Haloaldehyde polymers: 11. Polybromal

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Bromal has been purified by stirring it with SbF_3 at elevated temperatures. This treatment removed small amounts of impurities which had prevented the polymerization of bromal previously. Monomer grade bromal polymerized readily with selected anionic and cationic initiators at low temperatures. While the chemical structure of the polymer as a polyacetal was similar to that of other perhaloaldehyde polymers, the interplanar spacings of polybromal as determined by wide-angle X-ray studies indicated a significant deviation of the crystal structure from that of other perhaloacetaldehyde polymers, for example, polychloral or even polydibromochloroacetaldehyde. Polybromal degraded thermally to give a quantitative yield of monomer and had a 1 M ceiling temperature of $-75°C$. Copolymerization attempts of bromal with chloral under anionic conditions gave polymers incorporating only trace amounts of bromal, but bromal copolymers with phenyl isocyanate of various compositions, even of a 1:1 composition, could be readily prepared.

INTRODUCTION

Polymerization of aldehydes with bulky side groups has been shown to give stereoregular polymers exclusively without the necessity of stereospecific initiators, because the side group bulkiness permits the addition of each monomer unit in only one configuration. A good example for this kind of stereocontrol of polymerization is the polymerization of chloral which forms isotactic polymer exclusively, even with chloride as the initiating anion[1,2]. Aldehyde polymerization, particularly haloacetaldehyde polymerization, is a very good example for this study because perhaloacetaldehydes[3] with various side group sizes are either known or are expected to be easily synthesizable[4-8]. In addition, the anionic or cationic polymerization of these aldehydes should give no special problems, provided the monomers do not contain detrimental impurities which prevent polymerization. Comparison of aldehyde polymerization (e.g. chloral) with the polymerization of the corresponding olefins with perhalomethyl side groups (e.g. 3,3,3-trichloropropene), is not possible because these olefins, although known, do not polymerize readily regardless of the mechanism by which this was attempted.

The recent success in the polymerization of bromodichloroacetaldehyde[9] and dibromochloroacetaldehyde[10,11] to crystalline, presumably isotactic polymers and their copolymerization with chloral or phenyl isocyanate, made the investigation of the polymerization of bromal particularly desirable. Not only were previous polymerization attempts[12] which included the use of lithium tertiary butoxide and triphenylphosphine as initiators at $-78°C$ for extended periods of time unsuccessful, but as a consequence of this it was believed that a side group of the size of the tribromomethyl group was too large to allow a polyacetal structure with a tribromomethyl group attached to every other atom of the polymer backbone to be formed, and space-filling models indicated that polybromal would be a very crowded polymer chain.

It was the purpose of this work to renew the efforts of polymerizing bromal with particular attention to the purity of the monomer and to develop a simple method to prepare polymerization grade bromal. The polymerization and copolymerization of bromal with anionic and cationic initiators was the ultimate objective.

EXPERIMENTAL

Materials

Bromal (Aldrich Chemical Co.), was purified according to a special procedure (v.i.).

Phenyl isocyanate, p-methylphenyl isocyanate and n-butyl isocyanate (Aldrich Chemical Co.) were carefully fractionated under reduced pressure before use.

Acetic anhydride, pyridine and quinoline (Eastman Kodak Co.) were used from freshly opened bottles or, in the case of quinoline, simply distilled to remove the colour.

Antimony pentachloride (Fisher Scientific Co.), was distilled at $75°C$ and 20 mm before use.

Chloral (Montrose Chemical Co.) was used after careful distillation as described previously[13].

Lithium tertiary butoxide (LTB) (Ventron Alfa Products) was sublimed at $150°C$ and 0.1 mm prior to its use.

Triphenylphosphine (Ph_3P) (Aldrich Chemical Co.), toluene (Mallinckrodt Chemical Co.), and antimony trifluoride (Allied Chemical Co.) were used as received.

Trifluoromethanesulphonic acid (Aldrich Chemical Co.) was used from a freshly opened bottle.

Measurements:

The infra-red spectra were recorded on a Perkin–Elmer 727 Infra-red Spectrometer at a 'normal' scan rate or on a Beckman Infrared Spectrometer at a slow scan rate. The potassium bromide and thallous bromide used for the preparation of the pellets were dried at $180°C$ at 0.1 mmHg over P_2O_5.

Proton magnetic resonance (p.m.r.) spectra were obtained on a 60 MHz Hitachi Perkin–Elmer R24 Spectrometer or on a 90 MHz Perkin–Elmer R32 Spectrometer.

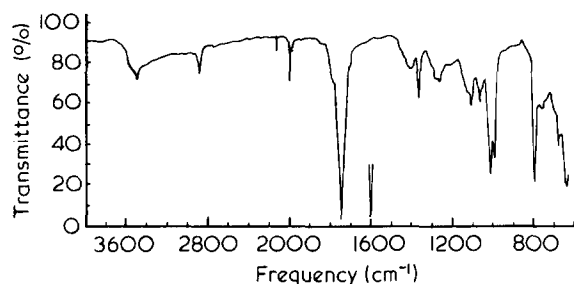Thermogravimetric (t.g.a.) data were recorded as thermal

Figure 1 I.r. spectrum of bromal (neat)

degradation spectra (d.t.g.) on a Perkin–Elmer TGS-1 Thermobalance under nitrogen at a heating rate of 20°C/ min.

