

# Driving Force for the Thermally Induced Solid State Polymerization of Alkali Metal Halogenoacetates: A Thermochemical Analysis

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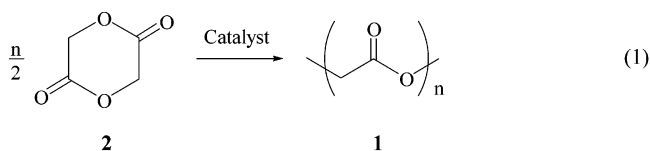
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Reaction-solution calorimetry was used to determine the standard molar enthalpies of formation of a series of lithium and sodium halogenoacetates in the crystalline state at 298.15 K. The obtained values were as follows:  $\Delta_f H_m^\circ(\text{ClCH}_2\text{COOLi, cr}) = -(763.6 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f H_m^\circ(\text{BrCH}_2\text{COOLi, cr}) = -(723.7 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f H_m^\circ(\text{ICH}_2\text{COOLi, cr}) = -(671.1 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f H_m^\circ(\text{ClCH}_2\text{COONa, cr}) = -(740.9 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f H_m^\circ(\text{BrCH}_2\text{COONa, cr}) = -(700.2 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1}$ , and  $\Delta_f H_m^\circ(\text{ICH}_2\text{COONa, cr}) = -(642.0 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$ . Microcombustion calorimetric studies of a polyglycolide sample with the empirical formula  $\text{C}_{2.000}\text{H}_{2.160}\text{O}_{2.032}\text{Cl}_{0.009243}\text{Na}_{0.004404}$  (PGA) led to  $\Delta_f H_m^\circ(\text{PGA, pol}) = -(379.1 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$ . These results were used to discuss the energetics of the solid-state polymerization of alkali metal halogenoacetates leading to polyglycolide. In agreement with experimental observations, it is concluded that for a given metal, the reaction becomes less favorable when the halogen changes along the series  $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ . The reaction is also considerably less favorable for the lithium than for the homologue sodium salts. These differences in reactivity seem to be mainly determined by the lattice enthalpy of the alkali metal halide salt formed in each reaction.

## Introduction

Polyglycolide, PGA, **1**, is a nontoxic and easily biodegradable polymer with great potential for application in medicine and pharmaceutical technology. It is used, for example, in controlled drug-delivery systems,<sup>1–3</sup> in scaffolds for extracorporeal tissue cultures (“tissue engineering”),<sup>3–5</sup> and in materials for internal bone fracture fixation (osteosynthesis),<sup>6–9</sup> teeth desensitization,<sup>10</sup> or absorbable surgical suture.<sup>11,12</sup> Conventionally, PGA is prepared from glycolide (1,4-dioxane-2,5-dione, **2**) by ring opening polymerization using a catalyst such as  $\text{SbF}_3$ .<sup>13</sup>



An alternative route is the direct solid-state polymerization of halogenoacetates ( $\text{M}$  = alkali metal;  $\text{X}$  = halogen):



which was discovered in 1857, when Hoffman, a student of Kekulé, reported on the thermally induced polycondensation of potassium chloroacetate.<sup>14</sup> Little attention was paid to this reaction until about 1996, when it was recognized that it could

be an efficient method to prepare polyglycolide polymers of controlled micromorphology and porosity.<sup>15</sup> Due to the deposition of crystals of the eliminated salt in the polymeric matrix, an intimate mixture of metal halide and polyglycolide is obtained. Removal of the metal halide by washing with water leads to highly porous polyglycolide samples whose overall porosity can be tuned, to a certain extent, by changing the starting material.<sup>15–18</sup> This possibility of controlling of porosity and micromorphology is, of course, very attractive in view of the medical applications referred to above. Another interesting aspect is the environmentally friendly nature of the reaction because it does not imply the disposal of solvents or metal catalysts.

Systematic structural and reactivity studies of the reaction in eq 2 have been undertaken recently using a variety of experimental techniques, including thermal analysis,<sup>16–19</sup> X-ray structure analysis,<sup>16,20–22</sup> in-situ X-ray absorption spectroscopy (EXAFS),<sup>19,23–25</sup> in-situ small- and wide-angle X-ray scattering (SAXS–WAXS),<sup>26</sup> in-situ solid-state NMR spectroscopy,<sup>27</sup> in-situ IR spectroscopy,<sup>28</sup> scanning electron microscopy,<sup>19</sup> mercury porosimetry,<sup>19</sup> viscometry,<sup>19</sup> and thermomicroscopy.<sup>29</sup> On the basis of the obtained results a general mechanism was formulated for the reaction, which according to all evidence appears to occur strictly in the solid state without any liquid intermediate.<sup>15</sup> The factors that govern the differences in reactivity of the  $\text{XCH}_2\text{COOM}$  compounds are, however, still not fully understood. It is not known for example, why  $\text{ClCH}_2\text{COONa}$  polymerizes readily at 471 K and  $\text{ICH}_2\text{COONa}$  decomposes at 493 K before any polymerization occurs.<sup>15–17</sup> To gain insight into the origin of these trends, a thermochemical analysis of

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reaction 2 for  $M = \text{Li, Na}$  and  $X = \text{Cl, Br, I}$ , was undertaken in this work, based on the results of reaction-solution and combustion calorimetric experiments.

## Experimental Section

**General.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Varian Gemini 200 (200 MHz) instrument. IR spectra were carried out on a Perkin-Elmer PE 1720 using KBr pellets. X-ray powder diffractograms (XRD) were recorded on a Philips PW1050/25 diffractometer equipped with a proportional counter, using nickel-filtered  $\text{Cu } K_\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Elemental analysis (C, H) were made on a Heraeus CHN-O-Rapid element analyzer, the typical accuracies for routine determination of C and H being 0.3% and 0.25%, respectively. The Cl content of the polyglycolide sample used in the combustion calorimetry studies was determined by potentiometric titration with  $\text{AgNO}_3$ . The corresponding Na content was obtained with a Perkin-Elmer 5000 flame atomic emission spectroscopy (FES) apparatus. Viscometry measurements were carried out with an Ubbelohde capillary viscometer (DIN 51562), using a solution of polyglycolide in 1,1,1,3,3,3-hexafluoro-2-propanol, HFIP, (99+ %). This solution was obtained as follows. A mixture of 120 mg of polyglycolide and 30 mL of 1,1,1,3,3,3-hexafluoro-2-propanol, HFIP, (99+ %), was stirred at room temperature for 3 d. The resulting clear yellowish solution was filtered before the viscometry measurements, leaving no precipitate in the filter. Only reduced viscosities at a concentration of  $4 \text{ mg}\cdot\text{mL}^{-1}$  were determined. The calculation of the molecular weights was based on viscosities in THF, which were derived from the experimentally measured values in HFIP using the equation recommended by Kenley et al.<sup>30</sup> The corresponding constants for the application of the Mark-Houwink equation ( $K_\eta = 4.8 \times 10^{-2}$ ,  $a = 0.73$ ) were derived by averaging data reported in the literature.<sup>18</sup> Differential scanning calorimetry experiments were performed under static air atmosphere with a Mettler TA 4000 instrument in aluminum crucibles sealed in air. The heating rate was  $5 \text{ K}\cdot\text{min}^{-1}$ , and the average sample mass was 2–4 mg. Combined thermogravimetric-mass spectrometry analysis was carried out on a Netzsch STA 409/Balzers QMS 421 system, under static air atmosphere, and using samples of ca. 80 mg mass placed in open alumina crucibles.

