The Thermally Induced Solid-State Polymerization Reaction in Halogenoacetates[☆]

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Nine salts of halogenoacetic acids $MOOC-CH_2-X$ were prepared and characterized by their thermochemical reactivity. It was found that in seven cases elimination of MX led to polymerization of the organic part of the molecule. The resulting polyester, polyglycolide, could be isolated easily by washing the reaction product with water. It has a distinct porous morphology. The reaction takes place at moderate temperatures (100–200 °C).

Photochemically induced dimerizations and polymerizations in the solid state have been studied for more than 30 years, pioneered by the work of Schmidt[1–5]. Usually, polyaddition of unsaturated compounds (alkenes or alkynes) is induced by irradiation in these cases. A prerequisite is a suitable orientation of the reacting parts of the molecule in the crystal. The structural aspects of these reactions are now well understood.

Only few examples of thermally induced polymerizations in the solid state were reported[6–8]. They are obviously more difficult to initiate because of the lower selectivity of the supplied energy (heat vs. light). One may speculate that it is even more important for a thermally induced solid state polymerization reaction that the monomers are oriented favorably in the crystal.

We recently reported on the unusual thermal elimination reaction that takes place in sodium chloroacetate[9].

$$\underset{\mathbf{1}}{Na^{+}\,{}^{-}OOC-CH_2-Cl(s)} \rightarrow NaCl(s) + 1/n\,[-OOC-CH_2-]_n(s) \quad (1)$$

The reaction leads quantitatively to the simplest polyester, called polyglycolide. This polymer is of high current interest as biomaterial, due to its good biodegradability[10–12].

The natural variation of reaction (1) would be the exchange of sodium for other metals and of chlorine for other halogens:

$$M^{+}\,{}^{-}OOCC-CH_2-X(s) \xrightarrow{?} MX(s) + 1/n\,[-OOC-CH_2-]_n(s) \quad (2)$$

with $M = 1/n\ M^{n+}$, e.g. K, NH_4^+, 1/2 Ca^{2+} and
X = F, Cl, Br, I

A thorough literature survey revealed that some of these compounds and their thermochemical reactivity were studied in almost "ancient" times. In 1857, Hoffmann obtained polyglycolide by heating of potassium chloroacetate **2**[13]. One year later, Kekulé, his mentor, studied the reaction himself[14]. Heintz in 1862[15] and Norton and Tcherniak in 1878[16] found the reaction in sodium chloroacetate **1**, and Beckurts and Otto[17] found it in silver chloroacetate **4** in 1881. Systematic studies were carried out by Bischoff and Walden in 1893–1894[18,19]. They heated sodium chloroacetate **1** and sodium bromoacetate **6**. They also demonstrated, following a suggestion of Anschütz[20,21], that the formed product was of polymeric nature, i.e., polyglycolide, and not the cyclic dimer $(-OOC-CH_2-)_2$, as it had been assumed before.

The reaction was studied only to a very little extent in this century[22–24], mainly on sodium chloroacetate. No systematic study was carried out in order to gain insight into the underlying principles of the reaction, e.g., its energetics, kinetics, or product morphology.

We studied the reactivity of sodium chloroacetate, employing various ex situ techniques (scanning electron microscopy, NMR in the liquid and in the solid state, X-ray powder diffractometry, EXAFS[9]) and in situ methods (IR spectroscopy[25], thermal analysis[9], EXAFS[26]). All results point to the fact that this is a true solid-state reaction with no liquid or solid intermediates. The reaction product NaCl is deposited as small cubes (d = 1–2 µm) in a polyglycolide matrix. It can be washed out with water, leaving a highly porous polyglycolide matrix with cubic holes (d = 1–10 µm) (Figure 1). Combustion of the polyglycolide at higher temperature leaves a sodium chloride "skeleton" of linked cubes[9].

The question remains whether this reaction occurs with all halogenoacetates of eq. 2, with different combinations of M and X. We prepared a number of homologous compounds and studied their polymerizability. In this paper we report on the results of these studies. It turned out that seven out of nine compounds form the desired polymer, although only five in quantitative yield.

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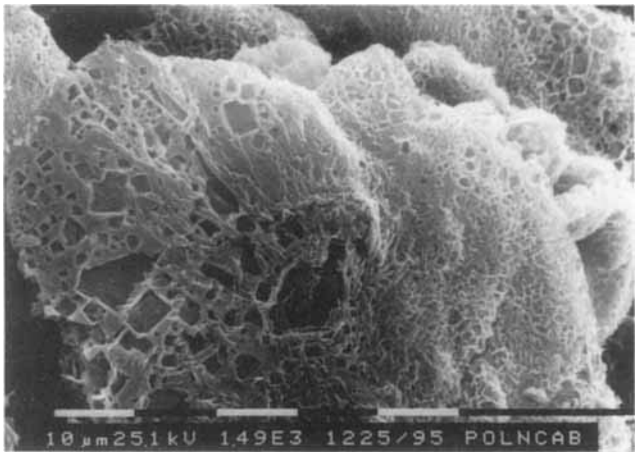
Figure 1. Scanning electron micrograph of polyglycolide. This sample was prepared by heating of sodium chloroacetate at 180 °C for 60 min and subsequent washing with water. Clearly visible are the "inverse sodium chloride cubes", i.e., the pores in the polymer where the NaCl was formed during the reaction



Results and Discussion

Nine halogenoacetates were prepared. We studied only salts of chloroacetic acid, bromoacetic acid and iodoacetic acid. Due to the extreme toxicity of fluoroacetic acid and especially its salts, we decided to leave these compounds for future studies.

