

Crystal-Lattice Controlled Photopolymerization of Di(benzylammonium) (*Z,Z*)-Muconates

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Abstract: A new type of photoreaction of the ammonium salts of butadiene-1,4-dicarboxylic acid in the solid state is reported. When the crystals of a series of di(benzylammonium) (*Z,Z*)-muconate (2,4-hexadienedioate) and its related derivatives were prepared and photoirradiated, either a tritactic polymer or an (*E,E*)-isomer was obtained as the photoproduct according to the structure of the ammonium part. The polymers produced were confirmed to be of high molecular weight and stereoregular by viscometry and NMR spectroscopy after solid-state polymer transformation. X-ray crystal structure analysis revealed that the crystal structures of benzylammonium muconates were classified into columnar-type and sheet-type on the basis of the molecular arrangement. Both types involve two-dimensional hydrogen bond networks between the primary ammonium cations and the carboxylate anions. In the former structure, the stacking of the diene moieties was suitable for topochemical polymerization to yield a tritactic polymer, while the latter has molecular packing favoring the isomerization or no reactivity. The stereocontrol of the tritactic polymer is in good agreement with the results expected from the crystal structure. This indicates that the molecular packing determines a reaction pathway in the crystalline state.

Introduction

Precise design and control of polymer-chain structures, such as stereoregularity, molecular weight, and its distribution as well as the chain-end structures, have been an ultimate goal in polymer syntheses.¹ Generally, free-radical polymerization under the usual conditions provides an atactic polymer with a wide molecular weight distribution. More recently, the living radical polymerization technique has intensively been developed to afford the polymers with a well-controlled structure including molecular weight distribution and the terminal structure.² However, the tacticity is still hard to regulate due to the inability to control propagation, in contrast with the established stereocontrol of polymer chains by coordination polymerization of vinyl monomers. Several attempts to control tacticity by free-radical polymerization have already been carried out in solution and in organized media.³ For example, higher isotactic polymers with a helical chain-structure were prepared from sterically

hindered methacrylate such as triphenylmethyl and 1-phenyl-dibenzosuberyl methacrylates.⁴ The presence of chiral auxiliary has been demonstrated to be effective to control the tacticity in the polymerization of acrylamide.⁵ The polymerization of 1,3-diene monomers in the inclusion canals of perhydrotriphenylene and steroid crystals produced asymmetric polymers with regulated stereochemical structures.⁶

[2+2] photopolymerization of 2,5-distyrylpyridine derivatives and thermal or radiation polymerization of diacetylenic compounds are typical examples of topochemical polymerization.⁷ They gave the polymers with primary controlled chain-structure. Although the discovery of these two polymerizations dates back to the late 1960s, few monomers had been found to proceed through topochemical polymerization. In 1994, Matsumoto et al. discovered that diethyl (*Z,Z*)-muconate (diethyl (*Z,Z*)-2,4-hexadienedioate) yields a tritactic polymer, i.e., *meso*-diisotactic-*trans*-2,5-polymer, by photoirradiation of the monomer crystals.⁸ X-ray diffractions and ESR studies revealed that this is the first example of topochemical polymerization of 1,3-diene derivatives

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via a radical chain mechanism.^{9,10} However, the topochemical polymerizability is so sensitive to the molecular structure that the alkyl esters other than diethyl (Z,Z)-muconate do not undergo photopolymerization at all. This sensitivity is explained by the drastic changes of packing and orientation of the monomer in the crystalline state. The difficulty of the crystal structure design prevents us from constructing topochemical polymerization systems.

Recently, the rational design of the packing and orientation of organic molecules in the crystalline state has attracted much attention in crystal engineering, because functions of the crystalline materials are closely related to the molecular orientation in the crystalline state.^{7a,11} Many efforts to design and search supramolecular synthons, partial structural motifs in the crystalline-state structure, have been reported by using multiple hydrogen bonds.¹² The selectivity and directionality of hydrogen bonding lead to its extensive use in construction and design of the structural motifs in the solid state.¹² More recently, organic salts have been employed as supramolecular synthons of the layer-type motifs.^{13–16} They construct robust structural motifs by polarized hydrogen bonds between cations and anions.

