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Structural Aspects of the Solid-State Polycondensation Reaction in Alkali 4-Halogenomethylbenzoates

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Sodium and potassium salts of 4-halogenomethylbenzoic acids undergo a polymerization reaction in the solid state upon heating. The reaction products are the corresponding alkali halide (NaCl, KCl, NaBr, KBr) and poly(4-hydroxymethylbenzoic acid). Solid-state ^{13}C NMR spectroscopy was used to characterize parent compounds and reaction products. Lithium 4-chloromethylbenzoate and lithium 4-bromomethylbenzoate do not undergo this reaction, and the underlying structural reasons can be understood on the basis of the crystal structures of these materials, which have been determined directly from synchrotron X-ray powder diffraction data. The sodium and potassium compounds could be obtained only as a microcrystalline mixture of polymorphs, a fact that rendered structure determination impossible. © **2001 Academic Press**

Key Words: **solid-state NMR spectroscopy; synchrotron X-ray diffraction; structure determination; molecular crystals; solid-state polymerization.**

INTRODUCTION

Many different types of solid-state polymerization reactions have been reported to occur within molecular crystals (1–7). The occurrence of polymerization reactions in molecular crystals can depend strongly on the relative orientations of the monomers in the crystal structure being geometrically appropriate for reaction, whereas the analogous reactions in solution or molten states are not subject to such geometric restrictions. Starting from the classical example of photodimerization in *trans*-cinnamic acid (3-phenylacrylic acid) and its derivatives, the terms "topochemical reaction" and "topochemistry" were coined by G. M. J. Schmidt in the 1960s for solid-state reactions that rely on minimal movement of the reactant molecules (8,9). Examples include polyaddition reactions of polyunsaturated hydrocarbons (diolefins (6) and diacetylenes (3,10)) and polycondensation reactions of halogenocarboxylates (halogenoacetates (11–13) and halogenopropionates (14)). The first type usually involves photochemical initiation, whereas the latter type usually involves thermal initiation.

We have recently reported a hitherto unknown solid-state polycondensation reaction involving the elimination of alkali halide from alkali 4-halogenomethylbenzoates (Scheme 1) (15). This reaction can be carried out with sodium, potassium, and rubidium salts, leading to poly(4-hydroxymethylbenzoic acid) as the organic product. The polymer was identified by elemental analysis, X-ray diffraction, infrared spectroscopy, and ^{1}H NMR spectroscopy in solution. The average chain length (number of monomer units) is between about 10 and 100, according to NMR end-group analysis and capillary viscosimetry (15), and thus the product is fully comparable with the same polymer obtained by liquid-phase polymerization (16). As with the similar solid-state polymerization reaction in metal halogenoacetates (12), the reaction leads to deposition of micrometer-sized salt crystals in the polymeric matrix. A highly porous polymer with pores in the micrometer range is obtained after extraction of the salt with water.

However, the structural basis for the polymerization reaction in alkali 4-halogenomethylbenzoates is still unclear as no crystal structures are available for compounds in this family. One question of fundamental importance concerns the fact that the lithium 4-halogenomethylbenzoates do not undergo the polymerization reaction, whereas the sodium, potassium, and rubidium compounds readily react. As none of these materials could be prepared in the form of crystals suitable for single-crystal X-ray diffraction experiments, two complementary methods have been

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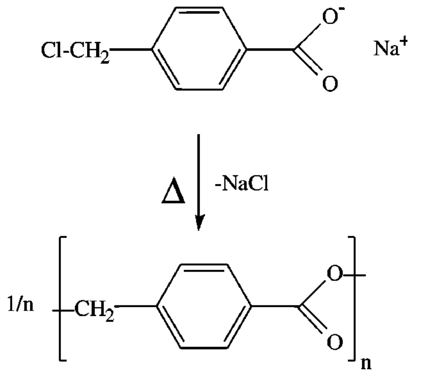

SCHEME 1. The thermally induced polycondensation in solid sodium 4-chloromethylbenzoate leads to sodium chloride and poly(4-hydroxymethylbenzoic acid).

employed in this work—structure determination from synchrotron X-ray powder diffraction data and solid-state NMR spectroscopy.

EXPERIMENTAL SECTION

Preparation

All alkali 4-halogenomethylbenzoate salts were prepared by neutralization of the corresponding acids with alkali hydroxide in diethylether/ethanol as reported in (15). They were characterized by elemental analysis (C, H, N), infrared spectroscopy, solution-state NMR spectroscopy (^{1}H in DMSO-d^6), and X-ray powder diffraction (check for the absence of alkali halide, alkali hydroxide, and halogenomethylbenzoic acid).