Scheme 1

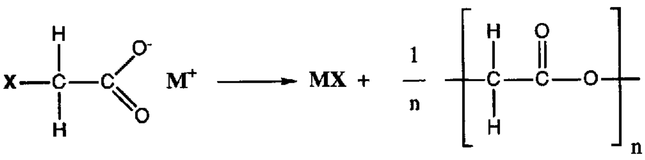


Table 1. Numbering scheme of the compounds **1** to **9**

Compound	1	2	3	4	5[a]	6	7	8	9
M	Na	K	NH_4	Ag	$1/2\ Ca^{2+}$	Na	Ag	Na	K
X	Cl	Cl	Cl	Cl	Cl	Br	Br	I	I

[a] This compound forms a monohydrate: $Ca(OOC-CH_2-Cl)_2 \cdot H_2O$.

The halogenoacetates were characterized by various spectroscopic methods: NMR in aqueous solution (^1H, ^{13}C), solid-state NMR (^{13}C), and IR spectroscopy. Additionally, the thermoanalytic techniques[27] differential scanning calorimetry (DSC) and thermogravimetry (combined with different thermal analysis, DTA, and mass spectrometry of evolved gases, TG-DTA-MS) were employed. Elemental analysis (C, H, N), and X-ray powder diffraction supplemented these investigations. Great care was bestowed to assure that no free halogenocarboxylic acid was present (absence of a melting peak in DSC), that no polyglycolide had already formed (IR, solid-state NMR) and that no metal halide MX or hydroxide MOH was present (powder diffractometry). In most cases, the purity of the starting compound was also confirmed by the weight loss determined by thermogravimetry after heating to 550 °C. Usually, it was consistent within the usual error limits caused by buoyancy with the one expected for remaining metal halide MX after complete combustion of polyglycolide (see Table 2).

The polymerizability of the halogenoacetates was checked by thermal analysis (DSC and TG-DTA-MS). A solid-state elimination as in eq. 2 is revealed by a strong exothermic peak, usually between 100 and 200 °C (see Table 2). Between 210 and 220 °C, the formed polyglycolide melts (endothermic peak). Above ca. 250 °C, combustion of polyglycolide occurs. A typical DSC scan is shown in Figure 2.

Except for the temperature range of the exothermic elimination peak, the DSC curves of the polymerizing halogenoacetates all look very similar to Figure 2. A completely different picture is shown by calcium chloroacetate monohydrate **5** that does not undergo the elimination reaction but only ill-defined decomposition (Figure 3). The endothermic dehydration between 95 and 150 °C (**A**) is followed by melting (**B**) without mass loss (T_{fus} = 197.8 °C). Above ca. 250 °C, multistep decomposition and combustion occur (**C** and **D**). The final mass loss corresponds with a residue of $CaCl_2$ (see Table 2).

Studies with combined TG-DTA-MS supplemented the information obtained by DSC. In cases of a successful polymerization, mass loss is observed above 220–230 °C, well after the polymerization reaction has occurred. Detected fragments are only H_2O (m/z = 17, 18) and CO_2 (m/z = 44) formed during the combustion of polyglycolide. This shows that it is possible to prepare polyglycolide by heating of the halogenoacetates above the elimination temperature but below the combustion temperature. Isothermal experiments are more suited for a planned synthesis than the non-isothermal experiments in DSC because wanted and unwanted reactions can be separated more easily.

We studied the reaction kinetics of the synthesized halogenoacetates towards isothermal elimination by isothermal DSC. This proved to be a valuable method for estimating reaction times because only a few milligrams of sample were needed and the extent of the reaction as a function of time could be derived easily from the exothermic elimination peak[27]. After a suitable temperature range for a complete reaction had been determined by DSC, a large-scale experiment was carried out by heating ca. 5 to 10 g of halogenoacetate in a round-bottom flask in an oil bath. With these quantities, it was necessary to stir the sample every few minutes to ensure isothermal conditions. Powders generally have a low thermal conductivity[28].

The external morphology of the sample (fine powder) did not change during the experiment, except for ammonium chloroacetate, where melting occurred. This preserved morphology is a first hint that this is a pure solid-state reaction, a fact that was, however, confirmed by various other in situ methods (see introduction). Electron microscopy revealed that the metal halide MX is formed as small cubic crystals (d = 0.1–10 µm) in a polymeric matrix[9]. The water-insoluble polymer could be isolated easily by washing the reaction product with water. The obtained polyglycolide was characterized by elemental analysis (C, H), IR spectroscopy,

Table 2. Thermochemical data of halogenoacetates. Thermogravimetry: The compounds were heated in open crucibles. Evolved gases were detected by mass spectroscopy. DSC: The compounds were heated in air in aluminum crucibles whose lid was pierced with a thin needle. Values in parantheses represent standard deviations of multiple experiments