**Materials.** All halogenoacetates were prepared by neutralizing the corresponding halogenoacetic acids (Merck) with  $\text{LiOH}$  (Merck) or  $\text{NaOH}$  (Merck), in ethanolic solution, at 273 K. The precipitated compounds were filtered, washed with cold ethanol, and dried in vacuum using a rotary pump. They were further recrystallized from ethanol/water (50:50 v/v), dried in vacuum (100 Pa), and kept in Schlenk tubes under argon prior to the calorimetric experiments. All samples were characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, XRD, and elemental analysis. The absence of residual solvent was confirmed by thermogravimetric and DSC analysis.

Lithium chloroacetate: IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$ : 3009, 2954 (C–H), 1611, 1596 (C=O), 1433, 1401 (COO, C–H), 1262 (C–O), 946, 935, 788, 688, 576, 516. X-ray powder diffraction (main reflections;  $2\theta$ ): 9.5, 19.1, 26.6, 28.3, 38.5.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 3.85 (s, 2H).  $^{13}\text{C}$  NMR (50.31 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 45.06 (s,  $\text{CH}_2$ ). Elemental analysis for  $\text{C}_2\text{H}_2\text{O}_2\text{-ClLi}$ : Expected: C, 23.92%; H, 2.01%. Found: C, 23.97%; H, 2.22% (average of two determinations).

Lithium bromoacetate: IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$ : 3013, 2958 (C–H), 1586 (C=O), 1425, 1394 (COO, C–H), 1178 (C–O), 851, 679, 542. X-ray powder diffraction (main reflections;  $2\theta$ ): 9.2, 20.5, 20.8, 21.3, 26.2, 27.1, 27.4, 27.7, 28.0, 37.3.

$^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 3.60 (s, 2H).  $^{13}\text{C}$  NMR (50.31 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 32.35 (s,  $\text{CH}_2$ ). Elemental analysis for  $\text{C}_2\text{H}_2\text{O}_2\text{BrLi}$ : Expected: C, 16.58%; H, 1.39%. Found: C, 16.54%; H, 1.55% (average of two determinations).

Lithium iodoacetate: IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$ : 3001, 2947 (C–H), 1586, 1575 (C=O), 1425, 1378 (COO, C–H), 1178 (C–O), 851, 679, 542. X-ray powder diffraction (main reflections;  $2\theta$ ): 8.8, 21.1, 25.7, 26.3, 27.2, 35.4, 41.6.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 3.45 (s, 2H).  $^{13}\text{C}$  NMR (50.31 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 2.81 (s,  $\text{CH}_2$ ). Elemental analysis for  $\text{C}_2\text{H}_2\text{O}_2\text{-ILi}$ : Expected: C, 12.52%; H, 1.05%. Found: C, 12.59%; H, 1.22% (average of two determinations).

Sodium chloroacetate: IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$ : 2972 (C–H), 1602 (C=O), 1420, 1399 (COO), 1258, 1249 (C–H), 1167 (C–O), 934, 771. X-ray powder diffraction (main reflections;  $2\theta$ ): 8.25, 16.44, 29.91, 33.24, 41.88.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 3.90 (s, 2H).  $^{13}\text{C}$  NMR (50.31 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 44.79 (s,  $\text{CH}_2$ ), 175.97 (s, COO). Elemental analysis for  $\text{C}_2\text{H}_2\text{O}_2\text{ClNa}$ : Expected: C, 20.62%; H, 1.73%. Found: C, 20.71%; H, 1.88% (average of two measurements).

Sodium bromoacetate: IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$ : 3009, 2967 (C–H), 1592 (C=O), 1409, 1384 (C–H, COO), 926 (O–H), 898, 699, 669, 568. X-ray powder diffraction (main reflections;  $2\theta$ ): 7.8, 22.3, 25.1, 25.8, 26.1, 26.3, 28.4, 31.6, 47.3.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 4.65 (s, 2H).  $^{13}\text{C}$  NMR (50.31 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 29.39 (s,  $\text{CH}_2$ ), 173.26 (s, COO). Elemental analysis for  $\text{C}_2\text{H}_2\text{O}_2\text{BrNa}$ : Expected: C, 14.93%; H, 1.25%. Found: C, 14.86%; H, 1.33% (average of two measurements).

Sodium iodoacetate: IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$ : 2994, 2947 (C–H), 1578 (C=O), 1427, 1397 (COO), 1176 (C–H), 923 (O–H), 853, 673, 652. X-ray powder diffraction (main reflections;  $2\theta$ ): 7.2, 14.6, 21.9, 25.0, 29.3, 44.8.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 3.63 (s, 2H).  $^{13}\text{C}$  NMR (50.31 MHz,  $\text{D}_2\text{O}/\text{TMS}$ ,  $\delta$ ): 2.82 (s,  $\text{CH}_2$ ), 178.53 (s, COO). Elemental analysis for  $\text{C}_2\text{H}_2\text{O}_2\text{INa}$ : Expected: C, 11.55%; H, 0.97%. Found: C, 11.62%; H, 1.36% (average of two measurements).

Polyglycolide was prepared by heating sodium chloroacetate for 3 h at 453 K as previously described.<sup>18</sup> The NaCl/polymer mixture was washed several times with cold water (277 K) for 4 h to remove the salt. PGA was filtered off and dried in vacuum (ca. 13 Pa). The obtained sample was further heated at 393 K in vacuum (1 Pa), during 6h, and kept in a Schlenk tube under argon atmosphere prior to the combustion experiments. IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$ : 2961 (C–H), 1745 (C=O), 1628 (COO), 1420 (C–H), 1154, 1091 (C–O), 902, 810, 720. Elemental analysis (C, H, O, Cl, and Na) led to the empirical formula  $\text{C}_{2.000}\text{H}_{2.160}\text{O}_{2.032}\text{-Cl}_{0.009243}\text{Na}_{0.004404}$ . The obtained Na content is the average result of fourteen FES experiments using solutions of the polymer in aqueous  $\text{HCl}$  (2),  $\text{H}_2\text{SO}_4$  (6), and  $\text{HNO}_3$  (6). X-ray powder diffraction measurements made with the Philips PW1050/25 diffractometer led to the following results (main reflections;  $2\theta$ ): 21.1, 22.1, 25.4, 28.3, 28.7, 30.8, 35.8, 39.3, 41.0, 42.3, 47.9. These experiments indicated the absence of solid crystalline NaCl in the polymer. This was further confirmed in X-ray powder diffraction experiments using synchrotron radiation, with detection limit for NaCl of about 0.1 wt %. The synchrotron experiments were carried out at HASYLAB (DESY, Hamburg, beamline B2), with the sample sealed in a rotating glass capillary of 1 mm diameter, at room temperature. DSC measurements of the temperature and enthalpy of fusion of PGA led to  $T_{\text{fus}} = 470.3 \text{ K}$  (peak onset)/  $491.3 \text{ K}$  (peak maximum) and  $\Delta_{\text{fus}}H_{\text{m}} = 7.4 \text{ kJ}\cdot\text{mol}^{-1}$ , for the average of two measurements, based on a molar mass of  $58 \text{ g}\cdot\text{mol}^{-1}$  for  $1/n(\text{C}_2\text{H}_2\text{O}_2)_n$ . The degree of

crystallinity was estimated as 62% from the ratio of the  $\Delta_{\text{fus}}H_m$  value quoted above to the mean value  $\Delta_{\text{fus}}H_m = 11.86 \text{ kJ}\cdot\text{mol}^{-1}$  of the enthalpies of fusion of fully crystalline PGA reported by Lebedev et al.<sup>31</sup> and Ginde et al.<sup>32</sup> Viscometry gave an average chain length of 27 monomers, based on a molar mass of the monomer of  $58 \text{ g}\cdot\text{mol}^{-1}$ .

