Study of a solid-state polymerisation reaction: thermal elimination of NaCl from sodium chloroacetate†

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The thermal elimination of sodium chloride from sodium chloroacetate can be accomplished by heating the compound to 150–200 °C. The remaining polyester ['polyglycolide', poly(1-oxy-1-oxoethylene)] is obtained in high yield. The reaction was quantitatively studied by thermal analysis (DSC, TG–DTA–mass spectrometry), NMR spectroscopy in solution and in the solid state, X-ray powder diffractometry, electron microscopy and X-ray absorption fine structure spectroscopy (EXAFS). Proton NMR spectroscopy, X-ray diffractometry and chlorine K-edge EXAFS are all well suited to determine the extent of reaction with high accuracy. The reaction proceeds in the solid state in one step without intermediates. Sodium chloride crystals (d = 1–2 μm) are deposited in a polyglycolide matrix while the external crystal morphology is preserved. Combustion of the polyglycolide leaves a sodium chloride framework. Washing out the sodium chloride with water leaves a porous polyglycolide matrix with cubic holes ('inverse NaCl crystals').

Solid-state photopolymerisation reactions of organic compounds are known for unsaturated hydrocarbons, *i.e.* alkenes and alkynes. For example, it is possible to synthesise polyacetylenes by these methods. The study of this field of organic solid-state chemistry has been pioneered by Schmidt[1] and continued, *e.g.* by the groups of Cohen,[2–4] Enkelmann,[5,6] Hasegawa,[7] Lahav,[8] Thomas[9] and Wegner.[10] In these reactions the necessary energy for the polymerisation step is provided by radiation, *i.e.* photopolymerisation occurs. In general, it is a photoaddition involving unsaturated organic compounds. Such topochemical reactions are now well understood from the viewpoint of crystallography.

Much less is known about thermally induced polymerisation reactions in the solid state. We now report a detailed study on the thermal elimination of sodium chloride from sodium chloroacetate which leads to a polyester [equation (1)]. This

$$ClCH_2CO_2^-Na^+ \longrightarrow NaCl + \tfrac{1}{n}(\text{–}CH_2CO_2\text{–})_n \quad (1)$$

strongly exothermic reaction occurs upon simply heating sodium chloroacetate above 140 °C. The organic part of the molecule polymerises to the simplest polyester, called 'polyglycolide' [poly(1-oxy-1-oxoethylene)]. The reaction was first discovered in 1894 by Bischoff and Walden.[11] It was studied to some extent in the first half of this century,[12,13] but no mechanistic studies have been performed to date. Here, the course of the reaction was followed by differential scanning calorimetry (DSC), combined thermogravimetry–differential thermal analysis–mass spectroscopy (TG–DTA–MS), NMR spectroscopy in solution and in the solid state, X-ray diffractometry (XRD), X-ray absorption spectroscopy (extended X-ray absorption fine structure, EXAFS) at the chlorine K-edge and scanning electron microscopy (SEM).

Results and Discussion

Sodium chloroacetate is metastable with respect to the thermal elimination. Unfortunately, the enthalpy of formation is not known for sodium chloroacetate or for the product polyglycolide. Non-isothermal DSC experiments gave an enthalpy of reaction (1) of -25.2 kJ mol^{-1} (see below). This is a pure solid-state reaction, provided that the polyglycolide occurs in the solid state, *i.e.* does not melt during the reaction. According to our results from DSC and electron microscopy this is the case. Thus, it is of interest in the context of fundamental studies of the mechanisms of organic solid-state reactions.

The polyglycolide formed is of interest from the viewpoint of preparative chemistry. Such polyesters are usually prepared in solution. They are used, for instance, as tablet supports, because they are non-toxic, easy to handle and easily biodegradable in the body.[14]

The fact that a solid-state decomposition leads quantitatively to a polymeric substance is unusual. A favourable arrangement of the molecules in the crystal most likely facilitates this condensation. We tried to clarify the reaction pathway by various methods. From a crystallographic point of view the ultimate information would be the crystal structures of sodium chloroacetate and polyglycolide, from which a possible mechanism could be derived. Unfortunately, all our attempts to obtain single crystals of sodium chloroacetate were unsuccessful. Crystallisation by cooling or by slow evaporation only led to very thin platelets with visible stacking disorder. Slow crystallisation by the diffusion method also led to thin platelets, in other cases to decomposition and deposition of NaCl after 2 months. Other structure-dependent methods are X-ray powder diffractometry, X-ray absorption spectroscopy, solid-state NMR spectroscopy and (scanning) electron microscopy. While the first requires long-range ordered samples, the other three can be applied to disordered or amorphous samples as well.

