Haloaldehyde polymers: 20. Thermodynamics of polymerization

P. Kubisa and O. Vogl
Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, USA
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The thermodynamics of polymerization of halogenated aldehydes of the general formula CX_3CHO, where X = F, Cl or Br, have been studied. The dependence of the equilibrium monomer concentration on temperature has been determined for nine homo- and hetero-halogen-substituted acetaldehydes. From this data, ceiling temperatures, enthalpies and entropies of polymerization have been calculated. Both enthalpy and entropy of polymerization become less negative when passing from fluorine to chlorine and bromine substituents. Thus, from the point of view of enthalpy alone, trifluorosubstituted acetaldehyde shows the highest and tribromosubstituted acetaldehyde the lowest polymerizability; the opposite is true if the entropy alone is considered. As the enthalpy factor prevails, the trend in the ceiling temperature follows that of the enthalpy and thus ceiling temperature is highest for fluoral and lowest for bromal polymerization with intermediate values for mixed substituted perhaloaldehydes. An attempt has been made to correlate the thermodynamic parameters of polymerization with electronic and steric effects of the substituents on the haloacetaldehydes.

INTRODUCTION

Addition of a monomer molecule to the growing species in polymerization (propagation) is a reversible reaction:

$$M_n^* + M \overset{K}{\rightleftharpoons} \sim M_{n+1}^* \qquad (1)$$

The equilibrium constant of this reaction is a function of the Gibbs free energy change, ΔG, which in turn is governed by the changes of enthalpy, ΔH, and entropy, ΔS, during reaction:

$$\Delta G = -RT \ln K \qquad (2)$$

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

Polymerization is thermodynamically possible if the ΔG value for the transformation of a monomer molecule into polymer unit is negative. For the majority of polymerization systems (polymerization of sulphur being an exception) both enthalpy and entropy of polymerization have been found to be negative[1].

ΔH_{polym} reflects the difference in bonding energies in monomer and polymer. For polymerizations which proceed by the opening of a carbon–carbon double bond, ΔH_{polym} reflects the energy difference between the double bond (average value 611 kJ mol^{-1} (145.8 kcal mol^{-1}) and two single bonds [2 x 346 kJ mol^{-1} (82.6 kcal mol^{-1})], which leads to a ΔH_{polym} value close to −84 kJ mol^{-1} (−20 kcal mol^{-1})[2]. For polymerizations which proceed through the opening of a carbon–oxygen double bond, with an average bond energy of 737 kJ mol^{-1} (176 kcal mol^{-1}), the predicted average value of ΔH_{polym} is between 0 and −21 kJ mol^{-1} (−5 kcal mol^{-1}). The nature of the substituent(s) on the double bond affects the ΔH_{polym} in two ways. Firstly, it may influence the energies of the bonds in the monomer and polymer (for example by resonance stabilization of double bonds) and, secondly, it may destabilize the polymer due to steric repulsion between substituents.

Because the polymerization is an association reaction, the entropy of polymerization is negative and the overall entropy change is a sum of contributions involving changes of translational, rotational and vibrational entropies. In one of the first comprehensive reviews of polymerization thermodynamics, Dainton and Ivin[3] stated that the loss of external rotational entropy nearly balances the gain in vibrational and internal rotational entropy during the polymerization step. Consequently, ΔS_{polym} reflects mainly the loss of translational entropy, and thus is fairly independent of the structure of the monomer[3]. Analysis of ΔS_{polym} values for different bond-opening polymerizations indeed indicates that the $-\Delta S_{gc}$ values (gaseous monomer → condensed polymer) are generally within 150–200 J $(^\circ\text{C mol})^{-1}$ [~40–50 cal $(^\circ\text{C mol})^{-1}$] while $-\Delta S_{lc}$ values (liquid monomer → condensed polymer) are between 80–120 J $(^\circ\text{C mol})^{-1}$ [~20–30 cal $(^\circ\text{C mol})^{-1}$] [2,4].

The position of equilibrium in a polymerization is governed by both enthalpy and entropy factors. Because the entropy factor $T\Delta S$, even for relatively high ΔS_{polym} values, contributes usually no more than 4.0 kJ mol^{-1} (−1.0 kcal mol^{-1}) to the ΔG_{polym} value, the position of equilibrium depends mainly on the ΔH_{polym} value. If, as in the case of the polymerization of typical vinyl monomers, ΔH_{polym} is strongly negative (<−20 kcal mol^{-1}) the equilibrium constant of reaction (1) is high and the equilibrium position is shifted to the right-hand side. For all practical purposes, the propagation step may be treated as an irreversible reaction, although in every case low, but definite amounts of monomer remain in equilibrium with the polymer. In the polymerization of styrene, for example, this equilibrium monomer concentration is about 10^{-6} mol l^{-1} at room temperature[1].

For these systems, for which ΔH_{polym} is lower than

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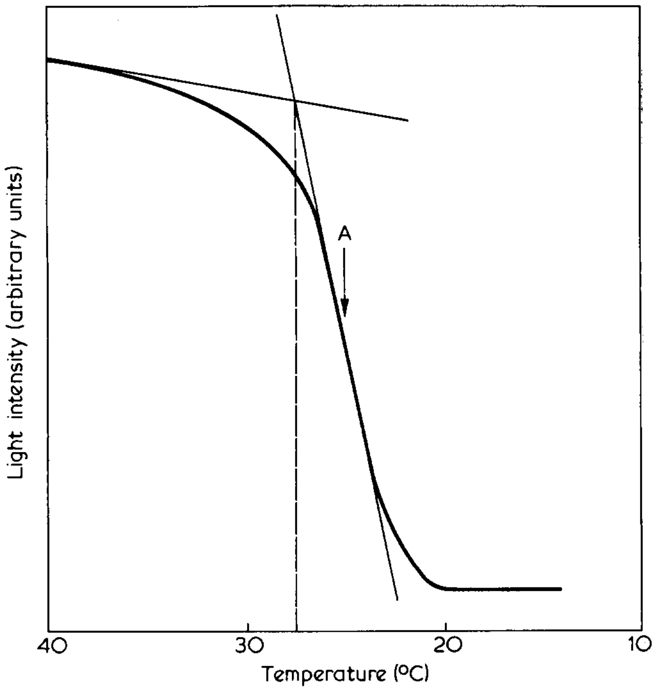

