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Award Lecture

AN IN SITU IR-SPECTROSCOPIC STUDY OF THE SOLID-STATE FORMATION REACTION OF POLYGLYCOLIDE

Thermal elimination of NaCl from sodium chloroacetate

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Abstract

The thermal elimination of NaCl from sodium chloroacetate, a polymerization reaction that takes place between 150 and 200°C in the solid state, leads quantitatively to the simplest polyester, polyglycolide. By *in situ* IR-spectroscopy, we have shown that the reaction proceeds smoothly and directly without intermediates or by-products. The endgroups of the polymeric product – ionised carboxylate groups (–COONa) and hydrogen-bonded alcohol groups (–COH) – are clearly detectable. It is therefore concluded that the polymer forms extended chains, not rings, during the course of this solid-state reaction. That corresponds well with the idea of a polymerization reaction in the solid state. However, this experiment does not exclude the formation of polyglycolide rings as further product because they do not contain any terminating groups.

Keywords: in situ IR-spectroscopy, solid-state polymerization, thermal elimination

Introduction

Heating of sodium chloroacetate above 100°C leads to the formation of polyglycolide, the simplest polyester, by elimination of sodium chloride:

$$Cl{-}CH_2COO^-Na^+ \longrightarrow NaCl + 1/n\ [{-}CH_2COO{-}]_n \qquad (1)$$

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Such a thermally-induced, quantitative solid-state polymerization reaction from an almost inorganic precursor is unusual. However, a thorough literature survey gave the surprising result that this reaction has been known for almost a century and a half.

Polyglycolide was first synthesized by Dessaignes in 1854 [1]. The first one to prepare it by heating a halogenoacetate, thus eliminating an alkali halide, was Hoffmann, a scholar of Kekulé, in 1857. Hoffmann heated potassium chloroacetate to 110°C and obtained polyglycolide [2]. So unusual was this reaction type that it prompted his mentor, A. Kekulé, to study the reaction himself [3]. At this time, a dimeric six-membered ring $(CH_2COO)_2$ was still assumed to be the structure of the glycolide. Further experiments along this line were subsequently carried out by Heintz, who prepared sodium chloroacetate [4], Norton and Tcherniak, who developed a method to prepare polyglycolide from sodium chloroacetate [5] and Beckurts and Otto, who prepared it from silver chloroacetate [6].

Systematic studies were carried out by Bischoff and Walden in 1893–1894 [7, 8], who proved that the organic product formed was actually polyglycolide. They prepared polyglycolide by heating sodium bromoacetate and sodium chloroacetate, respectively. Distillation of polyglycolide in vacuum gave the above mentioned diglycolide, which upon heating polymerized again.

This reaction, of ancient lineage, was studied spasmodically and somewhat tentatively earlier this century (see [9] for a review, and also [10–13]), but no attempt was made to elucidate either the underlying mechanism of this unusual reaction or the properties of the products. The formed polymer, polyglycolide, is of considerable interest as tablet support or biomaterial because of its easy biodegradability. It is currently under investigation for the manufacture of screws for the fixation of bone fractures [14–16]. Another important application is the preparation of microspheres that can serve as carriers for drugs or vaccines in the body [17].

We recently reported the investigation of this reaction with numerous solid-state chemical techniques [18], among them thermal analysis (DSC, TG-DTA-MS), X-ray diffraction, X-ray absorption spectroscopy (EXAFS) and electron microscopy. We found that the reaction takes place quantitatively within 2 h at 180°C. The crystals retain their original shape during the reaction; however, after the reaction they consist of NaCl microcrystals (d=1..2 μm) deposited in a polyglycolide matrix. Burning the polyglycolide matrix leaves a NaCl skeleton of interlinked cubes. Upon washing out the sodium chloride with water, a highly porous polyglycolide crystal with "inverse NaCl crystals" remains. The reaction is catalysed by the addition of sodium iodide through the intermediate formation of sodium iodoacetate [19].

