Solid-state polymerization of bis(but-3-enoato)zinc: the generation of a stereoregular oligomer

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Irradiation (^{60}Co γ-rays) of crystalline bis(but-3-enoato)-zinc, a two-dimensional coordination polymer with a bilayer packing motif, affords isotactic zinc poly(but-3-enoate).

Nearly four decades ago, Morawetz and Rubin demonstrated that ^{60}Co γ-irradiation of alkali metal acrylates and methacrylates produced high molecular weight, atactic polymer.[1] Irradiation of crystalline potassium acrylate **1** (2–8 kGy) led to high molecular weight polyacrylate (M_w = 100 000–400 000) with yields in the range 3–34%. Fankuchen reported that crystals of **1** were orthorhombic, space group $P2_12_12_1$, with a = 20.5, b = 4.15 and c = 5.73 Å.[2] Although structure–reactivity relationships have never been established for this interesting system, the short repeat distance of 4.15 Å requires that the crystal structure of **1** contains short contacts of *ca.* 4.15 Å, and the observed reactivity implies that the intermolecular orientation is appropriate for polymerization. In a recent study, we observed that upon ^{60}Co γ-irradiation, aquabis(but-3-enoato)-calcium **2** undergoes solid-state polymerization to high molecular weight polymer (M_w = 400 000) in high yield (97%).[3] The polybutenoates thus formed are again atactic, as also observed in a recent reinvestigation of polystyrenes formed by heating or irradiation of solid styryl monomers.[4] The crystal structure of **2** contains short –C=C–···–C=C– contacts (3.73–3.90 Å), usually considered as an important criterion for the onset of solid-state reactivity.[5] By contrast to the behavior of salts of vinylic monomers, irradiation or heating of *trans*-but-2-enoates affords a single dimer or trimer in cases where two, four or eight diastereomers are possible.[6–8] The relatively few examples of solid-state polymerization of metal salts of vinylic acids suggested to us that the ‘structure–reactivity database’ was too small to conclude that stereocontrol during polymerization was either unlikely or impossible for such materials. As part of our program in the discovery of new solid-state reactions, we undertook a study of the structure and reactivity of bis(but-3-enoato)zinc. Preliminary screening of several M^+ and M^{2+} systems with small radii, low coordination number and a high potential for bilayer formation[9] indicated that the zinc salt was both highly crystalline and sensitive to ^{60}Co γ-irradiation.

Anhydrous bis(but-3-enoato)zinc **3** was prepared readily by the slow addition of but-3-enoic acid to a stirred aqueous suspension of $ZnCO_3$. After stirring overnight, excess $ZnCO_3$ was removed by filtration; evaporation of the filtrate gave crystalline **3** in high yield (70–80%). Single crystals of **3** decomposed quickly at room temperature in an X-ray beam, suggesting that this was a highly reactive material. Exposure of **3** to large γ-ray doses resulted in a maximum conversion to polymer **4** of *ca.* 50%. NMR spectra of the crude material indicated the presence of monomer, polymer and a small amount of side product(s). Examples of dose/conversion data to polymer, based on extraction of monomer and side products: 61 kGy/2.9%; 102 kGy/9.8%; 316 kGy/21.9%; 592 kGy/47.8%. Further irradiation did not lead to significantly higher degrees of conversion (1570 kGy/48.9%). The NMR spectrum of the purified product, as the free acid in D_2O–DC1, showed the probable formation of a poly(but-3-enoate): δ_H 1.9–2.2 (2H, br d, CH_2CO_2H), 1.6–1.7 (1H, br), 1.3–1.5 (1H, br), 0.9–1.2 (1H, br); δ_C 180 (C), 29.0–40.5 (CH_2, CH). The stereochemistry of **4** was assigned as isotactic by analogy to the ^{1}H NMR spectrum of polypropylene and the expected shift due to a carboxy group. The backbone methylene protons are non-equivalent in isotactic polypropylene; thus three absorptions are seen for the backbone methylene and methine protons with an integration of 1:1:1 as in **4**.[10] The backbone methylene protons are equivalent in syndiotactic polypropylene, so that there are only two absorptions for the backbone protons with an integration of 1:2. A more complex pattern is observed in atactic polypropylene. The molecular weight of **4**, $\bar{M}_w$ = 2128, $\bar{M}_n$ = 1801, D = 1.2, determined by GPC, is consistent with the formation of a low molecular weight oligomer, containing 8–10 monomer units.

