Solid-State Reactions

Polymerization by Insertion of Molecular Oxygen into Crystals of 7,7,8,8-Tetrakis(ethoxycarbonyl)quinodimethane

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Polymerizations in crystals lead to polymers with highly controlled structures because of the structural restraints of the crystal lattice, and thus, they are promising methods for controlling polymer structures. However, it is still difficult to predict and control the polymerization properties of compounds in the crystal, because the arrangements of the monomers play a significant role. In particular, the monomers that undergo topochemical polymerizations, such as derivatives of 2,5-distyrylpyrazines[1] and diacetylenes,[2] triacetylenes,[3] dienes,[4] and quinodimethanes,[5] are known to have strict requirements for the monomer arrangements in the crystal. Therefore, the investigation of the crystal structures of monomers related to those that undergo solid-state polymerizations should enable us to control the reactivities of the monomers and provide us with models for the reaction pathway of the polymerization reactions.

Molecular oxygen is a well-known oxidizing agent in organic chemistry,[6] and in polymer chemistry it acts as an inhibitor and a retarder of radical polymerizations. Sometimes it can be incorporated as a comonomer to afford copolymers.[7] Until now, solution polymerizations of vinyl monomers[8] such as styrene, methyl methacrylate, vinylnaphthalene, α-methylstyrene, and unsubstituted quinodimethane[9] with oxygen afforded random copolymers. More recently, it was reported that solid-state polymerizations of dibenzofulvene[10] and alkyl sorbate[11] under air and oxygen produce a random copolymer and an alternating copolymer, respectively. However, this work did not report crystal

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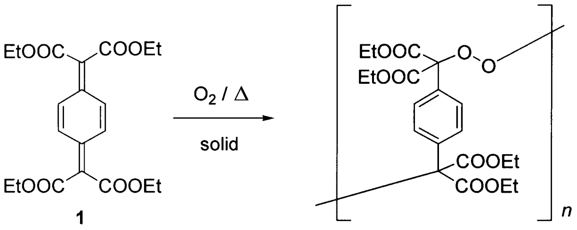
structures of the monomers suitable for copolymerization with molecular oxygen. In this communication we describe how 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (**1**) copolymerizes with molecular oxygen in the solid state to give a highly crystalline alternating copolymer [Eq. (1)]. An X-ray crystallographic study shows that the unique arrangement of **1** in the crystal is conducive to copolymerization with molecular oxygen.



(1)

Monomer **1** was prepared according to the method reported previously.[5] Knoevenagel condensation of 1,4-cyclohexanedione with diethyl malonate using titanium tetrachloride and pyridine as a dehydrating system[12] afforded 1,4-[bis(ethoxycarbonyl)methylene]cyclohexane (**2**) (43% yield). Oxidation of **2** with activated manganese dioxide in benzene heated at reflux gave **1** (34% yield), which was recrystallized from hexane to afford yellow needles. Crystals of **1** were polymerized under air or in vacuo by irradiation with a high-pressure Hg lamp at room temperature, or by heating in the dark. When crystals of **1** were exposed to UV light at 34 °C in air for 25 h, or heated at 60 °C in air for 24 h, polymers formed as white needlelike solids in 16% and quantitative yields, respectively (entries 1 and 4 in Table 1). In contrast, **1** did not polymerize in vacuo with irradiation or heating, or under air but in the dark and not heated, and **1** was recovered quantitatively (entries 2, 3, and 5 in Table 1). Therefore, polymer formation upon irradiation with UV light is due to photoinitiation, not to thermal initiation. These results strongly suggest the participation of oxygen in the polymerizations. To clarify role of oxygen, thermal polymerizations of **1** in the solid state at 60 °C were performed in the presence of oxygen and in the presence of nitrogen (entries 6 and 7 in Table 1). Monomer **1** polymerized only in the presence of oxygen to give a polymer in quantitative yield as a white needlelike solid. This indicates that oxygen truly participates in both thermal polymerizations and photopolymerizations in the solid state.

Table 1: Thermal polymerizations and photopolymerizations of **1** in the solid state, and thermal polymerization of **1** in benzene.