Solid-State NMR Spectroscopy

High-resolution solid-state ^{13}C NMR spectra were recorded at 75.49 MHz ($B_o = 7.05$ T) on a Chemagnetics CMX Infinity 300 spectrometer, using Chemagnetics 7.5- and 4-mm magic angle spinning probes. All spectra were recorded at 25°C for polycrystalline powder samples under conditions of magic angle spinning (MAS) (with typical MAS frequencies of 4000 ± 3 or 5000 ± 3 Hz) and high-power ^{1}H decoupling (using the TPPM decoupling sequence (17)) with decoupling field strength approximately 62.5 kHz. The $^1\text{H} \rightarrow {}^{13}\text{C}$ cross-polarization (CP) pulse sequence incorporating the total suppression of spinning sidebands (TOSS) technique was used. Recycle delays were between 12 and 120 s, depending on the sample. Solid-state ^{13}C NMR spectra were also recorded using the dipolar dephasing technique ("dd", with dephasing delay 45 ms), allowing the identification of carbon atoms that are not directly bonded to hydrogen. Isotropic ^{13}C chemical shifts are given relative to tetramethylsilane.

Structure Determination from Synchrotron Powder Diffraction Data

X-ray diffraction data were recorded at the powder diffractometer at beamline B2 at HASYLAB. The storage ring DORIS III was operated with 4.444 GeV. The data were recorded at room temperature in Debye–Scherrer mode in 0.5- and 1-mm glass capillaries. Lithium 4-bromomethylbenzoate was measured with a wavelength of 1.1895 Å (118.95 pm) using a secondary Ge(111) analyzing crystal. Lithium 4-chloromethylbenzoate was measured with a wavelength of 1.2006 Å (120.06 pm) using Soller slits between sample and detector (no secondary monochromator). The incoming beam was selected from the white beam with a Ge(111) double-crystal monochromator. A custom-made vacuum chamber was used to avoid air scattering. Data were collected from 3 to 40°2Θ in steps of 0.007°2Θ (bromine compound) and 3 to 48°2Θ in steps of 0.01°2Θ (chlorine compound) with an approximate counting time of 6 s at each point (scintillation counter).

For each sample, several scans were recorded to detect possible radiation damage. Only insignificant changes in the diffractograms were found in all cases, even after 10 or more hours of irradiation, indicating sufficient stability of the compounds toward irradiation. Individual scans were therefore summed prior to analysis. Raw data have been numerically corrected with respect to absorption based on a packing density of 80%.

Lists of peak positions were extracted from the raw data by profile fitting and used as input for the indexing program TREOR (18). The observed reflections were compatible with the extinction rules of the space group $P2_1/c$. Based on this symmetry, profile matchings were performed using the programs FULLPROF (19) and EXTRA (20) to refine both lattice parameters and profile parameters and to extract peak intensities. The lists of reflections and corresponding intensities were used as input data for the program SIRPOW-92 (21) for structure solution using direct methods. Structure solution gave the halogen position and five carbon atom positions of the benzene ring. The benzene ring was then completed using the built-in facilities of EXTRA. The geometry of the benzene ring was not fixed during the refinement and some distortion in the molecular geometry reflects this limitation of the refinement. Lithium atoms were found in the difference Fourier synthesis, but the hydrogen atoms could not be located and were omitted from the structure refinement. Note that the positions of the lithium atoms were stable under the refinement conditions, even with different starting parameters.

The following parameters were refined with the program GSAS (22): The scale factor S, two parameters for preferred orientation for the chlorine compound (G1 and G2 in March's function), the unit cell parameters (a, b, c, β), the zero-point shift parameter, two profile parameters (η, X), three parameters for the peak width (u, v, w), six anisotropic displacement parameters (β_{ij}) for the bromine atom, one isotropic displacement parameter for the chlorine atom, one common isotropic displacement parameter for all nonhalogen atoms (B_{iso}; for C, O, Li) and 36 coordinates for 12 independently refined atoms. Anisotropic peak broadening was taken into account for the bromine compound within the frame of a phenomenological model (23). Altogether, 52 independent parameters were refined for lithium 4-chloromethylbenzoate and 61 independent parameters were refined for lithium 4-bromomethylbenzoate.

