Alkali Metal Salts of 10,12-Pentacosadiynoic Acid and Their Dosimetry Applications

Amy V. Hall^a, Osama M. Musa^b, David K. Hood^b, David C. Apperley^a, Dmitry S. Yufit^a, and Jonathan W. Steed^{*a}

a Durham University, Department of Chemistry, Lower Mountjoy, Stockton Road, Durham, DH1 3LE, UK. E-mail: jon.steed@durham.ac.uk

b Ashland LLC, 1005 Route 202/206, Bridgewater, NJ 08807, USA

Abstract

Wide dose range 2D radiochromic films for radiotherapy such as GAFchromic[™] EBT are based on the lithium salt of 10,12-pentacosadiynoic acid (Li-PCDA) as the photosensitive component. We show that there are two solid forms of Li-PCDA – a monohydrated Form A and an anhydrous Form B. The form used in commercial GAFchromic[™] films is Form A due to its short needle shaped crystals which provide favourable coatability properties. However, Form B provides an enhanced photoresponse compared to Form A but adopts a long needle crystal morphology which is difficult to process. The two forms were characterised by powder X-ray diffraction, Fourier transform infrared spectroscopy, CP-MAS ¹³C solid-state NMR spectroscopy, and thermogravimetric analysis. In sum this data suggests a chelating bridging bidentate coordination mode of the lithium ions. The sodium salt of PCDA (Na-PCDA) is also reported which is an ionic cocrystal with a formula of Na⁺PCDA⁻·3PCDA. The PCDA and PCDA⁻ ligands display monodentate and bridging bidentate coordination to the sodium ion, in contrast to the coordination sphere of the Li-PCDA forms. Na-PCDA is photostable in contrast to its lithium analogues.

Introduction

Radiochromic films are commercially important materials, especially in medical physics, and provide reliable and accurate dose assessments. Their mode of operation involves the polymerisation of crystalline diacetylene monomers (e.g. 10,12-pentacosadiynoic acid, PCDA) to give a colour change that is proportional to the radiation dose.^{1, 2} It is well understood that diacetylene monomers such as PCDA can undergo a solid-state 1,4-addition polymerisation reaction when exposed to heat, ultraviolet, X-ray, or y-radiation to yield a coloured polydiacetylene.³⁻⁶ However, the reaction will only occur under optimal topochemical conditions - adjacent dialkyne moieties of the monomer must be separated by a distance less than or equal to the van der Waals contact distance (d) of 3.8 Å, with a translational period repeat spacing (r) of 4.9 Å or less, along with the monomers at an orientation angle (θ) to the crystal axis close to 45 ° (Scheme 1).^{3, 7, 8} The X-ray structure and topochemical parameters of PCDA have recently been reported.³ As PCDA exhibits some photoreactivity, it has been incorporated into radiochromic films in the past (e.g. GAFchromicTM MD-55),⁹ however, the PCDA films are relatively insensitive and can only be used to measure doses around 5 Gy.^{9, 10} More recently, sensitive, self-developing films such as GAFchromic[™] External Beam Therapy (EBT) have been developed by Ashland that are based on the lithium salt of PCDA (Li-PCDA),¹¹⁻¹⁸ and span dose ranges of 0.01-40 Gy.^{1, 2, 19} As the more recent models of GAFchromic[™] EBT films (especially EBT3 and EBT-XD) exhibit high spatial resolution,^{20, 21} near-tissue equivalence,^{21, 22} dose rate

and energy dependence,^{23, 24} along with being insensitive to visible light,²⁵ they are routinely employed in low dose gradient (e.g. a quality assurance tool in intensity modulated radiation therapy)²⁵⁻²⁸ and high dose gradient settings (e.g. brachytherapy^{29, 30}).^{18, 23, 31} Therefore, continued research into photoactive ingredients with tuneable reactivity is very important to improve dosimetry technologies for different therapeutic uses. In this paper, we highlight the spectroscopic characterisation of lithium salts of PCDA and the crystallographic characterisation of a sodium PCDA salt and compare their photoreactivity, particularly in the context of the impact of solid state crystal form.



Scheme 1. Parameters required for topochemical polymerisation of diacetylene monomers to result in a polydiacetylene. The C1-C4' distance (*d*) of the monomers must be ≤ 3.8 Å, and within the translational repeat distance (*r*) of ≤ 4.9 Å, with a tilt angle (θ) of 45°.

