and lowered into an oil bath maintained at 25°C . Freshly distilled DBCA (3 ml, 30 mmol) was added with a dry syringe and the temperature inside the test tube was allowed to reach 50°C . Pyridine (0.6 ml of a 1-M solution in toluene, 2 mol%, 0.6 mmol) was added and the tube was agitated. The NMR tube was removed from the oven, clamped in a vertical position, purged with dry nitrogen for 3 min, and placed in the 50°C oil bath to a depth of 7.5 cm. The initiated solution was then transferred from the test tube to

the NMR tube so that 6 cm of the NMR tube were filled with initiated monomer. The syringe needle connected to the nitrogen source was removed and very quickly the tube was closed with a pressure cap and the top of the NMR tube was wrapped with Parafilm. The NMR tube was removed from the 50°C bath, wiped off, and the zero time aldehyde proton ($\delta=8.9$) intensity was recorded. (The methyl group resonances of the toluene was used as an internal standard.) It was then placed in a -78°C bath along with test tube which contained the remaining initiated monomer which was used as a control sample. The NMR tube was removed from the -78°C bath after periods of 2, 5, 10, 20, 40, 60, 120, and 360 min and the aldehyde peak intensity was determined by integration. An infrared spectrum of the control sample after extraction of unreacted DBCA could be superimposed on previous spectra for the polymer.

Ceiling-Temperature Determination for DBCA in Toluene with Pyridine. Four polymerization tubes were washed in 1-N HCl, rinsed with distilled water four times and dried for 72 hr at 120°C . One test tube was removed from the oven. A syringe needle connected to a source of dry nitrogen was inserted. The tube was purged with nitrogen and then freshly distilled DBCA (3.0 ml, 30 mmol) was added while the flow of dry nitrogen was maintained. The lower half of the tube was cooled in liquid nitrogen. Toluene (2.7 ml) and pyridine (0.3 ml of a 1-M solution in toluene, 0.3 mmol, 1 mol%) were added; the tube was sealed and placed in an isopropanol bath at 50°C . The bath was cooled at a rate of $2^\circ\text{C}/\text{min}$ by a copper coil with a regulated flow of cold nitrogen. The intensity of light transmitted through the sample was recorded. The flow of cold gas continued until the temperature reached -60°C . The tube was removed from the cold bath and a self-supporting polymer gel was observed in the sealed tube. A cloud point of -10°C was recorded as the polymerization threshold temperature at a 8.33-molar monomer concentration. In separate experiments cloud points of -12°C for a 6.67-molar solution, -21°C for 5.0-molar solution and -27.5°C for a 2.5-molar solution were recorded respectively. Infrared

spectra of the tube contents in each experiment indicated that poly-DBCA had been formed.

RESULTS AND DISCUSSION

Dibromochloroacetaldehyde (DBCA) was obtained in a 50-% overall yield from chloroacetaldehyde diethyl acetal and bromine. It was purified, characterized, homopolymerized, copolymerized, and the characteristics of the polymers were determined.

Bromination of chloroacetaldehyde diethyl acetal had to be carried out at 100°C in a rapidly stirred solution in such a way that the bromine would almost immediately be discharged as it was added. If the conditions were not carried out exactly, side reactions occurred (eq 1).

The reaction product of the bromination is actually DBCA monoethyl acetal which was thermally decomposed at 150°C to give DBCA and ethanol. DBCA monoethyl acetal was isolated and purified by fractional distillation at reduced pressure at a temperature well below the decomposition point. The PMR spectrum and elemental analyses confirmed this structure. The decomposition of the hemiacetal was more conveniently carried out thermally without

the use of sulfuric acid which is commonly needed for the decomposition of acetals. The monoethyl acetal at the end of step one was of good purity in the reaction flask and DBCA was obtained in good yield. DBCA was finally purified by distillation through a spinning band column at 100 mm and the pure product was analyzed by GC. At a column temperature of 110°C, DBCA had a retention time of 15 min and 42 sec on the column described in the Experimental Part and the total impurities level was less than 0.2%.