The extent of reaction, without direct mechanistic information, can be measured on aliquots taken during a reaction, *e.g.* by ^1H NMR spectroscopy or by argentometric titration of the sodium chloride formed. Additionally, isothermal or non-isothermal DSC can be employed (heating rate $\beta = 0$ or >0, respectively). A TG–DTA–MS scan of sodium chloroacetate is shown in Fig. 1. The thermal elimination takes place between 185 and 215 °C, accompanied by an exothermic DTA peak and

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† *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

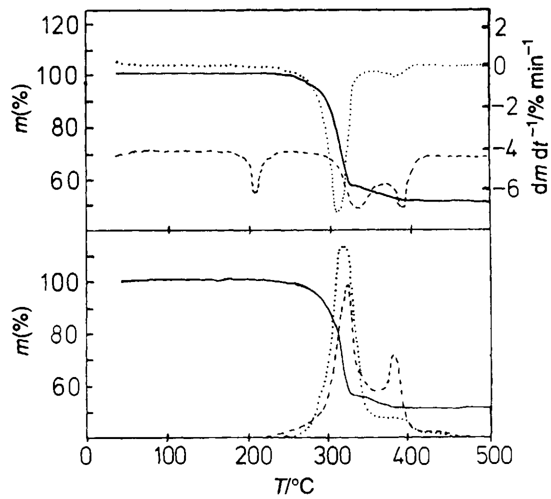

Fig. 1 A TG–DTA–MS experiment on sodium chloroacetate (air, 50 cm^3 min^{-1}, 5 K min^{-1}). In the upper part the relative sample mass m (TG) (——), the differentiated sample mass dm dt^{-1} (DTG) (. . .) and the DTA signal (- - -) (downwards = exothermic) are shown. The lower part shows the mass spectrometric signals with m/z = 18 (H_2O) (. . .) and 44 (CO_2) (- - -)

no mass loss. Exothermic combustion of the formed polyglycolide occurs between 250 and 400 °C. During this reaction, only the combustion gases H_2O (m/z = 18) and CO_2 (m/z = 44) are detected. The final mass loss of 49.3% corresponds well with the calculated one of 49.8% for a total burn up of polyglycolide. Only NaCl remains.

The observation that elimination and combustion are well separated is important. Consequently, a planned synthesis of polyglycolide can be accomplished by suitable isothermal heating programs. Isothermal DSC experiments at 150, 160, 170, 180 and 190 °C demonstrated that such a synthesis is possible. An exothermic reaction peak is detected from which the reaction extent $\alpha(t)$ can be calculated.[15] We obtained sigmoidal curves of α *vs.* t, a fact that could, with some caution, be interpreted as a nucleation-controlled mechanism.[16] The shape of the $\alpha(t)$ curves is almost independent of the temperature in the range of 150–190 °C, suggesting that the decomposition mechanism does not change in this temperature interval. The time required to reach $\alpha = 0.5$ ($\alpha = 1$) decreases from 313 (845) min at 150 °C to 22 (60) min at 180 °C to 9.2 (23 min) at 190 °C.

Non-isothermal DSC experiments at heating rates of 0.1–10 K min^{-1} gave an enthalpy of reaction of −25.2(14) kJ mol^{-1}. The polyglycolide formed occurs in the solid phase, and is revealed by a broad endothermic melting peak around 220 °C. This is also corroborated by electron microscopy (see below). The reported melting temperature for polyglycolide is 223–233 °C.[17] The onset temperature of the reaction peak changes from 145 °C at 0.1 K min^{-1} to 220 °C at 20 K min^{-1}.

Using this kinetic information, we synthesised a larger amount of polyglycolide by heating sodium chloroacetate ($\approx$ 10 g) in a glass container in an oil-bath (180 °C, 3 h). To monitor the reaction, sample aliquots were taken every few minutes and subjected to chloride titration (argentometry), ^{1}H NMR spectroscopy, X-ray powder diffractometry, X-ray absorption spectroscopy and scanning electron microscopy. The morphology of the powder does not change during the reaction; only the colour turned from white to yellowish. This corroborates the assumption that the polyglycolide formed occurs in the solid state.