The  $\text{As}_2\text{O}_3$  aqueous solution used in the combustion calorimetric experiments was prepared by dissolving solid  $\text{As}_2\text{O}_3$  (B. D. H.; mass fraction 0.998) in boiling distilled and deionized water. After cooling to room temperature, the solution was filtered and titrated with a  $2.00 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$  aqueous solution of  $\text{KMnO}_4$  (Merck Titrisol).

A  $\text{HCl}\cdot 553.41\text{H}_2\text{O}$  solution ( $0.1 \text{ mol}\cdot\text{dm}^{-3}$ , Riedel–deHaën, Fixanal), or diluted solutions prepared from this one were used in reaction-solution calorimetric studies. The  $\text{LiCl}$  (Aldrich, 99.99+%) and  $\text{NaCl}$  (J. M. Gomes dos Santos, 99.8%) used in the enthalpy of solution measurements were dried in an oven at 373 K and kept in a desiccator over  $\text{P}_2\text{O}_5$  prior to use. The enthalpies of solution of chloroacetic acid in the various calorimetric solutions were measured using a sample whose preparation and purification have been described.<sup>33</sup>

**Combustion Calorimetry.** Details of the micro combustion calorimetric apparatus and the general experimental procedure have been reported.<sup>34,35</sup> In a typical experiment, a pellet of the compound was placed in a platinum crucible containing *n*-hexadecane (B. D. H. mass fraction 0.99, batch number 1 253 750) and burned under 3.04 MPa of oxygen, in the presence of ca.  $1 \text{ cm}^3$  of  $6.18 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$   $\text{As}_2\text{O}_3(\text{aq})$ , inside a platinum lined bomb of  $19.63 \text{ cm}^3$  internal volume. The duration of the fore, main, and after periods of the experiment was 30 min each. The bomb rotation was automatically started 2 min after ignition and maintained for 15 min. The energy dissipated by the rotation of the bomb,  $\Delta_{\text{rot}}U$ , was calculated as  $\Delta_{\text{rot}}U = \langle V \rangle \langle I \rangle t$ , where  $\langle V \rangle$  and  $\langle I \rangle$  are the average values of the potential drop and of the current intensity, respectively, measured during the rotation period of duration  $t$  across the motor that drives the rotation. The sample and the combustion auxiliary were weighed to  $\pm 0.1 \mu\text{g}$  on a Sartorius 4504 Mp8–1 ultra-micro balance. The mass of  $\text{As}_2\text{O}_3(\text{aq})$  present inside the bomb in each experiment was determined to  $\pm 10^{-2} \text{ g}$  by weighing the bomb before and after addition of the solution in a Mettler PM 6100 balance. The  $\text{HNO}_3$  formed from traces of atmospheric  $\text{N}_2$  inside the bomb was determined as  $\text{NO}_3^-$ , using a Dionex 4000i ion chromatography apparatus. This apparatus was also used to determine the  $\text{As}_2\text{O}_5(\text{aq})$  produced in the reaction of  $\text{As}_2\text{O}_3(\text{aq})$  with  $\text{Cl}_2$ . The  $\text{Na}^+$  present in the final bomb solution was determined by flame photometry, using an Evans Electro Selenium apparatus.

**Reaction-Solution Calorimetry.** The apparatus and method used in the reaction-solution calorimetry experiments were essentially identical to those previously described.<sup>36–39</sup> The calorimeter consisted of a transparent Dewar vessel closed by a lid, which supported a stirrer, a quartz crystal thermometer probe, a resistor for electrical calibration, and an ampule breaking system. The assembled vessel was immersed in a thermostatic water bath whose temperature was controlled at  $298 \pm 10^{-3} \text{ K}$  by a Tronac PTC-40 unit. In a typical experiment, the sample was sealed in a thin-walled glass ampule and weighed to  $\pm 10^{-5} \text{ g}$  on a Mettler AT201 balance. The reaction or solution process under study was started by breaking the glass ampule in 125 mL of calorimetric solution. This was preceded by an electrical calibration, in which a potential difference of ca. 2.6 V was applied to a  $48 \Omega$  resistance during ca. 200 s.

TABLE 1: Auxiliary Thermochemical Data

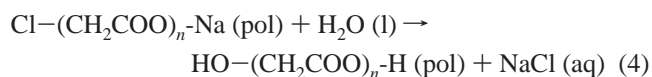
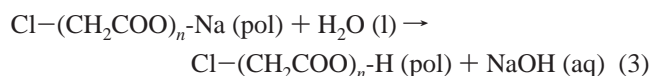
|   | $\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$ |
|---|--|
| $\text{CO}_2, \text{g}$                               | $-393.51 \pm 0.13^a$                                 |
| $\text{H}_2\text{O}, \text{l}$                        | $-285.830 \pm 0.040^a$                               |
| $\text{H}^+, \text{g}$                                | $1536.246^b$   |
| $\text{Li}^+, \text{g}$                               | $685.719^b$  |
| $\text{Na}^+, \text{g}$                               | $609.343^b$  |
| $\text{Cl}^-, \text{g}$                               | $-233.954^b$   |
| $\text{Br}^-, \text{g}$                               | $-219.008^b$   |
| $\text{LiCl}, \text{cr}$                              | $-408.266 \pm 1.142^b$                               |
| $\text{LiBr}, \text{cr}$                              | $-350.9 \pm 0.4^b$                                   |
| $\text{LiI}, \text{cr}$                               | $-270.08 \pm 0.40^b$                                 |
| $\text{NaCl}, \text{cr}$                              | $-411.120 \pm 0.340^b$                               |
| $\text{NaBr}, \text{cr}$                              | $-361.41 \pm 0.42^b$                                 |
| $\text{NaI}, \text{cr}$                               | $-287.86 \pm 0.80^b$                                 |
| $\text{ClCH}_2\text{COOH}, \text{cr}$                 | $-509.74 \pm 0.49^c$                                 |
| $\text{ClCH}_2\text{COOH}, \text{g}$                  | $-427.55 \pm 1.04^c$                                 |
| $\text{BrCH}_2\text{COOH}, \text{cr}$                 | $-466.98 \pm 1.08^c$                                 |
| $\text{BrCH}_2\text{COOH}, \text{g}$                  | $-383.48 \pm 3.14^c$                                 |
| $\text{ICH}_2\text{COOH}, \text{cr}$                  | $-415.44 \pm 1.53^c$                                 |
| $\text{ClCH}_2\text{COO}^-, \text{g}$                 | $-560.5 \pm 8.5^d$                                   |
| $\text{BrCH}_2\text{COO}^-, \text{g}$                 | $-522.2 \pm 9.0^d$                                   |
| $\text{HCl}\cdot 553.41\text{H}_2\text{O}, \text{aq}$ | $-166.598^e$   |
| $\text{HCl}\cdot 600\text{H}_2\text{O}, \text{aq}$    | $-166.619^e$   |

<sup>a</sup> Ref 41. <sup>b</sup> Ref 42. <sup>c</sup> Ref 33. <sup>d</sup> Ref 44. <sup>e</sup> Ref 43.

## Results and Discussion

The 1995 standard atomic masses<sup>40</sup> and the auxiliary thermochemical data listed in Table 1 were used in the calculations.<sup>33,41–44</sup>

As mentioned in the Experimental Section, the combustion calorimetric experiments on polyglycolide were made using a sample with empirical formula  $\text{C}_{2.000}\text{H}_{2.160}\text{O}_{2.032}\text{Cl}_{0.009243}\text{Na}_{0.004404}$ . The deficiency of Na versus Cl, and the excess of H and O versus C contents observed in this formula result from the partial hydrolysis of the polymer endgroups. The hydrolysis mainly occurs in the purification process, during the aqueous extraction of  $\text{NaCl}$  from the polymeric matrix. In-situ IR spectroscopy studies indicated, however, that it may also take place along with the polymerization of sodium chloroacetate due to the presence of atmospheric water.<sup>28</sup> Possible reactions are as follows



Hence, in addition to  $\text{Cl}-(\text{CH}_2\text{COO})_n\text{-Na}$ , the sample used in the combustion calorimetric experiments also contains some products of hydrolysis, e.g.,  $\text{Cl}-(\text{CH}_2\text{COO})_n\text{-H}$ , and  $\text{HO}-(\text{CH}_2\text{COO})_n\text{-H}$ .