Compound		Weight loss in Thermogravimetry (air, β=5 K min^{-1}, to 550 °C): T_{onset} / °C	% found	(% calcd.)[a]	Exothermic elimination reaction by DSC T_{Onset} / °C (β=5 K min^{-1})	Δ_rH / kJ mol^{-1}
Sodium chloroacetate	**1**	230	49.3	(49.8)	197.6(52)	-25.2 (7)
Potassium chloroacetate	**2**	220	42.4	(43.8)	157.4(80)	-40.3(31)
Ammonium chloroacetate	**3**	150	93.0	(100.0) [b]	107.0(26)	-21.8(16)
Silver chloroacetate	**4**	130 [c]	29.7	(28.8)	134.0(18)	-64.2(20)
Calcium chloroacetate	**5**	a) 90	8.2	(7.3) [d]	95.2	+48.3
hydrate		b) 260	54.6	(54.7)	197.8 [e]	+15.1 [e]
Sodium bromoacetate	**6**	230	35.0	(36.1)	186 (10)	-23.4(20)
Silver bromoacetate	**7**	270	20.7	(23.6)	77.6(30)	-63.9(58)
Sodium iodoacetate	**8**	200	33.5	(27.9) [f]	204.4(10) [f]	-72 (14) [f]
Potassium iodoacetate	**9**	250	25.6	(25.9)	192.4 (6)	-23.5(17)

[a] For the complete combustion of polyglycolide (only MX remains). – [b] The resulting NH_4Cl sublimates. – [c] Slow mass loss starts at 90 °C. – [d] Loss of 1 mol of crystal water. DSC (5 K min^{-1}): T_{Onset} = 95.2 °C; $\Delta_{dehydr}H$ = 48.3 kJ mol^{-1}. – [e] Endothermic fusion process. – [f] Decomposition with release of elemental iodine occurs is indicated by a well-defined exothermic DSC peak. Its onset temperature and enthalpy of reaction are given. The exothermic peak is preceded by a phase transition with a variable onset temperature of 167–183 °C.

Figure 2. DSC scan of potassium iodoacetate **9** (β = 5 K min^{-1}). The strongly exothermic elimination reaction (**A**) around 200 °C is followed by endothermic melting of polyglycolide (210–220 °C; **B**) and exothermic combustion of polyglycolide (T > 250 °C; two stages; **C** and **D**). Polyglycolide can be isolated by stopping the reaction between **B** and **C**

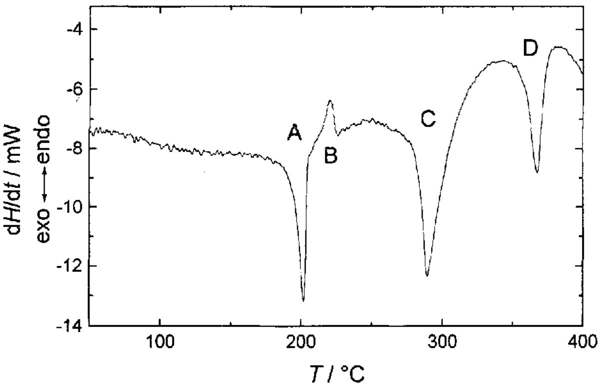
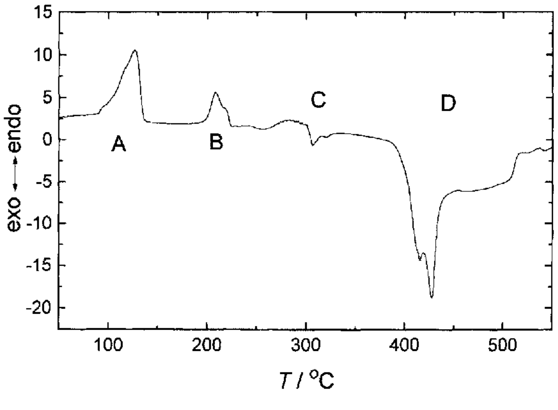


Figure 3. DSC scan of calcium chloroacetate monohydrate **5** with β = 5 K min^{-1}. Endothermic dehydration between 95 and 150 °C (**A**) is followed by endothermic melting at 197.8 °C (**B**). Above 250 °C, a multistep decomposition occurs (**C**, **D**). This compound does not undergo elimination to polyglycolide



solid-state NMR spectroscopy (^{13}C), NMR spectroscopy in solution (^{1}H and ^{13}C), and DSC.

Polyglycolide is insoluble in practically all solvents. The best results were obtained with 1,1,1,3,3,3-hexafluoroisopropanol. However, complete dissolution could be achieved only at reflux temperature, and upon cooling again, a part of the dissolved polymer precipitated again. The polymer is soluble in a mixture of $CDCl_3$/trifluoroacetic acid (volume ratio 3:1)[29]. Thus, polyglycolide could be identified by means of the chemical shifts observed in its ^{1}H- and ^{13}C-NMR spectra recorded in this solution. However, we have the strong suspicion that this highly acidic solvent causes some hydrolysis that makes it unsuitable for a determination of the degree of polymerization by quantitative determination of end groups.