The results of the X-ray diffractometry measurements are shown in Fig. 2. During the reaction the peaks due to sodium chloroacetate disappear and those of sodium chloride and of polyglycolide form. No crystalline intermediates were detected. The reaction proceeds in the solid state without an amorphous or liquid intermediate. There seems to be some structural relationship between sodium chloroacetate and polyglycolide, as suggested, *e.g.*, by the peaks at 2θ = 22, 37 and 41° which remain almost unchanged in position during the reaction.* The intensity and width of these peaks changes. Since neither crystal structure is known, any further interpretation would be just speculation.

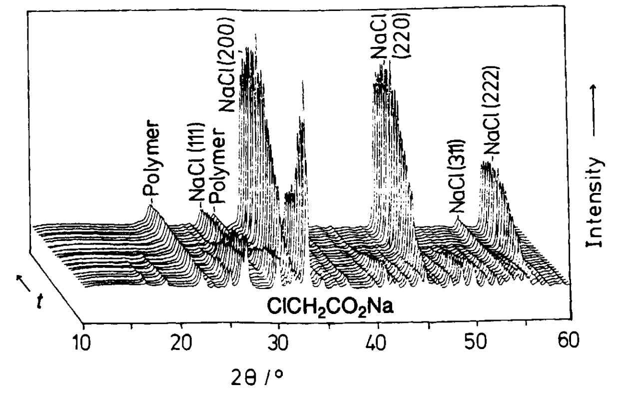

Fig. 2 Pseudo-three-dimensional plot of the obtained X-ray diffractometric data for aliquots from thermal elimination at 180 °C. The time intervals between the scans are not constant

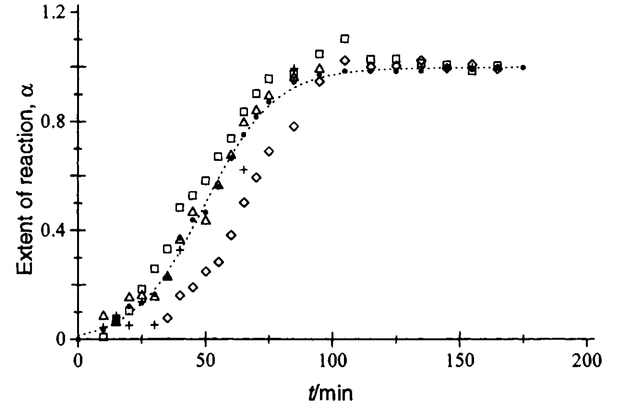

Fig. 3 Reaction extent α *vs.* time for the thermal elimination of NaCl from sodium chloroacetate at 180 °C. The reaction extent was determined by argentometric chloride titration of NaCl (●), by ^{1}H NMR spectroscopy in solution (+) and by X-ray powder diffractometry on selected non-overlapping peaks. The mean extent was calculated from three peaks of sodium chloroacetate and sodium chloride, respectively. The dashed line represents a sigmoidal fit to the argentometric data. Note the time lag in the growth of the polyglycolide peak. △, Mean reaction extent from the sodium chloroacetate peaks at 2θ = 18.3, 24.9 and 33.0°; □, mean reaction extent from the sodium chloride peaks at 2θ = 31.6 (200), 45.4 (220) and 56.5° (222); ◇, reaction extent from the polyglycolide peak at 2θ = 28.6°

The reaction extent determined by argentometry, ^{1}H NMR spectroscopy and X-ray diffractometry[18,19] is displayed in Fig. 3. Note that the relative integral peak-intensity ratio in X-ray diffractometry is proportional to the reaction extent α for this reaction.† The reaction is a little slower when compared to an isothermal DSC experiment at 180 °C (see above). This is probably due to the low thermal conductivity of sodium chloroacetate which leads to temperature gradients inside big samples, as previously reported.[12] The values from all methods

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* They do change enough, however, to reject the idea that they are due to any inert impurity.

† Generally, the integral X-ray peak intensity is proportional to the volume fraction of the component. For a single-step solid-state reaction A (s)→B (s) without mass loss it is directly proportional to the reaction extent α (see refs. 18 and 19 for details).

are in good agreement, therefore demonstrating their applicability to the determination of the extent of solid-state reactions.