Primary ammonium carboxylates have great potential as supramolecular synthons to make robust hydrogen bonded networks. The primary ammonium cations act as triple hydrogen bond donors due to the three hydrogen atoms attached to the nitrogen atom. The carboxylate anions act as triple or quadruple hydrogen bond acceptors due to the four lone-pairs of electrons. The polarized hydrogen bond network between them yields a one-dimensional (1D) columnar array (Figure 1). The importance of the columnar structure has already been pointed out in a series of conglomerate primary ammonium carboxylates.¹⁷ From the viewpoint of synthetic chemistry, primary ammonium

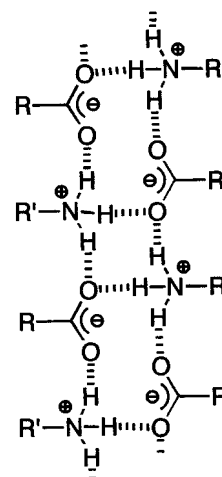


Figure 1. Hydrogen bond motif of primary ammonium carboxylates.

carboxylates are easily prepared by mixing acids and amines at 1:1 ratios and mostly isolated as crystalline materials with higher melting points from the appropriate solvents. This facile and easy preparation leads to their extensive use in the search for chiral recognition^{17,18} and selective reactions¹⁹ in the crystalline state. Therefore, we chose the hydrogen bonding of primary ammonium carboxylates as a supramolecular synthon of the solid state and started the search for topochemical polymerizable monomers.²⁰ In this report, we describe the photopolymerization behavior and crystal structures of a series of di(benzylammonium) (Z,Z)-muconates [di(benzylammonium) (Z,Z)-2,4-hexadienedioates] as well as the characterization of the resulting stereoregular polymers.

Results and Discussion

Photoreactions in the Crystalline State. A series of crystals of *N*-benzylammonium and related ammonium salts of the (Z,Z)-muconate derivatives were prepared and photoirradiated with a high-pressure Hg lamp at room temperature. Table 1 summarizes the photoreactivities. No change was observed in appearance during the reaction, i.e., the crystals were recovered after photoirradiation for all the cases. The unsubstituted **1**, the chloro-substituted derivative, **2-Cl**, **3-Cl**, and **4-Cl**, and 2-methyl-substituted **2-Me** provided insoluble photoproducts, which were isolated in 3–24% yield after 8 h of irradiation (Table 1, entries 1–5). These insoluble products were confirmed to be tritactic and high molecular weight polymers (vide infra). The soluble part was the unreacted (Z,Z)-monomer. Any other photoproducts such as (*E,Z*)-isomers, (*E,E*)-isomers, cyclodimers, and oligomers were not detected. This means that photopolymerization occurred exclusively. **4-Me**, **2-OMe**, and **3-OMe** provided the corresponding (*E,E*)-isomers in 56–66% conversion (entries 5–7) by photoirradiation. **4-OMe** and **3-Me** were inert to the photoirradiation under the present conditions. The dichloro-substituted salts **5** and **6** had no photopolymerization ability (entries 11 and 12), whereas the corresponding monochloro-substituted derivatives provided polymers (entries 2–4). We also

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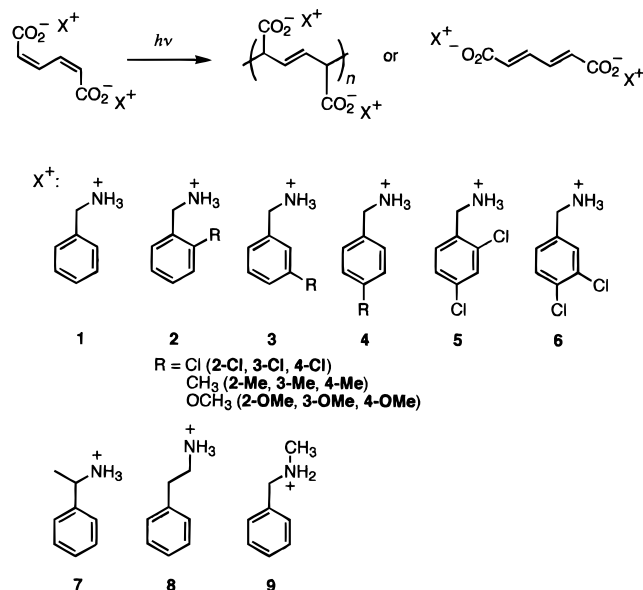
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Table 1. Photoreaction of Di(benzylammonium) (*Z,Z*)-Muconate and Its Related Derivatives in the Crystalline State under UV Irradiation with a High-Pressure Mercury Lamp at Room Temperature for 8 h