Entry	Amount of **1** [mg]	Light source	Atm.	*T* [°C]	*t* [h]	Conv. [%]	$M_n \times 10^3$[b]
1	20.4	Hg lamp	air	34	25	16	1.5
2	21.0	Hg lamp	vacuo	34	25	0	
3	11.1	dark	air	35	24	0	
4	10.5	dark	air	60	24	100	18
5	10.1	dark	vacuo	60	24	0	
6	10.9	dark	N_2	60	15	0	
7	11.4	dark	O_2	60	15	100	18
8[a]	370	dark	vacuo	60	50	72	2.5

[a] Solution-phase polymerization in benzene (1 mL) initiated by AIBN (5.1 mg). [b] Determined by GPC measurement with THF as the eluent and standard polystyrene as the reference.

The white needlelike solids obtained by the thermal polymerization of **1** in the solid state at 60 °C (entry 4 in Table 1) were characterized by ^{1}H and ^{13}C NMR and IR spectroscopy, GPC, elemental analysis, and powder X-ray diffraction. The data were also compared with those of the polymer obtained from the solution polymerization initiated by α,α′-azobisisobutyronitrile (AIBN; entry 8 in Table 1). Number-average molecular weights (M_n) of the products obtained by the solid-state polymerization and by the solution polymerization were 18000 and 2500, respectively. The solid-state polymerization produced higher-molecular-weight polymer than the solution polymerization. A characteristic absorption band at 1540 cm^{-1} assigned to the exocyclic conjugated C=C bond of **1** was absent in the IR spectra of both polymers, signals arising from the C=C bond of the ring were observed at 1486, 1445, and 1369 cm^{-1}, and a signal arising from the out-of-plane deformation of the *para*-disubstituted benzene was observed at 852 cm^{-1}. The changes in the IR spectrum observed in the solid-state polymerization of **1** lend support to the proposition that this reaction follows the conventional mode observed for substituted quinodimethane molecules: the polymerization takes place at the disubstituted exomethylene carbon atoms with formation of the corresponding stable aromatic structure.[13]

The ^{1}H NMR peak at $\delta = 7.53$ ppm assigned to the phenylene protons of the polymer obtained by the thermal solid-state polymerization was observed at a lower field than the corresponding one ($\delta = 6.70$ ppm) of the polymer obtained by the solution polymerization. In the ^{13}C NMR spectrum the peak at $\delta = 89.4$ ppm assigned to the quaternary carbon atom in the solid-state polymerization polymer was observed 19 ppm further downfield than the corresponding signal ($\delta = 70.0$ ppm) in the solution-phase polymerization polymer (Figure 1).

These deshieldings observed in the NMR spectra indicate the presence of electron-withdrawing groups such as oxygen atoms next to the units of **1** in the polymer. The elemental analysis of the polymer obtained from the solid-state polymerization (H 5.62, C 56.42) is not in good agreement with the found data for the homopolymer of **1** obtained from the solution polymerization (H 6.10, C 60.89), but is in good agreement with the figures calculated for the alternating copolymer of **1** with oxygen (H 5.70, C 56.60).

The thermogravimetric analysis (TGA) measurements showed that the solution-phase polymerization polymer begins to decompose at 217 °C, but the solid-state polymerization polymer shows a two-stage decomposition and begins to decompose already at 111 °C. The weight loss from 111 to 150 °C amounts to 17%, which corresponds approximately to the loss of an ethoxycarbonyl group from each unit of **1**. Upon heating the polymer obtained in the solid-state polymerization at 150 °C for 15 min, 1,4-bis(ethoxalyl)benzene (18% yield) was isolated. These results indicate that the polymer has thermally degradable bonds, which are reasonably assumed to be peroxide groups. It is concluded from the

