Crystal Structure, Solid-State Polymerization, and Ionic Conductivity of Alkali Salts of Unsaturated Carboxylic Acids, 4[◇]

Investigations on Lithium Sorbate

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The structure of lithium sorbate ($C_6H_7LiO_2$) was determined by single-crystal X-ray diffraction. It may be divided into organic and inorganic layers. The ionic part of the structure consists of a two-dimensional network of corner- and edge-sharing lithium oxotetrahedra, a structural pattern already known from other lithium carboxylates. Irradiation of the substance with X-rays or its thermal treatment results in the formation of a polymer exhibiting ionic conductivity at higher temperatures. Due to the rather large distances between potentially reactive atoms the polymerization results in a structural breakdown. Nevertheless, during the solid-state polymerization preferred orientations of building units are partially preserved. The probable course of the polymerization and the structure of the resulting polymer are discussed.

Polymers exhibiting ionic conductivity are interesting substances in view of their possible applications in electrochemical cells. Although the conductivities do not reach the values of liquid solutions, the use of such polymers may be advantageous due to their low weight, mechanical and chemical stability and flexibility in shape. Lithium ionconducting materials are especially interesting as a result of the high-energy density possible by using lithium-based electrodes.

The conductivity of heterogeneous systems prepared by dispersion of inorganic salts in inert polymer matrices is limited because the distribution of the charge carriers is not perfectly homogeneous, resulting in high local resistances between the conductive domains. To avoid these problems, our objective was to perform solid-state polymerizations of monomers already containing alkali ions, e.g. of salts of unsaturated carboxylic acids, which should result in more or less crystalline polymers with perfectly homogeneous distribution of potentially mobile ions. The determination and discussion of the monomer crystal structure is a key step in this development because the relative arrangement of the monomers determines the chances and the possible course of a solid-state polymerization whereas the ionic part of the structure accounts for an eventual ionic conductivity.

Structure and properties of lithium acrylates, methacrylates, crotonates, fumarates, and maleates were already discussed in previous contributions[1−3]. In all cases, the distances between the unsaturated carbon atoms − the potentially reactive centers of a solid-state polymerization − are too large for topochemical polymerizations and in some cases even too large for any reaction at all. The required

stacking of vinyl groups at rather small distances may not be achieved and even be unfavorable as a result of orbital symmetry restrictions according to the rules of Woodward and Hoffmann. For this reason, we extended our research to the lithium salt of sorbic acid (*trans,trans*-2,4-hexadienoic acid), an unsaturated compound containing conjugated double bonds in the hydrocarbon chain.

The Crystal Structure

The unit cell of lithium sorbate contains eight symmetrically equivalent molecules. The metrics of the structure are nearly orthorhombic with a small deviation of the monoclinic angle from 90°. The substance is organized in layers: along the *a*-axis planes containing lithium-oxygen tetrahedra alternate with organic double layers formed by the sorbate molecules. The structure is therefore divided into ionic and organic domains (Figure 1).

In the inorganic layers, pairs of edge-sharing lithium-oxygen tetrahedra are connected by the free corners to form an infinite two-dimensional network (Figure 2). This again appears to be a rather favorable answer to the structural problem of a fourfold oxygen-lithium coordination at an atomic ratio of only two to one when the formation of a three-dimensional network is prevented by bulky organic molecules. The lithium-oxygen structure appearing here is hence typical of solvent-free lithium carboxylates; it is found practically identical in the lithium salts of methacrylic[2], crotonic[1], and benzoic[4] acid. The tetrahedral coordination of a single lithium ion is always formed by oxygen atoms belonging to four different carboxylic acid molecules because the intramolecular oxygen distance of a carboxylate group is too short compared to the length of