DBCA was analyzed for all elements although the analyses for the halogens were difficult because of the interference of the presence of a high percentage of bromine with the analysis for chlorine. Derivatives of this aldehyde, such as the 2,4-dinitrophenylhydrazone and the oxime could not be prepared because they were apparently too unstable.

DBCA boiled at 148°C and 760 mm and had a density at 25°C of 2.27 g/cm³. The PMR spectrum showed a singlet at 8.70 ppm. In a comparison, chloral, under the same conditions, showed a singlet at 8.95 ppm. The ¹³C NMR spectrum shows a chemical shift of 176.3 ppm for a carbonyl carbon and 63.7 ppm for the trihalomethyl carbon, downfield from TMS. The infrared spectrum of DBCA is shown in Figure 1. It showed characteristic aldehyde carbonyl stretching assignments at 1768 cm⁻¹ in the gas phase, 1758 cm⁻¹ in *n*-hexane and 1750 cm⁻¹ neat. The comparative values for chloral are 1776 cm⁻¹, 1768 cm⁻¹, and 1760 cm⁻¹.

Figure 1. IR spectrum of DBCA (neat).

hyde, as its hydrolysis product. Dibromoacetaldehyde was not detected. The salt I was isolated and the structure confirmed by elemental analysis. This bromide salt was not the initiator for the DBCA polymerization. The chloral—triphenylphosphine (1:1) salt is a phosphonium chloride and neither did it nor did the bromal—triphenylphosphine (1:1) salt initiate DBCA polymerization. However, cesium chloride was a good initiator though cesium bromide was not under the reaction conditions. Thus the chloride ion was a good initiator for DBCA but not the bromide ion.

The yield and reaction rate of the polymerization of DBCA in the presence of acids, or generally cationic initiators, were markedly lower than in the polymerization of chloral and BDCA. Particularly surprising were the low yields of polymers obtained from sulfuric acid and

trifluoromethanesulfonic acid even after long reaction times; the yields of poly-DBCA were the same regardless of whether the polymerization was carried out at -20°C or -78°C , namely 3%. The polymerizations of DBCA initiated with antimony pentachloride and aluminum chloride gave higher yields; they were nearly the same as those of the anionic polymerizations.

Poly-DBCA shows an infrared spectrum which is fairly similar to that of other haloacetaldehyde polymers, particularly polychloral. A structure of a substituted polyacetal is indicated. Major absorptions of the IR spectra are shown in Table II and the spectrum is displayed in Figure 3. Only in the case of cationically prepared polymers were any OH end groups noticeable. Strong absorptions were in the region of the ether oxygen and carbon—halogen bonds

Figure 2. IR spectrum of dibromochloroethyl dibromochloroacetate (KBr pellet).

Figure 3. IR spectrum (KBr pellet) of poly-DBCA.

Table II. Major absorptions in infrared spectra of homopolymers of DBCA and chloral in cm^{-1} ($\pm 2 \text{ cm}^{-1}$)

Poly-DBCA	Polychloral
1372	1386
1348	1360
1320	1325
1115	1122
1075	1085
1040	1075
943	975

Table III. Wide angle X-ray studies. Interplanar spacings of poly-DBCA (in Å)

Poly-DBCA		Polychloral	
Spacing	Approx. intensity	Spacing	Approx. intensity
8.90	100	8.70	100
5.10	90	5.00	90
3.40	60	3.30	80
2.80	50	2.73	50
2.30	40	2.40	40

in the region of 1150 and 600 cm^{-1} . The carbon—hydrogen stretching frequency in all cases was near 2940 cm^{-1} .

Samples of poly-DBCA gave Debye—Scherrer diagram which indicated it to be a semicrystalline polymer with interplanar spacings similar to that for polychloral; the prominent lines are shown in Table III. A slight increase in the spacings of poly-DBCA as compared to that of polychloral and poly-BDCA indicates the increasing bulk of the side chain, and consequently an increase of the interchain distances.