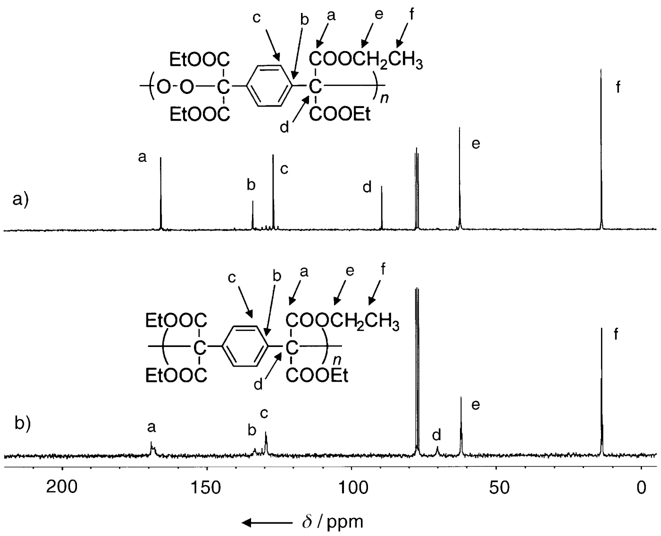


Figure 1. ^{13}C NMR spectra (in $CDCl_3$) of the polymers of **1** obtained from a) the solid-state polymerization under air and b) the solution-phase polymerization.

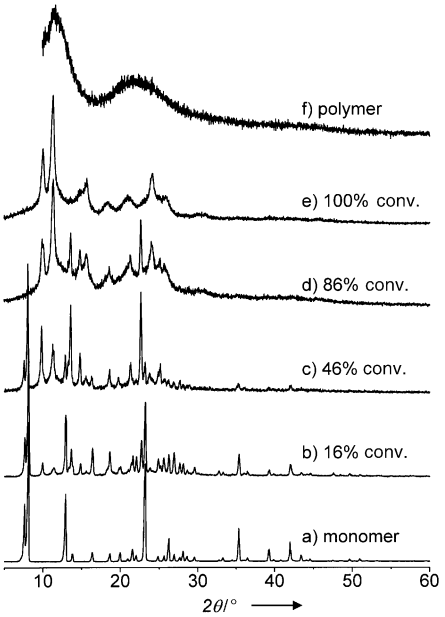


Figure 2. Powder X-ray diffraction patterns for a) monomer **1**, aliquots from the solid-state polymerization at b) 16% conversion, c) 46% conversion, d) 86% conversion, and e) 100% conversion, and f) reprecipitated polymer.

analysis results that the polymer produced in the solid-state polymerization under air and oxygen is a completely alternating copolymer of **1** with oxygen molecules. This is the first example for the alternating copolymerization of quinodimethanes with molecular oxygen in the solid state.

Thermal polymerization of **1** in the solid state under air was investigated by ESR spectroscopy. When crystals of **1** were heated in air at 62 °C, the ESR spectrum showed a broad triplet at a g-value of 2.0030 with a coupling constant of 5.0 G due to the two equivalent *ortho* hydrogens (H^a) of the phenylene group, which strongly supports the bis(ethoxycarbonyl)benzyl structure of the propagating radical. Thus, this indicates that polymerization reaction takes place at the disubstituted exomethylene carbon atoms and proceeds through a radical mechanism, and that the propagating species is a bis(ethoxycarbonyl)benzyl radical. The radical concentration in the polymerization reaction, 6.9×10^{-5} mol kg^{-1} in 1 h, was evaluated by using 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy as a standard, and was kept as high as 2.3×10^{-5} mol kg^{-1} in 24 h after even 100% conversion. This indicates that a long-lived radical is formed in this solid-state polymerization because of immobility of the polymer chain produced.

The powder X-ray diffraction (XRD) patterns of monomer **1**, reaction mixtures at conversions of 16%, 46%, and 86%, the polymer of **1** obtained at complete conversion by thermal polymerization in the solid state under air, and the polymer of **1** reprecipitated from chloroform–hexane are shown in Figure 2. The relatively sharp diffraction patterns of the reaction mixtures at conversions of 46% and 86%, and even at 100% conversion indicate that the monomer **1** maintains crystallinity during and after completion of the polymerization. However, there are no significant peaks in the powder XRD patterns of the reprecipitated polymer, which implies that it is amorphous (Figure 2 f). This indicates that the thermal polymerization of **1** in the solid state proceeds under the influence of the crystal lattice to form an alternating copolymer with a highly ordered structure.