From a solid-state chemical point of view as well as for a practical application of this reaction for polyglycolide synthesis it is important to learn more about the microscopic mechanism and about the properties of the formed products. A valuable technique for extracting this information is infrared-spectroscopy (IR). This is a highly sensitive probe for crystalline as well as for amorphous substances. We here report an *in situ* study using IR-spectroscopy with a view to detecting intermediates or by-products, if any, and to characterize the polymeric product.

Experiments and methods

Sodium chloroacetate was purchased from Fluka and recrystallized from ethanol. Its purity was checked by elemental analysis (C, H, Cl), ^{1}H- and ^{13}C-NMR spectroscopy in D_2O, ^{13}C-CP/MAS solid-state NMR spectroscopy, combined thermogravimetry-DTA-mass spectroscopy and DSC.

IR-spectroscopy was carried out with a Perkin-Elmer FT-IR 1725-X instrument equipped with a Spectratech diffuse reflectance unit (DRIFT). The sample temperature is measured in the sample holder with a thermocouple 2 mm below the surface. Approximately 250 mg of the pure sample were filled into the sample holder as a densly packed powder. The sample is subjected to ambient atmosphere during the experiment.

IR-spectra were measured from 400..4000 cm^{-1} with a resolution of 4 cm^{-1}. 32 scans were taken at each temperature and averaged to one dataset. The temperature was raised in steps of 3 K from 160 to 211°C. The sample remained at each temperature for the duration of one IR experiment (3 min). Thus, the average heating rate was 1 K min^{-1}. In another experiment, the sample was heated from room temperature to 200°C with an increased step height of 10 K and an annealing period of 10 min. No differences between the two experiments were detectable.

Results and discussion

During the reaction, considerable changes in the molecular vibrations occur (Fig. 1). The enlargements (Figs 2 to 4) show more clearly the variations in the single regions. As far as we can tell, there is no evidence for intermediates or other products during this reaction. The interpretation of the IR-spectra was done using standard references [20–22].

The formation of polyglycolide is most clearly seen in the C=O stretching region (1500..1800 cm^{-1}; Fig. 3) where the band of the ionised carboxyl group of sodium chloroacetate (1585 cm^{-1}) is vanishing and the broad C=O band of the ester group (1767 cm^{-1}) is forming. Other distinct changes occur in the C–H stretching region (2960..3010 cm^{-1}; Fig. 2) where the two bands are shifted to smaller wave numbers on account of the substitution of chlorine by oxygen on the methylene carbon. The C–O stretching band becomes much broader in the polymer (Fig. 4). Changes in the fingerprintregion below 1000 cm^{-1} (Fig. 4) are manifold and cannot be unambiguously assigned to single structural elements.

These spectral changes do all correspond to a one-step reaction from sodium chloroacetate to polyglycolide. However, there are unexpected bands occurring in the spectrum of the reaction product which indicate the occurrence of polymer endgroups.

The chains of the formed polyglycolide $[-CH_2COO-]_n$ must terminate in two different endgroups, one being alcoholic and the other carboxylic. Another

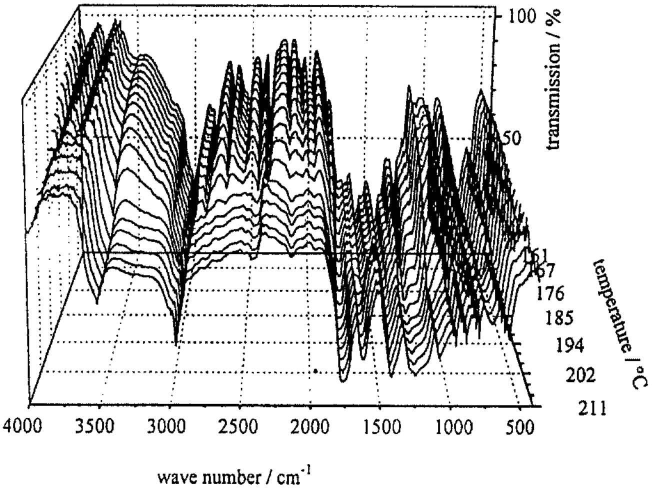

Fig. 1 Temperature-resolved IR-data taken during the transformation of sodium chloroacetate to sodium chloride and polyglycolide (400..4000 cm^{-1}). The average heating rate was 1 K min^{-1}