From Fig. 3 it is seen that the characteristic polymer peak at $2\theta = 28.64°$ develops after the other product peaks (NaCl) have formed. This, together with the full width at half maximum, of 0.589° at $2\theta = 22.05°$ and 0.595° at $2\theta = 28.64°$ compared to $\approx 0.37°$ for the peaks due to NaCl or sodium chloroacetate, suggests a poor crystallinity or a very small particle size for the polymer. It seems as if polyglycolide is initially formed in a highly disordered, probably partially amorphous, state which does not exhibit the long-range order needed to result in an X-ray diffraction peak. From Fig. 3 it is seen that after 35 min a long-range order crystallisation of the initially formed polyglycolide is achieved. Peaks due to NaCl are detectable after 10 mins of reaction.

Using chloride K-edge EXAFS we looked for non-crystalline phases that would be invisible by X-ray diffractometry. The results are displayed in Fig. 4. These Fourier transforms of the EXAFS function reflect the radial distribution function around the chlorine atom. For sodium chloroacetate (front plot) we see the neighbouring carbon atom at a distance of *ca.* 1.5 Å. The distances seen in the Fourier transform are lower than the crystallographic distances due to the effect of the scattering phase.[20] A quantitative evaluation of this spectrum gave a Cl–C distance of 1.76(2) Å, which corresponds very well with the value for aliphatic chlorine compounds of 1.767(2) Å from crystallographic experiments.[21]

Other co-ordination shells appear only weakly because mainly light back scatterers are present (C, O, H). The intensity of the Cl–C co-ordination shell decreases continuously during the reaction, and the structure of a cubic NaCl lattice develops (rear spectra). The peak around 2.4 Å corresponds to the Cl–Na nearest-neighbour shell in NaCl. Quantitative analysis gave a chlorine-sodium distance of 2.81(2) Å which is identical to the nearest-neighbour distance in bulk NaCl, 2.8201(2) Å.[21] The second peak in the Fourier transform of the rear spectra around 3.6 Å corresponds to the second co-ordination shell (Cl–Cl) in NaCl. The third (Cl–Na) and fourth (Cl–Cl) co-ordination shells in NaCl form the third peak, the fifth (Cl–Na) and sixth (Cl–Cl) shells the fourth peak in the Fourier transform. Contributions from Cl dominate these higher peaks since the heavier Cl atoms give a stronger signal than the lighter Na atoms. Also, multiple scattering paths contribute to these peaks.

At the end of the reaction (rear spectrum in Fig. 4) the Fourier transform is identical with that of pure NaCl. A theoretical calculation of the EXAFS and the EXAFS Fourier transform of bulk NaCl closely resembles the rear spectrum of Fig. 4 (see Experimental section). No intermediates were observed by EXAFS during the reaction. The measured Cl–C distance as well as the Cl–Na distance remain constant within 0.02 Å throughout the reaction. By successive measurements on a sample of pure sodium chloroacetate (three spectra over 2 h), it was confirmed that no radiation damage of the substance occurred during the EXAFS experiment.

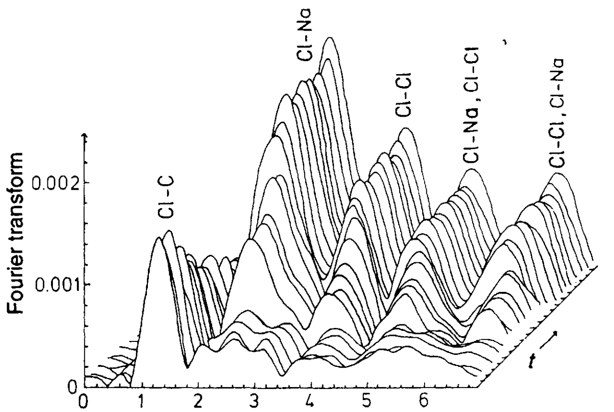

Fig. 4 Pseudo-three-dimensional plot of the chlorine K-edge EXAFS Fourier transforms of sample aliquots from Figs. 2 and 3 (weighted with *R*), showing the environment of the chlorine atoms during the transformation of sodium chloroacetate to sodium chloride. The time intervals between the scans are not constant (data not phase-shift corrected)

By quantitative evaluation of the EXAFS spectra it was possible to determine the extent of reaction α. The educt shell Cl–C and the product shell Cl–Na were consistently analysed in all spectra of Fig. 4 yielding the average Cl–C and Cl–Na co-ordination numbers in the sample by means of a two-shell fit (see Experimental section). In a two-component system these average co-ordination numbers are a measure of the individual concentrations and thus of the extent of reaction. The results are shown in Fig. 5, together with the argentometric data. The values from the two methods are in excellent agreement. This demonstrates the applicability of EXAFS to quantitative monitoring of reactions. Such analyses are seldom performed.*