The purity of the monomers and some solvents was monitored on a Varian Associates Model 920 Gas Chromatograph on a two metre column packed with 35% diisodecyl phthalate on Chromosorb W or on a one meter Porapak Q column.

Procedures

Purification of bromal. A three neck 250 ml round bottom flask was equipped with a nitrogen inlet tube and a reflux condenser connected to a bubbler tube and was then purged with nitrogen. Antimony trifluoride (5.0 g), bromal (50 ml) and a 3/4 in. Teflon covered stirring bar were added through the third neck and the flask was heated in an oil bath to 100°C for 2h with stirring. The flask was allowed to cool to room temperature; the bromal was then filtered under nitrogen pressure through a medium fritted funnel into a 250 ml round bottom flask which contained 3.0 g of of powdered P_2O_5 and was distilled at 50 mmHg under nitrogen bleed through a 20 cm Vigreux column. The first 5 ml of distillate were of red colour and were discarded. The subsequent colourless distillate was collected until 10 ml of liquid remained in the distillation flask. The bromal collected contained less than 0.1% impurities by volume according to analysis by gas chromatography (36% diisodecyl phthalate on Chromosorb W at 130°C), and was used immediately for the polymerization experiments. The infra-red spectrum of pure bromal showed a carbonyl absorption at 1742 cm^{-1} (neat), 1754 cm^{-1} (in hexane) or 1765 cm^{-1} (gas phase) (*Figure 1*).

Polymerization of bromal with pyridine. A 30 cm long (10 mm i.d.) Pyrex tube was sealed at one end, washed and flamed out. Freshly distilled bromal (4.0 ml, 39 mmol) and pyridine (0.8 ml of a 1 M solution in toluene; 0.8 mmol, 2 mol %) were then added. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mmHg pressure and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a dry ice/ acetone bath at –78°C for 72 h. The resultant plug of polymer was then cut into 2.5 cm sections; they were transferred to an Erlenmeyer flask containing acetic anhydride (40 ml) and acetone (40 ml), and stored in the refrigerator for 8 h at –10°C. The polymer was isolated, soaked in acetone for 16 h, collected on a fritted funnel and dried. Polybromal was obtained as small colourless translucent chunks (3.89 g, 47% yield). This experiment was repeated using 1.0, 2.5 and 5.0 mol % pyridine. The yields obtained were 46, 44 and 52%. In two experiments the initiator concentration was 0.5 mol % but no polymerization occurred.

An infra-red spectrum of polybromal showed absorptions at 2938 cm^{-1} (m) (C–H stretch); 1358 cm^{-1} (w); 1339 cm^{-1} (m), 1300 cm^{-1} (s) (C–H bending); 1048 cm^{-1} (vs), 1021 cm^{-1} (s), 910 cm^{-1} (vs), 1086 cm^{-1} (vs) (C–O stretching); 772 cm^{-1} (s), 740 cm^{-1} (s), 712 cm^{-1} (vs) (C–Br stretching), 535 cm^{-1} (m). Analysis calculated for C_2HBr_3O: C, 8.59%; H, 0.36%; Br, 85.37%. Found: C, 8.85%; H, 0.42%, Br, 85.11%.

Stabilization of polybromal by treatment with PCl_5[14].
To a flask which was being slowly purged with dry nitrogen were added polybromal (3.0 g) and PCl_5(60 ml of a 1 M solution in CCl_4). A reflux condenser was connected to the flask; the flask was heated to reflux with an oil bath for 2 h and was allowed to cool. The product was collected on a sintered funnel, rinsed with CCl_4 (50 ml) and dried under nitrogen (2.88 g, 96% yield). The product was washed with methanol (50 ml) and then dried under reduced pressure. The infra-red spectrum of the product could be superimposed on previous polybromal spectra. A d.t.g. analysis of this product indicated that the thermal stability was increased by this treatment.

Polymerization of bromal with LTB. A 30 cm long (10 mm i.d.) Pyrex tube was sealed on one end. Freshly distilled bromal (2.0 ml, 19 mmol), LTB (0.67 ml of a 0.3 M solution in methylcyclohexane; 0.2 mol, 1 mol %) and toluene (0.4 ml) were added with a dry syringe. The tube was inserted in a liquid nitrogen bath. sealed at 0.1 mmHg pressure, and then placed in a bath at –45°C for 10 min. The tube was shaken to mix the reactants thoroughly and was then placed in a dry ice/acetone bath at –78°C for 72 h. This polymerization, like the polymerization of bromal with pyridine, gave a homogeneous gel.

The tube was allowed to warm to room temperature and cut into several pieces. The polymer was then soaked in. acetic anhydride (25 ml) and acetone for 16 h. After isolation and drying, polybromal was obtained as small colourless translucent cylinders (2.07 g, 37% yield). An infra-red spectrum of this product could be superimposed on an infra-red spectrum of the polybromal prepared by pyridine initiation. In a separate experiment, where LTB was used in a 0.3 mol % concentration instead of a 1.0 mol % concentration, polybromal was obtained in only 6% yield. If the initiator and bromal were mixed in the sealed tube at 25°C very little polymer was isolated. At the higher mixing temperature some side reactions had taken place.