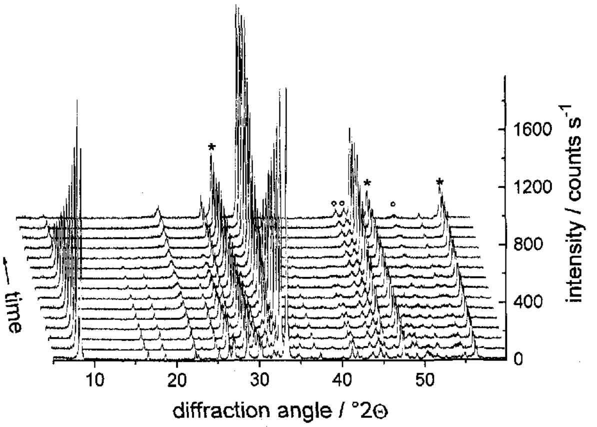
The end groups of the formed polyglycolide in the solid state were identified by in situ IR spectroscopy as COO^-M^+ and $HO-CH_2$[25]. Since this experiment was carried out in air, we assume that the $Cl-CH_2$ end group was hydrolyzed by atmospheric water. This is reasonable because halogenoacetic acids are hydrolyzed to hydroxyacetic acid in hot water[30,31].

In situ temperature-resolved X-ray diffractometry (TXRD)[32,33] was carried out to detect possible intermediates of the elimination reaction in sodium chloroacetate **1**. In ref.[9] we already reported on an ex situ experiment where no intermediates could be found. However, during cooling and storage of the aliquots for this experiment, solid-solid phase transformations or consecutive reactions may have occurred.

Sodium chloroacetate was mixed with an equal volume of silicon as 2Θ standard and heated rapidly to 130 °C. The sample was held at this temperature for 643 minutes, and powder diffractograms were recorded continuously every 46 minutes. Thus, the sample was continuously irradiated with X-rays.

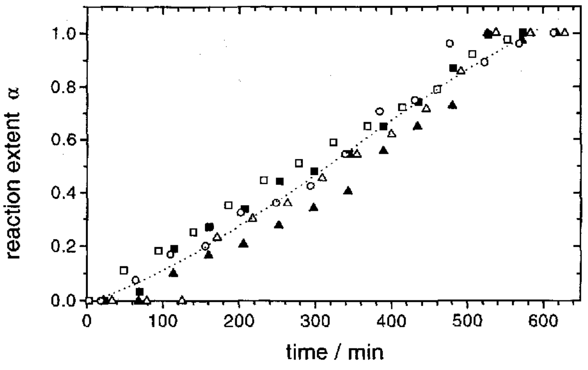
A pseudo-3D representation of the obtained diffractograms is shown in Figure 4. Sodium chloroacetate peaks shrink and peaks of sodium chloride and of polyglycolide grow. No intermediates are visible. A quantitative evalu-

Figure 4. Temperature-resolved X-ray powder diffractograms of the reaction of sodium chloroacetate leading to polyglycolide and sodium chloride. The first scan was taken at room temperature before heating of the sample. The reaction temperature was 130 °C (at the beginning of second scan), the total time for the experiment was 643 minutes. One scan took 45.9 minutes (2Θ = 5−60°; step width 0.01° 2Θ; integration time 0.5 s). Marked peaks originate from the added silicon powder (*) or from the sample holder (O)



ation is shown in Figure 5 where five characteristic strong peaks were integrated and their intensity was plotted against the reaction time. In this case of a pure solid-state reaction without mass loss, the scattered intensity is directly proportional to the mass fraction of the corresponding compound[34].

Figure 5. A quantitative evaluation of the diffraction data in Figure 3 shows the relative mass fractions of sodium chloroacetate **1**, polyglycolide and sodium chloride NaCl in the sample as a function of time. It seems as if the formation of NaCl occurs delayed compared with the consumption of sodium chloroacetate. The inserted curve represents a sigmoidal fit to all data points



−□− Sodium chloroacetate peak at 8.3° 2θ: $\alpha = 1 - I(t)/I(t = 0)$
−■− Sodium chloroacetate peak at 33.2° 2Θ: $\alpha = 1 - I(t)/I(t = 0)$
−▲− Sodium chloride (200) peak at 31.6° 2Θ: $\alpha = I(t)/I(t = \infty)$
−△− Sodium chloride (220) peak at 45.4° 2Θ: $\alpha = I(t)/I(t = \infty)$
−○− Polyglycolide peak at 27.3° 2Θ: $\alpha = I(t)/I(t = \infty)$

There is some scatter and inaccuracy in the X-ray intensities. However, it might be that the formation of sodium chloride occurs delayed compared to the disappearance of the sodium chloroacetate peaks. This could point to a possible intermediate or to very small NaCl crystals at the beginning of the reaction that cannot be detected by X-ray diffractometry. Considering the results of other in situ methods that were employed earlier and that showed no intermediates, we favor the second interpretation. This is corroborated also by a decreasing delay of the formation of sodium chloride with advancing reaction. That can be interpreted as a decreasing number of new nuclei due to progressively consumed starting material.

An important observation is the fact that the reaction is considerably accelerated by the continuous irradiation. It needs about 520 minutes at 130 °C and 180 minutes at 150 °C to be complete (experiment not shown). An isothermal DSC experiment at 150 °C needed 845 minutes for completion, and one at 160 °C needed 435 minutes. The shape of the *α*/*t* curve changes as well. For TXRD experiments, we observe an almost linear dependence whereas for isothermal DSC experiments and the ex situ experiments reported in ref.[9] a distinct sigmoidal shape was found. It may be that irradiation plays a decisive role both for the reaction kinetics and the mechanism. Generally, it should be checked for in situ studies with TXRD that are evaluated with respect to kinetics that irradiation does not influence the reaction, otherwise, misleading results may be obtained.