RESULTS AND DISCUSSION

Solid-state NMR spectroscopy has now developed into a standard tool in solid-state chemistry. Particular advantages of this technique lie in the possibility to study any material irrespective of its crystallinity (crystalline, glassy, or amorphous), and in the wealth of structural and dynamic information that can be obtained (24–26). We have recorded high-resolution solid-state ^{13}C NMR spectra for a number of alkali 4-halogenomethylbenzoates and their reaction product (i.e., the polymer). Numerical data are collected in Table 1, and the spectra are shown in Figure 1. Note that the ^{13}C NMR spectra were recorded using the TOSS technique, which allows spectra to be recorded in which no spinning sidebands are present.

TABLE 1
Isotropic ^{13}C Chemical Shifts for Alkali 4-Halogenomethylbenzoate Salts and Poly(4-hydroxymethylbenzoic Acid)

Compound	CH_2	C_6H_4	COO
Li/Cl	45.2*, 51.1*	129.1*, 131.0*, 133.7, 141.5	177.4
Na/Cl	47.3*	128.3*, 136.0, 139.0	174.0, 177.8
K/Cl	49.4*	125.3, 128.5, 131.9, 135.2, 136.3, 137.9, 139.4, 143.9	172.1, 173.9
Li/Br	—	128.8*, 130.9*, 133.3, 142.1	177.3
K/Br	35.2*	127.7*, 135.1*, 136.1, 138.7	172.0, 173.4
Polymer from Na/Cl	65.4*	129.8, 132.2*, 135.0*, 141.5	165.0
Polymer from K/Cl	65.1*	129.7, 132.1*, 134.7*, 141.5	164.8

Note. The acronyms in the first column denote the metal and the halogen; i.e., Li/Cl stands for lithium 4-chloromethylbenzoate. The signal due to the methylene carbon in Li/Br is not discernible in the spectrum, possibly because it is broadened severely by ^{13}C–$^{79/81}$Br residual dipolar interaction. Carbon atoms attached to hydrogen are marked with an asterisk (*). No dipolar dephasing spectrum was recorded for K/Cl.

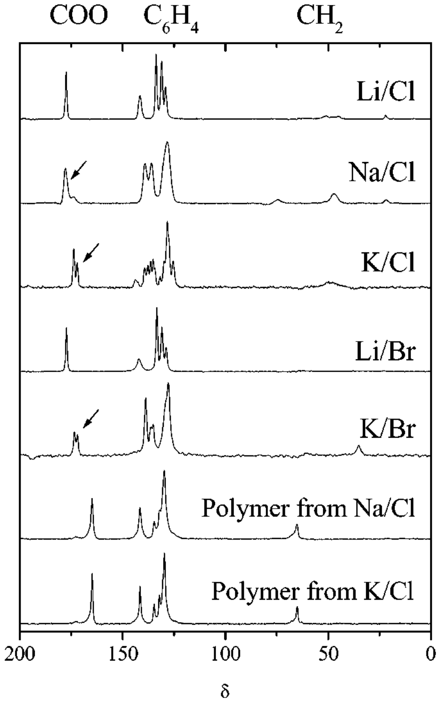

FIG. 1. High-resolution solid-state ^{13}C NMR spectra of alkali 4-halogenomethylbenzoates and the resulting polymer, poly(4-hydroxymethylbenzoic acid). The acronyms refer to the metal/halogen combinations in the samples. All spectra were recorded using the TOSS technique. The arrows mark the pairs of peaks observed for the carboxylate groups in some samples.

The spectra show the expected peaks for the carboxylate group, the benzene ring carbons (four signals for a *para*-substituted ring with appropriate symmetry), and the methylene group. The spectra also identify the reaction product as the expected polymer, and confirm the absence of byproducts. The chemical shift of the carboxylate group depends mainly on the metal (indicating a coordinative bond), whereas the chemical shift of the methylene group depends mainly on the halogen. For directly bonded ^{13}C–$^{35/37}$Cl and ^{13}C–$^{79/81}$Br spin pairs, residual dipolar interaction leads to splitting or broadening of the signal for the methylene group, in accordance with earlier observations on halogenated hydrocarbons (27–29).

Solid-state ^{13}C NMR spectra recorded using the dipolar dephasing (dd) technique provide a means of distinguishing carbon atoms that are directly bonded to hydrogen (for which the signals are suppressed, in the absence of molecular motion) from carbon atoms that are not directly bonded to hydrogen (for which the signals are not suppressed). This experiment has been performed for all compounds except potassium 4-chloromethylbenzoate. Representative results are shown in Fig. 2 for an alkali 4-halogenomethylbenzoate salt and a polymer. Note that the dipolar dephasing experiment suppresses the signals due to the CH_2 group and the CH groups in the benzene ring.