Polymerization of bromal with trifluoromethanesulphonic acid. To a polymerization tube was added bromal (8 ml, 78 mmol), dichloromethane (8 ml) and trifluoromethanesulphonic acid (0.1 ml) at 25°C. The stopcock was closed and the polymerization tube was place in a dry ice/acetone bath at –78°C. At the end of two weeks a white solid had collected at the bottom of the tube. The tube was removed from the cold bath and placed in a refrigerator at –20°C for one additional week. n-Hexane (5 ml) was added to the mixture and the solid polymer was collected, washed with cold acetone (30 ml) and dried. Polybromal was obtained as a white powder (0.57 g, 3% yield). The infra-red spectrum could be superimposed on previously described spectra for polybromal.

Solubility tests for bromal homopolymers. In each of 10 dry Erlenmeyer flasks with ground glass joints was placed 1 g of the solvent to be tested. The solvents acetone, dichloromethane, nitrobenzene, dimethyl sulphoxide, tri-

fluoracetic acid, hexafluoroisopropanol, o-chlorophenol, chloroform, and toluene were added successively to each test tube by syringe and the tubes were closed with ground glass stoppers. The flasks were allowed to stand for 72 h at 25°C. The solid materials remaining after 72 h were collected and the p.m.r. spectrum of each filtrate was taken to detect the presence of soluble polymer. The p.m.r. spectra showed solvent peaks, and in some cases small peaks corresponding to the protons in bromal and the hydrate of this aldehyde. These were the only peaks observed. The acetone, toluene, chloroform and dichloromethane filtrates were evaporated and in every case a trace of solid remained which was the hydrate of bromal. The dimethyl sulphoxide, trifluoroacetic acid, hexafluoroisopropanol and nitrobenzene filtrates were concentrated and then removed completely at reduced pressure. No residue remained behind after complete solvent removal.

The solubility tests were repeated employing mixed solvent systems: acetone/dichloromethane/toluene; dimethyl sulphoxide/benzene; nitrobenzene/o-dichlorobenzene. Polychloral and poly(dichlorobromoacetaldehyde) samples were also tested for their solubilities in these solvent combinations for comparison. No soluble material, neither from polychloral nor from polydichlorobromoacetaldehyde could be isolated from the filtrates after the polymers had been exposed for 72 h to these solvent mixtures.

Vacuum degradation of polybromal obtained from Br_3CCHO and pyridine. A 40 cm long Pyrex tube (12 mm i.d.) was bent into a U shape. One end of the U-tube was sealed and powdery polybromal (1.0 g) was placed in the U-tube. The tube was sealed on the other end at 0.1 mmHg pressure. One end of the U-tube was placed in a liquid nitrogen bath and the other end, containing the polymer, was placed in a silicone oil bath maintained at 180°C for 30 min. At the end of this time a colourless solid had collected in the cold end of the U-tube. No residue or char remained in the hot end of the U-tube. The solid was allowed to melt and the tube opened. A sample of the colourless liquid was drawn out with a 10 μl syringe and immediately injected into a gas chromatograph. The remainder of the colourless liquid was poured into a tared screw cap bottle (0.97 g or 97%). The analysis by gas chromatography (36% diisodecyl phthalate on Chromosorb W) indicated that the colourless liquid was bromal of 97% purity. An infra-red spectrum of the colourless liquid was superimposable on bromal i.r. spectra.

Copolymerization of bromal and phenyl isocyanate with pyridine (10% isocyanate in feed). A 30 cm long (10 mm i.d.) Pyrex tube was sealed at one end. Freshly distilled bromal (2 ml, 19 mmol), phenyl isocyanate (0.2 ml, 2 mmol) and pyridine (0.4 ml of 1 M solution in toluene; 0.4 mmol, 2 mol%) were added with dry syringes. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mmHg pressure, and then allowed to come to room temperature. The tube was shaken and was then placed in a dry ice/acetone bath at −78°C for 5 days. After 12 h a gel had formed but the tube was allowed to remain at −78°C to complete the reaction. The tube was allowed to warm to room temperature, opened and a reddish, hard gel which had formed was removed and placed in a 50 ml beaker with acetone (20 ml). The product was collected on a fritted funnel and dried. Bromal/phenyl isocyanate copolymer was obtained as slightly buff-white cylinders (3.11 g, 53% yield). The infra-red spectrum showed absorptions at 3040 cm^{-1} (w) (C−H stretching, aromatic); 2940 cm^{-1} (m) (C−H stretching, acetal); 1730 cm^{-1} (vs)

(C=O stretching, urethane); 1610 cm^{-1} (m), 1601 cm^{-1} (m), 1522 cm^{-1} (w), 1495 cm^{-1} (s), 1490 cm^{-1} (m), 1440 cm^{-1} (w), 1419 cm^{-1} (aromatic, phenyl absorptions); 1370 cm^{-1} (w), 1350 cm^{-1} (m), 1335 cm^{-1} (m) (C−H bending acetal), 1240 cm^{-1} (w), 1198 cm^{-1} (m), 1095 cm^{-1} (vs), 1050 cm^{-1} (vs), 940 cm^{-1} (vs), 805 cm^{-1} (w), 782 cm^{-1} (m), 760 cm^{-1} (s), 721 cm^{-1} (s), 697 cm^{-1} (s). Analysis for N: 0.77%. This corresponds to 9% isocyanate in the copolymer.