Figure 1. (111) Plane of lithium sorbate with shortest α-δ distances
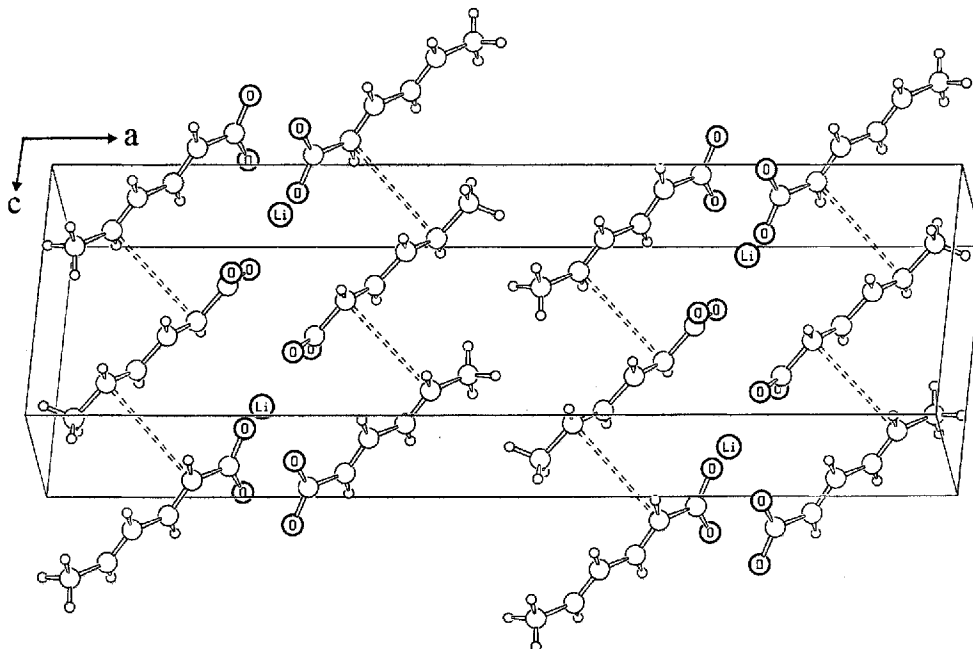
the edge of the tetrahedra (222 versus 283−341 pm in the case of lithium sorbate).

Figure 2. Network of lithium oxotetrahedra (along [100])
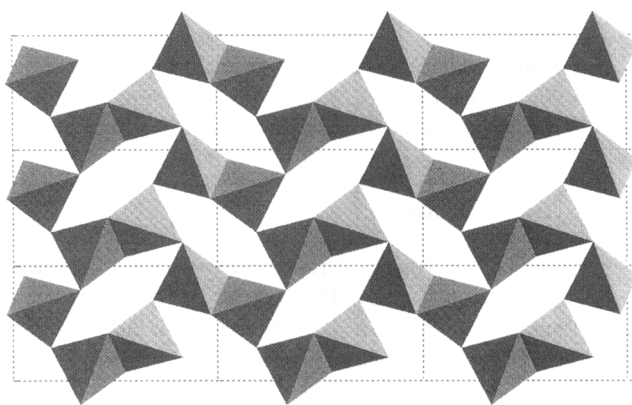
The organic part of the substance consists of layers as well, the sorbate molecules are arranged in planes nearly parallel to (602) in a zipper-like manner. They are not totally planar, the torsion angle is about 10° between the carboxylate and the first vinyl group and another 5° between the two double bonds. The variation of the temperature factors along the sorbate molecule emphasizes the predominance of the inorganic layers over the whole structure of the substance. While the oxygen and first carbon atoms are rather rigidly bound to the tetrahedral network, the terminal carbon atoms exhibit large thermal movements perpendicular to the axis of the molecule (Figure 3).

At first sight, the described arrangement of sorbate molecules in the (602) plane looks perfectly suitable to form a polymer chain by solid-state reaction, but the distances between adjacent molecules of about 455 pm (α- to β- or γ- to δ-C) and 570 pm (α- to δ-C) are far beyond the re-

Figure 3. Asymmetric unit of lithium sorbate, only nonhydrogen atoms shown
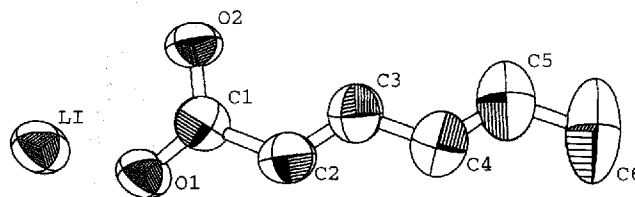
quired ones which should be below 400 pm according to[5]. The shortest distances found in the structure between potentially reactive centers, i.e. unsaturated carbon atoms, are 366 and 380 pm, belonging to β- to δ- and α- to γ-contacts or 388 and 412 pm for α- to δ-contacts.

Polymerization Experiments

Lithium sorbate can be transformed completely into a polymer substance by irradiation with X-rays or thermally. Progress and products of the reactions were analyzed by UV and ^{1}H-NMR spectroscopy and X-ray powder diffraction. Heating of the substance at temperatures above 220 °C in vacuo leads to complete transformation of the monomer into an amorphous product. In the case of the radiation-induced reaction, the process can be stopped at different degrees of polymerization, depending on the applied dose (Figure 4). Although the totally polymerized product is amorphous as well, a remaining structural organization of partially reacted samples can be seen in powder patterns. The (111) reflection remains relatively sharp and visible even at higher polymerization rates, i.e. the breakdown of the crystal structure is not isotropic but occurs preferably in such a way that the (111) layers are preserved to a certain extent. Considering that the shortest distances resulting in

an α-δ polymerization mentioned above are also located within the (111) layer, this might give a clue to the course of the reaction occurring on irradiation (Figure 1). The NMR spectra of polymerized samples are also consistent with a polymer chain formed by α-δ reaction; the thermally polymerized product appears to contain a more complex spectrum of products than the polymer samples prepared by irradiation.