Figure 1 Intensity of light transmitted through toluene solution of perhaloacetaldehyde as a function of temperature. Polymerization of bromodichloroacetaldehyde (BDCA) in toluene, [BDCA] = 8.33 mol l^{-1}, $[\mathrm{Pyridine}]_0$ = 1 mol %; cooling rate 0.25°C min^{-1}. A = temperature at which cloudiness of solution may be detected by visual observation

-60 kJ mol^{-1} (~ -15 kcal mol^{-1}), the equilibrium constant of polymerization (at temperature regions available for measurements) assumes a lower value and the concentration of monomer in equilibrium with polymer may easily be determined. If the dependence of the equilibrium monomer concentration on temperature is known, the equilibrium constant K and, consequently, the thermodynamic parameters of polymerization can be calculated.

Polymerization of aldehydes provides a convenient model system for studies of the thermodynamics of polymerization. This is due to the fact that the energy difference between carbonyl bonds in aldehydes and acetal bonds in polyaldehydes is considerably lower than that between the carbon–carbon double and single bonds. Due to the relatively low value of $\Delta H_{\mathrm{polym}}$ in aldehyde polymerization, the equilibrium character of the polymerization is clearly observed, even in the case of the parent compound, formaldehyde. Substitution usually reduces further the thermodynamic polymerizability and disubstituted derivatives (ketones) cannot be polymerized, although aldehydes can generally be polymerized to high molecular weight polymers.

Studies of aldehyde polymerization contributed to a large extent to our present understanding of the thermodynamics of polymerization. The thermodynamics of polymerization of formaldehyde and its cyclic trimer (trioxane) have been extensively studied. The commercial applications of polyformaldehyde became possible only after the thermodynamic reasons for its instability were understood and a method of polymer stabilization was developed.

Studies of aldehyde polymerization offer an excellent possibility for investigation of the effects of substituents on the thermodynamics of polymerization. By substituting the hydrogen atoms of the methyl group of acetaldehyde with halogen atoms, a series of monomers of the general formula CX_3CHO (where X denotes F, Cl or Br) may be obtained, having essentially the same character from the point of view of their chemical properties, but differing considerably with respect to the electronegativity and the size of CX_3 groups.

In the previous papers from this laboratory, the synthesis and polymerization of perhaloacetaldehydes of the general formula of CX_3CHO where X = F, Cl or Br (including substituted acetaldehyde with mixed halogen substitution) were described[5–18]; the only perhaloacetaldehyde not yet described is FClBrCCHO.

In this paper we describe the thermodynamics of perhaloacetaldehyde polymerization and discuss the influence of the nature of substituents on the ceiling temperature, enthalpy and entropy of polymerization.

EXPERIMENTAL

Materials

Syntheses, purifications and polymerizations of perhaloacetaldehydes of general formula CX_3CHO where X = F, Cl, or Br were described in a series of earlier papers[5–18].

Ceiling temperature determination

Apparatus[19]. Simple apparatus used for the determination of ceiling temperatures consisted of a GE Mazda projector bulb as a light source, and a selenium photocell (Lafayette Radio Co., No. 99–6243) as a detector which was connected to a recorder Linear Instruments Co. Model 161. A glass bottle, flattened on opposite sides to form planar windows which contained paraffin oil or isopropyl alcohol (depending on temperature range desired) as a bath liquid, was placed between the light source and detector. Below the flask was placed a magnetic stirrer coupled with a hot plate enabling effective mixing and heating of the bath liquid A copper coil connected to a Dewar flask containing liquid nitrogen was immersed in the bath in order to achieve cooling; the flow of cold nitrogen gas through the coil was regulated with the temperature probe and controller.

Measurements

Ceiling temperature. Pyrex ampoules used as reaction vessels were cleaned and dried for 72 h at 120°C and then purged with nitrogen for 10 min. Freshly distilled perhaloacetaldehyde was then added by dry syringe and the ampoule was immersed in the bath, preheated to a temperature 20–30°C higher than the expected ceiling temperature (estimated in preliminary experiments). After 5 min, solvent (toluene) and initiator solution were added with dry syringes. Pyridine was used as initiator throughout this work at a concentration of 1 mol %. After the components were mixed, the bath temperature was allowed to decrease at a controlled cooling rate of 0.25°C min^{-1}. The light source was then turned on and the intensity of light transmitted through the sample was recorded.

A typical recorder reading which shows the dependence of the intensity of transmitted light on the temperature is given in *Figure 1*. The intensity of transmitted light decreases slightly upon cooling; then a very significant drop of the intensity occurs within a narrow range of temperature, indicating the change of the optical properties of the system caused by precipitation of the polymer. The ceiling

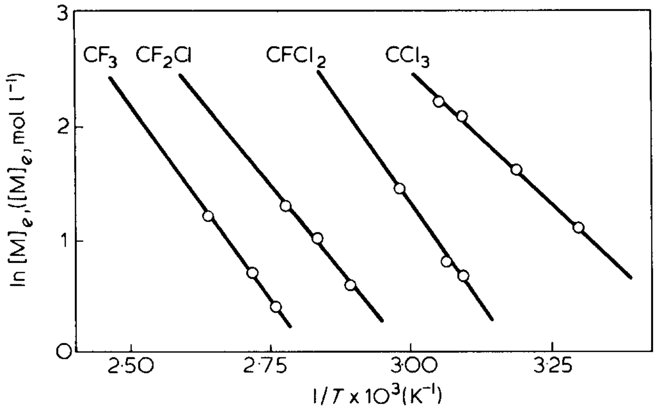

Figure 2 Dependence of $\ln[M]_e$ on $1/T$ for polymerization of perhaloacetaldehydes of the general formula: $CF_nCl_{3-n}CHO$; solvent, toluene, initiator, pyridine. Initiator concentration = 1 mol %

temperature was determined as an initial temperature at which the change of a slope of the plot of light intensity vs. temperature occurs. This temperature was obtained from extrapolation as indicated in *Figure 1*. Usually this temperature was 1°–2°C. higher than the ceiling temperature estimated on the basis of visual observation of the first onset of cloudiness.