Preparation of bromal–phenyl isocyanate 1:1 copolymer. A 30 cm long (12 mm i.d.) Pyrex tube was sealed at one end. Freshly distilled phenyl isocyanate (3.1 ml, 29 mmol) and then freshly distilled bromal (3.0 ml, 29 mmol) were added followed by pyridine (0.6 ml of a 1.0 molar solution in toluene; 0.6 mmol or 3 mol %) which was added carefully with minimal mixing. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mmHg pressure, removed from the cooling bath and allowed to warm to room temperature, shaken thoroughly and then placed immediately in a dry ice/acetone bath at −78°C. After 4 days the tube was removed from the both and was allowed to warm to room temperature. It was opened and a red wax was isolated and placed in acetone (30 ml). The wax completely dissolved and gave a viscous solution. Hexane (75 ml) was added to precipitate the polymer. The product was collected on a fritted filter and dried. The phenyl isocyanate–bromal 1:1 copolymer was obtained as a yellow powder (6.24 g, 74% yield). An infra-red spectrum (KBr) showed absorptions at 3040 cm^{-1} (aromatic C−H stretching), 2930 cm^{-1} (COH stretching, acetal); 1740 cm^{-1} (vs) (carbonyl stretch), 1595 cm^{-1} (m) (monosubstituted phenyl), 1495 cm^{-1} (m) (monosubstituted phenyl), 1372 cm^{-1} (w), 1320 cm^{-1} (s), 1270 cm^{-1} (vs), 1245 cm^{-1} (s), 1100 cm^{-1} (s), 970–1005 cm^{-1} (m, 6), 800 cm^{-1} (w), 750 cm^{-1} (s), 1730 cm^{-1} (s), 680 cm^{-1} (vs). The p.m.r. spectrum (CDCl$_3$) shows a broad peak at 6.5−7.1 (δ − TMS). Analysis for N: 3.61%; calculated for C$_9$H$_6$NO$_2$Br$_3$: N, 3.42%.

Polymerization rate of bromal at −78°C by p.m.r.. A p.m.r. tube and a 150 mm test tube were prepared for the experiment according to a consistent cleaning procedure[9] and finally dried at 120°C for 3 days. 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 and was heated with an air gun. It was allowed to cool to room temperature while a flow of nitrogen was maintained, and was then lowered into an oil bath maintained at 50°C. Freshly distilled bromal (3 ml, 29 mmol) was added with a dry syringe through the serum cap and the temperature inside the test tube was allowed to reach 50°C. Pyridine (0.6 ml of a 1 M solution in toluene, 0.6 mol, 2 mol %) was added with a dry syringe and the tube was agitated until mixing was complete. The p.m.r. tube was removed from the oven, clamped in a vertical position and purged with dry nitrogen and placed in the 25°C oil bath to a depth of 75 mm. The initiated solution was then transferred from the test tube with a dry syringe to the p.m.r. tube so that the p.m.r. tube was filled with initiated monomer to a depth of 60 mm. The syringe needle connected to the nitrogen was removed and very quickly the p.m.r. tube was closed with a pressure cap and the top of the p.m.r. tube was wrapped with Parafilm. The p.m.r. tube was removed from the 25°C bath, wiped off and the zero time aldehyde proton (δ = 8.9) intensity was recorded. The methyl group resonance of the toluene was used as an internal standard. The p.m.r. tube was placed in

a −78°C bath and removed after 2, 5, 10, 20, 40, 60, 120, and 360 min and the aldehyde peak intensity was determined together with the toluene methyl peak. The n.m.r. tube was kept at −78°C for 3 days and a final aldehyde peak intensity was determined to obtain the number for final conversion.

Ceiling temperature determination from bromal in toluene with pyridine. The ceiling temperature was determined by the turbidimetric method described in refs 9, 10 and 11. Four polymerization tubes were washed with 1 N HCl, rinsed with distilled water four times and dried for 3 days at 120°C. One tube was removed from the oven, and a syringe needle connected to a source of dry nitrogen was inserted. The test tube was purged with nitrogen for 10 min and then freshly distilled bromal (3.0 ml, 29 mmol) was added with a dry syringe. The lower half of the test 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 with a dry syringe. The tube was sealed, placed in an isopropyl alcohol bath at 25°C, and agitated. The bath was allowed to cool at 0.25°C/min and cold nitrogen gas was passed through a copper coil in the bath while the bath was stirred rapidly. The intensity of a beam of light passing through the sample tube was recorded. The tube was removed from the cold bath and a self-supporting gel was observed in the tube. The temperature at which the intensity of transmitted light began to decrease sharply was recorded as a threshold temperature of −36°C for a 8.33 molar bromal concentration. In similar experiments the threshold polymerization temperatures for bromal polymerization at other concentrations were measured as −39°C for a 6.67 molar and −49°C for a 5.0 molar bromal solution.

RESULTS AND DISCUSSION

Specially purified bromal could be polymerized with anionic and cationic initiators to insoluble and infusible polybromal. All attempts in the past to polymerize bromal had failed and it was thought that bromal could not be polymerized because of the bulkiness of its tribromomethyl group. Commercial bromal, which has a reddish brown colour, refluxed as a colourless liquid which when condensed in the condenser regained a reddish to pale brown colour. This material is not suitable for polymerization and no polymer has been obtained under several conditions tried, even when various initiators were used in large amounts. It was consequently suspected that one or more impurities were present in the bromal which could not be removed by distillation, even through a spinning band column.