Results and Discussion

Lithium PCDA

The lithium salt of PCDA is synthesised by dissolving PCDA in a basic solution (e.g. aqueous tetraethylammonium hydroxide) at elevated temperatures.³² When PCDA is dissolved, 30 wt. % aqueous solution of lithium hydroxide is added to form nuclei that are then ripened by Ostwald ripening to give the materials in a long needle shaped crystal morphology. Subsequent intense sonication gives shorter needle crystals that are more suited to coating to produce GAFchromicTM EBT3 films. However, the shorter needles are thought to give lower radiation

sensitivity. In this work we have examined the differences between the two crystal morphologies of Li-PCDA by powder X-ray diffraction (PXRD) which reveals that the two different morphologies represent two different crystalline forms. The short needle material, Form A, is stable when kept moist, while the initially prepared long needle samples are a mixture of this form and a second crystal modification termed Form B. Interestingly, the PXRD pattern of Form A closely resembles the recently reported free acid PCDA,³ with an almost identical lamellar spacing (Figure S1). The CP-MAS ¹³C solid-state NMR spectra (ssNMR) of the two forms displays two peaks for Form A and a single peak for Form B in the carboxylate region in the range of 187-183 ppm (Figure S2) implying lower symmetry for Form A. In addition, exposure of Form A to heat (100 °C for one hour or 80 °C for one day) or vacuum (one day) gives pure Form B (Figure S3), indicating that a phase transition has occurred. Thermogravimetric analysis (TGA) experiments confirm the transition from Form A to Form B corresponds to a dehydration of monohydrated Form A. The TGA consistently shows a significant initial weight loss (73.0 %) due to the moist nature of the sample followed by a distinct weight loss step (10.0 %) assigned to crystalline water calculated to be the mass of one water molecule (Figure S4). The heat induced transformation of Form A into Form B was replicated in GAFchromic[™] EBT3 films (consisting of Form A). The films, based on Form A, change colour in proportion to the amount of radiation they are exposed to and are initially yellow and change to almost black after 100 Gy of X-ray radiation (Figure 1). The PXRD pattern of the films both before and after irradiation show lowangle peaks at 5.7 ° and 9.4 ° that are indicative of the presence of Form A. However, when the films are heated to 80 °C for one day, the Li-PCDA in the films is dehydrated and transforms to Form B evident, for example, by the corresponding peaks at 5.0 ° and 8.3 ° 2θ (Figure 2).



Figure 1. Photographs of GAFchromicTM EBT3 films that have been irradiated with increasing doses of X-rays, ranging from 1 Gy to 100 Gy.



Figure 2. The PXRD patterns of the GAFchromic[™] EBT3 films containing Form A before and after X-ray irradiation (5.7 ° and 9.4 °), and Form B after heating at 80 °C for one day (5.0 ° and 8.3 °).

Though no X-ray crystal structure of either monohydrated or anhydrous Li-PCDA could be obtained as a result of the low solubility of the materials, the FTIR spectra of the two Li-PCDA forms reveals insights into their structure (Figure 3). The asymmetric and symmetric carboxylate

stretching bands between 1581-1558 cm⁻¹ and 1443-1412 cm⁻¹, respectively, are split as a result of the reduced carboxyl symmetry due to the coordination with the lithium ion.^{33, 34} The carboxylate stretching bands reveal the type of coordination of the metal centre, evident by the difference in wavenumber of the asymmetric and symmetric stretching bands: $\Delta v = v(COO)_{asym}$ $v(COO)_{symm}$,^{35, 36} and can be calculated from the position of the first asymmetric carboxylate stretching band minus the wavenumber of the first symmetric carboxylate stretching band. For Form A, Δv is 149 cm⁻¹ (1581-1432 cm⁻¹), and for Form B is 134 cm⁻¹ (1577-1443 cm⁻¹). This data is consistent with previous reports of the lithium salts of propanoic and pentanoic acids, in which the Δv values are greater than the value expected for chelating bidentate coordination but lower than the range expected for bridging coordination. Therefore, a combination of chelating and bridging bidentate coordination of the carboxylate to the lithium ion is anticipated for both forms.^{33, 35, 37} Additionally, short-chain lithium carboxylate salts display almost identical FTIR spectra to Li-PCDA, with Δv values averaging 142 cm⁻¹.^{34, 38-40} The lithium centres of long-chain carboxylates also show asymmetric chelating bidentate bonding, which implies a tetrahedral environment of the lithium ion.^{34, 38, 39} This lithium environment is also expected for the two Li-PCDA forms because of the similar spectra. The proposed coordination environment of the lithium ion in Form B is displayed in Figure 4, while the water molecule is likely coordinated to the lithium ion in Form A. Interestingly in the FTIR spectrum of Form B, a progression of evenly spaced methylene wagging bands are observed in the region of 1380-1100 cm⁻¹, indicating that all methylene groups crystallise in an all-trans conformation, similar to lithium pentanoate.^{33, 34} However, Form A displays additional wagging bands of a reduced intensity when compared to the anhydrous material (for example the bands at 1277 cm⁻¹ and 1269 cm⁻¹), suggesting gauche conformational features are present in the monohydrate structure. The Raman spectrum of Form A irradiated with 100 Gy of X-ray radiation also supports the FTIR interpretation.³ The CH₂ band with the greatest intensity is at approximately 722 cm⁻¹ for both materials and is representative of a methylene bending vibrational mode.^{34, 41} This methylene band is related to the hydrocarbon chain packing and as a result, can indicate what the crystal system may be. For instance, a sharp peak without splitting (observed in Form B) is indicative of triclinic or hexagonal packing,⁴² with triclinic being the most likely crystal system,^{43, 44} which is in agreement with the $P\overline{1}$ space group of the related Ag-docosanoate and long-chain lithium alkanoates.^{38, 41} However, if the methylene band is split (as observed in Form A) a monoclinic or orthorhombic crystal system is suggested, such as the $P2_1/c$ space group of short-chain lithium alkanoates.^{38, 42}