Sample aliquots were also studied by cross polarisation magic angle spinning (CP MAS) solid-state ^{13}C NMR spectroscopy. Again, no intermediates were found. Sodium chloroacetate shows two doublets (δ 175.5, 176.4, CO_2; 42.9, 49.9, CH_2). This is due to residual dipolar coupling between $^{35,37}Cl$ and ^{13}C.[22] After the reaction there are two peaks for polyglycolide at δ 167.2 (CO_2) and 62.3 (CH_2).

The morphological features of the reaction were studied by scanning electron microscopy on sample aliquots. Fig. 6 shows scanning electron micrographs of samples at 0, 37.2, 75.1 and 100% completion of reaction. In the course of the reaction the initially smooth crystalline facets of sodium chloroacetate are given a microstructure due to deposition of sodium chloride which crystallises in cubes of 1–2 μm edge length. No preference for a crystallographic orientation was observed, *i.e.* the deposition occurs isotropically. The released lattice energy of the sodium chloride formed (786 kJ mol^{-1})[21] is high enough to overcome diffusion barriers that could hinder the formation of such cubes.

Here we observe the preservation of the macroscopic morphology of the sodium chloroacetate crystals, although the

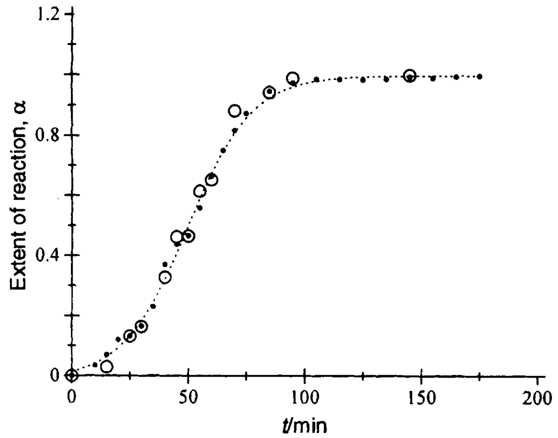

Fig. 5 Reaction extent α *vs.* time for the thermal elimination of NaCl from sodium chloroacetate at 180 °C determined by quantitative EXAFS evaluation (○). For comparison the values from the argentometric titration (●) are also shown. The dashed line represents a sigmoidal fit to the argentometric data

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* It should be emphasised that all quantitative analytical data (titration, XRD, EXAFS, ^{1}H NMR) were computed independently by different persons, without knowledge of the results of the other methods.