Gas chromatographic analysis of bromal revealed that commercial bromal had a retention time of 16 min and 30 sec at a column temperature of 130°C and contained three impurities which were present at the same levels after spinning band distillation. It was found, however, that two of the impurities could be completely eliminated and the third reduced to less than 0.1% when bromal was treated at 100°C with SbF_3 for 2 h. Subsequent distillation of this purified bromal from P_2O_5 gave polymerization grade material. The middle cut of this distillate was now a colourless liquid which remained colourless (in the absence of oxygen) and was used for our polymerization experiments. According to our preliminary characterizations, one of the impurities, which is believed to be the inhibitor of the bromal polymerization, is tribromoacetyl bromide.

Table 1 Polymerization of Br_3CCHO. Solvent, toluene (20%); polymerization bath temperature, −78°C; polymerization time, 72 h

Initiator (2.5 mol %)	Yield (%)
Pyridine	46
Quinoline	39
Et_3N	48
LTB[a]	16
CF_3SO_3H[b]	3

[a] 0.3 mol %; [b] reaction time 1 month

Bromal boils at 174°C at a pressure of 760 mmHg, but it is normally distilled under reduced pressure. The density of bromal at 25°C is 2.73 g/cm³. The p.m.r. chemical shift for the aldehyde proton of bromal is 8.45 ppm, which is upfield from the aldehyde proton of chloral which is at 8.95 ppm. The chemical shifts observed in the ¹³C spectra showed 176.9 ppm for the carbonyl carbon and 45.5 ppm for the carbon of the tribromomethyl group. The infra-red spectrum of bromal which is recorded in *Figure 1* showed the carbonyl infra-red stretching frequency of 1765 cm⁻¹ in the gas phase, 1754 cm⁻¹ in n-hexane solutions and 1742 cm⁻¹ in the neat monomer. The respective data for the carbonyl stretching frequency of chloral is 1777, 1768 and 1760 cm⁻¹. The absorption peaks in infra-red, p.m.r. and ¹³C n.m.r. reflect the low electron density on the carbonyl carbon and consequently the polarization of the carbonyl double bond which is important for the polymerizability of the monomer.

Polymerization

The polymerization of the purified bromal could be carried out at −78°C with aromatic tertiary amines such as pyridine and quinoline and also with triethylamine. Yields of nearly 50% (after extraction) could be obtained (*Table 1*). The polymerization with LTB was less effective and when LTB at a 1 mol % concentration, was mixed with the bromal at −45°C and the polymerization carried out for 3 days at −78°C a 37% yield was obtained. Under similar conditions at a 0.3 mol % LTB concentration, only a 16% yield was obtained. If the initiator and bromal were mixed at 25°C no polymer could be isolated which indicated that at higher temperatures some side reactions took place which rendered the initiator ineffective. The polymerization with trifluoromethanesulphonic acid as the initiator gave a very small yield of polybromal whose i.r. spectrum, however, was identical with that of anionically prepared polymers (equation 1):

$$CBr_3CHO \xrightarrow[R^+]{R^-} +\!\!\begin{array}{c} H \\ | \\ C \\ | \\ CBr_3 \end{array}\!\!-O\!\!\xrightarrow{}_n \qquad (1)$$
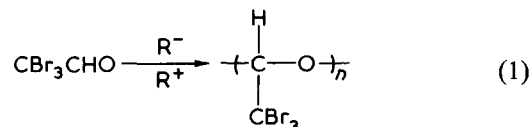
The polymerization of bromal was fairly delicate and had to be carried out under very accurately controlled conditions with purified materials and is not easily accomplished. It seemed that a minimum amount of initiator (pyridine) concentration was always required for a successful polymerization. Some solvent must also be present; if the diluent was not present, bromal crystallized at a temperature which was near or above its polymerization threshold temperature; also if methylcyclohexane or n-hexane was used as diluent, bromal crystallized out of solution and did not polymerize.

Table 2 Major absorptions in the i.r. spectra of polybromal and polychloral (cm⁻¹) (±2 cm⁻¹)

Polybromal	Polychloral
1382	1386
1355	1360
1322	1325
1142	1122
1019	1085
985	1075
	975
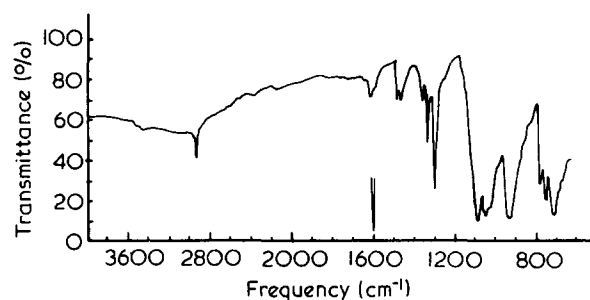
Figure 2 I.r. spectrum of polybromal (KBr pellet)

Very little polymer was obtained when the order of addition of the individual ingredients was reversed. When pyridine was added first before the toluene was added, the initiator could not be dispersed evenly throughout the bromal and a side reaction formed an impurity which prevented polymerization. Finally, it was absolutely necessary to use freshly distilled bromal. Even material that had been stored in a vacuum did not give successful and reproducible polymerizations.