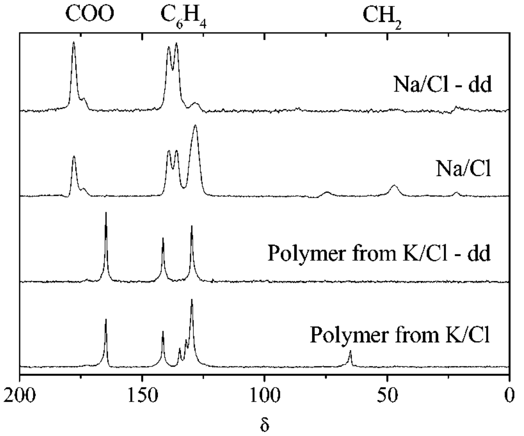

FIG. 2. High-resolution solid-state ^{13}C NMR spectra of sodium 4-chloromethylbenzoate and poly(4-hydroxymethylbenzoic acid) (obtained from the polymerization reaction in potassium 4-chloromethylbenzoate). All spectra were recorded using the TOSS technique to suppress spinning sidebands. Spectra recorded using the dipolar dephasing technique (also with TOSS) are labeled with dd—in such spectra, signals for carbon atoms directly bonded to hydrogen are suppressed.

A fundamental difference (see Fig. 1) between the two lithium salts studied and the sodium and potassium salts concerns the number of peaks. For the sodium and potassium salts, the signal due to the carboxylate group comprises two peaks. The underlying reason (excluding explanations based on the presence of impurities) is either that there are two kinds of molecules in the asymmetric unit of the crystal (with sufficiently different local environments to give different isotropic chemical shifts) or that two types of solid phases (polymorphs) of the same compound are present.

The fact that our attempts to index the powder diffraction patterns of the sodium and potassium compounds were unsuccessful suggests the presence of (at least) two polymorphic phases. Furthermore, the fact that the two carboxylate peaks in the solid-state ^{13}C NMR spectrum in general have unequal intensities implies (but does not prove) that the two peaks do not originate from having two molecules in the asymmetric unit. Nevertheless, a more definitive statement on these issues may be made only when the crystal structures are known.

Despite extensive efforts, it was not possible to grow crystals of any alkali 4-halogenomethylbenzoate that were suitable for structural characterization by single-crystal X-ray diffraction. All such trials resulted in very thin platelets with thickness too small for single-crystal diffraction experiments. Therefore, we set out to determine the crystal structures from high-resolution X-ray powder diffraction data recorded at the synchrotron source HASYLAB. In this regard, we recognize the opportunities that now exist for structure solution of molecular compounds of sometimes considerable complexity (13, 30–37) and for inorganic compounds (38–40) directly from powder diffraction data.

The traditional method (used here) for structure solution from powder diffraction data requires extraction of the intensities of individual diffraction maxima directly from the experimental powder diffraction pattern, followed by indexing and structure solution by the types of techniques (direct methods and Patterson methods) that are used for structure solution from single-crystal diffraction data (21, 41). Recently, however, there has also been much interest in the development of new strategies for structure solution from powder diffraction data that operate in direct space (42, 43). The relative merits of the traditional and direct-space approaches for structure solution are discussed elsewhere (43). Following structure solution, the structural model can be refined using the well-established Rietveld method (44).

As all information in the powder diffraction pattern is compressed into one dimension, indexing a powder pattern can turn out to be a major obstacle before a structure solution can be carried out. Small amounts of impurities or the presence of polymorphs and pseudopolymorphs (solvates) (45) can make successful indexing impossible, even when no chemical impurities are detectable in the sample.

We have encountered such problems during the structure determination of alkali 4-halogenomethylbenzoates. Thus, whereas the structure solution of lithium 4-chloromethylbenzoate and lithium 4-bromomethylbenzoate proceeded without problems by direct methods (see Experimental Section), we were not successful in indexing the powder diffraction patterns of potassium 4-chloromethylbenzoate and potassium 4-bromomethylbenzoate despite extensive attempts, and despite the fact that they were recorded on

TABLE 2
Lattice Parameters of Lithium 4-Chloromethylbenzoate and Lithium 4-bromomethylbenzoate

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å^3)	ρ_{calc} (g cm^{-3})	ρ_{exp} (g cm^{-3})
Li/Cl (benzoate)	18.3641(5)	5.0261(1)	8.6112(2)	96.356(3)	789.92(3)	1.484	1.506
Li/Cl (acetate)	9.3882(9)	4.8452(4)	9.0119(7)	94.330(5)	408.76(6)	1.632	—
Li/Br (benzoate)	18.6595(2)	5.0354(1)	8.6588(1)	96.036(1)	809.06(1)	1.813	1.786
Li/Br (acetate)	9.7165(11)	4.8610(6)	9.0228(11)	93.946(5)	425.15(9)	2.263	—

Note. For comparison, the values for lithium chloroacetate and lithium bromoacetate are given (35). The space group is $P2_1/c$ with $Z = 4$ in all cases.