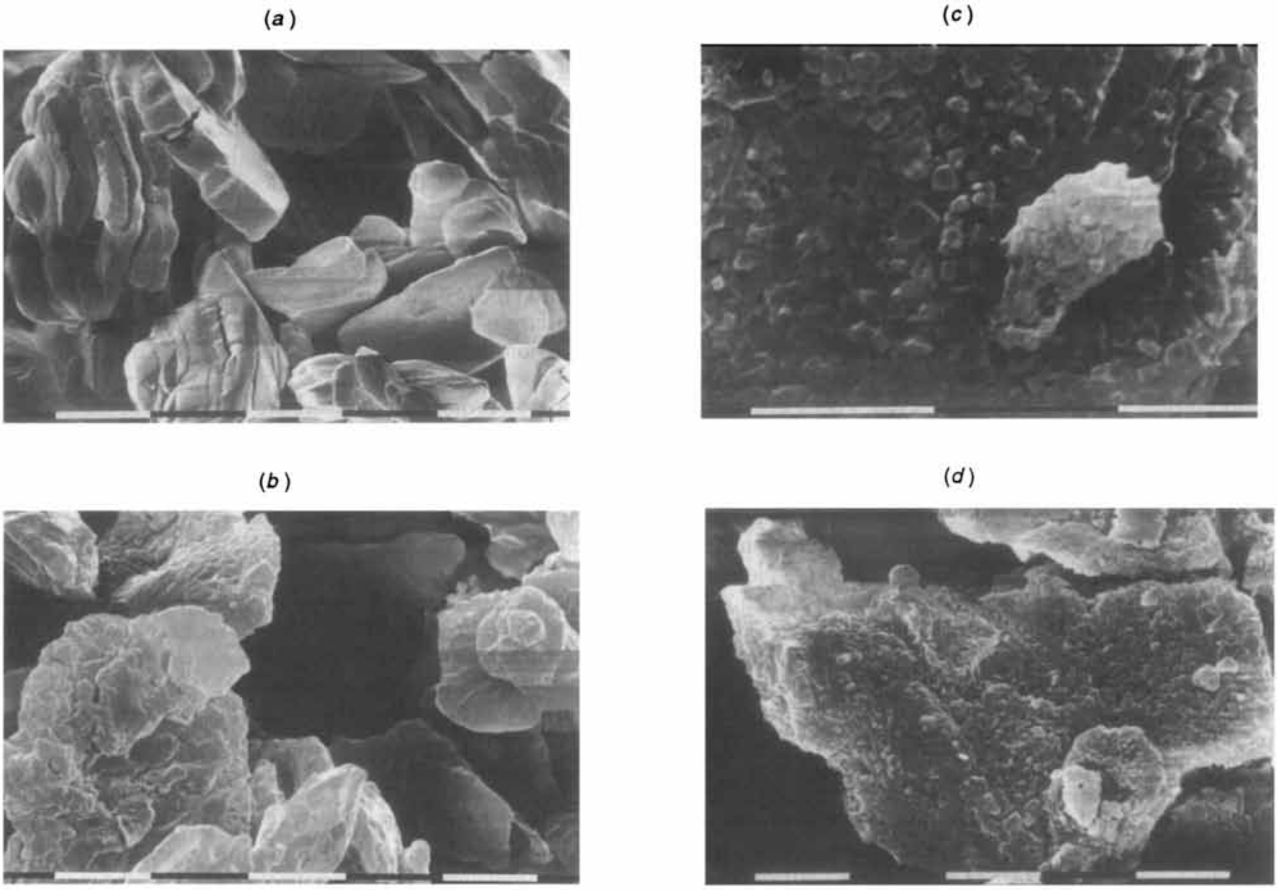

Fig. 6 Scanning electron micrographs of aliquots taken during the elimination of NaCl at 180 °C. The cracks in (*a*)–(*c*) are caused by radiation damage by the electron beam. (*a*) Unreacted sodium chloroacetate ($\alpha = 0\%$), (*b*)–(*d*) after 40 ($\alpha = 37.2$), 65 ($\alpha = 75.1$) and 155 min at 180 °C ($\alpha = 100\%$). Bar represents 10 μm

crystals seem to stick together to some extent [see Fig. 6(*d*)]. A complete melting of the polyglycolide formed during the reaction due to the released energy followed by solidification is unlikely because the particle size and morphology are almost retained. However, softening of the crystal surface may have occurred. Sodium chloride cubes deposit inside a polymeric matrix giving an intimate although still heterogeneous mixture. This is confirmed by the results of X-ray diffractometry and EXAFS which clearly show the presence of two well separated phases.

If such a sample of polyglycolide–NaCl is heated further, combustion of the polymer occurs (see Fig. 1). The sodium chloride frame-work remains. Fig. 7(*a*) shows the strongly interlinked round-edged cubes after heating to 500 °C. Further heating to 700 °C leads to well crystalline, sharp-edged crystals [Fig. 7(*b*)] due to thermal healing of the defect structure.

A polyglycolide matrix without sodium chloride is obtained after washing the insoluble polymer with water (Fig. 8). The external morphology is still preserved, but the surface now contains small cubic 'holes', left after the dissolution of sodium chloride. These holes have the same diameter (1–2 μm) as that of the NaCl crystals found in Fig. 6 and 7. The thoroughly washed polyglycolide was identified by solid-state ^{13}C NMR spectroscopy (see above) and by elemental analysis [Found (Calc.): C, 40.75 (41.40); H, 3.35 (3.45%)]. Thermogravimetry showed, however, that it still contained 3.5 wt% of sodium chloride, which was identified by scanning electron microscopy/analytical electron microscopy (energy-dispersive X-ray spectroscopy, EDX). The yield of polyglycolide was 84%.

In conclusion, this one-step reaction is easily carried out from an inexpensive precursor (sodium chloroacetate). Only non-toxic NaCl is formed as by-product which can be washed out with water. The porous network structure of the polymer could be of interest in pharmacology for controlled release of drugs or possibly for membrane-separation processes. The 'holes' in the structure are all in the same size range (1–2 μm).

