

# Synchronized Propagation Mechanism for Crystalline-State Polymerization of *p*-Xylylenediammonium Disorbate

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**Abstract:** We describe the results of the topochemical polymerization of *p*-xylylenediammonium disorbate as the bifunctional monomer in the crystalline state via a radical chain polymerization mechanism. The structure and properties of the resulting double-stranded polymer are investigated by X-ray crystal structure and thermal analyses as well as IR spectroscopy. The stereochemical structure of the polymer is confirmed by NMR spectroscopy after the solid-state transformation of the polymer side chain to give the single-stranded chains that are soluble in methanol. We propose a model for the reaction mechanism to provide a ladder polymer in the crystalline state on the basis of the results of single-crystal structure analysis and the observation of the  $\alpha$ -methyl and  $\alpha$ -carboxylate propagating radicals by ESR spectroscopy. The two reaction parts of the monomer are synchronized to simultaneously react with the conformational change in a sorbate moiety that is transformed into another sorbate through the diammonium part as the linker.

## Introduction

The synthesis of polymers with a well-controlled structure has intrigued polymer chemists, because the properties of polymers significantly depend on the primary chain structures, such as the repeating unit, molecular weight, molecular weight distribution,  $\alpha$ - and  $\omega$ -chain ends, branching, tacticity, and copolymer sequence. The control of the supramolecular architecture for the design of new organic polymer materials and three-dimensional polymer nanocomposites is a challenging topic of research.<sup>1</sup> Topochemical polymerization is the most promising method for controlling the stereo- and regiochemistries of polymer chains as well as the supramolecular ordering of polymer chains in the solid state.<sup>2</sup> We have recently demonstrated that the topochemical polymerization of 1,3-diene monomers is valid for the control of the polymer chain and crystal structures.<sup>3,4</sup> The diene mono- and dicarboxylic acid

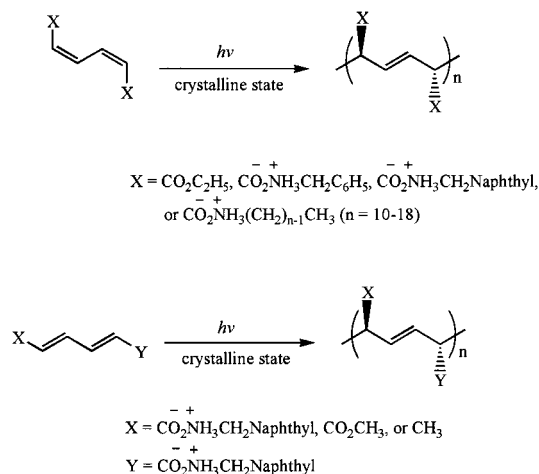
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## Scheme 1

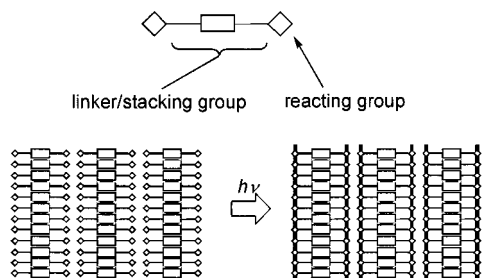


derivatives shown in Scheme 1 polymerize during photoirradiation in the crystalline state to yield a stereoregular polymer in the form of polymer crystals. Topochemical polymerization

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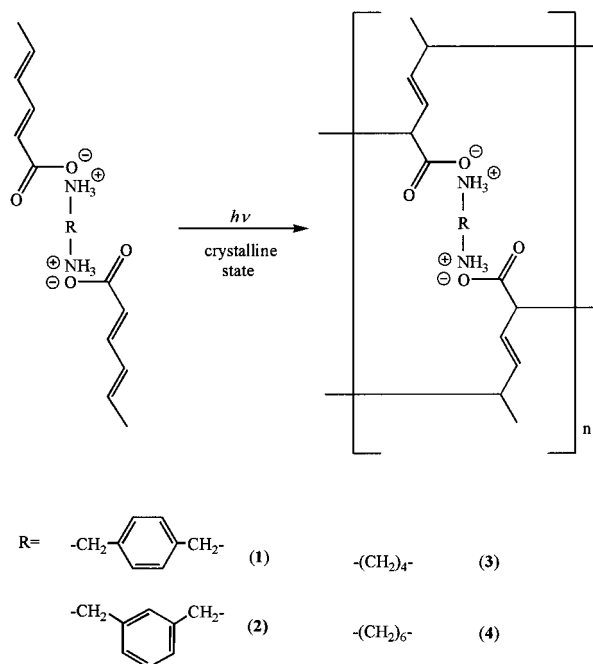


**Figure 1.** Molecular and stacking model of a bifunctional monomer for synthesis of a ladder polymer by topochemical polymerization.

would possess further potential to provide polymers with a more sophisticated structure. For example, a bifunctional monomer, of which two reacting groups are linked to a stacking group, may provide a ladder polymer by appropriate arrangement of the monomer molecules in the crystals (Figure 1). The controlled polymer synthesis from multifunctional monomers has been considered to be difficult through a chain reaction including radical polymerization because of cross-linking as a side reaction. In contrast, the topochemical polymerization of bifunctional monomers is expected to give a ladder polymer without any cross-linking reaction.