The method described gives correct and reproducible results, providing that two conditions are fulfilled: (a) polymerization proceeds quickly; and (b) the polymer is completely insoluble in the reaction medium. Independent measurements using ^{1}H n.m.r. spectroscopy indicated that for all perhaloacetaldehydes studied, rates of polymerization initiated by pyridine were high. These measurements were conducted by measuring the decrease of the intensity in the signal of the aldehyde proton of the monomers. In no case was a signal of the proton in the polymer observed, indicating that the polymers are insoluble in the reaction media.

RESULTS AND DISCUSSION

Ceiling temperature of polymerization

The ceiling temperature (T_c) of polymerization is defined as the temperature at which the ΔG_{polym} of a 1 M solution of monomer is equal to zero. Several methods for the determination of T_c of polymerization are described in the literature[7]. These methods are based on two approaches: either the monomer concentration is changed at constant temperature or the temperature is changed at constant composition of the reaction mixture. If the polymer is insoluble in the reaction medium, the latter method can be conveniently used and the T_c (or strictly speaking the threshold polymerization temperature for a given concentration of monomer), may be determined as the temperature at which, upon cooling, polymer starts to precipitate. Ceiling temperatures determined in this way correspond to the transformation of dissolved monomer into condensed (amorphous or crystalline) polymer and are denoted as T_{sc} or $T_{sc'}$.

In the present work, T_c for polymerization of nine haloaldehydes of general formula CX_3CHO (X = F, Cl or Br) were determined by following the intensity of light transmitted through the monomer solution in toluene upon cooling. This method has an advantage over visual observation because it permits an exact determination of the temperature at which the first slight cloudiness, not detectable by visual observation, occurs. As indicated in *Figure 1*, only after considerable change in the intensity of transmitted light was recorded could the precipitation of polymer be detected by visual observation. Consequently, the T_c determined by visual observation would be too low by approximately 2°C.

For each monomer the threshold polymerization temperatures for solutions having different initial monomer concentrations were determined. Because for given initial monomer concentration $[M]_0$ at the threshold temperature the equilibrium monomer concentration $[M]_e$ becomes equal to $[M]_0$, the determination of threshold temperatures for different $[M]_0$ is equivalent to the determination of the dependence of $[M]_e$ on temperature.

The equilibrium monomer concentration is equal to the equilibrium constant of propagation. This is a simple consequence of the fact that at equilibrium the rate of propagation becomes equal to the rate of depropagation:

$$\sim M_n^* + M \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \sim M_{n+1}^* \qquad (4)$$

$$[\sim M_n^*]\,[M]_e k_p = [\sim M_{n+1}^*]\,k_d \qquad (5)$$

because $[\sim M_n^*] = [\sim M_{n+1}^*]$ it follows that:

$$[M]_e = k_d/k_p = 1/K \qquad (6)$$

Since $K = k_p/k_d$, the dependence of K on temperature:

$$-\ln K = \ln(1/K) = \Delta H/RT - \Delta S/R \qquad (7)$$

may be written as

$$\ln[M]_e = \Delta H/RT - \Delta S/R \qquad (8)$$

By plotting $\ln[M]_e$ vs. $1/T$, a straight line should be obtained, permitting extrapolation to $[M]_e = 1$ and determination of T_c for a 1 M solution. From the same plot, thermodynamic parameters of polymerization may be determined: $\Delta H_{\text{polym}}/R$ as the slope of the plot of $\ln[M]_e$ vs. $1/T$ and $-\Delta S_{\text{polym}}/R$ as the intercept at $1/T \rightarrow 0$.

The plots of $\ln[M]_e$ vs. $1/T$ for fluorochloro-, fluorobromo- and chlorobromo-substituted perhaloacetaldehydes are shown in *Figures 2, 3* and *4*, respectively. Determined

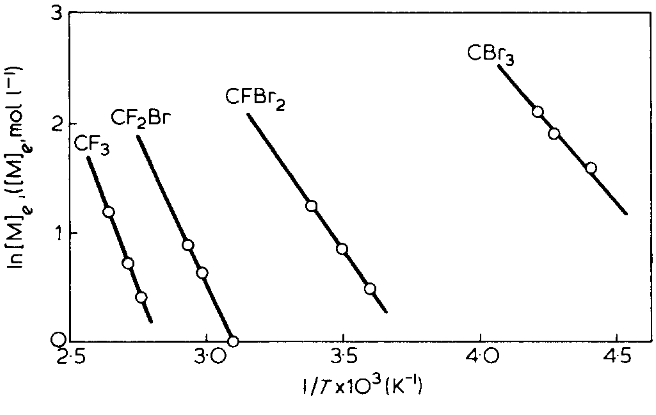

Figure 3 Dependence of $\ln[M]_e$ on $1/T$ for polymerization of perhaloacetaldehydes of general formula: $CF_nBr_{3-n}CHO$; solvent, toluene; initiator, pyridine. Initiator concentration = 1 mol %