A number of polymerizations of bromal with potential initiators, (compounds that had been known to act as initiators in some other perhaloacetaldehyde polymerizations) were attempted. Ph_3P, when added to the bromal/toluene mixture at room temperature and quickly cooled to $-78°C$, did not give any polymer. It has previously been shown that the reaction of Ph_3P with bromal gave a quaternary phosphonium salt with bromide as the anion (equation 2):

$$Ph_3P + Br_3CCHO \longrightarrow Ph_3\overset{+}{P}—OCH=CBr_2 \quad \underset{Br^-}{} \quad (2)$$
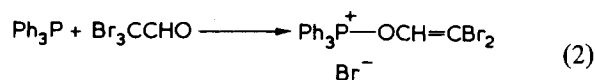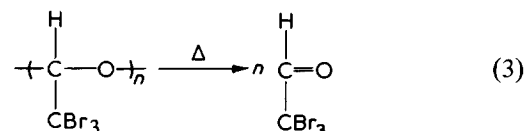
The bromide apparently is not capable of initiation of bromal. This has been found in polymerization attempts of DBCA and BDCA with bromide. No polymerization of bromal was obtained when tri-n-butyl phosphane, triethyl aluminium, PCl_5 and $SbCl_5$ were used as possible initiators.

Polybromal showed an infra-red spectrum which is similar to that of polychloral. The major absorption peaks of the i.r. spectra (KBr pellets) of polybromal are tabulated in *Table 2* and compared with similar absorption peaks of polychloral; a complete spectrum of polybromal is also recorded in *Figure 2*.

Debye—Scherrer diagrams have been taken for polybromal and the patterns have been compared with that of polychloral as shown in *Table 3*. The interplanar spacings of polybromal and polychloral are substantially different. While the polymers of bromodichloroacetaldehyde and di-

bromochloroacetaldehyde are very similar to that of chloral in spacing and intensities, the spacings of polybromal are not too different but have greater interplanar distances. However the intensities of the individual maxima are substantially different (*Table 3*) which indicates that a substantial change in the X-ray pattern and consequently the crystal structure of perhaloacetaldehyde polymers occurs when one compares dibromochloroacetaldehyde and bromal polymers.

Polybromal obtained with pyridine at $-78°C$ was thermally degraded in a sealed and evacuated tube without any char formation. Volatile products, obtained in nearly quantitative yields, were analysed by gas chromatography which showed them to be 97% bromal. The infra-red spectrum of the degradation product is almost superimposable on the i.r. spectrum of an authentic bromal sample.

$$
\begin{array}{ccc}
\underset{\overset{|}{CBr_3}}{\overset{\overset{\displaystyle H}{\overset{|}{}}}{+C—O+_n}} & \xrightarrow{\ \Delta\ } & n\ \underset{\overset{|}{CBr_3}}{\overset{\overset{\displaystyle H}{\overset{|}{}}}{C=O}}
\end{array}
\quad (3)
$$

D.s.c. analysis of a polybromal sample showed that there was no endothermic transition (which might indicate a glass transition temperature) from $-80°C$ to the point where polybromal started to degrade.

Polybromal (polymerized with pyridine as initiator) showed a maximum degradation rate temperature of $146°C$; after stabilization with PCl_5, a double maximum was obtained, one at $230°C$ and one at $283°C$ (*Table 4*). These degradation maxima are almost identical with maximum temperatures of degradation found for the degradation of perhaloacetaldehyde polymers prepared with various chloro- and bromo-substituents in the trihalomethyl group of the polymers. It has been accepted that the end groups obtained from the type of initiator used are primarily responsible for the onset of degradation and maxima temperatures of degradation of the stable chains are above $300°C$. The polyoxymethylene backbone chain substituted with a trihalomethyl group apparently has the same stability regardless of the size and the specific nature of the trihalomethyl group. The maximum degradation temperature for this backbone chain structure is near $400°C$.

Table 3 Wide-angle X-ray studies: interplanar spacings of polybromal and polychloral (Å)

| Polybromal		Polychloral	
Spacing	Approximate intensity	Spacing	Approximate intensity
9.30	100	8.70	100
5.40	90	5.00	90
3.60	100	3.30	60
2.80	30	2.73	50
		2.40	40

Table 4 D.t.g. of maxima degradation rate of polybromals. Heating rate 20°C/min, in nitrogen

Initiator for polymer formation	Degradation temperature maxima (°C)	
Pyridine	146	
Pyridine, PCl_5 treated	230	283

Table 5 Copolymerization of bromal with isocyanates. Initiator, pyridine (2.5 mol %); polymerization bath temperature, −78°C

Comonomer		Conversion to polymer (%)	Percent isocyanate in copolymer[a]
Type	Concentration (%)		
PhNCO	55		50
	50	74	43 (44)
	20	61	18
	10	50	11
	5	34	8
p-CH₃PhNCO	50	42	16
n-BuNCO	50	48	7

[a] determined by elemental nitrogen analysis
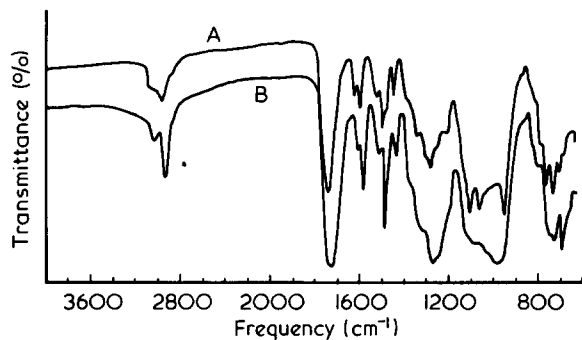
Figure 3 I.r. spectra of bromal/PhNCO copolymers (11 and 50% PhNCO content, KBr pellet)