In general, there are several strategies for the synthesis of ladder polymers.<sup>5,6</sup> Condensation polymerization includes a growing step of the double-stranded chain; for example, two tetrafunctional monomers are made to react with each other. Another approach is the synthesis of single-stranded polymers carrying required functionalities along the polymer chain, followed by the formation of the second strand. Both strategies have serious problems for controlled synthesis because of the incomplete chain growing reaction and undesired side reactions. Alternatively, Diels–Alder polyaddition is used as a new synthetic strategy for ladder polymers with well-defined structures using bifunctional components with both diene and dienophile functionalities.<sup>7</sup> Another problem with the ladder polymer synthesis is difficult polymer characterization because of poor solubility, as has been shown by the formation of ladder structures referred to during the solid-state polymerization of diacetylene derivatives.<sup>5,8</sup> In this study, we adopted alkylenediammonium disorbate monomers as the candidate of a bifunctional diene monomer for ladder polymer synthesis through topochemical polymerization (Scheme 2). The dicationic part of the polymers can be converted to other counterparts as monocations via a solid-state polymer transformation to determine the structure of the corresponding single-stranded chains in solution.

**Scheme 2**



**Table 1.** Photopolymerization of Alkylenediammonium Disorbates for 4 h

monomer	temp (°C)	polymer yield (%)
<b>1</b>	40	20
	60	41
	80	85
	100	96
<b>2</b>	60	0
<b>3</b>	60	trace
	100	4
<b>4</b>	60	0

## Results and Discussion

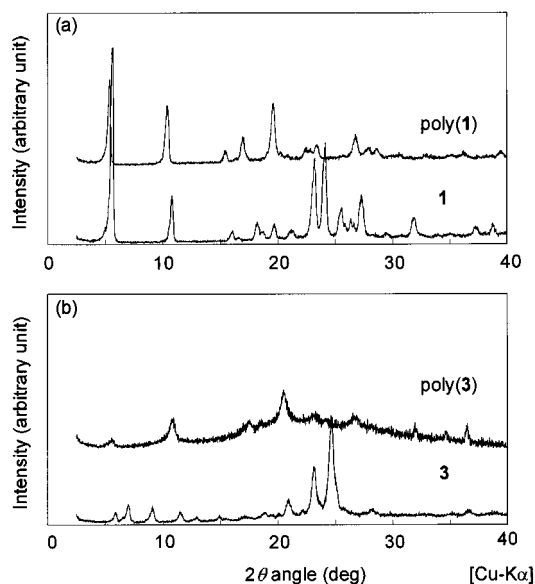
**Polymerization.** When the crystals of the bifunctional monomers were photoirradiated with a high-pressure mercury lamp under atmospheric conditions at 60 °C for 4 h, **1** and **3** gave insoluble polymers in 41% and trace yields, respectively. In contrast, **2** and **4** had no reactions (Table 1). The polymer yield of **1** increased with an increase in the reaction temperature and reached 96% yield at 100 °C, but **3** gave a polymer in only 4% yield even at a high temperature. Poly(**1**) was insoluble in all solvents, including the common organic solvent and fluorine-containing polar solvents such as trifluoroacetic acid. Therefore, the structure of the polymers was characterized in the solid state by IR spectroscopy and powder X-ray diffraction. The peak due to the stretching of the out-of-plane deformation vibration of a CH bond on *trans*-CH=CH was observed at 832 cm<sup>-1</sup> after polymerization. A shift in of the carbonyl stretching peak from 1512 cm<sup>-1</sup> of the monomer to 1542 cm<sup>-1</sup> of the polymer was also observed. These results suggest that the resulting polymer consists of the 2,5-*trans* repeating structure. Figure 2 shows the powder X-ray diffraction profiles of the monomers and the resulting polymers. The diffraction pattern of poly(**1**) consisting of sharp reflections indicates that the crystalline state is maintained during the polymerization of **1**. The interplanar distances were calculated to be 16.9 and 17.2 Å for **1** and poly(**1**), respectively, from reflecting in the low-angle region. These values are due to the thickness of the lamella structure consisting of the sorbate anion layers and the xylylenediammonium layers, as judged from the layered crystal structures of the

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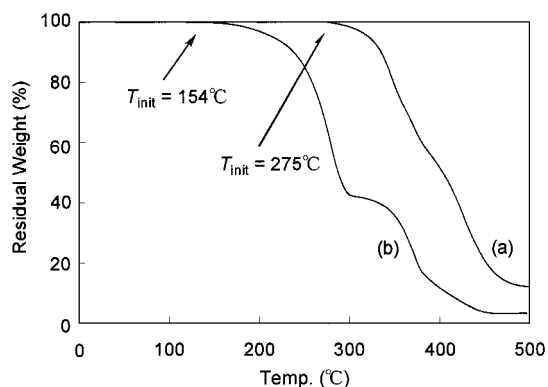
**Figure 2.** Powder X-ray diffraction profiles of (a) **1** and poly(**1**) and (b) **3** and poly(**3**).