Figure 3. The FTIR spectra of monohydrated (Form A) and anhydrous (Form B) Li-PCDA, with the important regions labelled. Form A also contains surface water.



Figure 4. The hypothesised chelating bridging bidentate coordination environment of the lithium ion in the anhydrous Form B of Li-PCDA, adapted from reference 34. $R = C_{25}H_{41}$.

While it is the monohydrated Li-PCDA (Form A) material that is currently used in GAFchromic[™] EBT3 films, it can be assumed that both Form A and Form B must conform to the topochemical postulate for photoreactivity since both display radiation sensitivity. This photoreactivity may be demonstrated by placing the two powdered forms on filter paper and exposure to UV (254nm) radiation for varying durations. Both materials show immediate darkening after 5 minutes of irradiation (Figure 5). The ssNMR spectra of Form A and Form B after one day of UV irradiation reveal the appearance of alkene peaks of the photopolymer as a result of the conjugated ene-yne backbone in the range of 130-100 ppm, indicating a slow conversion from monomer to polymer and implying a broad window of sensitivity which is a desired property from a dosimetry perspective (Figure 6). In Ashland's experience, a mixture of Form A and Form B (the pre-sonication long needle morphology material) is more responsive to radiation in a film context, however, the short needle morphology of Form A provides favourable film coating properties. Therefore, as the different materials have altered monomer-to-polymer conversions as a function of irradiation, the tunability of a range of different applications is possible.



Figure 5. Photographs of monohydrated (Form A) and anhydrous (Form B) forms of Li-PCDA powdered samples before and after different durations of UV irradiation (254 nm). As expected from the photoresponsive materials, the sample gradually darkens with prolonged radiation exposure. Note that the initial dark colour of Form B arises from surface colouration during the drying needed to remove Form A, however ssNMR data confirms that the bulk of the sample had not undergone appreciable photoreaction before UV irradiation.



Figure 6. The ssNMR of monohydrated (Form A) and anhydrous (Form B) Li-PCDA irradiated with UV (254 nm) for one day. The carboxylate region is 190-180 ppm while alkene peaks

arising from photopolymer occur in the 130-100 ppm region. Alkyne and alkane peaks are shown in the 80-60 ppm and 40-10 ppm region, respectively. The *x*-axis has added breaks to compact the spectra.

Sodium PCDA

To investigate group one alternatives to lithium salts that may adhere to the topochemical postulate of photoreactivity, the sodium salt of PCDA (Na-PCDA) was synthesised by combining sodium hydroxide and PCDA in a ball mill for 45 minutes in both 1:1 and 1:3 ratios, respectively. Characterisation of the 1:1 material revealed a mixture of PCDA and an Na-PCDA salt, while the 1:3 material consisted of only Na-PCDA. Serendipitous crystals of Na-PCDA were obtained from a mixture of PCDA and 3-aminopyridine by slow evaporation under ambient conditions. The resulting colourless plate crystals and were analysed at the I19 beamline at the Diamond Light Source. It is assumed that the sodium present was from contamination from the glass crystallisation vial. The X-ray structure of Na-PCDA reveals a PCDA sodium salt, free acid cocrystal that crystallises in space group $P\overline{1}$, with the sodium cation bound to one deprotonated PCDA (PCDA⁻) ligand and three neutral PCDA acid ligands to give a formula Na⁺PCDA⁻ ·3PCDA (Figure 7a). In addition, the PCDA salt ligand has a disordered carboxylic acid proton which and hence this site represents both an anion and a neutral molecule, as the proton has a site occupancy factor of 50 %. The sodium cation displays a distorted octahedral geometry (average O-Na-O bond angle of 85.7 °), with the sodium ion bound to carbonyl oxygen atoms at distances of 2.3580(13) Å and 2.3723(11) Å, and a Na-O distance from the sodium ion to the carboxylic acid OH group of the PCDA ligands at a distance of 2.6176(11) Å (Figure 7b). Two PCDA ligands coordinate to an adjacent sodium ion by bridging bidentate (syn-anti) oxygen atoms from the carboxyl ligands to form a continuous chain, while the remaining ligands have monodentate