TABLE 3
Figures of Merit in the Rietveld Refinement Calculations for Lithium 4-Chloromethylbenzoate and Lithium 4-Bromomethylbenzoate

Compound	χ^2	$R(F^2)$	R_{wp}	R_p	N
Li/Cl	2.13	11.98	4.35	3.15	52
Li/Br	1.74	3.82	7.40	5.60	61

Note. R_p is the profile R factor, R_{wp} is the weighted profile R factor, and N is the number of independently refined parameters.

TABLE 5
Fractional Atomic Coordinates for Lithium 4-Bromomethylbenzoate

Atom	x/a	y/b	z/c
Br	0.4368(1)	− 0.1337(4)	0.6506(3)
O1	0.0510(5)	− 0.3103(20)	0.5615(11)
O2	0.0503(6)	0.0393(18)	0.6963(10)
C1	0.1625(7)	− 0.0350(33)	0.5789(18)
C2	0.2002(8)	0.1752(3)	0.6550(14)
C3	0.2705(9)	0.2145(24)	0.6100(18)
C4	0.3032(7)	0.0244(31)	0.5278(19)
C5	0.2624(9)	− 0.1528(31)	0.4405(15)
C6	0.1871(8)	− 0.2196(22)	0.4788(17)
C7	0.0928(6)	− 0.1084(42)	0.6085(17)
C8	0.3780(5)	0.1088(30)	0.4977(15)
Li	− 0.0069(13)	− 0.3816(85)	0.3555(31)

a high-resolution diffractometer using synchrotron radiation. Sodium 4-chloromethylbenzoate and sodium 4-bromomethylbenzoate are of poor crystallinity (broad diffraction peaks), and indexing was also unsuccessful.

It appears that these four compounds contain at least two polymorphic phases after crystallization, as suggested by solid-state NMR spectroscopy (see above). Different attempts for crystallization from different solvents and annealing experiments were unsuccessful in giving monophasic samples of these compounds, although there were no indications from thermal analysis (DSC, thermogravimetry) that they underwent solid-state phase transformations or contained solvent molecules in the crystal. However, we must state that a structure determination was not possible in these cases, a fact that we ascribe to the presence of a mixture of polymorphic phases.

The structures of the two lithium compounds could be solved from powder diffraction data. Numerical data relating to the structure determination can be found in Tables 2 to 6. Both compounds are isostructural, with a monoclinic lattice. A Rietveld refinement plot is presented in Fig. 3, showing excellent agreement between experimental and calculated powder diffraction patterns for the final structure.

Figure 4 shows a packing plot of lithium 4-bromomethylbenzoate (viewed along [010]). The molecules assume a layer-like packing, with the halogen atoms pointing together and the lithium ions tetrahedrally coordinated by four oxygen atoms from four different carboxylate groups. These LiO_4 layers are interconnected to form infinite chains parallel to the crystallographic *bc* plane. This structure is very similar to those of lithium chloroacetate, lithium bromoacetate, and lithium iodoacetate (which are all isostructural), for which there is a similar layer-like structure with halogen layers and interconnected LiO_4 tetrahedra in the *bc* plane (35). In fact, the lithium 4-halogenomethylbenzoate structure is closely related to the lithium halogenoacetate structure by addition of a *para*-coordinated phenyl ring that

TABLE 4
Fractional Atomic Coordinates for Lithium 4-Chloromethylbenzoate

Atom	x/a	y/b	z/c
Cl	0.4374(2)	− 0.1412(8)	0.6536(6)
O1	0.0562(5)	− 0.3157(20)	0.5561(11)
O2	0.0555(4)	0.0357(15)	0.6915(10)
C1	0.1844(7)	− 0.0092(29)	0.5743(19)
C2	0.2028(9)	0.2147(29)	0.6595(16)
C3	0.2801(9)	0.1881(23)	0.6354(16)
C4	0.3174(6)	0.0368(27)	0.5208(18)
C5	0.2699(9)	− 0.1715(26)	0.4482(15)
C6	0.1917(7)	− 0.2159(22)	0.4658(19)
C7	0.1021(8)	− 0.0621(29)	0.6090(16)
C8	0.3908(5)	0.1007(25)	0.5039(14)
Li	− 0.0012(13)	− 0.4180(61)	0.3465(29)