1-naphthylmethylammonium sorbate (**5**) and related compounds.<sup>4e</sup> The crystal structure remains when the polymerization of **1** proceeds in the crystalline state. In contrast, the broad diffraction pattern of poly(**3**) suggests the collapse of the crystal structure of **3** during the photoirradiation, resulting in a low polymer yield.

#### Stereochemical Structure and Properties of the Polymer.

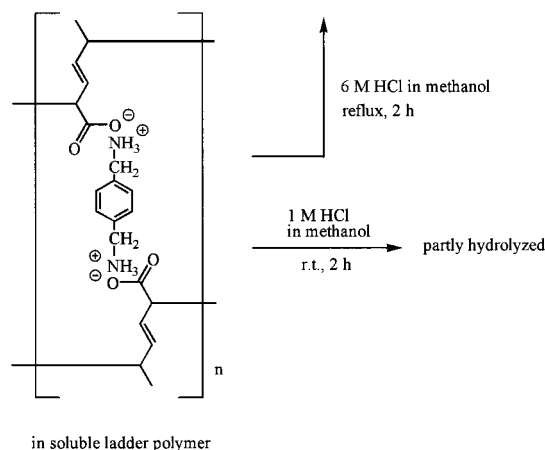
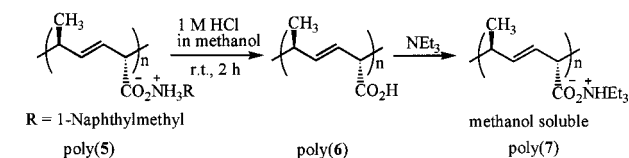
The side chain of poly(**1**) can be converted to any other counterpart by a polymer reaction in the solid state. We have already reported that the alkylammonium polymers of the muconic or sorbic acid derivatives obtained by topochemical polymerization are transformed into the corresponding acid polymers in the solid state.<sup>4e,f</sup> The polyacids are again converted to other ammonium salt polymers. Poly(**5**) was quantitatively hydrolyzed under mild conditions, that is, 1 M HCl in aqueous methanol at room temperature, but poly(**1**) was partly hydrolyzed under the identical conditions. With 6 M HCl under reflux in methanol, the protonation completely proceeded to give poly(sorbic acid), poly(**6**), as shown in Scheme 3. The acid resistance of poly(**1**) is possibly due to the robust structure of the double-stranded polymer crystals, compared to that of single-stranded poly(**5**). Poly(**6**) derived from poly(**1**) was further converted to poly(triethylammonium sorbate) (poly(**7**)), which is soluble in methanol and water. The <sup>13</sup>C NMR spectrum of poly(**7**) derived from poly(**1**) indicates the highly controlled stereochemical structure of the polymer, as it is identical to the spectrum of that derived from the previously described poly(**5**)<sup>4e</sup> (see Supporting Information). The repeating structure in the polymer chain was confirmed to be the *erythro*-diisotactic-2,5-*trans* structure.

The robust structure of the polymer influenced not only the hydrolysis but also the thermal decomposition behavior. Poly(**1**) and poly(**5**) started to decompose at 275 °C and 154 °C, respectively, as shown in the thermogravimetric (TG) curves (Figure 3). The decomposition of poly(**5**) proceeded in two steps, and the weight loss at 300 °C was 57%, suggesting side chain decomposition of poly(**5**) accompanied by liberation of the amine in the first step to give poly(**6**). In contrast, in the TG curve of poly(**1**), no clear two-step decomposition was observed. Thus, the TG analysis revealed the better thermal stability of poly(**1**) as compared to poly(**5**), similar to the resistance to acidolysis.