bonding, which differs from the hypothesised coordination sphere of Li-PCDA. Hydrogen bonds are also present within the structure, occurring from the hydrogen atom of the carboxyl group to neighbouring carbonyl oxygen atom, at an O···O distance of 2.6290(16) Å. The long PCDA aliphatic chains are in an all-*trans* conformation and pack in a bilayer arrangement and tail-totail, which is reflected by the long *c*-axis of the unit cell at 54.510(6) Å. The previously reported structure of sodium hydrogen dihexadecanoate is similar to Na-PCDA in that there are two aliphatic chains in the asymmetric unit, though the sodium ion coordination sphere involves a total of five oxygen atoms.⁴⁵ Two of the ligands consist of hexadecenoic acid chains, while the remaining three ligands are of hexadecanoate chains. Similar to Na-PCDA, two oxygen atoms from adjacent hexadecanoate ligands bridge a neighbouring sodium ion, to give a mono- and bidentate coordination to the sodium ion.⁴⁵ Additionally, the X-ray structure of Na-PCDA reveals that the dialkyne moieties in the structure are not within the optimal topochemical parameters for photopolymerisaiton (r = 4.045(3) Å, d = 4.244(3) Å, $\theta = 33$ °), and therefore, the material is expected to be unreactive when exposed to radiation.



Figure 7. a) The X-ray structure of Na-PCDA in the crystallographic (100) direction with the topochemical parameters added. b) An enlarged section of Na-PCDA head groups to show the hydrogen bonds between PCDA acid ligands and the salt ligands (with a disordered proton).

As Na-PCDA does not adhere to the topochemical postulate, the powder was irradiated to investigate if the powder was useful as a dosimetry material. The powder was placed on filter paper and exposed to different durations of UV (254 nm) radiation. The powder was moved around the paper and pressed with a spatula at approximately hourly intervals to ensure the bulk of the powder was exposed to radiation. The colour of the powder remained unchanged until after one day of UV irradiation where the powder darkened somewhat (Figure 8). Because of the lack of photoreactivity up until one day of irradiation, the powder darkening may be due to minor photodegradation. To confirm the lack of polymerisation and to investigate any changes in the structure upon prolonged irradiation for seven days, Na-PCDA was analysed by PXRD (Figure S5), FTIR (Figure S6), and ssNMR (Figure S7). Characterisation of the irradiated powder provides no evidence of photopolymerisation or photodegradation, particularly evident by the lack of alkene peaks in the region of 130-100 ppm of the ssNMR spectra.



Figure 8. Na-PCDA irradiated for increasing durations of UV (254 nm) radiation. The powders were placed on a glass slide and exposed to radiation without any rotation of the powder, and so only the surface of the powder was exposed.

Conclusion

The X-ray structures of short-chain lithium salts and PCDA give insights into the structures of Li-PCDA and its monohydrated and anhydrous forms,³³ and is further illustrated by the similarity of lamellar spacing in the PXRD patterns.³ It is hypothesised that Form A crystallises in a monoclinic space group with a similar lamellar spacing to PCDA itself, while Form B crystallises in a triclinic space group. Both carboxylate head groups of each form have the same mixed bridged-chelating bidentate coordination to the lithium ion, even though Form A has a coordinated water molecule to the lithium ion. Additionally, Form A can be transformed to Form B in the final dosimetry film by heating. Due to the photoreactive nature of both Li-PCDA forms, they must also adhere to the topochemical postulate, in a similar way to organic salts of PCDA.³ Li-PCDA has been shown to produce an ordered photopolymer when irradiated (evident by Raman spectroscopy analysis), though PCDA combined with organic cations gives materials with enhanced photoreactivity.³ In contrast to Li-PCDA, the X-ray structure of Na-PCDA demonstrates a different coordination environment to Li-PCDA involving both monodentate and bridging ligands and is not sensitive to radiation. The lack of photoreactivity in Na-PCDA reinforces the importance of the topochemical postulate to predict the photoreactivity of a system which can only be quantitatively confirmed by the X-ray structure. Therefore, sustained investigation into different salts of PCDA is required to continually improve and advance photoreactive materials and their dosimetry applications.