Poly-DBCA prepared with pyridine as the initiator was degraded in a sealed evacuated tube and the volatile materials collected. Degradation occurred at 180°C to give a 98% yield of a liquid which proved to be 98% pure DBCA. When the degradation of various samples of poly-DBCA was carried out in a TGA apparatus and the thermal degradation spectrum recorded, three regions of stability of these DBCA polymers were obtained, depending upon the initiators used for the polymerization as shown in Table IV. Polymers which were very unstable were usually prepared by anionic

Table IV. DTG maxima of degradation rate of DBCA homo- and DBCA—chloral copolymers^a

Initiator for polymer preparation	Maximum temp, $^\circ\text{C}$	
Homopolymers		
Pyridine	120	
Pyridine, PCl_5 treated	255	280
H_2SO_4	238	280
$\text{CF}_3\text{SO}_3\text{H}$	249	
SbCl_5		300
Copolymers		
Pyridine	125	
$\text{CF}_3\text{SO}_3\text{H}$	250	

^a Heating rate $20^\circ\text{C}/\text{min}$, in nitrogen

initiators such as pyridine and showed a maximum rate of degradation at 120°C . This instability is apparently caused by one unstable end group in the polymer which is believed to be an occluded active alkoxide end. Cationically prepared poly-DBCA was much more stable and usually showed two maxima, one around 250°C and one near 300°C .

The polymer prepared with pyridine as the initiator, which had a maximum of only 120°C , could be stabilized by treatment with PCl_5 . Maxima of degradation rates were found at 255 and 280°C , for the stabilized polymer. During this treatment the bromine in the polymer had not been replaced because the IR spectra of these polymers were superimposable on those taken before PCl_5 treatment. Also, the elemental analysis indicated no halogen exchange.

Copolymerizations

DBCA could be copolymerized with other haloaldehydes, primarily chloral (Table V) or with phenyl isocyanate (Table VI).

Table V shows the results of some copolymerizations of DBCA with chloral in the presence of pyridine and $\text{CF}_3\text{SO}_3\text{H}$. It was shown that

Table V. Preparation of DBCA—chloral copolymers^a

Chloral in feed, %	Polymerization initiator	Polymerization bath temperature, °C	Polymerization time, hr	Conversion, %	DBCA in product, %
75	Pyridine	-45	3	57	3
75	Pyridine	-45	3	63	10
25	Pyridine	-45	3	50	28
75 ^b	Pyridine	-78	3	62	5
50 ^b	Pyridine	-78	3	55	12
25 ^b	Pyridine	-78	3	27	28
75	CF ₃ SO ₃ H	-10	320	44	11
50	CF ₃ SO ₃ H	-10	320	41	27
25	CF ₃ SO ₃ H	-10	320	36	40

^a Initiator concentration (2 mol%)^b 20-% toluene as diluent.Table VI. Copolymerization of DBCA with isocyanates^a

Type	Comonomer		Conversion to polymer, %	Isocyanate ^b content in product, %
	Concentration, mol%			
PhNCO	50		91	38
	20		46	27
	10		54	13
	5		52	8
<i>n</i> -BuNCO	50		23	10

^a Initiator, pyridine (2.5 mol%); polymerization bath temperature, -78°C.^b Determined by elemental nitrogen analysis.

the chloral was more readily incorporated than DBCA in these copolymers regardless of the polymerization temperature or the initiator used (Figure 4).

An approximately equal maximum degradation rate temperature was observed for the homopolymer of DBCA and DBCA—chloral copolymers (Table IV). This similarity was no surprise because the degradation was determined by the stability of the end group and not by the slight changes in the side chain of the copolymer. Phenyl isocyanate could be very readily incorporated by copolymerization into a DBCA polymer chain and the monomer content was almost identical with the feed ratio of the monomers (Table VI). At higher phenyl isocyanate feed concentrations the conversion to the polymer, however, decreased somewhat. Butyl isocyanate was not as readily incorporated into the copolymer and only a 10-% comonomer content in the polymer was found at a feed ratio of 1 : 1. Figure 5 shows the infrared spectrum of a copolymer of DBCA and phenyl isocyanate. This particular sample had 13-% phenyl isocyanate

Figure 4. IR spectrum (KBr pellet) of copolymer (about 1 : 2) of DBCA and chloral.