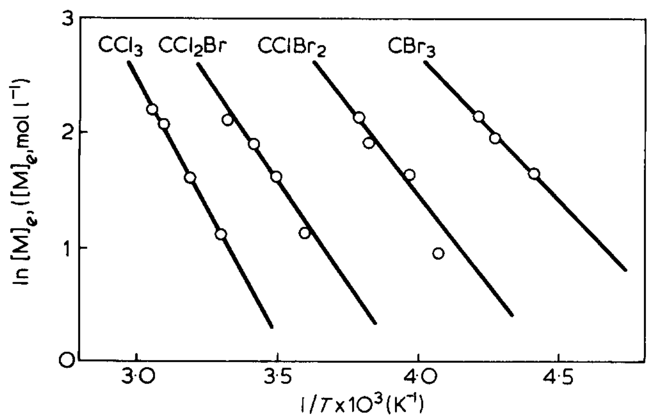

Figure 4 Dependence of $\ln[M]_e$ on $1/T$ for polymerization of perhaloacetaldehydes of general formula: $CCl_nBr_{3-n}CHO$; solvent, toluene; initiator, pyridine. Initiator concentration: 1 mol %

on this basis, values of T_c, ΔH_{polym} and ΔS_{polym} are listed in *Table 1*.

Effect of degree of polymer crystallinity on the thermodynamics of polymerization

The thermodynamics of polymerizations in which the solid polymer precipitates from solution is affected by the morphology of the polymer. If crystalline polymer is formed, both enthalpy (ΔH) and entropy (ΔS) of crystallization will contribute to the overall enthalpy and entropy change, consequently affecting the values of T_c. Thus, quantitative comparison of either T_c values or thermodynamic parameters (ΔH_{polym} and ΔS_{polym}) is possible only when the same type of transformation is being compared, namely dissolved monomer to amorphous (denoted by subscript *sc*) or crystalline (*sc*′) polymer.

Polymers prepared from haloaldehydes generally contain both crystalline and amorphous fractions, the former predominating in polymers prepared anionically and the latter in those prepared cationically.

Because crystallization is an exothermic process, the ΔH_{cryst} is negative. The ΔS_{cryst} is also negative, since crystalline polymer has a higher degree of order than amorphous polymer. Consequently, both overall ΔH_{polym} and ΔS_{polym} for the formation of crystalline polymer have larger negative values than the corresponding values for the formation of amorphous polymers. In order to compare quantitatively the thermodynamic parameters for *sc* and *sc*′ transformations, we must know the amount of crystalline fraction in the individual polymer and the thermodynamic parameters of crystallization. These parameters, namely ΔH_{cryst} and ΔS_{cryst} for perhaloacetaldehydes, are not known.

We may use known values of ΔH_{fusion} and ΔS_{fusion} for polyformaldehyde in order to estimate the magnitude of the contribution of the parameters of crystallization to the values of ΔH_{polym} and ΔS_{polym} for crystalline polymer. For ΔH of fusion of polyformaldehyde, values between 3.72 and 7.37 kJ mol^{-1} (0.89–1.76 kcal mol^{-1}) were reported[20], while entropy of fusion is equal to 8.21 J (°C mol)$^{-1}$ [1.96 cal (°C mol)$^{-1}$][21]. Thus, the contributtion of ΔH_{cryst} to the overall enthalpy change may be significant, especially for studied systems in which the overall ΔH_{polym} is rather low.

The degree of crystallinity however, affects T_c to a lesser extent, because changes of enthalpy and entropy due to crystallization partly compensate themselves. T_c is governed by the ratio of ΔH to ΔS, and, if this ratio is not very much different for crystallization than for polymerization, the resulting T_c may depend only slightly on the degree of crystallinity of the polymer:

$$T_{sc} = \frac{\Delta H_{sc}}{\Delta S_{sc}} \qquad (9)$$

$$T_{sc'} = \frac{\Delta H_{sc'}}{\Delta S_{sc'}} = \frac{\Delta H_{sc} + \Delta H_{cryst}}{\Delta S_{sc} + \Delta S_{cryst}} \qquad (10)$$

Because it has been established that polyaldehydes (especially chloro- and bromosubstituted) are predominantly crystalline, all values determined in this paper correspond rather to *sc*′ subscript-type transformation. Consequently, in further discussions we will use the *sc*′ subscript.

Ceiling temperature–correlation with other properties

Data collected in *Table 1* indicate that there is a well-defined trend for $T_{sc'}$ values. T_c is highest for trifluoroacetaldehyde and decreases gradually as fluorine is replaced by chlorine and bromine. The most interesting feature of this series of monomers is that the CX_3 group may be substituted in nine different ways with atoms belonging to the same periodic group, thus having different molecular weights, different electronegativity, different polarizability but the same configuration of outer electron orbitals. The perhaloacetaldehydes constitute a series of monomers which are close chemical analogues, differing only in those respects which are imposed by the nature of substituents in the CX_3 group. Consequently, perhaloacetaldehydes provide a model series of monomers for which it may be expected that different properties would change monotonically when fluorine is replaced by chlorine and bromine.

Indeed, as shown in *Table 2*, the change of $T_{sc'}$ values is parallel (with only a few exceptions) to changes of such properties as boiling point, density and spectral characteristics of those monomers.