**Figure 3.** TG curves of (a) poly(**1**) and (b) poly(**5**). The heating rate was 10 °C/min in a nitrogen stream.

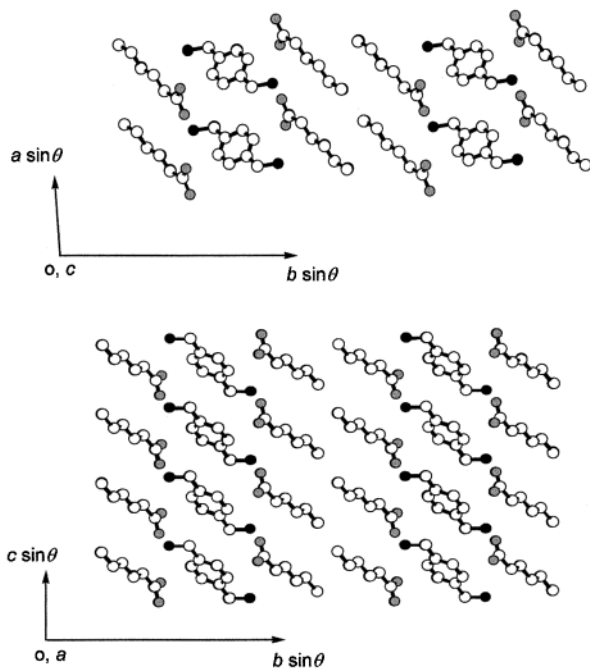
#### Scheme 3



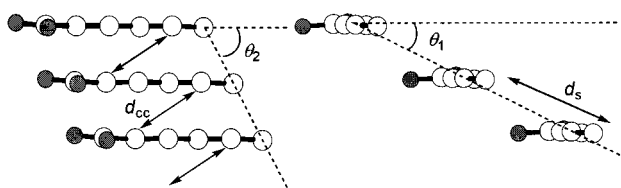
**Table 2.** Crystallographic Data for **1**

formula	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub> N <sub>1</sub>
formula weight	180.23
crystal system	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	5.6799
<i>b</i> , Å	16.997(2)
<i>c</i> , Å	4.9876(5)
$\alpha$ , deg	90.030(2)
$\beta$ , deg	96.110(3)
$\gamma$ , deg	93.385(3)
<i>V</i> , Å <sup>3</sup>	477.93
<i>Z</i>	2
<i>D<sub>c</sub></i>	1.252
unique reflns	2109
no. obsd reflns ( <i>I</i> > 2.00σ( <i>I</i> ))	1640
<i>R</i> , <i>R<sub>w</sub></i>	0.062, 0.104
GOF	1.73
2θ <sub>max</sub> , deg	55.0
<i>R/P</i>	11.71
temperature, °C	23

**Crystal Structure and Reaction Mechanism.** We have successfully determined the single-crystal structure of **1**. The structural parameters are summarized in Table 2. The views of the crystal from the crystallographic *c*- and *a*-axes are shown in Figure 4. In the crystal, the monomer molecules stack along



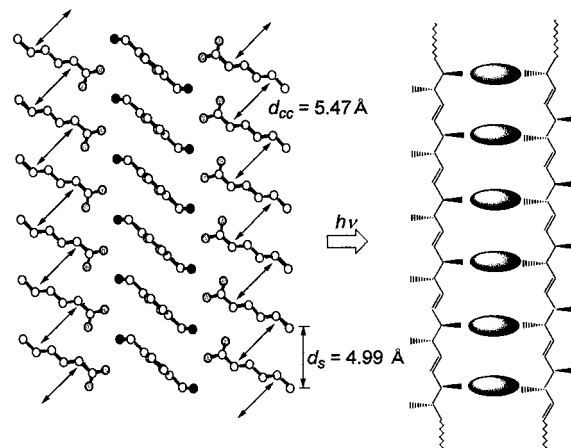
**Figure 4.** Crystal structure of **1** viewed from the crystallographic *c*- and *a*-axes. Hydrogen atoms are omitted for clarity.



**Figure 5.** Parameters of molecular stacking for evaluation of topochemical polymerization reactivity of sorbate derivatives in the crystalline state.  $d_{cc}$  is the intermolecular distance between the 2-carbon and 5'-carbon.  $d_s$  is the stacking distance.  $\theta_1$  and  $\theta_2$  are the angles between the stacking direction and the molecular plane in orthogonally different directions.

the *c*-axis to form a column structure appropriate for the polymerization with the aid of  $\pi$ - $\pi$  stacking and CH- $\pi$  interactions as well as the hydrogen bond network between the primary ammonium cations and the carboxylate anions, which act as triple hydrogen bond donors and acceptors, respectively.<sup>4d,e</sup> We can predict the polymerization behavior using the parameters related to the mutual angles and distances of the conjugate  $\pi$ -planes for these diene monomers (Figure 5). The intermolecular distance ( $d_{cc}$ ) between the 2-carbon and 5'-carbon is important for determining the reactivity during topochemical polymerization of the 1,3-diene compounds, but it is not enough to evaluate the reactivity. To precisely estimate the polymerization reactivity, we have to consider the stacking distance ( $d_s$ ) and two kinds of tilt angles of the stacking ( $\theta_1$  and  $\theta_2$ ), which are the angles between the stacking direction and the molecular plane in orthogonally different directions. The parameters determined for **1** and **5** are as follows:  $d_{cc} = 5.47$  Å,  $d_s = 4.99$  Å,  $\theta_1 = 25^\circ$ , and  $\theta_2 = 60^\circ$  for **1**, and  $d_{cc} = 5.37$  Å,  $d_s = 4.99$  Å,  $\theta_1 = 29^\circ$ , and  $\theta_2 = 61^\circ$  for **5**. All the parameters for both crystals have similar values to each other, indicating that both monomers have a similar stacking structure appropriate for topochemical polymerization.