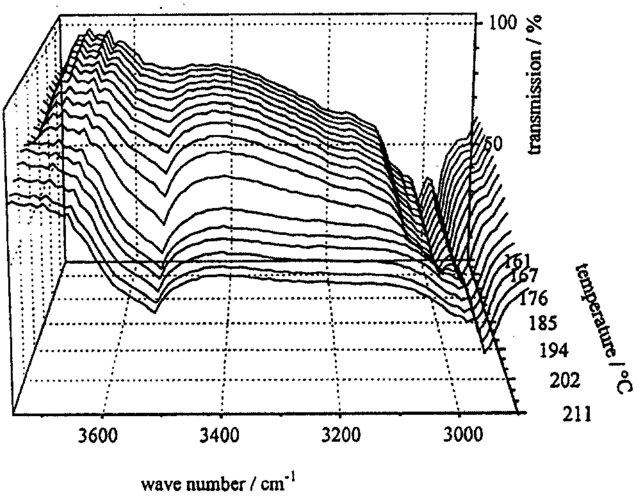

Fig. 2 Enlarged region of O–H and C–H stretch vibration frequencies. It clearly shows the formation of hydrogen-bonded OH–groups in polyglycolide (3514 cm^{-1}) and the changes in the C–H stretching region (2960..3010 cm^{-1})

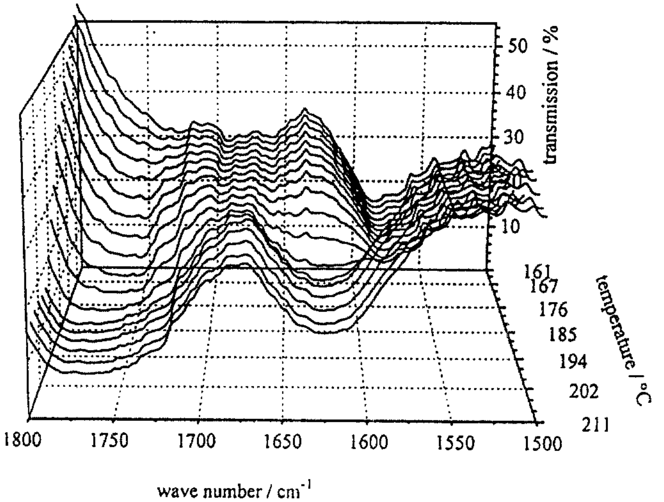

Fig. 3 Enlarged region of the C=O stretch vibration frequencies. The starting material sodium chloroacetate shows the ionised COO$^-$ group (1585 cm^{-1}). The formed polyglycolide shows the strong vibration of the covalent ester group (1767 cm^{-1}) and the smaller band of COO$^-$ endgroups (1626 cm^{-1})

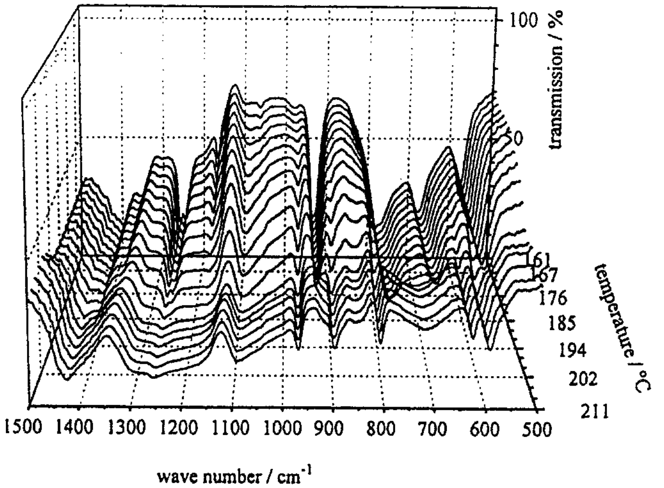

Fig. 4 Enlarged region of the lower wave number frequencies. Distinct changes in the molecular structure are clearly discerned (see text)

possibility is the formation of circular polymer chains which would not possess endgroups. In the following, we will identify the polymer endgroups by analysing the IR-spectrum of the reaction product.