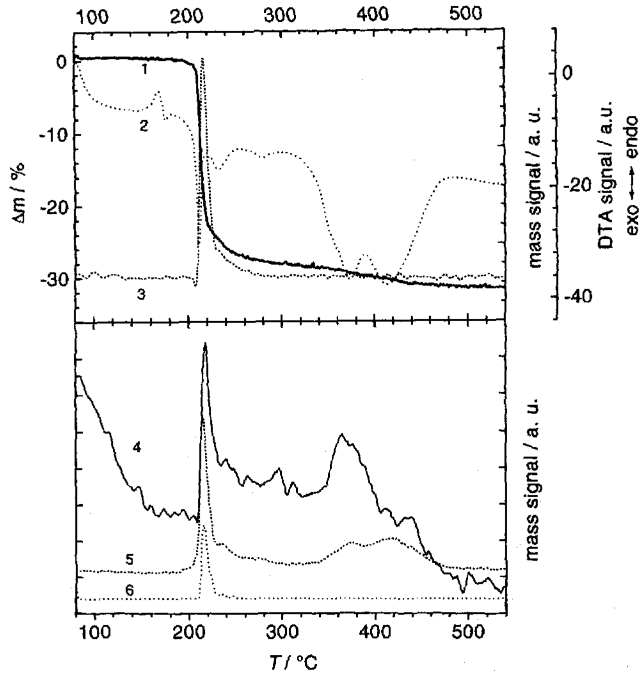
Two salts out of nine do not form polyglycolide. Calcium chloroacetate **5** melts without polymerization (see Figure 3). In that case, it is obviously difficult for the substance to eliminate $CaCl_2$ without collapse of the crystal structure. This may be due to the fact that the cation has the charge +2 instead of +1 in the other cases.

Sodium iodoacetate **8** gives an exothermic peak with an onset temperature of 204.4 °C. The enthalpy of reaction is the highest one of all halogenoacetates with −72.0 kJ mol^{-1}. Simultaneously with this exothermic reaction, a mass loss occurs, as visible by simultaneous TG-DTA-MS (Figure 6). Mass spectrometry of the evolved gases shows the release of methyl ($m/z = 15$), water ($m/z = 17, 18$), carbon dioxide ($m/z = 44$), and acetic acid ($m/z = 60$). We also identified released iodine by its violet color. The observed mass loss of 33.5 wt-% is considerably higher than the one expected for remaining sodium iodide NaI (27.9 wt%). Clearly, a partial combustion of the compound occurs, which explains the highly exothermic enthalpy of reaction.

Only sodium iodide is seen in X-ray powder diffraction after heating to 550 °C. Despite extensive experiments at low heating rates or under different gases (N_2, H_2/N_2) it was impossible to prevent the almost "explosive" decomposition of sodium iodoacetate. We surmise that the strongly exothermic decomposition leads to autocatalytic self-heating of the compound and thus combustion. No polyglycolide could be isolated in this case so far.

A similar observation was made for silver chloroacetate **4** which polymerizes around 120 °C with an enthalpy of reaction of −64.2 kJ mol^{-1}. If this compound is not heated slowly, self-heating leading to combustion may occur. Consequently, a quantitative isolation of larger quantities of polyglycolide is difficult. Silver bromoacetate has a comparable enthalpy of reaction (−63.9 kJ mol^{-1}), but the low reaction temperature of ca. 80 °C effectively prevents self-heating to temperatures where combustion may start. Polyglycolide was obtained quantitatively from silver bromoacetate.

Figure 6. A TG-DTA-MS scan of sodium iodoacetate **8** shows the endothermic/exothermic phase transition at 180–200 °C and the strong exothermic decomposition peak above 200 °C. This peak is accompanied by a rapid mass loss. The main detected mass fragments are 15 (CH_3), 17 and 18 (H_2O), 44 (CO_2) and 60 (acetic acid)



1: TG. – 2: DTA. – 3: m/z = 15. – 4: m/z = 18. – 5: m/z = 44. – 6: m/z = 60.

Prior to the exothermic reaction in sodium iodoacetate, an endothermic/exothermic event occurs reproducibly with a variable onset temperature of 167–183 °C (visible more pronounced in DSC). No mass loss is associated with this process, so that we ascribe this event to a phase transformation. Interestingly, sodium iodoacetate does not react at temperatures below 185 °C, as shown by isothermal DSC experiments, whereas a rapid reaction occurs at temperatures equal or higher than 185 °C. It seems as if the low-temperature phase is not able to follow the reaction pathway of the high-temperature phase. In situ X-ray powder diffractometry showed an almost instantaneous reaction affording sodium iodide at 145 °C. The continuous irradiation with X-rays destabilizes sodium iodoacetate and leads to enhanced decomposition.

The described results are compiled in Table 3. Seven out of nine prepared halogenoacetates undergo the desired polymerization reaction. In five cases, polyglycolide could be isolated quantitatively, in one case (silver chloroacetate) it was difficult to obtain larger amounts, and in another case (ammonium chloroacetate) mostly oligomers were formed.