To clarify the steric requirement of the polymerization, we investigated the crystal structure of **1** by X-ray crystallography.[15] In the crystal structure of **1**, the molecules form a one-dimension column by the stacking of the quinodimethane rings along the crystallographic c axis (Figure 3). The stacking axes are nearly perpendicular to the plane of the quinodimethane ring, and the stacked molecules are rotated successively by 60°. The face-to-face distance between units of **1** in

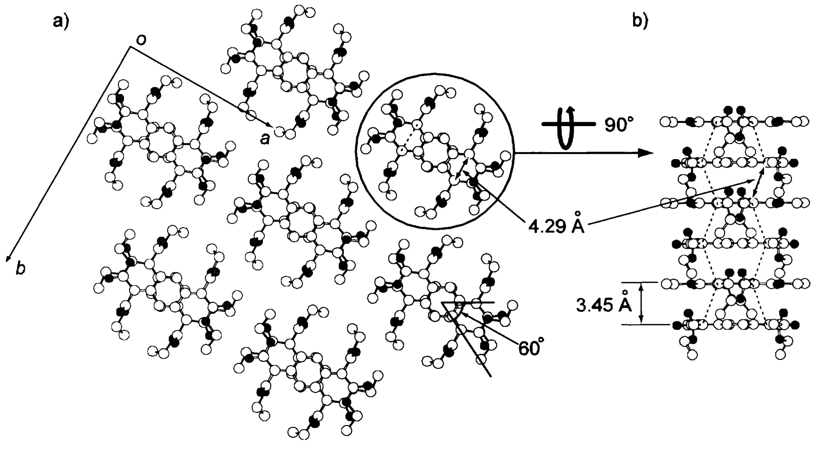


Figure 3. Crystal structure of **1** a) viewed down the crystallographic c axis and b) viewed down the crystallographic b axis. Hydrogen atoms are omitted for clarity. Open and filled circles represent carbon and oxygen atoms, respectively.

the stacked column is 3.45 Å, which corresponds to the π–π stacking distance of the aromatic rings.[14] The distance between the reacting exomethylene carbon atoms in the column is 4.29 Å. This packing of molecules of **1** in the crystal is quite different from that found for the methyl analogue, which undergoes topochemical polymerization.[5] Therefore, monomer **1** does not undergo homopolymerization in the solid state by thermal and photoinitiation due to the different packing mode in the crystals.

Instead, **1** copolymerizes with molecular oxygen. Molecular oxygen normally exists as a triplet (i.e. a diradical) in its ground state with a bond length of 1.21 Å, which is much shorter than the distance between the reacting exomethylene carbon atoms (4.29 Å) and also the face-to-face distance between the quinodimethane rings (3.45 Å). A dioxygen unit may act as a hinge to bind neighboring quinodimethane molecules at their exomethylene carbon atoms. These distances are just suitable for the insertion of oxygen into the polymer chains to yield copolymers. The reaction mechanism (polyaddition or chain reaction) is not clear at present and more experimental data are needed.

In conclusion, we described the first example of the solid-state alternating copolymerization of **1** with oxygen molecules, which leads to highly crystalline needlelike white solids by means of a radical mechanism. No thermal or photo solid-state polymerizations of **1** in vacuo were observed, which was explained by the lack of structural prerequisites for topochemical polymerization. In crystals of **1** the crystal packing is suitable for insertion of oxygen diradicals between the bis(ethoxycarbonyl)benzyl radicals. Detailed studies on the application of this peroxide polymer, the reaction mechanism of the polymerization, and the crystal structures and polymerization reactivities of other substituted quinodimethanes are now in progress.

Experimental Section

2: Compound **2** was synthesized from 1,4-cyclohexanedione and diethyl malonate by the same procedure reported previously[5]: white needles by recrystallization from hexane (43 % yield); m.p. 59–60 °C; IR (KBr): $\nu = 2940$ (CH), 1688 (C=O), 1610 (C=C), 1232 and 1050 cm^{-1} (C–O); UV/Vis (CH_3CN): 215 ($\varepsilon = 1.75 \times 10^4$) nm; ^{1}H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 4.26$ (q, $J = 7.26$ Hz, 8H, CH_2), 2.76 (s, 8H, CH_2), 1.29 ppm (t, $J = 7.26$ Hz, 12H, CH_3); ^{13}C NMR (67.7 MHz, $CDCl_3$, TMS): $\delta = 165.2$ (C=O), 157.7 (>C<), 123.5 (>C<), 61.1 (CH_2), 29.4 (CH_2), 14.1 ppm (CH_3); elemental analysis calcd for $C_{20}H_{28}O_8$: H 7.12, C 60.59, O 32.29; found: H 7.03, C 59.85, O 33.12.