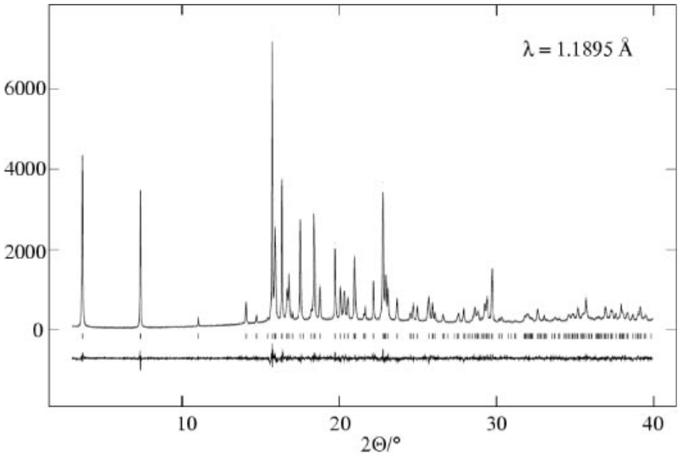

FIG. 3. Rietveld refinement plot of the powder diffraction pattern of lithium 4-bromomethylbenzoate.

TABLE 6
Displacement Parameters after Refinement and Absorption Correction (multiplied by $100/\text{Å}^2$)

Compound	Atom	u_{iso}	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Lithium 4-chloromethylbenzoate	Cl	10.2(3)	—	—	—	—	—	—
	Li, C, O	4.8(2)	—	—	—	—	—	—
Lithium 4-bromomethylbenzoate	Br	10.5(3)	4.7(2)	14.9(3)	11.9(3)	− 1.1(2)	0.7(2)	2.1(2)
	Li, C, O	1.2(2)	—	—	—	—	—	—

Note. Bromine in lithium 4-bromomethylbenzoate was refined anisotropically, whereas all other atoms were refined isotropically.

acts as "spacer" between the halogen and the LiO_4 layers (see Fig. 4). A comparison of the lattice parameters of lithium halogenoacetates and lithium 4-halogenomethylbenzoates supports this observation (see Table 2). The most significant difference between the lattice parameters concerns the elongated *a* axis in which the benzene ring acts as spacer.

In both cases (halogenoacetates and 4-halogenomethylbenzoates), the lithium salts do not undergo a polymerization reaction, in contrast to the sodium and potassium salts. In this regard, it is likely that the small, strongly polarizing lithium cation leads to a kinetic inhibition of the polymerization reaction, and the fact that the structures are governed by Li–O interactions supports this interpretation. However, as no thermodynamic data are available for any of these lithium salts, it cannot be established definitively whether the inhibition of the reaction has thermodynamic or kinetic reasons. In any case, the structure does not