A sharp band forms in the O–H stretching region at 3514 cm^{-1} (Fig. 2). This can be attributed either to a hydrogen bonded alcohol group C–OH or to a "free", unbonded acid group C(O)–OH. As we are dealing with a solid with a high concentration of electron donating oxygen groups, the occurrence of a free carboxylic group is unlikely. We therefore assign this peak to a terminating alcohol group in the polymer that is hydrogen-bond to another carbonyl group. This is also corroborated by the formation of another new band at 1089 cm^{-1} (Fig. 4) which we attribute to the C–O stretching vibration of an alcohol endgroup.

In the C=O double bond stretching region another unexpected band at 1626 cm^{-1} occurs. This belongs to an ionised carboxyl group, which, in comparison to the same band in the sodium chloroacetate, has lost the electronegative chlorine substituent. This indicates that the other endgroup of the formed polymer is COO^-Na^+.

These considerations show that the polymer is terminated by hydrogen-bonded alcoholic and by ionised carboxylic groups, and therefore has the structure

$$\cdots HO\text{–}[\text{–}CH_2COO\text{–}]_n\text{–}CH_2COO^-Na^+ \qquad (2)$$

The necessary OH-groups for formation of the alcohol endgroup are probably provided by atmospheric water through the reaction

$$Cl\text{–}CH_2\text{–}R\ (s) + H_2O\ (g) \longrightarrow HO\text{–}CH_2\text{–}R\ (s) + HCl\ (g) \qquad (3)$$

which is well known for the hydrolysis of chloroacetic acid in hot water.

Although we cannot exclude the formation of polyglycolide rings from these data, it is most unlikely that two ends of the polymerizing chain would meet during this solid-state reaction, where the mobility of the single chain elements is so small. Considering this, the formation of the linear aggregates that we detected fits perfectly well into the picture of a true solid-state reaction without liquid intermediate.

The spectra of samples of both sodium chloroacetate and polyglycolide were also monitored in transmission mode (as KBr pellet) because of the lower sensitivity of the reflection geometry arrangement. For sodium chloroacetate bands were obtained at 3008 (C–H stretch), 2978 (C–H stretch), 1601 (C=O stretch in COO^-), 1421/1400 (C–H deformation, COO^- bend), 1249 (C–O stretch), 934, 771 (C–Cl?), 673 (C–Cl?), 578 (C–Cl?) and 410 cm^{-1}. Polyglycolide shows IR-bands at 2993 (C–H stretch), 2962 (C–H stretch), 1746 (C=O stretch in ester group), 1611 (C=O stretch in COO^- endgroup), 1419 (C–H deformation, COO^- bend), 1212 (C–O stretch in ester), 1096 (C–O stretch in C–OH endgroup), 974, 904, 810, 711, 629 and 595 cm^{-1}. Adsorbed water on the KBr gave rise to a broad band between 3300 and 3700 cm^{-1} and masked possible O–H vibrations in the samples. The band positions are slightly different from those measured in reflection mode. However, we consider the data from the transmission experiments as more accurate because of the much higher beam intensity.

Conclusion

The solid-state elimination of sodium chloride from sodium chloroacetate has been monitored by *in situ* IR-spectroscopy. Polyglycolide is formed quantitatively without by-products or detectable intermediates. The terminating endgroups of the polymer were identified as hydrogen-bonded alcohol groups (C–OH) and as ionised carboxylic groups (COO^-Na^+), which points to the formation of linear polyglycolide chains. This underscores the presence of a polymerization in the solid state.

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