We can also predict the stereochemical structure of the produced polymer chains on the basis of the monomer crystal structure, because topochemical polymerization proceeds with the minimum movement of atoms in the crystals. In Figure 6,



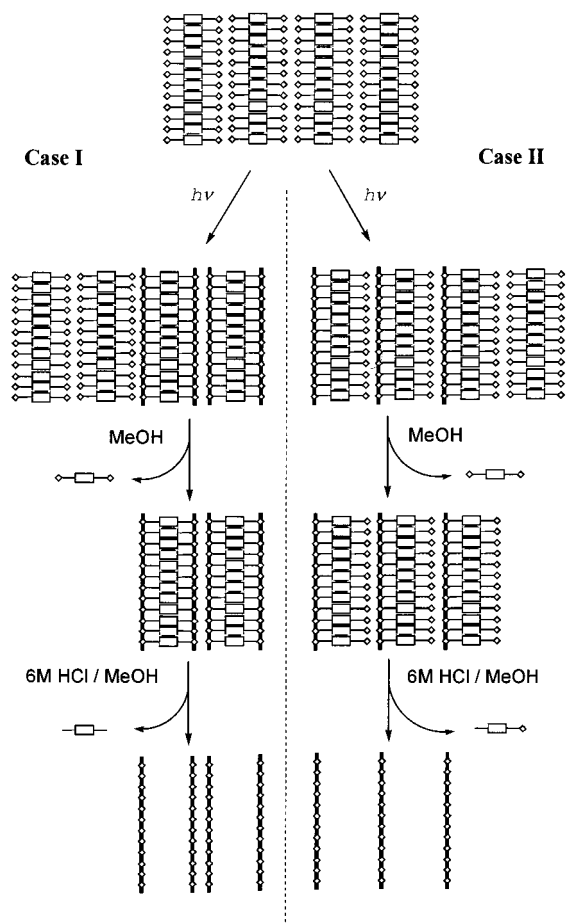
**Figure 6.** Stacking structure of **1** in the crystals and stereochemical structure of the polymer obtained from **1**.

the arrows represent the carbons, which make a new bond during topochemical polymerization. The predicted structure of the resulting stereoregular polymer is the *erythro*-diisotactic-*trans*-2,5-structure, which agrees with the result of the <sup>13</sup>C NMR spectroscopy. The diisotactic polymer has asymmetric carbon atoms with an identical sign along the single polymer chain, but the obtained polymer did not show any optical activity. It is due to the presence of both right- and left-handed chains, because the crystal of **1** has an inversion center.

There are two types of models for the solid-state polymerization of bifunctional monomers as the extreme case (Figure 7). In case I, both functional groups may simultaneously react to give a ladder polymer without any pendant group. On the other hand, either side part of the dienes exclusively reacts to give a polymer with unreactive groups as the pendant in case II. If a drastic conformation change of the monomer moiety in the crystals is accompanied by propagation, the conversion does not exceed 50%, and a polymer with a pendant group is produced. Polymer chains would be randomly formed, as the intermediate of cases I and II. When the polymer isolated as the methanol insoluble part is hydrolyzed, the parts of the linker in the polymer are removed. In case I, the residual weight of the isolated poly(**6**) after the hydrolysis would be 62% of the weight of the original poly(**1**). The pendant groups also contribute to the weight loss of the polymer in case II. The calculated value as the residual weight is 31%.

Table 3 shows the polymer yield for the photopolymerization and the residual weight after hydrolysis for different UV irradiation times. The values of the residual weight after hydrolysis are close to that expected for case I, independent of the irradiation time, that is, the polymer yield. The constant value of reduced viscosity ( $\eta_{sp}/c$ ), regardless of the polymer yield, means that a high molecular weight polymer is formed during an early stage of polymerization, because of fast propagation via a radical chain mechanism. If the polymer contains any pendant groups, a sorbic acid monomer would be contained in the soluble part. However, it is not detected in the <sup>1</sup>H NMR spectrum after hydrolysis with 6 M deuterium chloride in D<sub>2</sub>O and methanol-*d*<sub>4</sub> (see Supporting Information). This indicates that the polymer has no pendant group and that polymerization proceeds exactly via a reaction mechanism in case I.

Because sorbic acid is a 1,3-butadiene derivative having different substituents at the 1- and 4-positions,  $\alpha$ -methyl and  $\alpha$ -carboxylate radicals are possibly formed. If we assume that the propagation radical species is limited to the  $\alpha$ -carboxylate



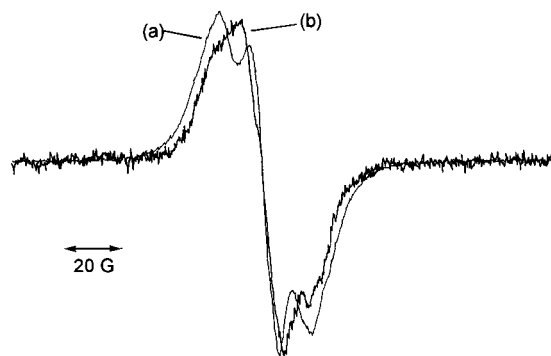
**Figure 7.** Model of polymerization of a bifunctional monomer as two extreme cases.