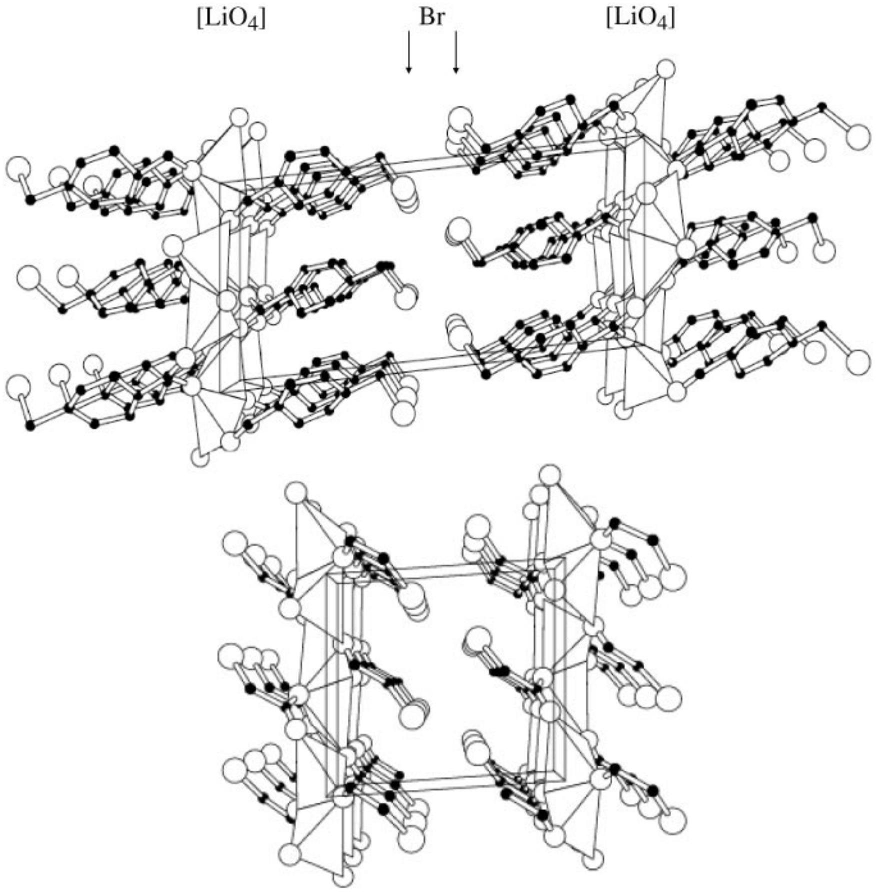

FIG. 4. (Top) Packing of the molecules in the structure of lithium 4-bromomethylbenzoate (viewed along [010]). The molecules assume a layered structure—the bromine atoms point together and the lithium cations are coordinated by four oxygen atoms from four different carboxylate groups (only the tetrahedra are shown for clarity). (Bottom) Packing plot of lithium bromoacetate along [010]. Note the structural similarity in which the *para*-coordinated phenyl rings may be regarded to act as "spacers."

support a topochemical reaction. In contrast, for the significantly different structures of sodium chloroacetate (13), sodium bromoacetate (29), and silver chloroacetate (46), direct topochemical reaction pathways could be postulated.

CONCLUSIONS

The crystal structures of lithium 4-chloromethylbenzoate and lithium 4-bromomethylbenzoate do not support a topochemical polymerization reaction in the solid state. This is ascribed to the polarizing effect of the small lithium cation that coordinates four oxygen atoms. The structures of the corresponding sodium and potassium compounds that undergo a solid-state polymerization reaction could not be obtained, most likely due to the presence of at least two polymorphic phases. Solid-state NMR spectroscopy unequivocally identifies the reaction product as poly(4-hydroxymethylbenzoic acid). It can therefore be concluded that this reaction type offers a new synthetic route to this polymer.