Experimental

General

Form A of Li-PCDA was supplied by Ashland LLC, with all other reagents and solvents purchased from standard commercial sources and used without further purification. IR spectra were measured with a Perkin-Elmer 100 FT-IR spectrometer with a uATR attachment. Raman spectra were collected on a Perkin Elmer Ramanstation 400F with 5-10 accumulations of 10-60 second scans, using an excitation laser with a wavelength of 785 nm. Thermogravimetric analysis thermograms were recorded using a TA Instruments Q 500 TGA analyser. Between 1 and 5 mg of sample was weighed into platinum pans and dry nitrogen was used as the purge gas (flow rate: 60 mL min 1). Solid-state NMR spectra were recorded at 100.63 MHz using a Bruker Avance III HD spectrometer and a 4 mm magic-angle spinning probe. Spectra were obtained using cross-polarisation with a 20 s recycle delay with 7 ms contact time at ambient probe temperature (approx. 25 °C) at a sample spin rate of 10 kHz with 400 repetitions. Spectral referencing was with respect to an external sample of neat tetramethylsilane. Single crystal data for Na-PCDA was collected at 100.0(2) K at I19 beamline (Dectris Pilatus 2M pixel-array photon-counting detector, undulator, graphite monochromator, $\lambda = 0.6889$ Å) at the Diamond Light Source, Oxfordshire. The structure was solved using direct methods and refined by fullmatrix least squares on F² for all data using SHELXL⁴⁶ and OLEX2 software.⁴⁷ All nonhydrogen atoms were refined with anisotropic displacement parameters. CH hydrogen atoms were placed in calculated positions and refined in riding mode. H atoms attached to oxygen atoms were located on the difference map but refined as part of a rotating group (AFIX 147); disordered H atoms of the OH groups were refined with fixed SOF = 0.5. X-ray powder diffraction patterns were performed on glass slides, using a Bruker AXS D8 Advance diffractometer, with a Lynxeye Soller PSD Detector, using Cu K α radiation at a wavelength of 1.5406 Å.

The powdered materials were placed on filter paper in a dark box and exposed to a 6-Watt handheld UV light at 254 nm.

Synthesis of Li-PCDA and Na-PCDA

Lithium 10,12-pentacosadiynoate monohydrate (Form A): Li-PCDA·H₂O supplied by Ashland contained excess surface water and was placed under vacuum at room temperature for one day before analysis (which subsequently changes the monohydrated sample to the anhydrous sample). Analysis calc. for C₂₅H₄₁O₂Li: C 78.91, H 10.86 %, found: C 78.76, H 10.76 %; FTIR (cm⁻¹): 3570-3040 v(OH), 2956 v(CH₃)_{asym}, 2934 v(CH₂)_{asym}, 2918 v(CH₃)_{symm}, 2847 v(CH₂)_{symm}, 1688 δ (HOH), 1581 v(COO)_{asym}, 1564 v(COO)_{asym}, 1457 δ (CH₂), 1432 v(COO)_{symm}, 1418 v(COO)_{symm}, 1370 ω (CH₂), 1355 ω (CH₂), 1338 ω (CH₂), 1318 ω (CH₂), 1311 ω (CH₂), 1306 ω (CH₂), 1297 ω (CH₂), 1277 ω (CH₂), 1254 ω (CH₂), 1241 ω (CH₂), 1231 ω (CH₂), 1219 ω (CH₂), 1208 ω (CH₂), 1197 ω (CH₂), 1182 ω (CH₂), 1119 ω (CH₂), 1103 ω (CH₂), 1090 v(C-C), 1058 v(C-C), 1050 v(C-C), 1030 v(C-C), 1026 v(C-C), 1009 v(C-C), 999 v(C-C), 990 v(C-C), 979 v(C-C), 877 v(C-C)COO, 780 p(CH₂), 722 p(CH₂), 634.

Lithium 10,12-pentacosadiynoate (Form B): Li-PCDA was prepared by heating Li-PCDA·H₂O in the oven at 100 °C for one hour. Analysis calc. for C₂₅H₄₁O₂Li: C 78.91, H 10.86 %, found: C 79.02, H 10.78 %; FTIR (cm⁻¹): 2956 v(CH₃)_{asym}, 2918 v(CH₂)_{asym}, 2880 v(CH₃)_{symm}, 2847 v(CH₂)_{symm}, 1577 v(COO)_{asym}, 1558 v(COO)_{asym}, 1467 δ (CH₂), 1443 v(COO)_{symm}, 1412 v(COO)_{symm}, 1371 ω (CH₂), 1356 ω (CH₂), 1333 ω (CH₂), 1310 ω (CH₂), 1304 ω (CH₂), 1277 ω (CH₂), 1269 ω (CH₂), 1254 ω (CH₂), 1229 ω (CH₂), 1202 ω (CH₂), 1195 ω (CH₂), 1120 ω (CH₂), 1103 ω (CH₂), 1097 v(C-C), 1050 v(C-C), 1032 v(C-C), 1026 v(C-C), 1007 v(C-C), 995 v(C-C), 981 v(C-C), 847 v(CC)COO, 792, 747, 723 ρ (CH₂), 617.