**Table 3.** Results of Photopolymerization of **1** at 60 °C in the Crystalline State

photoirradiation time (h)	polymer yield (%)	residual weight after hydrolysis (%)	$\eta_{sp}/c^a \times 10^{-2}$ (cm <sup>3</sup> /g)
2	17	53	
4	41	58	3.2
6	57	58	2.9
8	76	58	3.3

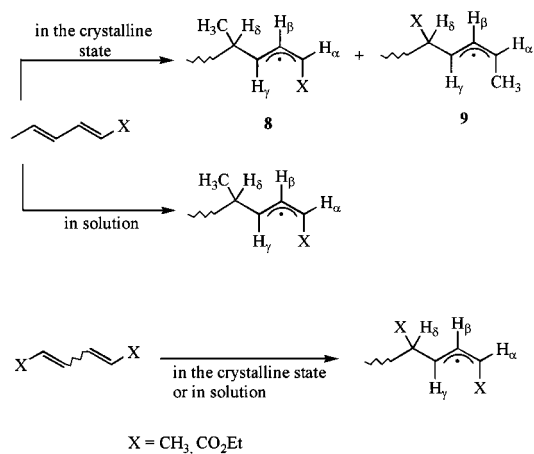
<sup>a</sup> Reduced viscosity of the polymer after hydrolysis and transformation into poly(triethylammonium sorbate).  $c = 1 \times 10^{-3}$  g/cm<sup>3</sup> in methanol at 30 °C.

radical, which is more stable than the  $\alpha$ -methyl radical, radical active species run from the top to bottom in a column in the crystals and run from the bottom to top in another column in Figure 6. Namely, the direction of propagation would be completely opposite in neighboring polymerization columns. Alternatively, when propagating radicals are produced on both the 2- and 5-carbons, the propagation can proceed simultaneously in the same direction. Therefore, an ESR measurement was carried out to detect the propagating radicals during UV irradiation of **1** in the crystalline state. The observed spectrum consists of broad lines with a  $g$ -value of 2.0029, as shown in Figure 8a. Here, another spectrum (b) is of the propagating radical from benzylammonium (*Z,Z*)-muconate ( $g$ -value = 2.0030) as a comparison. Both polymerizations proceed via a similar radical chain mechanism, but these spectra do not agree with each other. The line width of the entire spectrum of **1** is larger than that of benzylammonium (*Z,Z*)-muconate. As shown in Scheme 4, two types of radicals are possibly formed during the polymerization of sorbates; one is the  $\alpha$ -methyl radical, and



**Figure 8.** ESR spectra observed during propagation of (a) **1** and (b) benzylammonium (*Z,Z*)-muconate under UV irradiation in the crystalline state at room temperature.

**Scheme 4**



**Table 4.** Hyperfine Coupling Constants for Propagating Radicals Produced Form Diene Monomers ( $-\text{CH}_2\text{XCH}_2=\text{CH}_\beta-\text{CH}_\alpha\text{X}$ )

monomer	X	hyperfine coupling constant (mT)				
		$a(\text{H}_\alpha)$	$a(\text{H}_\beta)$	$a(\text{H}_\gamma)$	$a(\text{H}_\delta)$	$a(\text{X})$
2,4-hexadiene	CH <sub>3</sub>	1.30	0.30	1.30	1.10	0.95
diethyl ( <i>Z,Z</i> )-muconate	CO <sub>2</sub> Et	1.30	0.44	1.30	0.44	

the other is the  $\alpha$ -carboxyl radical. Considering the ESR coupling constant values reported for the propagating radical of diethyl (*Z,Z*)-muconate<sup>9</sup> and 2,4-hexadiene<sup>10</sup> in solution (Table 4), the propagating radicals of **1** are speculated to be the  $\alpha$ -methyl and  $\alpha$ -carboxyl radicals during the sorbate polymerization in the crystalline state.<sup>11</sup> The coupling to  $\alpha$ -methyl protons would broaden the line width of the spectrum of radical **9**. Thus, the ESR results support the existence of two kinds of propagating radicals, **8** and **9**. During the polymerization of the conjugated diene monomers in solution, the participation of both radicals during the propagation has not been reported. This reaction mechanism is peculiar to the solid-state polymerization. Any conformational change in a sorbate moiety can be transformed into another sorbate group through the diammonium part in the crystals. Consequently, the two reaction parts are possibly synchronized to react at the same time.

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(10) Kamachi, M.; Kajiwara, A.; Saegusa, K.; Morishima, Y. *Macromolecules* **1993**, *26*, 7369–7371.

(11) We attempted to obtain the ESR spectrum of the single crystal of **1** but failed because of the low concentration of the propagating radicals in a single crystal.