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REFERENCES

1. I. Paul and D. Curtin, *Acc. Chem. Res.* **6,** 217–225 (1973).
2. M. D. Cohen and B. S. Green, *Chem. Br.* **9,** 490–497, 517 (1973).
3. G. Wegner, *Pure Appl. Chem.* **49,** 443–454 (1977).
4. J. M. Thomas, *Pure Appl. Chem.* **51,** 1065–1082 (1979).
5. A. Gavezzotti and M. Simonetta, *Chem. Rev.* **82,** 1–13 (1982).
6. M. Hasegawa, *Chem. Rev.* **83,** 507–518 (1983).
7. G. R. Desiraju, "Organic Solid State Chemistry." Elsevier, Amsterdam, 1987.
8. G. M. J. Schmidt, *Pure Appl. Chem.* **27,** 647–678 (1971).
9. M. D. Cohen, *Angew. Chem.* **14,** 439–447 (1975); *Angew. Chem. Int. Ed. Engl.* **14,** 1386 (1975).
10. V. Enkelmann, G. Wegner, K. Novak, and K. B. Wagener, *Mol. Cryst. Liquid Cryst. A* **240,** 121–126 (1994).
11. R. Hoffmann, *Liebigs Ann. Chem.* **102,** 1–20 (1857).
12. M. Epple and H. Kirschnick, *Chem. Ber.* **129,** 1123–1129 (1996).
13. L. Elizabé, B. M. Kariuki, K. D. M. Harris, M. Tremayne, M. Epple, and J. M. Thomas, *J. Phys. Chem. B* **101,** 8827–8831 (1997).
14. M. Epple and H. Kirschnick, *Liebigs Ann. Chemie* 81–85 (1997).
15. O. Herzberg and M. Epple, *Macromol. Chem. Phys.* **200,** 2662–2666 (1999).
16. A. G. Pinkus, R. Subramanyam, and R. Hariharan, *J. Macromol. Sci. Pure Appl. Chem. A* **29,** 1031–1047 (1992).
17. A. E. Bennett, C. M. Rienstra, M. Auger, K. V. Lakshmi, and R. G. Griffin, *J. Chem. Phys.* **103,** 6951–6958 (1995).
18. P. E. Werner, L. Eriksson, and M. Westdahl, *J. Appl. Crystallogr.* **18,** 367–370 (1985).
19. J. Rodriguez-Carvajal, "Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France," p. 127, 1990.
20. A. Altomare, M. C. Burla, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, and G. Polidori, *J. Appl. Cryst.* **28,** 842–846 (1995).
21. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, and M. Camalli, *J. Appl. Cryst.* **27,** 435–436 (1994).
22. A. C. Larson and R. B. von Dreele, "Program GSAS-General Structure Analysis System," Los Alamos Lab. Report LA-UR-86-748. Los Alamos National Laboratory, Los Alamos, NM, 1987.
23. P. W. Stephens, *J. Appl. Crystallogr.* **32,** 281–289 (1999).
24. C. A. Fyfe, "Solid State NMR for Chemists." C.F.C. Press, Boca Rotan, FL, 1984.
25. G. Engelhardt and D. Michel, "High-resolution Solid-State NMR of Silicates and Zeolites." Wiley, Chichester, UK, 1987.
26. B. Blümich, *Adv. Mater.* **3,** 237–245 (1991).
27. S. H. Alarcon, A. C. Olivieri, S. A. Carss, and R. K. Harris, *Angew. Chem. Int. Ed. Engl.* **33,** 1624–1625 (1994).
28. A. E. Aliev, K. D. M. Harris, R. K. Harris, S. A. Carss, and A. C. Olivieri, *J. Chem. Soc. Faraday Trans.* **91,** 3167–3176 (1995).
29. A. E. Aliev, L. Elizabé, B. M. Kariuki, H. Kirschnick, J. M. Thomas, M. Epple, and K. D. M. Harris, *Chem. Eur. J.* **6,** 1120–1126 (2000).
30. R. E. Dinnebier, U. Behrens, and F. Olbrich, *Organometallics* **16,** 3855–3858 (1997).
31. R. E. Dinnebier, M. Pink, J. Sieler, and P. W. Stephens, *Inorg. Chem.* **36,** 3398–3401 (1997).
32. M. Tremayne, B. M. Kariuki, and K. D. M. Harris, *Angew. Chem. Int. Ed. Engl.* **36,** 770–772 (1997).
33. K. D. Knudsen, P. Pattison, A. N. Fitch, and R. J. Cernik, *Angew. Chem.* **110,** 2474–2478 (1998).
34. W. I. F. David, K. Shankland, and N. Shankland, *Chem. Commun.* 93 (1998).
35. H. Ehrenberg, B. Hasse, K. Schwarz, and M. Epple, *Acta Crystallogr. Sect. B* **55,** 517–524 (1999).
36. B. M. Kariuki, P. Calcagno, K. D. M. Harris, D. Philp, and R. L. Johnston, *Angew. Chem.* **111,** 860–864 (1999); *Angew. Chem. Int. Ed.* **38,** 1831–1835 (1999).
37. B. M. Kariuki, K. Psallidas, K. D. M. Harris, R. L. Johnston, R. W. Lancaster, S. E. Staniforth, and S. M. Cooper, *Chem. Commun.* 1677–1678 (1999).
38. T. Kraft and M. Jansen, *Angew. Chem.* **109,** 1842–1843 (1997).
39. S. Horstmann, E. Irran, and W. Schnick, *Angew. Chem.* **109,** 1938–1940 (1997).
40. J. D. Dunitz, K. D. M. Harris, R. L. Johnston, B. M. Kariuki, E. J. MacLean, K. Psallidas, W. B. Schweizer, and R. R. Tykwinski, *J. Am. Chem. Soc.* **120,** 13,274–13,275 (1998).
41. D. M. Poojary and A. Clearfield, *Acc. Chem. Res.* **30,** 414–422 (1997).
42. K. D. M. Harris and M. Tremayne, *Chem. Mater.* **8,** 2554–2570 (1996).
43. K. D. M. Harris, M. Tremayne, and B. M. Kariuki, *Angew. Chem.* (2000), in press.
44. H. M. Rietveld, *Acta Crystallogr.* **22,** 151–152 (1967).
45. T. L. Threlfall, *Analyst* **120,** 2435–2460 (1995).
46. M. Epple and H. Kirschnick, *Chem. Ber.* **130,** 291–294 (1997).