Sodium 10,12-pentacosadiynoate/10,12-pentacosadiynoic acid salt cocrystal was prepared by grinding 10,12-pentacosadiynoic acid (0.60 g, 1.59 mmol) and sodium hydroxide (0.021 g, 0.53 mmol) in a Retsch MM 200 mixer mill for 45 minutes at a frequency of 20 s⁻¹ to yield a peach-colored powder (yield = 0.57 g, 1.15 mmol, 91 %). Analysis calc. for $C_{100}H_{167}O_8Na$: C 78.76, H 10.84 %, found: C 78.40, H 10.81 %; FTIR (cm⁻¹): 2957 v(CH₃)_{asym}, 2916 v(CH₂)_{asym}, 2851 v(CH₂)_{symm}, 1712 v(C=O), 1472 δ (CH₂), 1421, 1408, 1323 ω (CH₂), 1287 ω (CH₂), 1254 ω (CH₂), 1222 ω (CH₂), 1192 ω (CH₂), 1100 v(C-C), 936 vC-C(COO), 715 ρ (CH₂). The X-ray structure of Na-PCDA came from a failed crystallisation of PCDA and 3-aminopyridine in a 3:1 ratio, respectively, from the slow evaporation of acetone at room temperature which yielded colorless plate crystals. It is assumed that the presence of sodium was from a contamination in the glass vial.

Crystal data: M = 1520.32 g/mol, $0.203 \times 0.029 \times 0.008$ mm³, triclinic, space group $P\overline{1}$ (no. 2), a = 5.3007(6) Å, b = 7.9037(9) Å, c = 54.510(6) Å, a = 91.674(3) °, $\beta = 92.680(3)$ °, $\gamma = 92.463(4)$ °, V = 2278.0(4) Å³, Z = 1, $D_c = 1.108$ g/cm³, $\mu = 0.068$ mm⁻¹, F(000) = 842.0, synchrotron radiation, $\lambda = 0.6889$ Å, T = 100(2) K, 20max = 50.00°, 27970 reflections collected, 8701 unique (*R*int = 0.1030). Final GooF = 1.005, $R_1 = 0.0998$ (5841 reflections with $I > = 2\sigma(I)$, w $R_2 = 0.2559$ (all data), 497 parameters, 0 restraints. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2054687.

Corresponding Author

*Author to whom correspondence should be addressed.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

Ashland LLC and the Engineering and Physical Sciences Research Council.

Acknowledgments

We thank Ashland LLC and the Engineering and Physical Sciences Research Council for studentship funding. We thank Ashland for the X-ray irradiation of the radiochromic films. We also thank the Diamond Light Source for an award of instrument time on the Station I19 (CY 22240) and the instrument scientists for their support and patience. We also thank Mr. W. Douglas Carswell for his assistance with TGA measurements.

References

(1) Devic, S.; Tomic, N.; Lewis, D., Reference radiochromic film dosimetry: Review of technical aspects. *Eur. J. Med. Phys.* **2016**, 32, 541-556.

(2) Casolaro, P.; Compajola, L.; Breglio, G.; Buontempo, S.; Consales, M.; Cusano, A.; Cutolo, A.; Di Capua, F.; Fienga, F.; Vaiano, P., Real-time dosimetry with radiochromic films. *Sci. Rep.* **2019**, 9, 5307.

(3) Hall, A. V.; Yufit, D. S.; Apperley, D. C.; Senak, L.; Musa, O. M.; Hood, D. K.; Steed, J.
W., The crystal engineering of radiation-sensitive diacetylene cocrystals and salts. *Chem. Sci.*2020, 11, 8025-8035.

(4) Wegner, G., Z. Topochemical reactions of monomers with conjugated triple bonds I.
Polymerizations of 2,4-Hexadiynyl-1,6-diol derivatives in the crystalline state. Z. Naturforsch.,
B: J. Chem. Sci. 1969, 24, 824-832.

(5) Lauher, J. W.; Fowler, F. W.; Goroff, N. S., Single-crystal-to-single-crystal topochemical polymerizations by design. *Acc. Chem. Res.* **2008**, 41, 1215-1229.

(6) Fan, H. H.; Jiang, H. J.; Zhu, X. F.; Zhu, M. S.; Zhang, L.; Liu, M. H., Homo- and heterochirality regulated blue and red phase polymerization of diacetylene with enantiomeric and racemic gelators. *Eur. Polym. J.* **2019**, 118, 146-152.

(7) Enkelmann, V., Structural Aspects of the Topochemical Polymerization of Diacetylenes.*Adv. Polym. Sci.* 1984, 63, 91-136.

(8) Sun, A. W.; Lauher, J. W.; Goroff, N. S., Preparation of poly(diiododiacetylene), an ordered conjugated polymer of carbon and iodine. *Science* **2006**, 312, 1030-1034.

(9) Klassen, N. V.; van der Zwan, L.; Cygler, J., GafChromic MD-55: investigated as a precision dosimeter. *Med. Phys.* **1997**, 24, 1924-34.

(10) Rink, A.; Lewis, D. F.; Varma, S.; Vitkin, I. A.; Jaffray, D. A., Temperature and hydration effects on absorbance spectra and radiation sensitivity of a radiochromic medium. *J. Med. Phys.* **2008**, 35, 4545-55.

(11) Balakrishnan, S.; Lee, S.; Kim, J. M., Thermochromic reversibility of conjugated polymers derived from a diacetylenic lipid containing lithium salt. *J. Mater. Chem.* **2010**, 20, (12), 2302-2304.