It is not possible to definitively explain why the two remaining salts do not undergo polymerization. The reason could lie in crystallography, thermodynamics, and kinetics. First, the arrangement of the molecules in the crystal may be unfavorable for an elimination, e.g. a very long distance between M and X or between the two ends of the organic group. This question could be solved by knowledge and comparison of the crystal structure of the halogenoacetates. Unfortunately, no crystal structure of an halogenoacetate has been known to date, and despite extensive efforts, we were not able to obtain single crystals suitable for X-ray diffractometry. Generally, all compounds crystallize as very thin platelets or needles that show a distinct stacking disorder, even to the bare eye.

Concerning thermodynamics, one would need the enthalpies of formation of the halogenoacetates and of polyglycolide to compute the enthalpy of reaction. None of these was found in the literature. Chemical kinetics determine whether the desired reaction pathway is suitable or

Table 3. The polymerizability of halogenoacetates: seven out of nine compounds undergo the desired reaction

Compound		Formula	Polymerizability	Elimination products
Sodium chloroacetate	**1**	$NaOOCCH_2$-Cl	yes, quantitatively	NaCl, polyglycolide
Potassium chloroacetate	**2**	$KOOCCH_2$-Cl	yes, quantitatively	KCl, polyglycolide
Ammonium chloroacetate	**3**	NH_4OOCCH_2-Cl	oligomerization, little fraction of poly-glycolide (~2 wt%)	NH_4Cl, polyglycolide, oligomers
Silver chloroacetate	**4**	$AgOOCCH_2$-Cl	yes	AgCl, polyglycolide
Calcium chloroacetate hydrate	**5**	$Ca(OOCCH_2\text{-}Cl)_2 \cdot H_2O$	no	——
Sodium bromoacetate	**6**	$NaOOCCH_2$-Br	yes, quantitatively	NaBr, polyglycolide
Silver bromoacetate	**7**	$AgOOCCH_2$-Br	yes, quantitatively	AgBr, polyglycolide
Sodium iodoacetate	**8**	$NaOOCCH_2$-I	no	——
Potassium iodoacetate	**9**	$KOOCCH_2$-I	yes, quantitatively	KI, polyglycolide

whether another one, e.g. unwanted decomposition, is preferred. Properties to be known would be the defect structure of the crystals, diffusion coefficients etc.[35,36].

Of course, structure, thermodynamics, and kinetics are related to one another and cannot be separated. This is a general feature in solid state reactivity. In case of the discussed reaction presented here, much more information is necessary to make a decisive statement about the feasibility and general applicability for halogenoacetates. The approach must be regarded as phenomenological so far. We may nevertheless conclude that polyglycolide can be prepared by smooth solid-state reaction from inexpensive precursors. Future work must show how the properties of the formed polymer (degree of polymerization, micromorphology) can be tailor-made by varying the precursor compound. Possible applications of microstructural polyglycolide could be membranes with a defined pore structure, drug carrier systems, and biomaterials.

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Experimental

Analytic techniques: Differential scanning calorimetry (DSC) was carried out with a Mettler DSC 27 HP heat-flux calorimeter at ambient pressure. The calorimeter was calibrated (T and heat-flux) by melting water, naphthalene, indium, lead, and zinc[37–39]. Sealed aluminum crucibles with a small pinhole in the lid served as sample holders. As reference, empty aluminum crucibles were used. The sample mass was 5–10 mg. The accuracy was estimated to ±0.5 K for temperature determinations and ±3.5% for enthalpy determinations. For isothermal experiments, the calorimeter was heated to the annealing temperature without sample crucible and left a few minutes to equilibrate. Then the sample crucible was placed into the instrument that was closed immediately and the experiment started as soon as possible (equilibration time $\approx$ 1 min). Simultaneous thermogravimetry (TG), differential thermal analysis (DTA), and mass spectrometry (MS) of evolved gases were carried out with a Netzsch STA 409/Balzers QMS 421 system in dynamic air atmosphere (50 ml min^{-1}). Samples (50–150 mg) were placed in open alumina crucibles. – X-ray powder diffractometry was carried out with a Philips PW 1050/25 diffractometer with Nickel-filtered Cu-K_α radiation (λ = 154.178 pm). For high-temperature X-ray powder diffractometry (TXRD) we used a Philips XPERT diffractometer equipped with a Paar HTK 10 camera and a stainless steel heating strip. Cu-K_α radiation (secondary monochromator) was used. The temperature signal was calibrated with the II-I-phase transition of KNO_3 at 128 °C. – High-resolution solid-state CP/MAS NMR: Bruker MSL-300 NMR (75.5 MHz; ^{13}C). Samples were placed in 7-mm ZrO_2 rotors and spun with 4 kHz. – The solvent for solution NMR was D_2O in all cases. ^1H-NMR spectroscopy: Bruker WP-80 (80 MHz) and Varian Gemini 200 (200 MHz). The solvent peak of HOD was set to δ_H = 4.65. For ^{13}C-NMR spectroscopy: Varian Gemini 200 (50.31 MHz).

Chemicals: Halogenoacetic acids, metal hydroxides, and silver nitrate were purchased from Merck in "pro analysi" quality.