Solid-state polymerization of alkali and alkaline earth acrylates and methacrylates (^{60}Co γ-rays),[1] as well as crystalline styryl monomers (^{60}Co γ-rays or heating)[4] leads to *atactic* polymer. Despite the observed lack of stereocontrol, it now seems apparent that topochemical effects are responsible for at least the *onset* of reactivity in a number of cases;[4,8] later, other factors (*e.g.* crystal degradation) intervene such that the product obtained is atactic. However, elegant studies of methacrylate solid-state polymerization have demonstrated that stereocontrol is indeed operative in the *early* stages of solid-state polymerization.[11,12] The dearth of structural information available for reactive, solid materials containing terminal vinyl groups limits our understanding of the structural factors responsible for solid-state reactivity. With this in mind, but also perhaps in order to provide insight into the isotactic nature of the product as well as the maximum *ca.* 50% conversion, we carried out an X-ray structure determination of **3**. The structure determination was carried out at 173 K on a Nonius Kappa-CCD diffractometer in order to prevent the X-ray induced decomposition observed at room temperature on a conventional diffractometer; no decomposition was observed at 173 K on the CCD instrument.

The crystal structure of **3** consists of tetrahedral zinc ions, bridged infinitely by two symmetry-independent but-3-enoate moieties.† The result, shown in Fig. 1, is a two-dimensional coordination polymer, roughly parallel to crystal *bc* planes. As

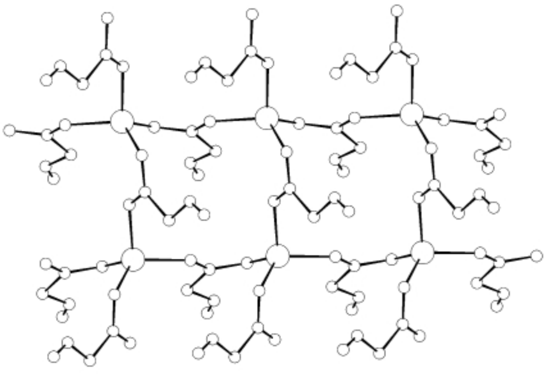

Fig. 1 View of the two-dimensional coordination polymer in **3** showing zinc ions bridged in a *syn, anti*-fashion by the but-3-enoate ligands.

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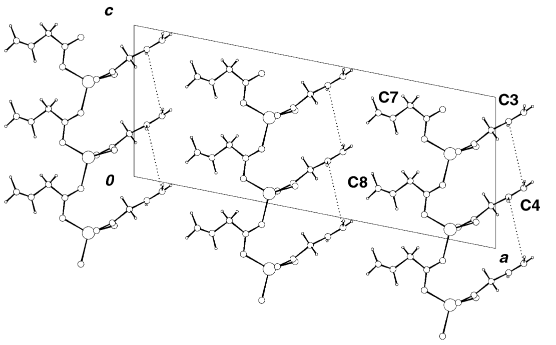

Fig. 2 View of the unit cell of **3**, showing C(3)···C(4) contacts of 4.21 Å (dotted lines), and identification of the 'unreactive' vinyl group [C(7), C(8)], separated by 4.42 Å (no connection shown).