(12) Soliman, Y. S.; Abdel-Fattah, A. A.; Hamed, A. A.; Bayomi, A. M. M., A radiationsensitive monomer of 2,4-hexadiyn-1,6-bis(p-toluene sulphonyl urethane) in PVA as a radiochromic film dosimeter. *Radiat. Phys. Chem.* **2018**, 144, 56-62.

(13) Cho, J. D.; Son, J.; Sung, J. W.; Choi, C. H.; Kim, J. S.; Wu, H. G.; Park, J. M.; Kim, J. I., Flexible film dosimeter for in vivo dosimetry. *Med. Phys.* 2020, 47, 3204-3213.

(14) Darafsheh, A.; Zhao, T. Y.; Khan, R., Spectroscopic analysis of irradiated radiochromic EBT-XD films in proton and photon beams. *Phys. Med. Biol.* **2020**, 65, 1-11.

(15) Schoenfeld, A. A.; Wieker, S.; Harder, D.; Poppe, B., Changes of the optical characteristics of radiochromic films in the transition from EBT3 to EBT-XD films. *Phys. Med. Biol.* **2016**, 61, 5426-5442.

(16) Williams, M.; Metcalfe, P., Radiochromic Film Dosimetry and its Applications in Radiotherapy. *AIP Conf. Proc.* 2011, 1345, 75-99.

(17) Leon-Marroquin, E. Y.; Mulrow, D.; Darafsheh, A.; Khan, R., Response characterization of EBT-XD radiochromic films in megavoltage photon and electron beams. *Med. Phys.* **2019**, 46, 4246-4256.

(18) Cueto, J.; Osorio, V. P.; Saiz, C. M.; Guirado, F. N.; Villalon, F. J. C.; Montenegro, P. G., A universal dose-response curve for radiochromic films. *Med. Phys.* 2015, 42, 221-231.

(19) Lewis, D. F.; Chan, M. F., Technical Note: On GAFChromic EBT-XD film and the lateral response artifact. *Med. Phys.* **2016**, 43, 643-649.

(20) Morales, J. E.; Butson, M.; Crowe, S. B.; Hill, R.; Trapp, J. V., An experimental extrapolation technique using the Gafchromic EBT3 film for relative output factor measurements in small x-ray fields. *Med. Phys.* **2016**, 43, 4687-4692.

(21) Callens, M. B.; Crijns, W.; Depuydt, T.; Haustermans, K.; Maes, F.; D'Agostino, E.; Wevers, M.; Pfeiffer, H.; Van den Abeele, K., Modeling the dose dependence of the visabsorption spectrum of EBT3 GafChromic (TM) films. *Med. Phys.* **2017**, 44, 2532-2543.

(22) Niroomand-Rad, A.; Chiu-Tsao, S. T.; Grams, M. P.; Lewis, D. F.; Soares, C. G.; Van Battum, L. J.; Das, I. J.; Trichter, S.; Kissick, M. W.; Massillon-Jl, G.; Alvarez, P. E.; Chan, M. F., Full report of AAPM Task Group 235 radiochromic film dosimetry: An update to TG-55. *Med.* Phys. 2020, DOI: 10.1002/mp.14497.

(23) Bekerat, H.; Devic, S.; DeBlois, F.; Singh, K.; Sarfehnia, A.; Seuntjens, J.; Shih, S.; Yu, X.; Lewis, D., Improving the energy response of external beam therapy (EBT) GafChromic (TM) dosimetry films at low energies (<= 100 keV). *Med. Phys.* 2014, 41, 1-14.

(24) Chiu-Tsao, S. T.; Ho, Y.; Shankar, R.; Wang, L.; Harrison, L. B., Energy dependence of response of new high sensitivity radiochromic films for megavoltage and kilovoltage radiation energies. *Med. Phys.* **2005**, 32, 3350-3354.

(25) Fuss, M.; Sturtewagen, E.; De Wagter, C.; Georg, D., Dosimetric characterization of GafChromic EBT film and its implication on film dosimetry quality assurance. *Phys. Med. Biol.*2007, 52, 4211-4225.

(26) Borca, V. C.; Pasquino, M.; Russo, G.; Grosso, P.; Cante, D.; Sciacero, P.; Girelli, G.; La Porta, M. R.; Tofani, S., Dosimetric characterization and use of GAFCHROMIC EBT3 film for IMRT dose verification. *J. Appl. Clin. Med. Phys.* **2013**, 14, 158-171.

(27) Vaiano, P.; Consales, M.; Casolaro, P.; Campajola, L.; Fienga, F.; Di Capua, F.; Breglio, G.; Buontempo, S.; Cutolo, A.; Cusano, A., A novel method for EBT3 Gafchromic films read-out at high dose levels. *Phys. Med.* 2019, 61, 77-84.