Figure 4. Polymer yield as a function of X-ray dose (analyzed by UV spectroscopy at λ = 254 nm)
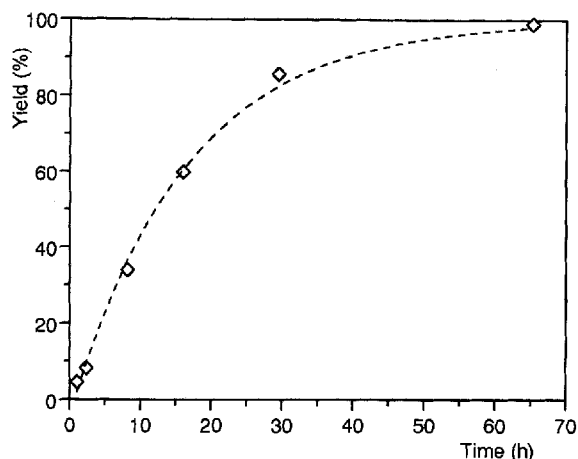
It is interesting to note that at least the radiation-induced polymerization seems to prefer the α-δ reaction although the distances between the reaction centers are longer than in the case of a hypothetical α-δ/δ-β polymerization. Probably, the required rotation of the sorbate molecule is an important factor in the selection of the reaction pathway. Due to the longer intramolecular distance between the α- and δ-carbon atoms, the entire molecule has to rotate less to connect the reaction centers.

Ionic Conductivity

The described arrangement of lithium-oxygen tetrahedra in the lithium sorbate structure is empirically known to be rather unfavorable for ionic conductivity probably due to the lack of suitable interstitial sites for moving lithium ions. None of the already analyzed substances with comparable structure[1,2] exhibit ionic conductivity at ambient temperatures, nor does lithium sorbate.

Upon polymerization the electric properties of lithium sorbate change drastically. A thermally polymerized sample already exhibits a small ionic conductivity under ambient conditions rising to values in the range of 10^{-4} S/cm at 250 °C (Figure 5). Since the material becomes plastic and begins to decompose at about this temperature, no further heating was tried. Analysis of the temperature dependence results in an activation energy of 2.0 eV.

The breakdown of the structure hence favors ionic conductivity in lithium sorbate because the unfavorable lithium-oxygen arrangement in the monomer structure is replaced by a more or less statistical distribution of oxygen-coordinated lithium in the polymer.

Figure 5. Temperature dependence of the ionic conductivity of thermally polymerized lithium sorbate
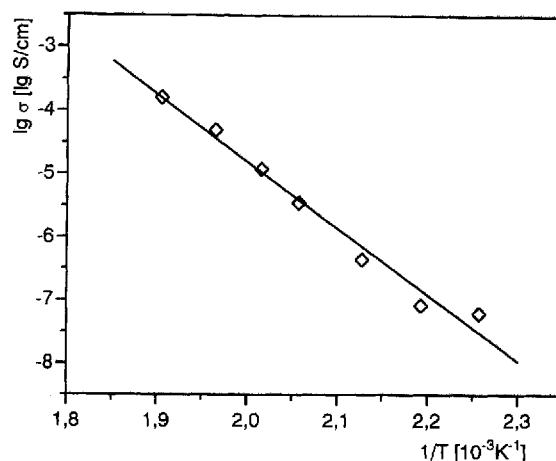
Experimental

Preparation of the Monomer: Lithium sorbate is prepared by dissolving 5.0 g (4.5 mmol) of sorbic acid and 1.9 g (4.5 mmol) of lithium hydroxide monohydrate in 50 ml of deionized and carbonate-free hot water. The pH of the resulting solution is adjusted to about 8 by addition of small amounts of sorbic acid or lithium hydroxide. Then 50 ml of 2-propanol is added and the cooled solution is separated from undissolved material by filtration. About 800 ml of 2-propanol is refluxed and stirred in a 2-l flask and the sorbate solution is added dropwise during two hours. The resulting suspension is cooled to ambient temperature and the crystals are separated by using a glass filter crucible and dried in vacuo. Yield: ca. 2.5 g (2.1 mmol/47%); the substance should be kept in the dark. – Crystals suitable for structure analysis are prepared by dissolving 100 mg of lithium sorbate in 30 ml of 2-propanol/water (10:1). The filtered solution is slowly concentrated in a trimethylsilane-coated glass vessel after a few additional drops of water have been added. A small amount of ground lithium sorbate suspended in 2-propanol is used as seed after 24 h. Thin crystal plates form within a few days. – ^{1}H-NMR (Bruker AC 200, F, D$_2$O): δ = 1.6 (d, 6-H), 5.6 (d, 2-H), 6.0 (m, 4-H, 5-H), 6.8 (dd, 3-H). – C$_6$H$_7$LiO$_2$ (118.06): calcd. C 61.04, H 5.98; found C 60.91, H 6.06.