shown in Fig. 2, the two-dimensional coordination polymers pack in a bilayer motif. Bilayer packing arrangements occur with $>90\%$ frequency for metal carboxylate coordination polymers where the acids have $\geqslant 4$ carbon atoms.[9] As we have described previously, the two-dimensional coordination polymer, generated by metal carboxylate interactions, including carboxylate bridging, serves as a bifunctional template.[13] The first function of such a template is to generate a bilayer structure: the organic tails of the carboxylate groups will be oriented in a roughly perpendicular direction to the bilayer. Secondly, depending on the nature of the bridging, the tails may be forced into very short contact. In the crystal structure of compound **3** (Fig. 2), one set of but-3-enoates is nearly parallel (interplanar angle 9.1°), with a C(3)–C(4) $(x, -2-y, z-\frac{1}{2})$ distance of 4.21 Å. The other set of but-3-enoates are separated, within the bilayer, by a minimum distance C(7)–C(8) $(x, -2-y, z-\frac{1}{2})$ of 4.42 Å and an interplanar angle of 119.0°. There are pairs of 'dimeric' contacts *across* the bilayer [C(3)–C(8) $(\frac{1}{2}+x, \frac{1}{2}+y, z)$, 4.01 Å, not shown in Fig. 2]. While such contacts might lead to a dimeric product and may account for observed traces of side product, the resultant reaction pathway cannot account for polymer formation. Thus the 'head-to-head', nearly parallel arrangement shown in Fig. 2 leads to isotactic polymer, in a genuine topochemical fashion.[5] Further, since the C(7)=C(8) double bonds are separated by an amount significantly greater than 4.2 Å,[5] no reactivity is observed (or expected) for this set of but-3-enoates, and the maximum yield possible will be 50%. Topochemical factors thus control both the product stereochemistry and the extent of reaction.

In summary, we have discovered a new solid-state reaction that leads to isotactic oligomer. Such an event is unprecedented for reactive solid materials containing terminal vinyl groups. The present case, as well as the trimerization of sodium *trans*-but-2-enoate[7] to yield sodium (2*R**,3*R**,4*S**,5*R**)-2,4-dimethylhept-6-ene-1,3,5-tricarboxylate **5** represent the only two examples of high-yield, solid-state oligomerization reactions of compounds containing RCH=CH– groups that lead to stereoregular products. The formation of both **4** and **5** lend strong support to the ideas advanced some time ago by the groups of Morawetz and Lando, that the early stages of solid-state polymerization often show strong evidence of stereoregularity, and thus likely occur under topochemical control.[11,12] Further, the stereoregularity observed for **4** and **5** may represent a 'snapshot' of the early stages of a broader class of solid-state polymerization reactions. The synthesis, structure determination and solid-state polymerization of related new materials will help to uncover additional examples that clarify this issue. Such experiments, as well as conventional and 'tail' UV-irradiation[14] of **3**, are underway in our laboratories.

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Notes and references

† *Crystal data* for **3**: $C_8H_{10}O_4Zn$, $M = 235.54$, monoclinic, space group *Cc* (no. 9), colorless plates, $a = 22.6251(18)$, $b = 4.8003(4)$, $c = 9.2901(11)$ Å; $\beta = 101.2915(50)°$; $Z = 2$; $U = 989.44$ Å^3; $D_m = 1.58(3)$, $D_c = 1.581$ g cm^{-3}; $T = 173$ K. Data were collected on a Nonius Kappa-CCD diffractometer [λ(Mo-Kα) = 0.710 73 Å]; no absorption corrections were made. Full matrix least squares refinement (based on $|F|$) of positional and anisotropic displacement parameters for all nonhydrogen atoms, and isotropic displacement parameters for H atoms (fixed at geometric positions; total parameters = 119) led to $R = 0.0371$ and $R_w = 0.0400$, using 997 data for which $I > 1.96\sigma(I)$; maximum residual ρ 0.47 e Å^{-3}]. Programs used: SIR92,[15] CRYSTALS,[16] CAMERON.[16] Bond lengths and angles lie in normal ranges (C(3)–C(4) and C(7)–C(8) bond lengths are affected by disorder of atoms C(4) and C(8)).

CCDC 182/1805. See http://www.rsc.org/suppdata/cc/b0/b007334m/ for crystallographic files in .cif format.

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