Sodium Chloroacetate (**1**), *Potassium Chloroacetate* (**2**), *Calcium Chloroacetate Monohydrate* (**5**), *Sodium Bromoacetate* (**6**), *Sodium Iodoacetate* (**8**): A concentrated solution of halogenoacetic acid in ethanol was neutralized at room temp. with an equimolar amount of the corresponding hydroxide in ethanol. The solvent was removed in a rotary evaporator. The residue was recrystallized from ethanol and dried in vacuo. Yield 80–90%, white platelets. – IR (KBr) of **1**: $\tilde{\nu}$ = 3008/2972 cm^{-1} (w, C–H), 1601 (s, C=O), 1421 (s, COO$^-$, C–H), 1249 (s, C–O), 933 (m), 771 (m), 674 (m), 578 (m), 430 (m). – **2**: $\tilde{\nu}$ = 2991/2964 cm^{-1} (w, C–H), 1604 (s, C=O), 1408 (s, COO$^-$, C–H), 1247 (s, C–O), 933 (m), 768 (m), 671 (m), 569 (m), 425 (m). – **5**: $\tilde{\nu}$ = 3031/2955 cm^{-1} (w, C–H), 1627/1578 (s, C=O), 1447/1418/1403 (m, COO$^-$, C–H), 1270/1252 (s, C–O), 939 (m), 793 (m), 777 (m), 704 (m), 571 (m), 460 (m). – **6**: $\tilde{\nu}$ = 3009/2967 cm^{-1} (w, C–H), 1590 (s, C=O), 1415/1385 (m, COO$^-$, C–H), 1222/1213 (s, C–O), 926 (m), 898 (m), 699 (m), 669 (m). – **8**: $\tilde{\nu}$ = 2994/2947 cm^{-1} (w, C–H), 1578 (s, C=O), 1427/1397 (m, COO$^-$, C–H), 1176 (s, C–O), 923 (m), 853 (m), 673 (m), 652 (m). – ^1H NMR (D_2O) of **1**: δ = 3.85 (s). – **2**: δ = 3.94 (s); **5**: δ = 4.02 (s). – **6**: δ = 3.93 (s). – **8**: δ = 3.63 (s). – ^{13}C NMR (D_2O) of **1**: δ = 44.79 (s, CH_2), 175.97 (s, COO). – **2**: δ = 44.75 (s, CH_2), 175.75 (s, COO). – **5**: δ = 44.81 (s, CH_2), 176.09 (s, COO). – **6**: δ = 32.12 (s, CH_2), 175.76 (s, COO). – **8**: δ = 2.82 (s, CH_2), 178.16 (s, COO). – ^{13}C CP/MAS NMR of **1**: δ = 46.40 (d, J = 528 Hz, CH_2), 175.95 (d, J = 68 Hz, COO); **2**: δ = 46.87 (d, J = 517 Hz, CH_2), 172.43 (s, COO); **5**: δ = 45.01 (d, J = 349 Hz, CH_2), 176.07 (d, J = 186 Hz, COO). – **1**: $C_2H_2ClNaO_2$ (116.5): calcd. C 20.62, H 1.73, Cl 30.43; found C 20.54, H 1.63, Cl 30.90. – **2**: $C_2H_2ClKO_2$ (132.6): calcd. C 18.12, H 1.52, Cl 26.74; found C 18.48, H 1.83, Cl 25.98. – **5**: $C_4H_6CaCl_2O_5$ (245.1): calcd. C 19.60, H 2.47; found C 19.61, H 2.47. – **6**: $C_2H_2BrNaO_2$ (160.9): calcd. C 14.93, H 1.26; found C 14.92, H 1.26. – **8**: $C_2H_2INaO_2$ (207.9): calcd. C 11.55, H 0.97; found C 11.58, H 0.92.

Ammonium Chloroacetate (**3**): To a concentrated ethanolic solution of chloroacetic acid an excess of a concentrated aqueous solution of NH_3 was given. Water and ethanol were removed in a rotary evaporator. The white residue was recrystallized from diethyl ether/ethanol (1:5). Yield 90%, white hygroscopic crystals. – IR (KBr): $\tilde{\nu}$ = 2901 cm^{-1} (w, C–H), 1594 (s, C=O), 1450/1375 (s, COO$^-$, C–H), 1082 (m), 935 (m). – ^1H NMR (D_2O): δ = 4.06 (s, CH_2). – ^{13}C NMR (D_2O): δ = 44.67 (s, CH_2), 175.65 (s, COO). – ^{13}C CP/MAS NMR: δ = 45.35 (d, J = 484 Hz, CH_2), 175.65 (s, COO). – $C_2H_6ClNO_2$ (111.4): calcd. C 21.54, H 5.42, N 12.56; found C 21.01, H 5.44, N 12.69.