Several attempts were made to copolymerize bromal and chloral with pyridine as well as with trifluoromethanesulphonic acid as the initiators. Most polymer samples showed no incorporation of bromal. It was common that with increasing bromal concentration in the comonomer feed, the yield of polymers decreased but the polymer which was obtained was the homopolymer of chloral. For example, pyridine initiation of a mixture containing 75 mol % chloral gave 41% yield of polychloral, a 50:50 mixture gave a 30% conversion and a comonomer mixture with 25 mol % chloral in the feed gave an 18% conversion to polychloral. Trifluoromethanesulphonic acid was also used as the initiator of a comonomer mixture with 75% of chloral in the feed; it gave 17% homopolymer. A 50:50 comonomer mixture gave 12% conversion and 25 mol % of chloral in the feed gave an 8% conversion to chloral homopolymer.

On careful investigation, however, it was found that a small amount of copolymerization occurred with LTB as initiator in a 50:50 percent mixture by volume which amounts to 50 mol % of bromal in the comonomer mixture. When this comonomer mixture was polymerized, 1.8 mol % of bromal was incorporated in the polymer after careful extraction of monomers and unstable fractions and a 10 mol % bromal containing mixture gave 0.9 mol % of bromal in the copolymer. This shows that reaction conditions, initiator and temperatures when carefully controlled, can produce a small amount of incorporation of bromal into the polychloral when large amounts of bromal are used in the comonomer feed mixture.

Bromal copolymerized[15] readily in the presence of 50 mol % of phenyl isocyanate with 2.5 mol % of pyridine at −78°C. In a 74% conversion, a 1:1, probably alternating, copolymer of bromal and phenyl isocyanate was produced (*Table 5*). The incorporation dropped down to 13% isocyanate content of the copolymers at a 20 mol % feed and a 61% conversion. The isocyanate content of the copolymer was about the same at the comonomer feed ratio of 10 mol

% at a conversion of 50% (*Figure 3*). The molecular weight of the 1:1 copolymer of phenyl isocyanate and bromal was determined to be more than 7000 according to vapour phase osmometry in dichloromethane. Copolymers of iso-cyanates and perhaloacetaldehydes with low isocyanate content are insoluble; however, the solubility of chloral/phenyl isocyanate copolymers becomes significant above 20 mol % of phenyl isocyanate in the polymer and the 1:1 bromal/phenyl isocyanate copolymer is soluble.

$$(4)$$
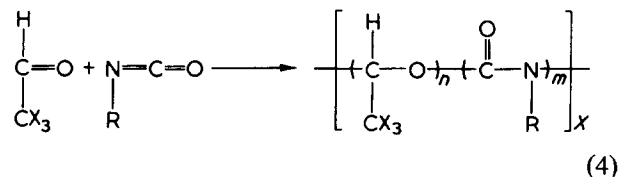
Phenyl isocyanate was much more reactive in copolymerization with bromal than was p-tolyl isocyanate or n-butyl isocyanate. When a 1:1 mixture of n-butyl isocyanate and bromal were copolymerized the product had only 7% of isocyanate in the polymer (*Figure 4*). p-Tolyl isocyanate was also less reactive than phenyl isocyanate and 16 mol % of p-tolyl isocyanate was incorporated at a 42% conversion. The yields for the copolymerization of bromal and isocyanates are higher than the yields for the homopolymerization of bromal. The copolymers are also initially more thermally stable and lose less weight on extraction with acetone than homopolymer (*Figure 5*).

Vacuum thermal degradation was also used as an analysis for the incorporation of bromal into polychloral as indicated earlier. Polymers made with several feed mixtures from 75% chloral and 25% bromal up to 25% chloral and 75% bromal with trifluoromethanesulphonic acid or pyridine as initiators gave always essentially pure chloral monomer on degradation and analysis of the products.

The rate of homopolymerization of bromal was determin-
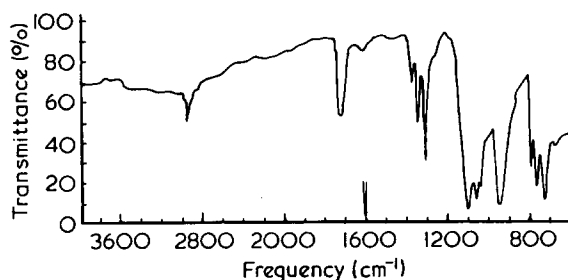
Figure 4 I.r. spectra of bromal/n-BuNCO copolymer (6.5% n-BuNCO) (KBr pellet)
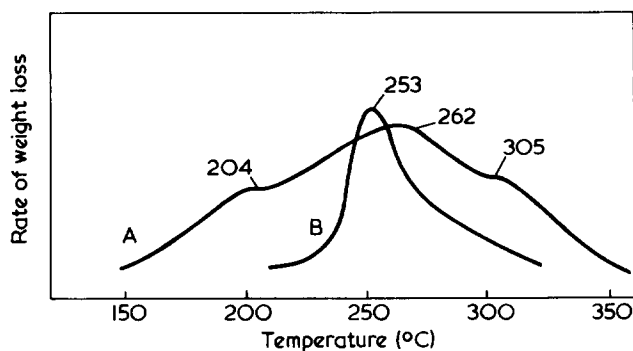
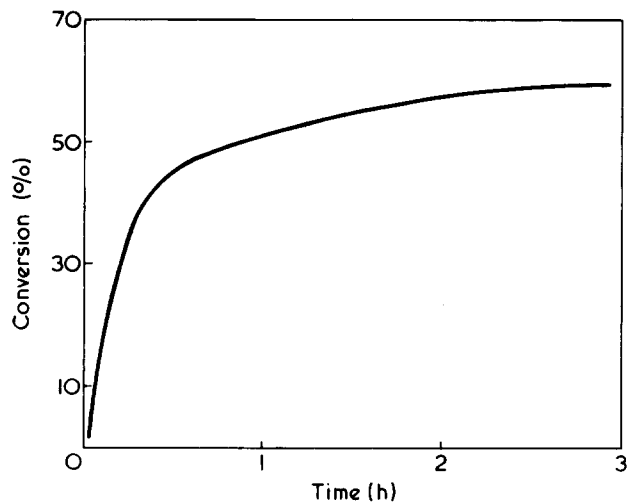**Figure 5** D.t.g. curves of bromal/PhNCO copolymers (initiator, pyridine), heating rate, 20°C/min