(28) Fiandra, C.; Ricardi, U.; Ragona, R.; Anglesio, S.; Giglioli, F. R.; Calamia, E.; Lucio, F., Clinical use of EBT model Gafchromic (TM) film in radiotherapy. *Med. Phys.* **2006**, 33, 4314-4319.

(29) Aldelaijan, S.; Devic, S.; Bekerat, H.; Papaconstadopoulos, P.; Schneider, J.; Seuntjens, J.; Cormack, R. A.; Buzurovic, I. M., Positional and angular tracking of HDR Ir-192 source for brachytherapy quality assurance using radiochromic film dosimetry. *Med. Phys.* **2020**, DOI: 10.1002/mp.14540.

(30) Devic, S.; Liang, L. H.; Tomic, N.; Bekerat, H.; Morcos, M.; Popovic, M.; Watson, P.; Aldelaijan, S.; Seuntjens, J., Dose measurements nearby low energy electronic brachytherapy sources using radiochromic film. *Phys. Med.* **2019**, 64, 40-44.

(31) Devic, S., Radiochromic film dosimetry: Past, present, and future. *Phys. Med.* 2011, 27, 122-134.

(32) Anyumba, J.; Lewis, D. F.; Shih, H.-Y.; Yu, X. Lithium salt of polyacetylene as radiation sensitive filaments and preparation and use thereof. EP1614002A4, **2004**.

(33) Casado, F. J. M.; Riesco, M. R.; Perez, M. V. G.; Redondo, M. I.; Lopez-Andres, S.; Cheda, J. A. R., Structural and Thermodynamic Study on Short Metal Alkanoates: Lithium Propanoate and Pentanoate. *J. Phys. Chem. B* **2009**, 113, 12896-12902.

(34) Nelson, P. N.; Ellis, H. A.; White, N. A. S., Solid state C-13-NMR, infrared, X-ray powder diffraction and differential thermal studies of the homologous series of some mono-valent metal (Li, Na, K, Ag) n-alkanoates: A comparative study. *Spectrochim. Acta, Part A* **2015**, 145, 440-453.

(35) Deacon, G. B.; Phillips, R. J., Relationships between the carbon-oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination. *Coord. Chem. Rev.* **1980**, 33, 227-250.

(36) Nakamoto, K.; Fujita, J.; Tanaka, S.; Kobayashi, M., Infrared Spectra of Metallic Complexes. IV. Comparison of the Infrared Spectra of Unidentate and Bidentate Metallic Complexes. *J. Am. Chem. Soc.* **1957**, 79, 4904-4908.

(37) Pereira, R. F. P.; Valente, A. J. M.; Fernandes, M.; Burrows, H. D., What drives the precipitation of long-chain calcium carboxylates (soaps) in aqueous solution? *Phys. Chem. Chem. Phys.* **2012**, 14, 7517-7527.

(38) White, N. A. S.; Ellis, H. A.; Nelson, P. N.; Maragh, P. T., Thermal and odd-even behaviour in a homologous series of lithium n-alkanoates. *J. Chem. Thermodyn.* **2011**, 43, 584-590.

(39) White, N. A. S.; Ellis, H. A., Room temperature structures and odd-even behaviour of a homologous series of anhydrous lithium n-alkanoates. *J. Mol. Struct.* **2008**, 888, 386-393.

22

(40) Bui, H. L.; de Klerk, A., Lithium C-1-C-12 n-Alkanoates: Thermal Behavior from-30 degrees C to 600 degrees C. J. Chem. Eng. Data 2013, 58, 1039-1049.

(41) Blanton, T. N.; Rajeswaran, M.; Stephens, P. W.; Whitcomb, D. R.; Misture, S. T.; Kaduk, J. A., Crystal structure determination of the silver carboxylate dimer Ag(O2C22H43) (2), silver behenate, using powder X-ray diffraction methods. *Powder Diffr.* **2011**, 26, 313-320.

(42) Marques, E. F.; Burrows, H. D.; Miguel, M. D., The structure and thermal behaviour of some long chain cerium(III) carboxylates. *J. Chem. Soc., Faraday Trans.* **1998**, 94, 1729-1736.

(43) Snyder, R. G., Vibrational spectra of crystalline n-paraffins : II. Intermolecular effects. J.Mol. Spectrosc. 1961, 7, 116-144.

(44) Nielsen, J. R.; Hathaway, C. E., Infrared spectra of normal paraffins in the hexagonal crystal form. *J. Mol. Spectrosc.* **1963**, 10, 366-377.

(45) Lynch, M. L.; Wireko, F.; Tarek, M.; Klein, M., Intermolecular interactions and the structure of fatty acid-soap crystals. *J. Phys. Chem. B* **2001**, 105, 552-561.

(46) Sheldrick, G. M., Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3-8.

(47) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., J. *Appl. Crystallogr.* OLEX2: a complete structure solution, refinement and analysis program. **2009**, 42, 339-341.



For Table of Contents Only