Experimental

Differential scanning calorimetry was carried out with a Mettler DSC 27 HP high-pressure heat-flux calorimeter, operated at ambient pressure. The calorimeter was calibrated (T and heat flux) by melting naphthalene, indium, lead and zinc.[23–25] Sealed aluminium capsules with a small pinhole in the lid served as sample holders. Empty aluminium capsules were used as reference. The sample mass was 5–10 mg and the heating rates were 0.1–20 K min^{-1}. Simultaneous thermogravimetry, differential thermal analysis and mass spectrometry of evolved gases was carried out on a Netzsch STA 409/Balzers QMS 421 system. Samples (50–150 mg) were placed in open alumina crucibles. The atmosphere was either air or nitrogen (50 cm^3 min^{-1}).

X-Ray powder diffractometry was carried out on a Siemens D5000 diffractometer equipped with a secondary monochromator and Braun 50 m position-sensitive detector (Cu-Kα radiation, $\lambda = 154.178$ pm, 25 kV, 20 mA). Peak intensities for determination of extent of the reaction were calculated as integrals using pseudo-Voigt functions.[26] X-Ray absorption fine structure spectra (EXAFS) were measured at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen-Synchrotron (DESY), Hamburg, at beamline E4 (EXAFS II). This is equipped with a nickel mirror and an Si(111) double-crystal monochromator, yielding approximately 10^{10} photons s^{-1} mm^{-2} at the sample. Experiments were performed at the chlorine Kα-edge ($\approx$2820 eV)

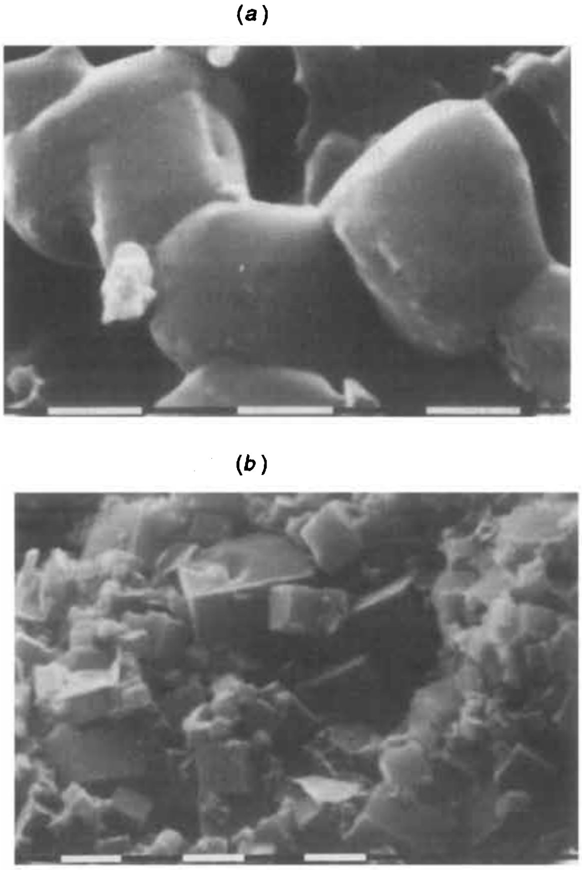

Fig. 7 Scanning electron micrographs of the sodium chloride matrix after combustion of the polymer. Crystal sizes are of the order of 1–2 μm: (*a*) after heating to 500 °C round-shaped crystals remain; (*b*) upon further heating to 700 °C, well crystalline, sharp-edged cubes form. Bar represents 1 μm