In qualitative terms these correlations are a simple consequence of the fact that substitution of fluorine by chlorine and bromine results in changes of electronegativity and size of CX_3 group which affects the T_c of polymeriza-

Table 1

Substituent	$T_{sc'}$* (°C)	$-\Delta H_{sc'}$* kJ mol^{-1} (kcal mol^{-1})	$-\Delta S_{sc'}$* J(°C mol)$^{-1}$ (cal(°C mol)$^{-1}$)
CF_3	81	54.9 (13.1)	155 (36.9)
CF_2Cl	63	51.0 (12.2)	152 (36.3)
$CFCl_2$	41	56.2 (13.4)	179 (42.8)
CCl_3	9	37.8 (9.0)	134 (32.0)
CF_3	81	54.9 (13.1)	155 (36.9)
CF_2Br	48	43.4 (10.35)	135 (32.2)
$CFBr_2$	−19	29.0 (6.90)	114 (27.2)
CBr_3	−77	19.6 (4.70)	100 (23.8)
CCl_3	9	37.8 (9.0)	134 (32.0)
CCl_2Br	−17	31.2 (7.45)	122 (29.2)
$CClBr_2$	−40	26.0 (6.2)	116 (27.8)
CBr_3	−77	19.6 (4.70)	100 (23.8)

* Calculated from data shown in *Figures 2, 3* and *4* by least squares method

Table 2

				N.m.r. chemical shifts (ppm)			I.r.		
CX_3	$T_{sc'}$ (°C)	B.p. (°C)	Density ($g\ cm^{-3}$)	^1H ppm δ	^{13}C	^{19}F	Gas	Hexane solution [C=O bands (cm^{-1})]	Neat
CF_3	81	−18	1.47	9.36	–	–	1785	1780	–
CF_2Cl	63	18	1.45	9.25	–	5.52	1770	1770	–
CF_2Br	48	43	1.80	9.09	–	8.53	1770	1762	1755
CF_2Cl_2	41	56	1.43	9.15	–	0.32	1760	1772	1770
CCl_3	9	98	1.45	8.95	93.7	–	1777	1768	1760
CF_2Br_2	−19	52/90 mmHg	2.25	8.86	–	0.45	1760	1755	1751
$CClBr_2$	−40	148	2.27	8.10	63.5	–	1768	1758	1750
CCl_2Br	−7	127	1.87	8.87	79.4	–	1774	1763	1754
CBr_3	−77	174	2.73	8.45	45.5	–	1765	1754	1742

Table 3

xx^a	$-\Delta H_{xx}$ ($kJ\ mol^{-1}$)	($kcal\ mol^{-1}$)	$-\Delta S_{xx}$ $J(°C\ mol)^{-1}$	[$cal\ (°C\ mol)^{-1}$]	Solvent	Temperature (°C)	Reference
	Fluoral						
gc	64.5	(15.4)	187	(44.6)		45	22
sc	50.8	(12.1)	142.7	(34)	CH_2Cl_2		23
sc	54.9	(13.1)	155	(36.9)	Toluene		This work
	Chloral						
gc'	71 ± 8	(17 ± 2)	190 ± 30	(45.3 ± 7.1)		50	24
gc'	65.5	(15.6)				−50	25
gc	51	(12.1)				−50	25
lc'	38 ± 8	(9.1 ± 2)	95 ± 30	(22.7 ± 7.2)		50	24
lc'	34.5	(8.2)				−50	25
lc	20	(4.8)				−50	25
ss	14.5	(3.5)	52	(12.4)	THF	−50	26
sc'	33.5	(8.0)	117	(28.0)	Pyridine	13	24
sc'	40	(9.3)	142	(33.9)	n-Heptane	10	25
sc'	37.8	(9.0)	134	(32.2)	Toluene		This work

[a] *x* indicates the general symbol for *g, c, l, s* and *c'*

tion. At the same time, electronegativity and polarizability of substituents influences both n.m.r. and i.r. spectra of haloaldehydes (this effect is especially pronounced for ^1H n.m.r. chemical shifts of the aldehyde proton) while molecular weight and size of the CX_3 group influences density and boiling point. Quantitatively, these effects should be discussed rather in terms of ΔH_{polym} and ΔS_{polym}.

Enthalpy of polymerization

$\Delta H_{sc'}$ values, calculated from the linear dependence of ln $[M]_e$ on $1/T$ and listed in *Table 1*, indicate that, with increasing atomic number of halide substituents, the negative value of ΔH decreases; consequently the enthalpy factor makes polymerization less favourable.

In one case, namely for the $CFCl_2$ substituent, the ΔH value does not fit the general trend, and is much too high. Nevertheless, when all values are compared, there is a definite trend, and ΔH_{polym} decreases significantly when fluorine is replaced by chlorine and by bromine. The corresponding $-\Delta H_{sc'}$ values for polymerization of fluoral, chloral and bromal are equal to 54.9, 37.8 and 19.6 kJ mol^{-1} (13.1, 9.0 and 4.7 kcal mol^{-1}), respectively. For mixed substitution intermediate values were obtained.

The thermodynamic parameters of polymerization of fluoral and chloral have been determined earlier. In *Table 3* values of ΔH_{polym} and ΔS_{polym} of those monomers reported in the literature are compared with those obtained in the present work. The data indicate that there is good agreement between thermodynamic parameters of polymerization determined by various authors. The difference between ΔH_{gc} and ΔH_{lc} for chloral polymerization corresponds closely to the known value of the heat of vaporization of chloral which is equal to 35.48 kJ mol^{-1} (8.47 kcal mol^{-1}). However, the difference between ΔH_{sc} and ΔH_{ss} should reflect the heat of dissolution of chloral polymer; this difference is approximately 20 kJ mol^{-1} (~5 kcal mol^{-1}). The ΔH of dissolution of polychloral is not known because this polymer is insoluble in all solvents.

It should be remembered that the polymerization of perhaloacetaldehydes leads to the formation of partly crystalline and partly amorphous polymer, with the crystalline fraction predominating in anionic polymerization. Thus, the ΔH values measured in this work are not directly comparable, since the exact amounts of crystalline and amorphous fraction formed in pyridine initiated polymerization are not known to be the same for all the aldehydes.