Crystallography: C$_6$H$_7$LiO$_2$Li (118.06), monoclinic space group C2/c (No. 15), a = 28.380(6), b = 5.037(2), c = 8.843(2) Å, β = 90.83(3)°, V = 71264.0(6) Å^3, Z = 8, ρ$_{calcd.}$ = 1.241 g/cm^3. Atomic positions and temperature factors are compiled in Table 1[6]. A preliminary structural model could be found by using a rudimentary data set and direct methods of CRYSTAN[7]. Data collection for this publication was performed with a Siemens P4 diffractometer with Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator) at 294 K. The whole reciprocal lattice of a crystal of about 0.3 × 0.4 × 0.02 mm was measured in the range 3° < 2Θ < 60°, resulting in 4282 measured reflections. In the least-squares full-matrix refinement (SHELXTL PLUS[8]), 850 independent observations with I > 2σ(I) were used, no absorption (μ = 0.83 cm^{-1} for Mo-K_α) or extinction correction was applied. Refinement of nonhydrogen atoms was performed anisotropically, whereas only two isotropic thermal parameters were used for the description of the vinyl or methyl hydrogen atoms, resulting in 105 parameters. R = 6.7%, R$_w$ = 4.8%, w = σ^{-2}(F$_o$).

Table 1. Fractional coordinates and isotropic temperature factors of lithium sorbate

	x/a	y/b	z/c	U eq.
Li	.2523(2)	.1507(10)	-.3509(5)	.036(2)
O(1)	.2197(1)	.2918(4)	-.1786(2)	.033(1)
O(2)	.2127(1)	-.0797(4)	-.0449(2)	.034(1)
C(1)	.2023(1)	.1605(6)	-.0716(3)	.028(1)
C(2)	.1680(1)	.2933(6)	.0277(3)	.035(1)
C(3)	.1417(1)	.1695(7)	.1271(3)	.037(1)
C(4)	.1076(1)	.2899(7)	.2239(4)	.046(1)
C(5)	.0796(2)	.1679(8)	.3162(4)	.056(1)
C(6)	.0443(2)	.2879(11)	.4180(5)	.080(2)
H(1)		.4806(62)	.0086(30)	.054(5)
H(2)		-.0286(60)	.1335(31)	.054(5)
H(3)		.4728(60)	.2158(32)	.054(5)
H(4)		-.0117(61)	.3163(35)	.054(5)
H(5)		.2364(91)	.5152(46)	.131(11)
H(6)		.2181(91)	.3915(41)	.131(11)
H(7)		.4853(90)	.4060(47)	.131(11)

Polymerization: For thermal polymerization the substance is treated for 24 h at elevated temperatures in vacuo; polymerization yield is nearly 100% above 220 °C. DTA (Netzsch STA 409, 2 K/ min) shows an exothermic polymerization effect between 225 and 285 °C. Irradiation of the monomer with X-rays was performed in an X-ray fluorescence analysis system (type Siemens SRS 200) by using unfiltered Cr radiation (40 kV/40 mA, under ambient conditions). The substance turns yellowish in both cases. Due to the strong UV absorption of the conjugated double bonds in the monomer (lg ε_{254nm}) = 4.36 in H_2O) the polymerization yield can easily be determined by UV spectroscopy. Alternatively, the proportion of protons bound to the vinyl or saturated carbon atoms determined by integration of ^{1}H-NMR spectra (measured in D_2O)

may be used to follow the progress of the reaction. After a complete thermal reaction (verified by NMR) a small UV absorption (about 5% at 254 nm) remains. Major ^{1}H-NMR peaks after irradiation: broad signals at δ = 0.5−0.9 (methyl protons), 1.9−2.5 (methylene protons), 4.9−5.5 (vinyl protons).

Conductivity Measurements: The substance under investigation was pressed to pellets between thin copper disks and placed between copper stamps located in a small electrically heated tube. During the measurement, a steady nitrogen stream was passed through the tube to prevent oxidation of the sample at elevated temperatures. The actual measurement was performed with a HP 4192 LF Impedance Analyser, the sample temperature was recorded by using a thermocouple inserted into one of the copper stamps. The ionic conductivity was calculated by extrapolation of Nyquist plots to the real axis at the low-frequency side.

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