The results of the combustion calorimetric experiments are shown in Table 2, where  $m(\text{PGA})$  is the mass of sample;  $m(\text{aux})$  is the mass of *n*-hexadecane used as combustion auxiliary;  $n(\text{HNO}_3)$  is the amount of substance of nitric acid formed in the bomb process;  $n^i(\text{As}_2\text{O}_3)$  and  $n^f(\text{As}_2\text{O}_5)$  represent the amounts of substance of  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$  in the initial and final bomb solution, respectively;  $\epsilon_i$  and  $\epsilon_f$  are the energy equivalents of the bomb contents in the initial and final states of the bomb process, respectively;  $T_i$  and  $T_f$  represent the initial and final temperatures of the experiment;  $\Delta T_c$  is the contribution to the observed temperature rise of the calorimeter proper due to the heat exchanged with the surroundings and the heat dissipated by the temperature sensor;  $\Delta U_{\text{ign}}$  is the electrical



TABLE 2: Results of the Combustion Experiments on Polyglycolide

|   |           |           |           |           |           |           |           |
|---|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| $m(\text{PGA})/\text{mg}$                                       | 33.0205   | 32.1866   | 34.4417   | 24.8466   | 33.3564   | 28.8027   | 34.6027   |
| $m(\text{aux})/\text{mg}$                                       | 6.7919    | 6.3220    | 7.4890    | 7.0139    | 6.7363    | 7.9710    | 5.6985    |
| $10^6 n(\text{HNO}_3)/\text{mol}$                               | 1.67      | 1.98      | 2.06      | 1.59      | 2.46      | 1.83      | 1.82      |
| $10^5 n(\text{As}_2\text{O}_5)/\text{mol}$                      | 6.18      | 6.18      | 6.18      | 6.24      | 6.30      | 6.18      | 7.97      |
| $10^6 n(\text{As}_2\text{O}_5)/\text{mol}$                      | 1.40      | 2.00      | 0.85      | 1.50      | 0.70      | 0.45      | 0.26      |
| $\epsilon^\circ/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ | 4.93      | 4.93      | 4.94      | 4.95      | 5.01      | 4.93      | 6.37      |
| $\epsilon^\circ/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ | 6.78      | 6.77      | 6.78      | 6.80      | 6.85      | 6.78      | 8.20      |
| $T_i/\text{K}$  | 298.14983 | 298.16936 | 298.16263 | 298.19268 | 298.16613 | 298.16577 | 298.13181 |
| $T_f/\text{K}$  | 298.64636 | 298.64475 | 298.67809 | 298.64037 | 298.66065 | 298.66142 | 298.61653 |
| $\Delta T_c/\text{K}$   | 0.09585   | 0.09284   | 0.08594   | 0.09597   | 0.09276   | 0.09242   | 0.10121   |
| $\Delta U_{\text{ign}}/\text{J}$                                | 1.76      | 1.76      | 1.76      | 1.76      | 1.76      | 1.76      | 1.76      |
| $\Delta U_{\text{rot}}/\text{J}$                                | 0.15      | 0.21      | 1.20      | 0.84      | 1.20      | 1.22      | 0.73      |
| $-\Delta U_{\text{IBP}}/\text{J}$                               | 725.49    | 692.55    | 776.81    | 636.01    | 726.46    | 729.09    | 694.24    |
| $\Delta U_{\Sigma}/\text{J}$                                    | 3.04      | 2.93      | 3.22      | 2.64      | 3.07      | 2.98      | 3.29      |
| $\Delta U(\text{HNO}_3)/\text{J}$                               | 0.10      | 0.12      | 0.12      | 0.09      | 0.15      | 0.11      | 0.11      |
| $\Delta U(\text{As}_2\text{O}_5)/\text{J}$                      | 0.46      | 0.66      | 0.28      | 0.49      | 0.23      | 0.15      | 0.08      |
| $\Delta U(\text{aux})/\text{J}$                                 | 321.10    | 297.96    | 352.96    | 330.57    | 317.49    | 375.68    | 268.58    |
| $\Delta U(\text{PGA})/\text{J}$                                 | 401.79    | 390.88    | 420.23    | 302.22    | 405.52    | 350.17    | 422.18    |
| $-\Delta_c u^\circ(\text{PGA})/\text{J}\cdot\text{g}^{-1}$      | 12167.16  | 12144.18  | 12201.20  | 12163.43  | 12157.19  | 12157.54  | 12200.78  |

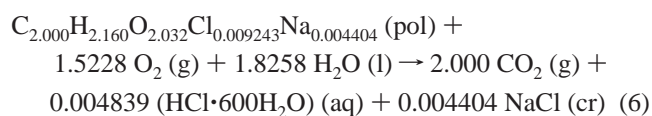
energy supplied for ignition of the sample;  $\Delta U_{\text{rot}}$  is the energy dissipated by the rotation of the bomb;  $\Delta U_{\text{IBP}}$  is the internal energy change associated with the bomb process under isothermal conditions, at 298.15 K;  $\Delta U_{\Sigma}$  represents the sum of all corrections necessary to reduce  $\Delta U_{\text{IBP}}$  to the standard state (Washburn corrections),  $\Delta U(\text{HNO}_3)$  and  $\Delta U(\text{As}_2\text{O}_5)$  are the energy changes associated with the formation of nitric acid and  $\text{As}_2\text{O}_5$ , respectively;  $\Delta U(\text{aux})$  and  $\Delta U(\text{PGA})$  are the contributions of *n*-hexadecane, and polyglycolide to the energy of the isothermal bomb process, respectively; and finally,  $\Delta_c u^\circ(\text{PGA})$  is the standard massic energy of combustion of polyglycolide.

The values of  $T_i$ ,  $T_f$ , and  $\Delta T_c$  were calculated by using a computer program based on the Regnault–Pfaundler method,<sup>34</sup> and  $\Delta U_{\text{IBP}}$  was derived from

$$\Delta U_{\text{IBP}} = \epsilon_o(T_i - T_f + \Delta T_c) + \epsilon_f(T_i - 298.15) + \epsilon_f(298.15 - T_f + \Delta T_c) + \Delta U_{\text{ign}} + \Delta U_{\text{rot}} \quad (5)$$