Silver Chloroacetate (**4**): All operations were carried out in vessels wrapped in aluminum foil. An equimolar amount of KOH in ethanol was added to a diluted ethanolic solution of $AgNO_3$ at −50 °C. A dispersion of "AgOH" formed. A solution of an equimolar amount of chloroacetic acid in ethanol was added. Colorless needles precipitated. The dispersion was stirred for 1 h at −50 °C. The salt was filtered off with a cooled Buchner funnel, recrystallized from water at 50 °C, and dried in vacuo. Yield 50%, very thin, white-grey light-sensitive needles. – IR (KBr): $\tilde{\nu}$ = 2989/2963 cm^{-1} (w, C–H), 1604 (s, C=O), 1410/1399/1340 (s, COO$^-$, C–H), 1248 (s, C–O), 933 (m), 919 (m). – ^1H NMR (D_2O): δ = 4.18 (s, CH_2). – ^{13}C NMR (D_2O): δ = 44.96 (s, CH_2), 175.90 (s, COO). – ^{13}C CP/MAS-NMR: δ = 47.11 (d, J = 562 Hz, CH_2), 174.59 (s, COO). – $C_2H_2AgClO_2$ (201.4): calcd. C 11.93, H 1.00; found C 11.81, H 1.14.

Silver Bromoacetate (**7**): Light was excluded as far as possible. A solution of sodium bromoacetate in ethanol was slowly added to an equimolar solution of $AgNO_3$ in ethanol at 0 °C. A white precipitate formed. The dispersion was stirred for 4 h, the precipitate was filtered off, washed with cold water, ethanol and diethyl ether, and dried in vacuo. Yield 89%, white-grey light-sensitive crystals. The neutralization of bromoacetic acid with KOH at 50°C as with **4** afforded AgBr, but not the desired product **7**. – IR (KBr): $\tilde{\nu}$ = 3014/2961 cm^{-1} (w, C–H), 1610/1572 (s, C=O), 1459/1391 (s, COO$^-$, C–H), 1224/1208 (s, C–O), 916 (m), 703 (m), 669 (m). – ^{1}H NMR (D_2O): δ = 3.68 (s, CH_2). – ^{13}C NMR (D_2O): δ = 31.12 (s, CH_2), 175.01 (s, COO). – $C_2H_2AgBrO_2$ (245.8): calcd. C 9.77, H 0.82; found C 9.56, H 0.83.

Potassium Iodoacetate (**9**): To an ethanolic solution of iodoacetic acid an equimolar solution of KOH in ethanol was added at −50°C. The solvent was almost fully removed in vacuo at −50°C. The white precipitate was filtered off, washed with little cold ethanol and dried in vacuo. Yield 78%, white crystals. – IR (KBr): $\tilde{\nu}$ = 2994/2947 cm^{-1} (w, C–H), 1597 (s, C=O), 1415/1382/1365 (s, COO$^-$, C–H), 1172/1165 (s, C–O), 912 (m), 853 (m), 664 (m), 543 (m). – ^{1}H NMR (D_2O): δ = 3.59 (s, CH_2). – ^{13}C NMR (D_2O): δ = 3.27 (s, CH_2), 178.09 (s, COO). – $C_2H_2IKO_2$ (224.0): calcd. C 10.72, H 0.90, I 56.64; found C 10.72, H 0.94, I 54.98.

Preparation of Polyglycolide by Thermal Elimination from Halogenoacetates: Ca. 5–20 g of mortared halogenoacetate was annealed in a round-bottom flask in an oil bath. The sample should be heated carefully to avoid self-heating that may lead to combustion. Reaction conditions: Sodium chloroacetate (**1**): 60 min at 180°C; potassium chloroacetate (**2**): 60 min at 150°C; ammonium chloroacetate (**3**): 30 min at 110°C; silver chloroacetate (**4**): 60 min at 180°C; sodium bromoacetate (**6**): 60 min at 160°C; silver bromoacetate (**7**): 10 min at 100°C; potassium iodoacetate (**9**): 60 min at 180°C. The sample changed from a white to a yellow or grayish powder but retained its morphology, except ammonium chloroacetate (see below). The polyglycolide was separated from the also formed metal halide by multiple washing with water. Yield quantitative. Ammonium chloroacetate reacts to afford a viscous yellow liquid with suspended polyglycolide (small white particles; about 2 wt-%). The yellow liquid is probably a mixture of oligomers, as shown by ^{1}H-NMR (δ_H = 3.98–4.78; many peaks). *Polyglycolide*: White powder, insoluble in common solvents, partially soluble in 1,1,1,3,3,3-hexafluoro-2-propanol. – IR (KBr): $\tilde{\nu}$ = 2992/2961 cm^{-1} (w, C–H), 1744 (s, C=O ester), 1630 (w, C=O, acetate end group: COO$^-$M$^+$), 1419 (m, COO$^-$, C–H), 1229 (s, C–O, ester bond), 1096 (m, C–OH end group), 974 (w), 904 (w), 808 (w), 628 (w), 594 (w). – ^{1}H NMR ($CDCl_3$/trifluoroacetic acid, 3:1): δ = 4.89 (m, CH_2O) (ref.[29] 4.91 in 1,1,1,3,3,3-hexafluoro-2-propanol). – ^{13}C NMR ($CDCl_3$/trifluoroacetic acid, 3:1): δ = 61.49 (s, CH_2O), 168.3 (s, COO) (ref.[29]: 61.4/168.4 in 1,1,1,3,3,3-hexafluoro-2-propanol). – ^{13}C CP/MAS NMR: δ = 62.3 (s, CH_2), 166.9 (s, COO). – $1/n(C_2H_2O_2)_n$ (58.0): calcd. C 41.39, H 3.47; found C 39.32, H 3.48.

☆ Dedicated to Prof. *Günther Klar* on the occasion of his 60th birthday.

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