Figure 5. IR spectrum (KBr pellet) of copolymer of DBCA and PhNCO (13% PhNCO content in polymer).

in the copolymer and the IR spectrum shows clearly the carbonyl band of the urethane linkage in the polymer at 1740 cm^{-1} .

The thermal degradation of phenyl isocyanate—DBCA copolymers in nitrogen is similar to that of the chloral—phenyl isocyanate copolymers. Two maximum rates of degradation occurred at 220°C and 250°C .

By DSC poly-DBCA and DBCA copolymers showed no endotherms from -80°C to the degradation points indicating that no glass transition temperatures of the homopolymers or the copolymers with high concentration of DBCA could be observed.

Chloral—DBCA copolymers could also be vacuum degraded in a sealed tube to the monomers which were then analyzed by GC for the copolymer composition. The data in Table V describing the composition of the copolymers were obtained by vacuum degradation to the monomers because the copolymers could not be analyzed very well by elemental analysis owing to the difficulties in the halogen analysis.

Because of the insolubility of the polymers, molecular weights could not be determined directly by solution techniques; it has been estimated that both pyridine and SbCl_5 initiated DBCA polymers have DP's in excess of 100. This estimate was obtained by treatment of the SbCl_5 initiated polymer with acetic anhydride

and end group analysis for an acetyl carbonyl by IR spectroscopy. This constitutes a maximum value because it is well-known that the acetylation reaction is not quantitative, even under vigorous conditions. The DP of the pyridine initiated polymer was estimated by *in situ* chain termination with an acid chloride as previously described.¹³

The rate of polymerization of DBCA was determined by PMR spectroscopy by observing the disappearance of the aldehyde monomer proton peak by the method used for chloral in ref 14. The polymerization mixture when taken below the threshold temperature formed a homogeneous gel in which the acetalic protons of the polymer were unobservable due to excessive line broadening, but the monomer proton peak showed very little broadening as observed in the system chloral—polychloral in ref 15. Hence the decrease of the aldehyde monomer peak integral served as a quantitative measurement of the rate of the polymerization.

In one particular case the rate study was carried out at -60°C . In general, it is desirable, in the case of perhaloacetaldehyde polymerizations, to carry out a rate study at about 20°C below the ceiling temperature of polymerization for consistency in thermodynamics. With pyridine as the initiator at a 2-mol% level, it was shown that the reaction levels off at 75% after

about 1.5 hr; after 15 min, about 50% of the polymerization was completed. The rate of chloral polymerization is much faster at 20°C below the ceiling temperature. At 0°C, 50% of the polymerization is completed in less than 2 min. At -78°C, in bulk, the polymerization is much faster and an ultimate conversion of 85% is reached after about 1 hr; a 50% conversion is achieved in about 10 min for DBCA (Figure 6).

The ceiling temperature of DBCA polymerization was estimated visually but a more accurate determination was carried out by an instrumental method; the polymer was insoluble in the monomer form and the point of the first appearance of opacity was detected passing a light beam through the solution and measuring the intensity of transmitted light (Figure 7A). The threshold temperature was determined at monomer concentrations of 8.33 mol, 6.67 mol, 5.0 mol, and 2.5 mol in toluene. Extrapolation of the data to a one-molar solution gave a ceiling temperature for a one-molar solution of -40°C (Figure 7B).

Polymerization of DBCA gave homopolymer and copolymers similar to other perhaloacetaldehyde polymers. DBCA was much less reactive

Figure 6. NMR study of DBCA polymerization rate: bath temperature, A, -78°C; B, -60°C; initiator, pyridine (2 mol%); monomer concentration, 8.3 M in toluene.

Figure 7A. DBCA polymerization threshold temperature determination: solvent, toluene; initiator, pyridine (3 mol%); monomer concentration, 5 mol.

Figure 7B. Graphic ceiling temperature determination of DBCA polymerization.

with cationic initiators than BDCA; it was also less reactive under anionic conditions than BDCA or chloral. This lower reactivity reflected clearly the lower ceiling temperature of DBCA polymerization. Also in copolymerizations, with chloral, chloral is more readily incorporated into the copolymers, especially at higher temperatures.

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