The energy equivalent of the calorimeter and its standard deviation  $\epsilon^\circ = (1808.64 \pm 0.34) \text{ J}\cdot\text{K}^{-1}$ , was determined from the combustion of benzoic acid (B. D. H. thermochemical standard), whose energy of combustion under certificate conditions and standard deviation were  $-(26433 \pm 2) \text{ J}\cdot\text{g}^{-1}$ . The calculation of  $\Delta U_{\Sigma}$  was based on the scheme recommended for  $\text{CHOC}$  compounds,<sup>45–47</sup> modified to account for the presence of sodium in the polyglycolide sample. The auxiliary values used in this calculation were: for *n*-hexadecane  $c_p^\circ = 2.215 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ ,<sup>48</sup>  $\rho = 0.773 \text{ g}\cdot\text{cm}^{-3}$ ,<sup>49</sup> and  $-(\partial u/\partial p)_T = 0.347 \text{ J}\cdot\text{MPa}^{-1}\cdot\text{g}^{-1}$ ,<sup>49</sup> for polyglycolide:  $c_p^\circ = 1.15 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ ,<sup>31</sup>  $\rho = 1.5 \text{ g}\cdot\text{cm}^{-3}$  (obtained in this work by weighing several pellets of known dimensions), and  $-(\partial u/\partial p)_T = 0.12 \text{ J}\cdot\text{MPa}^{-1}\cdot\text{g}^{-1}$ .<sup>50</sup> In addition, the internal energy of solution of the NaCl present in the final bomb solution,  $\Delta_{\text{sol}} U_m^\circ(\text{NaCl}) = 3.833 \text{ kJ}\cdot\text{mol}^{-1}$ , was assumed to be identical to the enthalpy of solution of NaCl in water.<sup>43</sup> The value of  $\Delta U(\text{HNO}_3)$  was obtained from  $\Delta_f H_m^\circ(\text{HNO}_3, \text{aq}, 0.1 \text{ mol}\cdot\text{dm}^{-3}) = -59.7 \text{ kJ}\cdot\text{mol}^{-1}$ .<sup>43</sup> The calculation of  $\Delta U(\text{aux})$  was based on  $\Delta_c u^\circ(\text{aux}) = -(47\,131.02 \pm 1.47) \text{ J}\cdot\text{g}^{-1}$ .<sup>34</sup>

The values of the standard massic energy of combustion of polyglycolide in Table 2 correspond to the reaction



and were calculated from

$$\Delta_c u^\circ(\text{PGA}) = [\Delta U_{\text{IBP}} + \Delta U_{\Sigma} - \Delta U(\text{HNO}_3) - \Delta U(\text{aux})]/m(\text{PGA}) \quad (7)$$

These results lead to  $\Delta_c u^\circ(\text{PGA}) = -(12170.21 \pm 8.39) \text{ J}\cdot\text{g}^{-1}$ ,  $\Delta_c U_m^\circ(\text{PGA}) = -(719.72 \pm 1.04) \text{ kJ}\cdot\text{mol}^{-1}$ , and  $\Delta_c H_m^\circ(\text{PGA}) = -(718.54 \pm 1.04) \text{ kJ}\cdot\text{mol}^{-1}$ . In accordance with common practice in combustion calorimetry, the uncertainty given for  $\Delta_c u^\circ(\text{PGA})$  is the standard deviation of the mean, and those indicated for  $\Delta_c U_m^\circ(\text{PGA})$  and  $\Delta_c H_m^\circ(\text{PGA})$  represent twice the over-all standard deviation of the mean and include the contributions from the calibration with benzoic acid and from the energy of combustion of the auxiliary oil.<sup>51,52</sup> By using eq 8

$$\begin{aligned} \Delta_f H_m^\circ(\text{PGA}, \text{pol}) &= -\Delta_c H_m^\circ(\text{PGA}) + 2\Delta_f H_m^\circ(\text{CO}_2, \text{g}) + \\ &0.004839\Delta_f H_m^\circ(\text{HCl}\cdot 600\text{H}_2\text{O}, \text{aq}) + \\ &0.004404\Delta_f H_m^\circ(\text{NaCl}, \text{cr}) + 1.0776\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) \quad (8) \end{aligned}$$

and the auxiliary data in Table 1 it is concluded that  $\Delta_f H_m^\circ(\text{PGA}, \text{pol}) = -(379.1 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$  (per mol of monomer). Note that by convention<sup>43</sup>  $\Delta_f H_m^\circ(\text{HCl}\cdot 600\text{H}_2\text{O}, \text{aq})$  represents the enthalpy of formation of  $\text{HCl}(\text{g})$  plus the enthalpy of solution of 1 mol of  $\text{HCl}(\text{g})$  in 600 mol of  $\text{H}_2\text{O}$ . Hence, the contribution of the term  $600 \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l})$  is already included in  $\Delta_f H_m^\circ(\text{HCl}\cdot 600\text{H}_2\text{O}, \text{aq})$  and only 1.0776 mol of  $\text{H}_2\text{O}$  ( $= 0.004\,839 \times 600 - 1.8258$ ) need to be considered in eq 8.

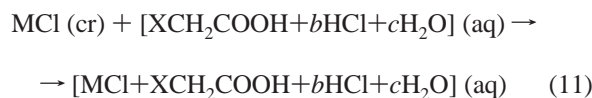
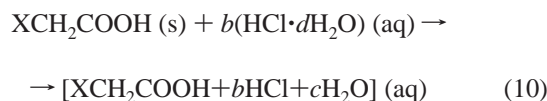
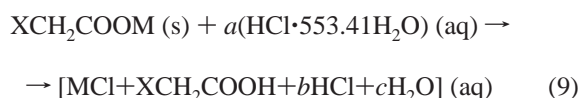
The value of  $\Delta_f H_m^\circ(\text{PGA}, \text{pol})$  indicated above corresponds to a sample with estimated crystallinity and average chain length of 62% and about 27 monomers, respectively (see Experimental Section). Lebedev and co-workers<sup>31</sup> previously reported  $\Delta_f H_m^\circ(\text{PGA}, \text{pol}) = -(367.2 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$  for a PGA sample with 100% crystallinity and  $\Delta_f H_m^\circ(\text{PGA}, \text{pol}) = -(355.6 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$  for an amorphous PGA sample, both prepared by ring opening polymerization and with average chain lengths in the range of 36000–52000 monomers. Note, however, that the three results are not directly comparable. Lebedev's data refer to high molecular weight polymers, for which the enthalpic contribution of the endgroups is negligible.<sup>53</sup> This is not the case for an oligomeric material with an average chain length of 27 monomers.<sup>53</sup> It is therefore not unexpected that, the enthalpy of formation of polyglycolide (per mole of monomer) obtained in this work, albeit referring to a polymer of 62% crystallinity, is outside the range of Lebedev's results for amorphous and 100% crystalline polymers.

**TABLE 3: Results of the Reaction-solution Calorimetry Experiments at 298.15 K (data in kJ·mol<sup>-1</sup>)**

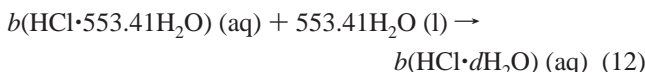
|                                | XCH <sub>2</sub> COOLi |                   |                   | XCH <sub>2</sub> COONa |                   |                   |
|--------------------------------|------------------------|-------------------|-------------------|------------------------|-------------------|-------------------|
|                                | X = Cl                 | X = Br            | X = I             | X = Cl                 | X = Br            | X = I             |
| a                              | 4.17298                | 5.17048           | 6.92393           | 4.16002                | 5.18192           | 6.87509           |
| b                              | 3.17298                | 4.17048           | 5.92393           | 3.16002                | 4.18192           | 5.87509           |
| c                              | 2309.37                | 2861.39           | 3831.77           | 2302.20                | 2867.73           | 3804.74           |
| d                              | 727.82                 | 686.11            | 646.83            | 728.54                 | 685.74            | 647.61            |
| $\Delta_f H_m^\circ(9)$        | $-7.56 \pm 0.25$       | $-5.21 \pm 0.19$  | $-3.10 \pm 0.18$  | $5.37 \pm 0.20$        | $7.70 \pm 0.17$   | $4.04 \pm 0.33$   |
| $\Delta_{sol} H_m^\circ(10)$   | $15.15 \pm 0.10$       | $15.05 \pm 0.11$  | $18.57 \pm 0.10$  | $15.15 \pm 0.10$       | $15.05 \pm 0.11$  | $18.57 \pm 0.10$  |
| $\Delta_{sol} H_m^\circ(11)$   | $-34.68 \pm 0.37$      | $-35.06 \pm 0.45$ | $-35.38 \pm 0.53$ | $3.77 \pm 0.17$        | $4.15 \pm 0.14$   | $3.71 \pm 0.35$   |
| $\Delta_{dil} H_m^\circ(12)^a$ | -0.21                  | -0.23             | -0.24             | -0.22                  | -0.23             | -0.24             |
| $\Delta_f H_m^\circ(13)$       | $12.18 \pm 0.46$       | $15.03 \pm 0.50$  | $13.95 \pm 0.57$  | $-13.33 \pm 0.28$      | $-11.27 \pm 0.25$ | $-18.00 \pm 0.49$ |
| $\Delta_f H_m^\circ(cr)$       | $-763.6 \pm 1.3$       | $-723.7 \pm 1.7$  | $-671.1 \pm 2.0$  | $-740.9 \pm 0.7$       | $-700.2 \pm 1.2$  | $-642.0 \pm 1.6$  |

<sup>a</sup> Ref 43.