The absolute values of ΔH_{polym} are relatively high, especially for fluorosubstituted aldehydes. From the difference between bond energies between carbon–oxygen double bonds (for which the average value of bond energy is 737 kJ mol^{-1} (176 kcal mol^{-1}) and two carbon–oxygen single bonds (358 kJ mol^{-1} 85.5 kcal mol^{-1}), the positive value of 21 kJ mol^{-1} (5 kcal mol^{-1}) for the enthalpy of aldehyde polymerization was predicted. More refined calculation led to the value of approximately −20 kJ mol^{-1} (−5 kcal mol^{-1})[2]. This value is still lower than the experimentally determined ΔH_{polym} of the simplest 'unsubstitut-

Table 4

CX_3	Van der Waals radius of X (Å)	Length of CX bond in (Å) [28]	Radius of CX_3 group (Å) *
CH_3	1.2	1.086	2.3
CF_3	1.35	1.332	2.7
CCl_3	1.80	1.76	3.55
CBr_3	1.95	1.94	3.90
$C(CH_3)_3$	2.0	1.54 [29]	3.55

* Length of C—X bond and radius of X substituent

ed' aldehyde, formaldehyde. For the polymerization of gaseous formaldehyde to solid polymer the ΔH_{gc} values reported in the literature vary between –50 and –70 kJ mol^{-1} (–12 to –17 kcal mol^{-1})[4]. This value, however, is a sum of ΔH_{polym} and ΔH of phase transition. Because the enthalpy of condensation may be taken as equal to the heat of vaporization (24.79 kJ mol^{-1}, 5.92 kcal mol^{-1} for formaldehyde)[27], the value of ΔH_{lc} for formaldehyde polymerization should be less negative by approximately 25 kJ mol^{-1} (~6 kcal mol^{-1}) than the ΔH_{gc} value, which would lead to a value between –25 and –45 kJ mol^{-1} (–6 to –11 kcal mol^{-1}) for ΔH_{lc}.

Substitution of one hydrogen with a CH_3 group leads to considerable decrease of the value of ΔH_{polym}. The ΔH_{polym} of acetaldehyde (ΔH_{lc} is reported to be close to zero at 25°C [2]. This is in agreement with general rules according to which substitution reduces the polymerizability by affecting the ΔH_{polym} value. Steric strain in the polymer tends to make ΔH_{polym} less negative as a result of bond stretching, bond angle deformation and interaction between non-bonded atoms (a typical and well-known example of this effect is the reduced polymerizability of α-methylstyrene in comparison with styrene).

If ΔH_{polym} were affected only by steric factors we would expect that further substitution of hydrogen atoms within a CH_3 group with more bulky halide atoms should reduce the polymerizability even further. This is clearly not the case – substitution of all hydrogens with fluorine makes polymerization more exothermic (ΔH_{polym} = –55 kJ mol^{-1}, –13.1 kcal mol^{-1}) which implies that, in contrast to acetaldehyde, fluoral is rather easily polymerized and as far as ΔH_{polym} is concerned it may be compared with methyl methacrylate (ΔH_{lc} = –55 kJ mol^{-1}, –13.1 kcal mol^{-1})[4].

This phenomenon, namely the increase of exothermicity of polymerization upon substitution with strongly electronegative groups, is also well-known for other groups of monomers. Typical examples are polymerizations of vinyl chloride (ΔH_{lc} = –95.9 kJ mol^{-1}, –22.9 kcal mol^{-1}) nitroethylene (ΔH_{cc} = –90.0 kJ mol^{-1}, –21.7 kcal mol^{-1}), vinylidene fluoride (ΔH_{lc} = –130 kJ mol^{-1}, –31 kcal mol^{-1}), and tetrafluoroethylene (ΔH_{lc} = –155 kJ mol^{-1}, –37 kcal mol^{-1})[2]. According to Sawada increased ΔH_{polym} may be due to a reduction, upon polymerization, of repulsion between non-bonding electrons associated with electrophilic groups. Alternatively they may arise because of the stabilization of the polymer caused by a degree of ionic resonance[2].

In the series of substituted aldehydes, the electron withdrawing effect of the substituent may be estimated on the basis of the chemical shift of the aldehyde protons in the ^1H n.m.r. spectra. The frequency of the C=O stretching band in the i.r. spectra also gives an indication of the relative electron-withdrawing effects of different groups. Chemical shifts of aldehyde protons and i.r. frequencies for C=O bands together with some data on ^{19}F and ^{13}C n.m.r. are given in *Table 2*.

As judged from the chemical shift of protons attached directly to the carbonyl carbon atoms, there is a considerable difference among the electron withdrawing effects of different substituents. The corresponding value for fluoral is 9.36 ppm δ, for chloral 8.95 ppm δ and for bromal 8.45 ppm δ, respectively. Replacement of fluorine for chlorine and for bromine, apart from influencing the electron density and consequently the strength of double bonds, results also in considerable change of the size of the CX_3 group. The size of the CX_3 group may be expressed in terms of a radius of a sphere into which specific CX_3 groups can be fitted; calculated in this way values for radii of CH_3, CF_3, CCl_3, CBr_3 and, for comparison $C(CH_3)_3$ groups are given in *Table 4*.

As mentioned earlier, with increasing size of the substituent attached to the double bond, the value of ΔH_{polym} becomes less negative, due to steric repulsion between substituents in β positions in the polymer. Consequently, both electronic and steric effects affect the ΔH_{polym} in the same way, reducing the polymerizability of haloaldehydes (in terms of ΔH_{polym}) as fluorine is replaced by chlorine and bromine. In order to estimate to what extent each of these factors affects the ΔH_{polym} value, it would be necessary to compare ΔH_{polym} values for monomers for which steric factors (size of substituent) are the same but electronic factors (electron-withdrawing power) are different or *vice versa.* Of course, such treatment would be of only semi-quantitative value because chemically different groups may lead to different steric interactions even if their calculated diameters are the same. Nevertheless, it is informative to carry out even such approximate analyses of the relative importance of electronic and steric effects on the ΔH_{polym}.