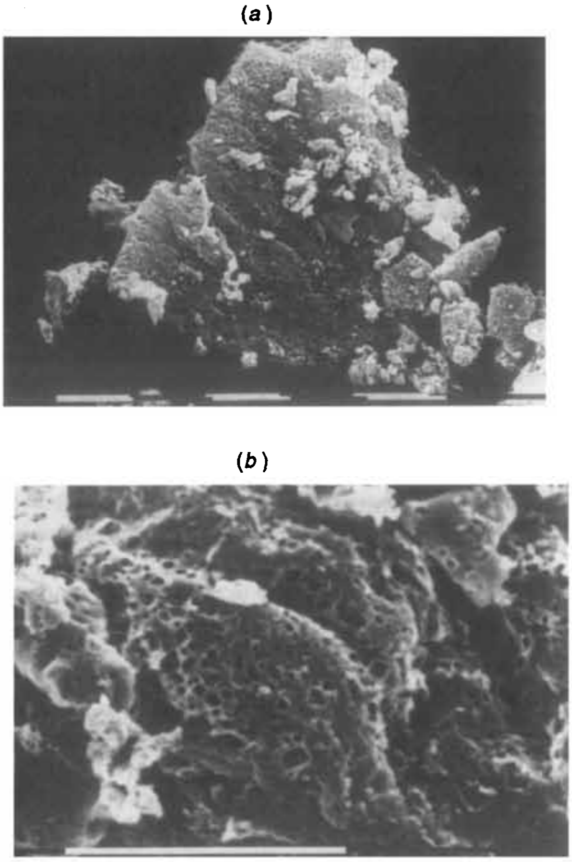

Fig. 8 Scanning electron micrographs of the polyglycolide matrix of a reacted sample after thoroughly washing with water. (*a*) A polyglycolide crystal, (*b*) magnification of the surface. Bar represents 10 μm

in transmission mode at room temperature. A few milligrams of mortared sample were thoroughly mixed with polyethylene ($\approx 1:3$) and pressed to a pellet (diameter 14 mm) which was placed in the beam. For data evaluation the program NUMERIC was used (Fig. 4).[27]

Quantitative evaluation of the EXAFS data employed the programs AUTOBK and FEFFIT from the University of Washington package.[28] Theoretical calculations of the bulk NaCl spectra were performed using the multiple scattering code FEFF 5.04 (ref. 29) which also provided the theoretical standards used in the quantitative fits of the data.[30] The extent of reaction was calculated by analysing the Cl–C shell of sodium chloroacetate (educt) and the first Cl–Na shell of sodium chloride (product) in a combined two-shell fit as follows. The EXAFS data were Fourier transformed in the range $k = 1.9$–9.0 Å^{-1} of the photoelectron wave vector using a k^3 weighting. The fitting was performed in r space in the range $r = 1.0$–2.6 Å. Generally, the number of free-fitting parameters in the two-shell fit should be at least eight: a mean co-ordination number, interatomic distance, mean-square relative displacement (m.s.r.d.) between the atoms and an energy shift between experimental and standard for each Cl–C and Cl–Na shell. However, we were able to reduce this number to only four by fixing the m.s.r.d. and energy shifts to the values obtained from one-shell fits of the pure educt and product [ΔE(Cl–C) = 2.5, ΔE(Cl–Na) = -1.9 eV, m.s.r.d.(Cl–C) = 0, m.s.r.d. (Cl–Na) = 0.022 Å^{-1}, relative to theoretical standards]. This assumes no significant change in the disorder of sodium chloroacetate and the NaCl formed in the course of the reaction. Fits with variable m.s.r.d. did not show a clear variation and support this assumption.

In a two-component system the ratio of a measured mean co-ordination number (over a macroscopic volume of the sample) and the co-ordination number in the corresponding pure compound directly gives the extent of reaction. It can be individually determined from the Cl–C as well as from the Cl–Na contribution. However, by assuming that there is no other contribution, a combination of both yields a more accurate result. This was done in Fig. 5. The estimated error of α is ± 0.05.

High-resolution solid-state CP MAS ^{13}C NMR spectroscopy was carried out on a Bruker MSL-300 spectrometer (75.5 MHz). Samples were placed in 7 mm ZrO_2 rotors and spun at 4 kHz. Proton NMR spectroscopy for quantitative analysis was carried out with a Bruker WP-80 instrument at 80 MHz. Samples were dissolved in D_2O containing a constant concentration of sodium acetate. The integral ratio of the methylene protons of chloroacetate (δ 4.03) and acetate (δ 1.88) gives the extent of reaction. We confirmed the linearity of this ratio by measuring defined mixtures of sodium chloroacetate and sodium acetate.

Scanning electron microscopy was performed on a Philips XL-20 instrument operating at 25 kV with gold-sputtered samples.

The extent of reaction of the samples was also determined by potentiometric titration of Cl^- with $AgNO_3$. Chlorine of $ClCH_2CO_2Na$ is not precipitated by $AgNO_3$, therefore only the NaCl content is measured.

Sodium chloroacetate was obtained from Fluka and recrystallised 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 NMR spectroscopy and DSC.

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