The enthalpies of formation of XCH<sub>2</sub>COOM (M = Li, Na; X = Cl, Br, I), were determined from reaction-solution calorimetric studies of reaction shown in eq 9 and of the dissolution processes shown in eqs 10 and 11



The corresponding results are shown in Table 3, where the uncertainties quoted represent twice the standard deviation of the mean of at least five independent determinations. These values taken with the enthalpy of the dilution process  $\Delta_{dil} H_m^\circ(12)$



indicated in Table 3 were used to derive the enthalpy of the standard state reaction 13 (M = Li, Na; X = Cl, Br, I)

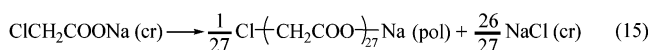


as

$$\Delta_f H_m^\circ(13) = \Delta_f H_m^\circ(9) - \Delta_{sol} H_m^\circ(10) - \Delta_{sol} H_m^\circ(11) - \Delta_{dil} H_m^\circ(12) \quad (14)$$

The enthalpies of formation of the sodium and lithium acetates were finally calculated from the corresponding  $\Delta_f H_m^\circ(13)$  and the auxiliary data in Table 1. The obtained values are indicated in Table 3.

An estimation of the enthalpy of reaction 15, at 298.15 K



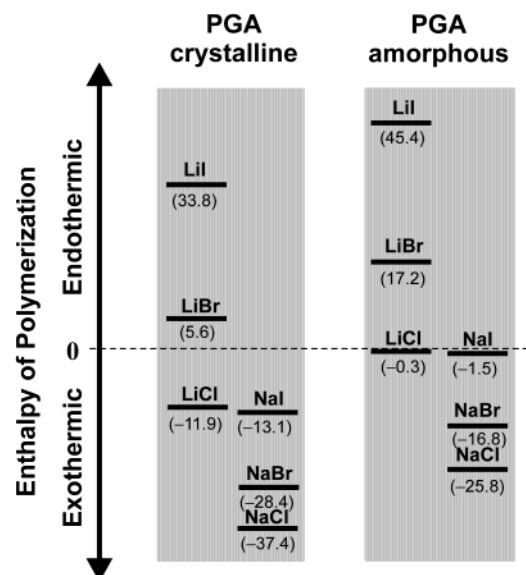
can be made from  $\Delta_f H_m^\circ(\text{ClCH}_2\text{COONa, cr})$  and the auxiliary data in Table 1, and taking the enthalpy of formation of the polyglycolide sample obtained in this work as approximately

**TABLE 4: Enthalpies of Polymerization of XCH<sub>2</sub>COOM (data in kJ·Mol<sup>-1</sup>)**

| M  | X  | DSC <sup>a</sup> | $\Delta_f H_m^\circ(15)^b$ | $\Delta_f H_m^\circ(2)$ |                        |                     |
|----|----|------------------|----------------------------|-------------------------|------------------------|---------------------|
|    |    |                  |                            | PGA-100%cr <sup>c</sup> | PGA-62%cr <sup>d</sup> | PGA-am <sup>e</sup> |
| Li | Cl |                  |                            | $-11.9 \pm 1.9$         | -7.5                   | $-0.3 \pm 2.2$      |
|    | Br |                  |                            | $5.6 \pm 1.9$           | 10.0                   | $17.2 \pm 2.2$      |
|    | I  |                  |                            | $33.8 \pm 2.2$          | 38.2                   | $45.4 \pm 2.4$      |
| Na | Cl | -25.2            | -34                        | $-37.4 \pm 1.1$         | -33.0                  | $-25.8 \pm 1.5$     |
|    | Br | -23.4            |                            | $-28.4 \pm 1.5$         | -24.0                  | $-16.8 \pm 1.8$     |
|    | I  |                  |                            | $-13.1 \pm 2.0$         | -8.7                   | $-1.5 \pm 2.2$      |

<sup>a</sup> Refs 15–17. <sup>b</sup> Based on  $\Delta_f H_m^\circ\{1/27[\text{Cl}-(\text{CH}_2\text{COO})_{27}\text{Na}], \text{pol}\} = -379.1 \text{ kJ} \cdot \text{mol}^{-1}$  estimated in this work (see text). <sup>c</sup> Based on  $\Delta_f H_m^\circ(\text{PGA, pol}) = -(367.2 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$  for a polyglycolide sample with 100% crystallinity (Reference 31). <sup>d</sup> Based on an estimated  $\Delta_f H_m^\circ(\text{PGA, pol}) = -362.8 \text{ kJ} \cdot \text{mol}^{-1}$  for a polyglycolide sample with 62% crystallinity (see text). <sup>e</sup> Based on  $\Delta_f H_m^\circ(\text{PGA, pol}) = -(355.6 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$  for an amorphous PGA sample (Reference 31).

representing the enthalpy of formation of  $\{1/27[\text{Cl}-(\text{CH}_2\text{COO})_{27}\text{Na}]\}$  (pol), i.e.,  $\Delta_f H_m^\circ\{1/27[\text{Cl}-(\text{CH}_2\text{COO})_{27}\text{Na}], \text{pol}\} = -379.1 \text{ kJ} \cdot \text{mol}^{-1}$ . The derived value,  $\Delta_f H_m^\circ(15) = -34 \text{ kJ} \cdot \text{mol}^{-1}$ , is compared in Table 4 with our previously reported DSC results for the polymerization of sodium chloro- and bromoacetate in the solid state, at the reference temperatures of 471 and 459 K, respectively.<sup>16,17</sup> The agreement can be considered as rather good, given the approximations made in the calculation of the enthalpy of formation of the polymer and the fact that it is not known if in the DSC experiments the polymer is formed in a crystalline or in an amorphous state. Note that, although the melting temperature of polyglycolide and the onset temperature for the polymerization of sodium chloroacetate obtained by DSC are rather close, studies of this reaction by many other techniques suggest that the polymer is not formed in the liquid state (see Introduction).<sup>15</sup> This is particularly evident from thermomicroscopy experiments on the polymerization of a single crystal of ClCH<sub>2</sub>COONa<sup>29</sup> and also from direct observation of the solid powder present during the synthesis of PGA described in the Experimental section. We cannot, nevertheless, exclude the possibility of a temporary liquefaction of the polymer on a microscopic scale in the reaction zone. However, that intermediate liquid phase, if present, must immediately solidify and, as such, the enthalpy of reaction obtained by DCS should refer to the formation of a solid polymer. The difference between  $\Delta_f H_m^\circ(15)$  obtained in this work and the corresponding differential scanning calorimetry data in Table 4 is not likely to be significantly changed by correcting the DSC results to 298.15 K. In fact, using  $C_{p,m}^\circ(\text{ClCH}_2\text{COONa, cr}) = 114.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,  $C_{p,m}^\circ\{1/27[\text{Cl}-(\text{CH}_2\text{COO})_{27}\text{Na}], \text{pol}\} = 65.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , and  $C_{p,m}^\circ(\text{NaCl, cr}) = 51.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , estimated by Kopp's