The radius of CF_3 groups (2.7 Å) is considerably larger than the radius of CH_3 groups (2.3 Å); nevertheless the ΔH_{sc} for polymerization of fluoral is a relatively large negative value (–55 kJ mol^{-1}, –13.1 kcal mol^{-1}) while the ΔH_{sc} for polymerization of acetaldehyde is close to zero. This would indicate that if purely steric reasons were considered, ΔH_{polym} for fluoral polymerization should be even less favourable (less negative ΔH_{polym}); in fact electronic factors alone are apparently responsible for bringing the ΔH value at least from about 0 to –55 kJ mol^{-1}(–13.1 kcal mol^{-1}).

Similar conclusions can be reached if the polymerizabilities of chloral and trimethylacetaldehyde (pivalaldehyde) are compared. The calculated radii of CCl_3 and $C(CH_3)_3$ substituents are nearly the same (3.55 Å) but ΔH_{polym} of chloral polymerization is equal to –39 kJ mol^{-1} (–9.3 kcal mol^{-1})[25] while for trimethylacetaldehyde it has apparently a positive value because all attempts to polymerize this monomer were unsuccessful. Again, in this case electronic factors are solely responsible for bringing the ΔH value to –39 kJ mol^{-1} (–9.3 kcal mol^{-1})[25].

It is interesting to note that the ΔH increment resulting from replacing one fluorine atom by one chlorine atom and one chlorine atom by one bromine atom in the CX_3 group seems to be the same. Indeed if the ΔH_{polym} values are plotted so that CF_3 and CCl_3 groups are the terminal points of a monotonic scale based on increasing heterohalogen substitutions then straight lines are obtained for the following haloaldehyde types: $CF_nCl_{n-3}CHO$, $CF_nBr_{3-n}CHO$ and $CCl_nBr_{3-n}CHO$. The linearity of this plot indicates that replacement of each fluorine by chlorine and each chlorine

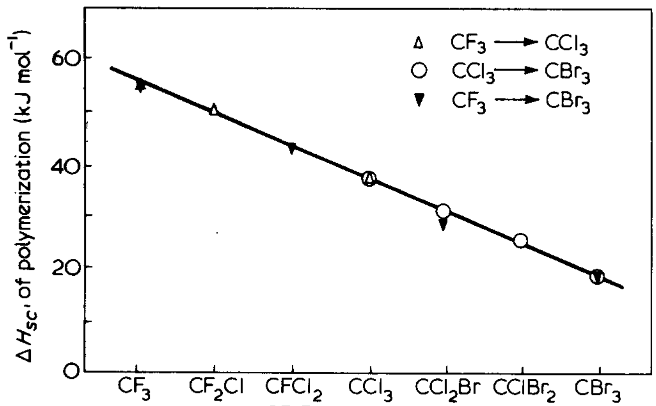

Figure 5 Dependence of $\Delta H_{sc'}$ of polymerization on the nature of CX_3 groups for polymerization of perhaloacetaldehydes of the general formula CX_3CHO

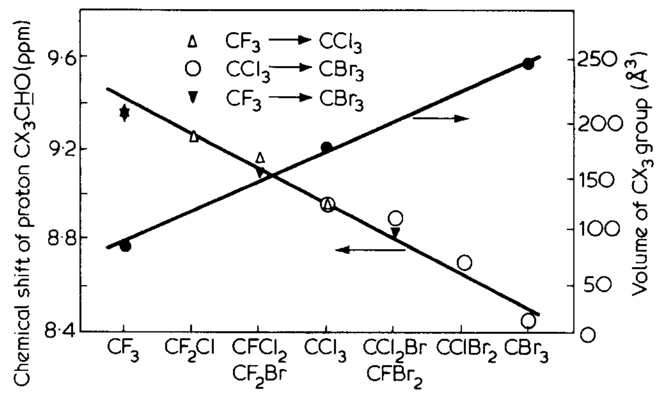

Figure 6 Dependence of proton chemical shifts and the calculated spherical ($Å^3$) volume of CX_3 groups on the nature of CX_3 substituents in perhaloacetaldehydes of general formula CX_3CHO

by bromine affects the individual ΔH_{polym} values in the same way. Because ΔH_{polym} values for $CF_3 \rightarrow CBr_3$ substituents also fall on the same line it is evident that replacement of two fluorine atoms by two chlorine atoms is from the point of view of ΔH_{polym} equivalent to replacement of one fluorine by bromine. This is a simple consequence of the fact that both factors affecting ΔH_{polym} value, namely steric and electronic effects, also seem to be additive values for the series of perhalogenated acetaldehydes. This is shown in *Figure 6* in which chemical shifts of aldehyde protons (as the measure of electronic effects) and the volume of CX_3 groups (calculated on the basis of the radii listed in *Table 4*) are plotted in the same coordinates as *Figure 5*. Again, good linear dependence is observed for both chemical shift values and volumes of CX_3 groups, indicating that both electronic and steric properties of perhaloacetaldehydes change monotonically and linearly when passing from fluorine to chlorine and bromine.

Entropy of polymerization

The Gibbs free energy of polymerization ΔG_{polym} depends on both ΔH_{polym} and ΔS_{polym}. The contribution of enthalpy and entropy factors depends on absolute values of ΔH, ΔS and on the temperature. As data collected in *Table 1* indicate, in the polymerization of perhaloacetaldehydes ΔH_{polym} and ΔS_{polym} change in opposite directions (from the point of view of their influence on ΔG_{polym}) when passing from CF_3 to CBr_3 substituents. ΔH_{polym} becomes less negative making the polymerization less favourable. At the same time, the ΔS_{polym} also becomes less negative, making polymerization more favourable; thus the two effects tend to compensate each other.

Because the contribution of the entropy factor is smaller than the contribution of enthalpy, ΔG_{polym} changes in the same direction as ΔH_{polym}. Thus, the difference between ΔH_{lc} for the polymerization of fluoral and bromal is -35.8 kJ mol^{-1} (-8.55 kcal mol^{-1}) while the difference between the entropy factors ($T\Delta S$) at room temperature is only ~20 kJ mol^{-1} (4 kcal mol^{-1}).