1: A solution of compound **2** (678 mg, 1.71 mmol) in benzene (50 mL) was added in one portion to activated manganese dioxide (5.42 g) and molecular sieves 4 Å (2.84 g) in benzene (350 mL) at reflux. After the reaction mixture had been stirred for 15 min at reflux, the activated manganese dioxide and molecular sieves were removed by filtration and the solvent was removed by evaporation under reduced pressure. The crude yellow solids were purified by column chromatography (SiO_2, chloroform) followed by recrystallization from hexane to give **1** as yellow needles (225 mg, 34 %): m.p. 72–73 °C; IR (KBr): $\nu = 2938$ (CH), 1690 (C=O), 1639 (C=C), 1542 (C=C), 1209, and 1044 cm^{-1} (C–O); UV/Vis (CH_3CN): 360 ($\varepsilon = 5.75 \times 10^4$) nm; ^{1}H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 7.45$ (s, 4H, CH), 4.32 (q, $J = 7.26$ Hz, 8H, CH_2), 1.33 ppm (t, $J = 7.26$ Hz, 12H, CH_3); ^{13}C NMR (67.7 MHz, $CDCl_3$, TMS): $\delta = 164.7$ (C=O), 138.8 (>C<), 130.0 (CH), 126.1 (>C<), 61.7 (CH_2), 14.0 ppm (CH_3); elemental analysis calcd for $C_{20}H_{24}O_8$: H 6.16, C 61.22, O 32.62; found: H 6.15, C 60.77, O 33.08.

Polymerization: A given amount of **1** (see Table 1) was put in a Pyrex ampoule, which was sealed either without degassing (in air) or with degassing under reduced pressure (in vacuo). Thermal polymerizations were carried out by setting the ampoule in an oil bath at 35 or 60 °C for a given time. The conversion was determined by removing an aliquot from the reaction system after a certain reaction time, dissolving it in $CDCl_3$, and recording the ^{1}H NMR spectrum. The conversion was calculated from the ratio of the peak area at $\delta = 7.45$ ppm due to quinonoid structure of **1** to that at $\delta = 7.53$ ppm due to the phenylene group of polymer. Photopolymerizations were carried out at 34 °C under UV irradiation by using a high-pressure mercury lamp (Fuji Glass Work Type HB-400, 400 W) at a distance of 12 cm. Conversion was determined by the same procedure as that described above.

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[15] Crystal structure data for **1** (single crystal from isopropyl ether): $C_{10}H_{12}O_4$, $M_r = 196.20$, crystal dimensions $0.15 \times 0.30 \times 0.10$ mm, orthorhombic, space group *Iba*2 (no. 45), $a = 13.483(2)$, $b = 21.392(3)$, $c = 6.8956(9)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1988.9(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.310\ g\,cm^{-3}$, $2\theta_{max} = 136.3°$, Rigaku RAXIS-RAPID Imaging Plate diffractometer ($Cu_{K\alpha}$, $\lambda = 1.54178$ Å, graphite monochromator), ω scans, $T = 296$ K, 860 measured reflections, all 832 independent reflections used in the refinement, Lorenz and polarization factors were applied, $\mu = 8.56\ cm^{-1}$. Structure solution and refinement: direct methods (SIR92), full-matrix least-squares refinement of F^2, 127 parameters, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located in ideal positions without further refinement, $R_1 = 0.072$, $R = 0.291$, $Rw = 0.156$, GOF = 1.56, $\Delta\rho_{max} = 0.45$ e Å^{-3}, $\Delta\rho_{min} = -0.61$ e Å^{-3}. CCDC-214888 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).