**Figure 1.** Standard enthalpies of polymerization of lithium and sodium halogenoacetates, at 298.15 K (data in  $\text{kJ}\cdot\text{mol}^{-1}$ )

rule,<sup>54</sup> it is concluded that  $\Delta_r C_{p,m}^\circ(15) = 0.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The reliability of Kopp's rule was assessed, in this case, by noting that the estimated  $C_{p,m}^\circ\{1/27[\text{Cl}-(\text{CH}_2\text{COO})_{27}-\text{Na}], \text{pol}\}$  and  $C_{p,m}^\circ(\text{NaCl}, \text{cr})$  values quoted above, are very close to the experimental values, at 298.15 K,  $C_{p,m}^\circ[-(\text{CH}_2\text{COO})_n, \text{pol}] = 68.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (as measured by Lebedev et al. for a PGL polymer with 33% crystallinity)<sup>31</sup> and  $C_{p,m}^\circ(\text{NaCl}, \text{cr}) = 50.509 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .<sup>42</sup>

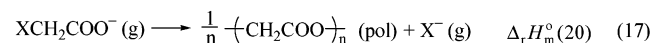
The enthalpy of reaction 2, which refers to a polymer with a number of monomers large enough to make the enthalpic contribution of the endgroups negligible, can also be calculated, at 298.15 K, by using the  $\Delta_f H_m^\circ(\text{PGA}, \text{pol})$  values for 100% crystalline (PGA-100%cr) and fully amorphous (PGA-am) polymer, reported by Lebedev and co-workers,<sup>31</sup> and quoted above. The obtained results are indicated in Table 4 and in Figure 1. Also included in Table 4 are the estimated enthalpies of reaction 2 for the production of a polymer with 62% crystallinity (PGA-62%cr), thus similar to the crystallinity of the sample used in the present work. These values are based on  $\Delta_f H_m^\circ(\text{PGA}, \text{pol}) = -362.8 \text{ kJ}\cdot\text{mol}^{-1}$ , calculated by interpolation from the  $\Delta_f H_m^\circ(\text{PGA}, \text{pol})$  given by Lebedev and co-workers<sup>31</sup> for the fully crystalline and the fully amorphous polymers. It is noted that for sodium chloroacetate the estimated values of  $\Delta_f H_m^\circ(2)$  and  $\Delta_f H_m^\circ(15)$  in Table 4, which refer to polymer of identical crystallinity, are in excellent agreement.

As seen in Table 4 and in Figure 1, for a given metal, reaction 2 becomes less favorable when X varies along the series  $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ . It is also systematically more favorable (exothermic) for  $\text{M} = \text{Na}$  than for  $\text{M} = \text{Li}$ . The results in Table 4 therefore support the experimental observations that sodium chloro- and bromoacetates smoothly undergo polymerization whereas lithium bromo- and iodoacetates do not polymerize. Lithium chloroacetate and sodium iodoacetate are borderline cases in that a polymerization is not experimentally observed but might be thermodynamically feasible. These conclusions are not likely to be significantly changed by entropic considerations because a small entropy contribution is expected for a solid-state reaction such as that in eq 2.<sup>55</sup>

**TABLE 5: Decomposition of the Enthalpy of Reaction 2 in Terms of the Lattice Enthalpies of  $\text{XCH}_2\text{COOM}$  and MX and the Enthalpy of Reaction 17 (data in  $\text{kJ}\cdot\text{mol}^{-1}$ )**

| M  | X  | $\Delta_{\text{lat}} H_m^\circ(\text{XCH}_2\text{COOM})$ | $\Delta_r H_m^\circ(17)$ | $-\Delta_{\text{lat}} H_m^\circ(\text{MX})$ | $\Delta_r H_m^\circ(2)$ |
|----|----|--|--------------------------|---|-------------------------|
| Li | Cl | 888.8  | -40.7                    | -860.0                                      | -11.9                   |
|    | Br | 887.2  | -64.0                    | -817.6                                      | 5.6                     |
| Na | Cl | 789.7  | -40.7                    | -786.5                                      | -37.4                   |
|    | Br | 787.3  | -64.0                    | -751.7                                      | -28.4                   |

Further insight into the origin of these trends can be obtained by decomposing reaction 2 into the following hypothetical reactions



The enthalpy of reaction 16 corresponds to the lattice enthalpy of  $\text{XCH}_2\text{COOM}$ ,  $\Delta_{\text{lat}} H_m^\circ(\text{XCH}_2\text{COOM})$ , and the enthalpy of reaction 18 represents the symmetrical of the lattice enthalpy of MX,  $\Delta_{\text{lat}} H_m^\circ(\text{MX})$ . In reaction 17, the carbon-halogen bond is cleaved to generate polyglycolide and  $\text{X}^-$ . Arbitrarily assuming that the PGA formed in reaction 2 has 100% crystallinity, and using the enthalpies of formation of  $\text{XCH}_2\text{COOM}(\text{cr})$  obtained in this work and the auxiliary data in Table 1, it is possible to calculate the values of  $\Delta_{\text{lat}} H_m^\circ(\text{XCH}_2\text{COOM})$ ,  $\Delta_r H_m^\circ(17)$ , and  $\Delta_{\text{lat}} H_m^\circ(\text{MX})$  for  $\text{M} = \text{Li}, \text{Na}$  and  $\text{X} = \text{Cl}, \text{Br}$  listed in Table 5. The results in Table 5 show that the lattice enthalpy of the acetate salts is independent of X. Furthermore, although in reaction 17 the cleavage of the C-Br bond with the formation of  $\text{Br}^-$  is more favorable than the cleavage of the C-Cl bond with the formation of  $\text{Cl}^-$  by 23.3  $\text{kJ}\cdot\text{mol}^{-1}$ , this difference is not sufficient to overcome the larger lattice enthalpy of MCl compared to that of MBr. Hence, the decrease of the tendency of the  $\text{XCH}_2\text{COOM}$  ( $\text{M} = \text{Li}, \text{Na}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) compounds to polymerize when X varies along the series  $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ , seems to be controlled by the magnitude of the lattice enthalpy of the MX salts.

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## References and Notes

- (1) Langer, R. *Nature* **1998**, 392 Supp., 5.
- (2) Uhrich, K. E.; Cannizzaro, S. M.; Langer, R. S.; Shakesheff, K. M. *Chem. Rev.* **1999**, 99, 3181.
- (3) Langer, R. *Acc. Chem. Res.* **2000**, 33, 94.
- (4) Dee, K. C.; Bizios, R. *Biotechnol. Bioeng.* **1996**, 50, 438.
- (5) Niklason, L. E.; Gao, J.; Abbott, W. M.; Hirschi, K. K.; Houser, S.; Marini, R.; Langer, R. S. *Science* **1999**, 284, 489.
- (6) Ashammakhi, N.; Rokkanen, P. *Biomaterials* **1997**, 18, 3.
- (7) Vasenius, J.; Helevirta, P.; Kuisma, H.; Rokkanen, P.; Törmälä, P. *Clinical Mater.* **1994**, 17, 119.
- (8) Hofmann, G. O. *Arch. Orthop. Trauma Surg.* **1995**, 114, 123.
- (9) Hollinger, J. O.; Leong, K. *Biomaterials* **1996**, 17, 187.
- (10) Masterman, T. C.; Spencer, J. L. *PCT Int. Appl. WO 96 14*, 825, **1996**; *Chem. Abstr.* **1996**, 125, 95 622r.
- (11) Gilding, D. K.; Reed, A. M. *Polymer* **1979**, 20, 1459.
- (12) Chu, C. C. In *ACS Symp. Ser.*; Vigo, T. L., Ed.; American Chemical Society: Washington, **1991**; Vol. 457, p 167.