Figure 6 Polymerization rate determination of bromal by p.m.r., polymerization initiator, pyridine (2 mol %); polymerization bath temperature, −78°C

ed at an 8 molar concentration in toluene solutions at −78°C. It was shown (*Figure 6*) that the polymerization levels off at around 65% conversion which is reached after about 2 or 3 h. A 50% conversion is obtained in slightly more than 0.5 h. A 40−45% conversion was the maximum obtainable poly-bromal yield of a 5 molar solution.

The ceiling temperature of bromal polymerization (1 M in toluene) was determined with 2 mol % pyridine as the initiator and found to be −75°C. (*Figure 7b*). The threshold temperature of polymerization of an 8.33 molar bromal solution was −36°C. It was −39°C for a 6.67 molar solution and it was −49°C for a 5.0 molar bromal solution (*Figure 7a*).

In this context, 'ceiling temperature' is defined as the temperature at which polymer is in equilibrium with a 1 M concentration of monomer and the 'threshold temperature' corresponding to any other monomer concentration is the temperature at which polymer is in equilibrium with that concentration of monomer.

From these experiments, it must be concluded that bromal very readily polymerizes and copolymerizes. but the monomer must be scrupulously freed of undesirable impurities which might interfere with the polymerization. Polymerization temperature and monomer concentration in the polymerization mixture must be suitable for the formation of the polymer. In anionic and cationic polymerizations, bromal is less reactive than any of the other haloaldehyde monomers studied and does not readily copolymerize with chloral with cationic or anionic initiators. Bromal does, however, readily copolymerize with phenyl isocyanate, for example, as well as with other isocyanates, primarily aromatic isocyanates, to form polyacetals containing urethane linkages.
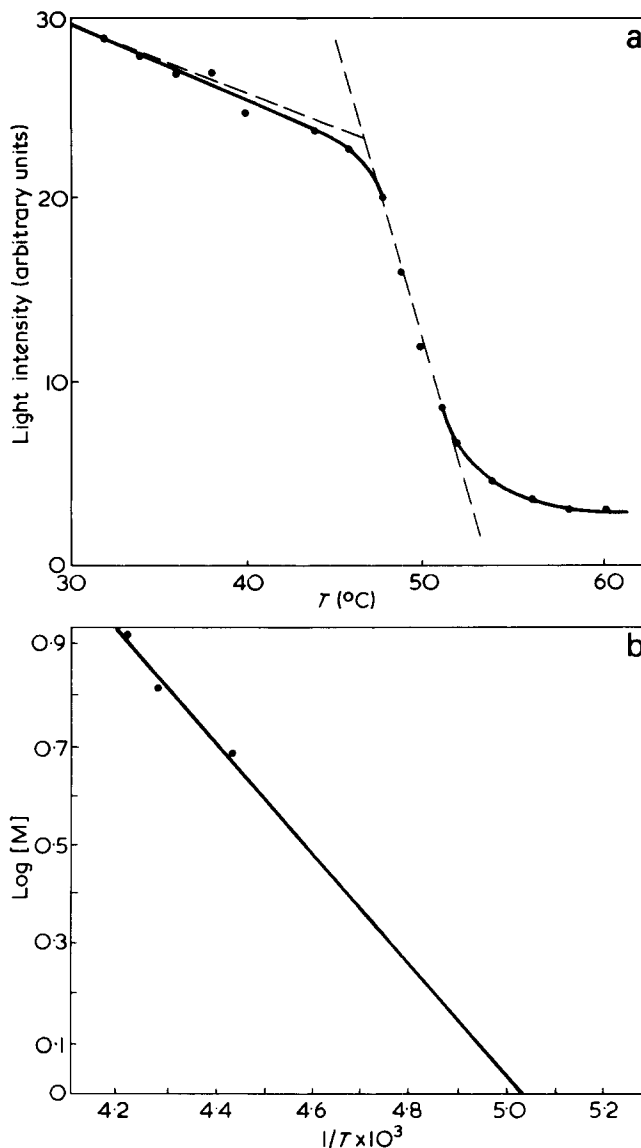
ACKNOWLEDGEMENTS

Figure 7 (a) Bromal polymerization threshold temperature determination. Solvent, toluene; initiator, pyridine (3 mol %); monomer concentration, 5 M. (b) Graphic ceiling temperature determination of bromal polymerization

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