## Conclusion

For a long time, it has been considered that a ladder polymer with a well-controlled structure is not prepared via a chain reaction such as radical polymerization. In this study, however, we have proposed a new way to the efficient synthesis of a ladder polymer via a radical chain polymerization using topochemical polymerization of a bifunctional monomer in the crystalline state.

As has already been described in our previous papers,<sup>4d,e</sup> the ammonium polymer crystals, which are obtained from sorbic and muconic acid derivatives by topochemical polymerization, have a two-dimensional hydrogen bond network structure. The primary ammonium cations form the hydrogen bonds with three neighboring carboxylate anions, and the carboxylate anions form them with three neighboring ammonium cations. The two-dimensional hydrogen network runs perpendicular to the molecular plane of the diene carboxylate anions in the monomer crystal. Because such a hydrogen bond structure is also maintained in the polymer crystals, the ammonium polymer crystal is regarded as the polymer with a structure three-dimensionally linked by covalent and hydrogen bonds. If any ester monomer instead of the diammonium derivatives can be polymerized through a topochemical reaction mechanism, a true ladder polymer will be efficiently obtained, and the resulting double-stranded polymer chains will be characterized in solution. In the present stage of the work on the topochemical polymerization of diene monomers, a design for the polymerization of any ester monomer is not easy compared to that for ammonium monomers, but it will possibly be realized soon. The design and control of molecular crystal structure and reactivity based on crystal engineering would be helpful for supramolecular architecture providing new polymer materials with a well-controlled high dimensional structure.

## Experimental Section

**Materials.** Alkylenediammonium disorbates were prepared by the addition of the ether solution of a corresponding alkylenediamine (0.5 equiv) to sorbic acid in diethyl ether with stirring at room temperature. The precipitants were filtered and dried in a vacuum, followed by recrystallization from methanol.

*p*-Xylylenediammonium disorbate (**1**): platelet (MeOH); mp over 160 °C (decomp); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 7.49 (s, Ar, 4H), 7.02 (dd, *J* = 10.8 and 15.2 Hz, CH=CHCO<sub>2</sub>, 2H), 6.22–6.15 (m, CH<sub>3</sub>CH=CH, 2H), 6.06–5.96 (m, CH<sub>3</sub>CH=CH, 2H), 5.78 (d, *J* = 15.2 Hz, CH=CHCO<sub>2</sub>, 2H), 4.07 (s, NH<sub>3</sub>CH<sub>2</sub>, 4H), 1.80 (d, *J* = 6.8 Hz, CH<sub>3</sub>CH=CH, 6H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 175.71 (C=O), 142.10 (CH=CHCO<sub>2</sub>), 136.52 (CH<sub>3</sub>CH=CH), 136.36 (Ar), 131.73 (CH<sub>3</sub>CH=CH), 130.48 (Ar), 126.78 (CH=CHCO<sub>2</sub>), 44.05 (NH<sub>3</sub>CH<sub>2</sub>), 18.56 (CH<sub>3</sub>CH=CH); IR (KBr) 1624 (ν<sub>C=C-C=C</sub>), 1513 (ν<sub>C=O</sub>) cm<sup>-1</sup>; UV (CH<sub>3</sub>OH) λ<sub>C=C-C=C</sub> 248 nm (ε = 20 000).

*m*-Xylylenediammonium disorbate (**2**): powder (MeOH); mp 139 °C (decomp); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 7.51 (d, *J* = 27.2 Hz, Ar, 4H), 6.98 (dd, *J* = 10.4 and 15.2 Hz, CH=CHCO<sub>2</sub>, 2H), 6.20–6.14 (m, CH<sub>3</sub>CH=CH, 2H), 6.04–5.96 (m, CH<sub>3</sub>CH=CH, 2H), 5.78 (d, *J* = 15.2 Hz, CH=CHCO<sub>2</sub>, 2H), 4.10 (m, NH<sub>3</sub>CH<sub>2</sub>, 4H), 1.80 (d, *J* = 7.2 Hz, CH<sub>3</sub>CH=CH, 6H); <sup>13</sup>C NMR (100 MHz CD<sub>3</sub>OD) δ 175.91 (C=O), 142.03 (CH=CHCO<sub>2</sub>), 136.54 (CH<sub>3</sub>CH=CH), 136.27 (Ar), 131.68 (CH<sub>3</sub>CH=CH), 130.79–130.35 (Ar), 126.91 (CH=CHCO<sub>2</sub>), 44.10 (NH<sub>3</sub>CH<sub>2</sub>), 18.58 (CH<sub>3</sub>CH=CH); IR (KBr) 1627 (ν<sub>C=C-C=C</sub>), 1515 (ν<sub>C=O</sub>) cm<sup>-1</sup>; UV (CH<sub>3</sub>OH) λ<sub>C=C-C=C</sub> 248 nm (ε = 48 700).