- (13) Kricheldorf, H. R. *Handbook of Polymer Synthesis*; Marcel Dekker: New York, 1992.
- (14) Hoffmann, R. *Justus Liebigs Ann. Chem.* **1857**, 102, 1.
- (15) Herzberg, O.; Epple, M. *Eur. J. Inorg. Chem.* **2001**, 1395.
- (16) Epple, M.; Kirschnick, H. *Chem. Ber.* **1996**, 129, 1123.
- (17) Epple, M.; Herzberg, O. *J. Mater. Chem.* **1997**, 7, 1037.
- (18) Schwarz, K.; Epple, M. *Macromol. Chem. Phys.* **1999**, 200, 2221.
- (19) Epple, M.; Tröger, L. *J. Chem. Soc., Dalton Trans.* **1996**, 11.
- (20) Ehrenberg, H.; Hasse, B.; Schwarz, K.; Epple, M. *Acta Crystallogr.* **1999**, B55, 517.
- (21) Elizabé, L.; Kariuki, B. M.; Harris, K. D. M.; Tremayne, M.; Epple, M.; Thomas, J. M. *J. Phys. Chem. B* **1997**, 101, 8827.
- (22) Epple, M.; Kirschnick, H. *Chem. Ber.* **1997**, 130, 291.
- (23) Epple, M.; Kirschnick, H.; Greaves, G. N.; Sankar, G.; Thomas, J. M. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 5035.
- (24) Epple, M.; Sazama, U.; Reller, A.; Hilbrandt, N.; Martin, M.; Tröger, L. *J. Chem. Soc. Chem. Commun.* **1996**, 1755.
- (25) Epple, M.; Sankar, G.; Thomas, J. M. *Chem. Mater.* **1997**, 9, 3127.
- (26) Herzberg, O.; Gehrke, R.; Epple, M. *Polymer* **1999**, 40, 507.
- (27) Aliev, A. E.; Elizabé, L.; Kariuki, B. M.; Kirschnick, H.; Thomas, J. M.; Epple, M.; Harris, K. D. M. *Chem. Eur. J.* **2000**, 6, 1120.
- (28) Epple, M.; Kirschnick, H.; Thomas, J. M. *J. Thermal Anal.* **1996**, 47, 331.
- (29) Herzberg, O.; Epple, M. *J. Therm. Anal. Cal.* **1999**, 57, 151.
- (30) Kenley, R. A.; Lee, M. O.; Mahoney, T. R.; Sanders, L. M. *Macromolecules* **1987**, 20, 2398.
- (31) Lebedev, B. V.; Yevstropov, A. A.; Kiparisova, Y. G.; Belov, V. I. *Polym. Sci. USSR* **1978**, 20, 32.
- (32) Ginde, R.; Gupta, R. *J. Appl. Polym. Sci.* **1987**, 33, 2412.
- (33) Lagoa, A. L. C.; Diogo, H. P.; Dias, M. P.; Minas da Piedade, M. E.; Amaral, L. M. P. F.; Ribeiro da Silva, M. A. V.; Martinho Simões, J. A.; Guedes, R. C.; Costa Cabral, B. J.; Schwarz, K.; Epple, M. *Chem. Eur. J.* **2001**, 7, 483.
- (34) Diogo, H. P.; Minas da Piedade, M. E. *J. Chem. Thermodyn.* **1995**, 27, 197.
- (35) Santos, R. C.; Diogo, H. P.; Minas da Piedade, M. E. *J. Chem. Thermodynamics* **1999**, 31, 1417.
- (36) Calado, J. C. G.; Dias, A. R.; Martinho Simões, J. A.; Ribeiro da Silva, M. A. V. *Rev. Port. Quim.* **1979**, 21, 129.
- (37) Calhorda, M. J.; Carrondo, M. A. A. F. C. T.; Dias, A. R.; Galvão, A. M.; Garcia, M. H.; Martins, A. M.; Minas da Piedade, M. E.; Pinheiro, C. I.; Romão, C. C.; Martinho Simões, J. A.; Veiros, L. F. *Organometallics* **1991**, 10, 483.
- (38) Diogo, H. P.; Minas da Piedade, M. E.; Moura Ramos, J. J.; Simoni, J. A.; Martinho Simões, J. A. *J. Chem. Educ.* **1992**, 69, 940.
- (39) Diogo, H. P.; Minas da Piedade, M. E.; Martinho Simões, J. A.; Teixeira, C. *J. Organomet. Chem.* **2001**, 632, 188.
- (40) IUPAC, *J. Phys. Chem. Ref. Data* **1997**, 26, 1239.
- (41) CODATA Key Values for Thermodynamics; Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds.; Hemisphere: New York, 1989.
- (42) NIST-JANAF Thermochemical Tables; 4th ed.; Chase, M. W., Jr., Ed.; *J. Phys. Chem. Ref. Data* **1998**, Monograph No. 9, Parts I and II.
- (43) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *The NBS Tables of Chemical Thermodynamic Properties*, *J. Phys. Chem. Ref. Data* **1982**, 11; Supplement no. 2.
- (44) The values of  $\Delta_f H_m^\circ(\text{ClCH}_2\text{COO}^-, \text{g}) = -(560.5 \pm 8.5) \text{ kJ} \cdot \text{mol}^{-1}$ , and  $\Delta_f H_m^\circ(\text{BrCH}_2\text{COO}^-, \text{g}) = -(522.2 \pm 9.0) \text{ kJ} \cdot \text{mol}^{-1}$  were derived from the gas-phase acidity data,  $\Delta_{\text{acid}} H_m^\circ(\text{ClCH}_2\text{COOH}) = 1403.3 \pm 8.4 \text{ kJ} \cdot \text{mol}^{-1}$ , and  $\Delta_{\text{acid}} H_m^\circ(\text{BrCH}_2\text{COOH}) = 1397.5 \pm 8.4 \text{ kJ} \cdot \text{mol}^{-1}$ , reported by Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, 56, 1, and the enthalpies of formation of  $\text{H}^+(\text{g})$ ,  $\text{ClCH}_2\text{COOH}(\text{g})$  and  $\text{BrCH}_2\text{COOH}(\text{g})$  given in Table 1.
- (45) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 5.
- (46) Hu, A. T.; Sinke, G. C.; Månsson, M.; Ringnér, B. *J. Chem. Thermodyn.* **1972**, 4, 283.
- (47) Tan, Z.; Kamaguchi, A.; Nagano, Y.; Sakiyama, M. *J. Chem. Thermodynamics* **1989**, 21, 615.
- (48) *Handbook of Chemistry and Physics*, 74th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, **1993–94**.
- (49) Vargaftik, N. B. *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed.; John Wiley: New York, 1975.
- (50) Assumed identical to the  $(\partial u/\partial p)_T$  value given for benzoic acid in Johnson, W. H.; Prosen, E. J. *J. Res. Natl. Bur. Stand. (U. S.)* **1975**, 79A, 481.
- (51) Olofsson G. In *Experimental Chemical Thermodynamics*, Vol. 1; Sunner, S., Månsson, M., Eds.; Pergamon Press: London, 1979; chapter 6.
- (52) Bjellerup, L. *Acta Chem. Scand.* **1961**, 15, 121.
- (53) Dainton, F. S.; Ivin, K. J. In *Experimental Thermochemistry*; Skinner, H. A., Ed.; Interscience: New York, 1962; Vol. 2, Chapter 12.
- (54) *Lange's Handbook of Chemistry*; Dean, J. A., Eds.; 12<sup>th</sup> Ed.; McGraw-Hill: New York, 1979.
- (55) Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*; 2nd Ed.; Cambridge University Press: Cambridge, 1982.