Because the T_c is a function of ΔG_{polym}, $T_{sc'}$ changes in the same direction as $\Delta H_{sc'}$, although the contribution of the entropy factor makes the differences between T_c less pronounced than the differences between $\Delta H_{sc'}$ values.

ΔS_{polym} reflects mainly the loss of translational entropy of monomer, with changes in rotational (internal and external) and vibrational entropy compensating each other to a large extent. For the systems which have been studied, we may expect certain contributions from the rotational entropy in the polymer because an increasing size of the substituents in the β positions may inhibit the rotation around the carbon–carbon bond. Rotation around the carbon–carbon bond is not completely free even in the monomer molecule. For fluoral the energy barrier for rotation was found to be equal to 3.707 kJ mol^{-1} (0.885 kcal mol^{-1})[30]. This value is lower than the energy barrier for the rotation in acetaldehyde (4.817 kJ mol^{-1}, 1.150 kcal mol^{-1})[30], due to the increasing bond length of the carbon–carbon bond from 1.50 Å in CH_3CHO to 1.54 Å in CF_3CHO [28]. For chloro- and bromo-substituted acetaldehydes the length of the carbon–carbon bond is 1.52 Å [28] when the hydrogen atoms of the CH_3 group are substituted by fluorine atoms, and because of increasing size of the substituent, the energy barrier for rotation should be higher. This effect should be much more pronounced in polymers due to the mutual interaction between CX_3 substituents in the β positions, thus one would expect that internal rotational entropy would decrease more upon polymerization of bromal than upon polymerization of fluoral.

The overall entropy change during the polymerization follows however a different pattern; $\Delta S_{sc'}$ is highest for fluoral and lowest for bromal polymerization with intermediate values for polymerization of chloral.

Again, as in the case of ΔH_{polym}, there is a definite trend. The ΔS values for heterosubstituted perhaloacetaldehydes are (with the exception of the $CFCl_2$-substituted acetaldehyde) between the values for the corresponding homosubstituted haloaldehydes. This trend of entropy changes indicates that indeed the contribution of internal rotational entropy to the overall $\Delta S_{sc'}$ value is small and that the ΔS_{polym} is governed mainly by other factors.

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REFERENCES

1 Ivin, K. J. in 'Encyclopedia of Polymer Science and Technology', (Eds. H. F. Mark and N. M. Bikales), Interscience, 1977, Suppl. Vol. II, p 70
2 Sawada, H. in 'Reviews in Macromolecular Chemistry', (Eds. G. B. Butler and K. F. O'Driscoll), Marcel Dekker, 1970, Vol IV, p 313
3 Dainton, F. S. and Ivin, K. J. *Quart. Rev.* 1958, **12**, 61
4 Ivin, K. J. in 'Polymer Handbook', (Eds. J. Brandrup and E. H. Immergut) Wiley–Interscience, New York, 1975, Chapter II, p 421
5 Vogl, O., Miller, H. C. and Sharkey, W. H. *Macromolecules* 1972, **5**, 658
6 Kubisa, P. and Vogl, O. *Polymer J. (Jpn)* 1975, **4**, 186
7 Kubisa, P., Neguleseu, I., Hatada, K., Lipp, D. W., Starr, J., Yamada, B. and Vogl, O. *Pure Appl. Chem.* 1976, **48**, 275
8 Lipp, D. W., Campbell, R. W. and Vogl, O. *Polym. Prepr.* 1977, **18**, 40
9 Yamada, B., Campbell, R. W. and Vogl, O. *J. Polym. Sci. (Polym. Chem. Edn)* 1977, **15**, 1123
10 Yamada, B., Campbell, R. W. and Vogl, O. *Polymer J. (Jpn)* 1977, **9**, 23
11 Lipp, D. W., and Vogl, O. in 'Ring Opening Polymerization', (Eds. T. Saegusa and E. Goethals), *ACS Symposium Series*, 1977, **59**, p 111
12 Lipp, D. W. and Vogl, O. *Polymer J. (Jpn)*, 1977, 9, 499
13 Lipp, D. W. and Vogl, O. *Polymer* 1977, **18**, 1051
14 Lipp, D. W. and Vogl, O. *J. Polym. Sci. (Polym. Chem. Edn)* 1978, **16**, 1311
15 Vogl, O. and Corley, L. S. *Polym. Prepr.* 1978, **19**, 210
16 Campbell, R. W. and Vogl, O. *Makromol. Chem.* 1979, **180**, 633
17 Campbell, R. W. and Vogl, O. *Monatsh. Chem.* 1979, **119**, 1087
18 Vogl, O. *Polymer News* 1979, 5(4), 150
19 Lipp, D. W. *PhD Thesis,* University of Massachusetts (1977)
20 Miller, R. L. in 'Encyclopedia of Polymer Science and Technology', (Eds. H. F. Mark, N. G. Gaylord and N. M. Bikales), Interscience, New York, 1966, Vol. IV, p 449
21 Starkweather Jr, H. W. and Boyd, R. H. *J. Phys. Chem.* 1960, **64**, 410
22 Busfield, W. K. *Polymer* 1966, **7**, 541
23 Busfield, W. K. *Eur. Polym. J.* 1973, **9**, 1143
24 Busfield, W. K. and Whalley, E. *Trans. Faraday Soc.* 1963, **59**, 679
25 Mita, I., Imai, I. and Kambe, H. *Makromol. Chem.* 1970, **137**, 169
26 Mita, I., Imai, I. and Kambe, H. *Makromol. Chem.* 1970, **137**, 143
27 'Handbook of Chemistry and Physics', 59th Edn, CRS Press, 1978–1979
28 Hagen, G. *Acta Chem. Scand.* 1971, **25**, 813
29 'Handbook of Chemistry and Physics', 59th Edn, CRC Press, 1978–1979
30 Woods, R. C. *J. Chem. Phys.* 1967, **46**, 4789