Tetramethylenediammonium disorbate (**3**): powder (MeOH); mp 157 °C (decomp); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 7.0 (dd, *J* = 10.8 and

14.8 Hz, CH=CHCO<sub>2</sub>, 2H), 6.18 (m, CH<sub>3</sub>CH=CH, 2H), 6.05–5.98 (m, CH<sub>3</sub>CH=CH, 2H), 5.79 (d, *J* = 14.8 Hz, CH=CHCO<sub>2</sub>, 2H), 2.94 (m, NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, 4H), 1.81 (d, *J* = 7.2 Hz, CH<sub>3</sub>CH=CH, 6H), 1.72 (m, NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, 4H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 176.09 (C=O), 141.82 (CH=CHCO<sub>2</sub>), 136.39 (CH<sub>3</sub>CH=CH), 131.70 (CH<sub>3</sub>CH=CH), 127.22 (CH=CHCO<sub>2</sub>), 39.92 (NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.67 (NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 18.59 (CH<sub>3</sub>CH=CH); IR (KBr) 1609 (ν<sub>C=C-C=C</sub>), 1519 (ν<sub>C=O</sub>) cm<sup>-1</sup>; UV (CH<sub>3</sub>OH) λ<sub>C=C-C=C</sub> 248 nm (ε = 49 700).

Hexamethylenediammonium disorbate (**4**): needles (MeOH); mp 160 °C (decomp); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 6.98 (dd, *J* = 10.7 and 15.6 Hz, CH=CHCO<sub>2</sub>, 2H), 6.21–6.14 (m, CH<sub>3</sub>CH=CH, 2H), 6.03–5.98 (m, CH<sub>3</sub>CH=CH, 2H), 5.79 (d, *J* = 15.6 Hz, CH=CHCO<sub>2</sub>, 2H), 2.9 (dd, *J* = 7.6 and 15.1 Hz, NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, 4H), 1.80 (d, *J* = 6.8 Hz, CH<sub>3</sub>CH=CH, 6H), 1.66 (m, NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 4H), 1.43 (m, NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 4H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 176.01 (C=O), 141.74 (CH=CHCO<sub>2</sub>), 136.19 (CH<sub>3</sub>CH=CH), 131.78 (CH<sub>3</sub>CH=CH), 127.27 (CH=CHCO<sub>2</sub>), 48.36 (NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 28.56 (NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 26.97 (NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 18.51 (CH<sub>3</sub>CH=CH); IR (KBr) 1625 (ν<sub>C=C-C=C</sub>), 1520 (ν<sub>C=O</sub>) cm<sup>-1</sup>; UV (CH<sub>3</sub>OH) λ<sub>C=C-C=C</sub> 248 nm (ε = 47 600).

**Polymer Transformation.** The hydrolysis of poly(**1**) and poly(**3**) was carried out in 6 M HCl in aqueous methanol at reflux for 2 h. The produced poly(sorbic acid) was filtered and washed with methanol. To the obtained polymeric acid was added an excess triethylamine and methanol-*d*<sub>4</sub> in an NMR tube, and then the solution was used for the NMR measurement. Similarly, the methanol solution was used for the viscosity measurement with an Ubbelohde-type viscometer.

Poly(**7**) derived from poly(**1**); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 181.77 (C=O), 137.26 (C=C), 130.12 (C=C), 61.88 (CH), 39.92 (CH), 18.63 (CH<sub>3</sub>), 47.03 (CH<sub>2</sub>), 10.89 (CH<sub>3</sub>).

Poly(**7**) derived from poly(**3**); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 181.79 (C=O), 137.28 (C=C), 130.07 (C=C), 61.92 (CH), 39.84 (CH), 18.51 (CH<sub>3</sub>), 47.01 (CH<sub>2</sub>), 10.32 (CH<sub>3</sub>).

**Photoreaction Procedures.** Photoirradiation was carried out in air with a high-pressure Hg lamp (Toshiba SHL-100-2, 100 W) at a distance of 16 cm through a Pyrex filter. The polymer yield was gravimetrically determined after removing any unreacted monomer with methanol.

**Measurements.** The NMR spectra were recorded using a JEOL JMN A400 spectrometer in CD<sub>3</sub>OD at room temperature. IR spectra were taken with a JASCO FT/IR 430 spectrometer. UV spectra were recorded on a Shimadzu UV-160 spectrometer. Powder X-ray diffraction profiles were measured on a RIGAKU RINT2100 diffractometer with Cu Kα radiation. Single-crystal X-ray data were collected on a Rigaku RAXIS RAPID-F diffractometer using Mo Kα radiation monochromated by graphite. The structure was solved by the direct method with the program SIR92 and refined using full-matrix least-squares procedures. All the calculations were performed using a CrystalStructure crystallographic software package. The ESR spectra were measured with a Bruker ESP300 spectrometer.

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**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the monomers **1–4**, <sup>13</sup>C NMR spectra of poly(**7**)s derived from poly(**1**) and poly(**2**), <sup>1</sup>H NMR spectrum of a soluble part obtained after the hydrolysis of poly(**1**). FT-IR spectra of **1**, and **3**, poly(**1**), and poly(**3**) and crystallographic data of **1** (PDF/CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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