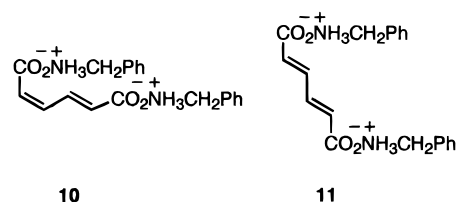
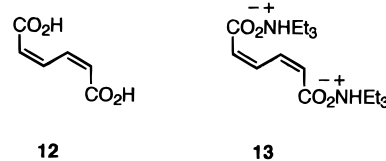
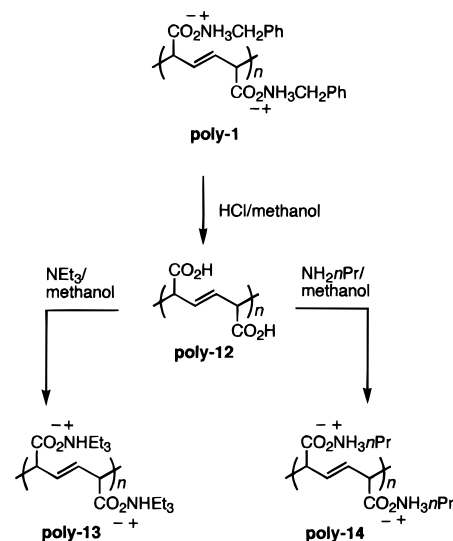
entry	substrate	<i>N</i> -substituent	yield of photoproduct (%)	
			polymer	(<i>E,E</i>)-isomer
1	1	benzyl	21	0
2	2-Cl	2-chlorobenzyl	24	0
3	3-Cl	3-chlorobenzyl	21	0
4	4-Cl	4-chlorobenzyl	3	0
5	2-Me	2-methylbenzyl	3	0
6	3-Me	3-methylbenzyl	0	0
7	4-Me	4-methylbenzyl	0	59
8	2-OMe	2-methoxybenzyl	0	56
9	3-OMe	3-methoxybenzyl	0	66
10	4-OMe	4-methoxybenzyl	0	0
11	5	2,4-dichlorobenzyl	0	0
12	6	3,4-dichlorobenzyl	0	0
13	7	1-phenylethyl	0	0
14	8	2-phenylethyl	0	88
15	9	<i>N</i> -methyl- <i>N</i> -benzyl	0	0
16	10	benzyl	0	2
17	11	benzyl	0	100

Scheme 1

investigated the photoreactions of the crystals of several derivatives with related chemical structures of the ammonium moiety (7–9 in Scheme 1). No reaction proceeded for the crystals of **7** and **9**, which are the α - and *N*-methyl-substituted derivatives of **1**, respectively (entries 13 and 15). In contrast, derivative **8** provided the (*E,E*)-isomer in the highest yield (entry 14). The photoreactivity of **10** and **11** as the geometrical isomers of **1** was also examined. **10** provided **11** in low yield and **11** was utterly stable under photoirradiation, being in contrast with the photopolymerization ability of **1** (entries 16 and 17).

It is noted that the photoreactions in the crystalline state provide a single photoproduct, either polymer or (*E,E*)-isomer. In contrast, isotropic solutions resulted in a mixture of several products, i.e., the unreacted (*Z,Z*)-derivative and the (*E,Z*)- and (*E,E*)-isomers, as well as a mixture of dimers. This suggests that the reaction path is exclusively controlled by the crystal lattice in the solid state, but not by the chemical nature of the diene compounds.

Polymer Characterizations. The photopolymer obtained by the crystalline-state polymerization of **1** was not soluble in any solvents, for example, common organic solvents such as

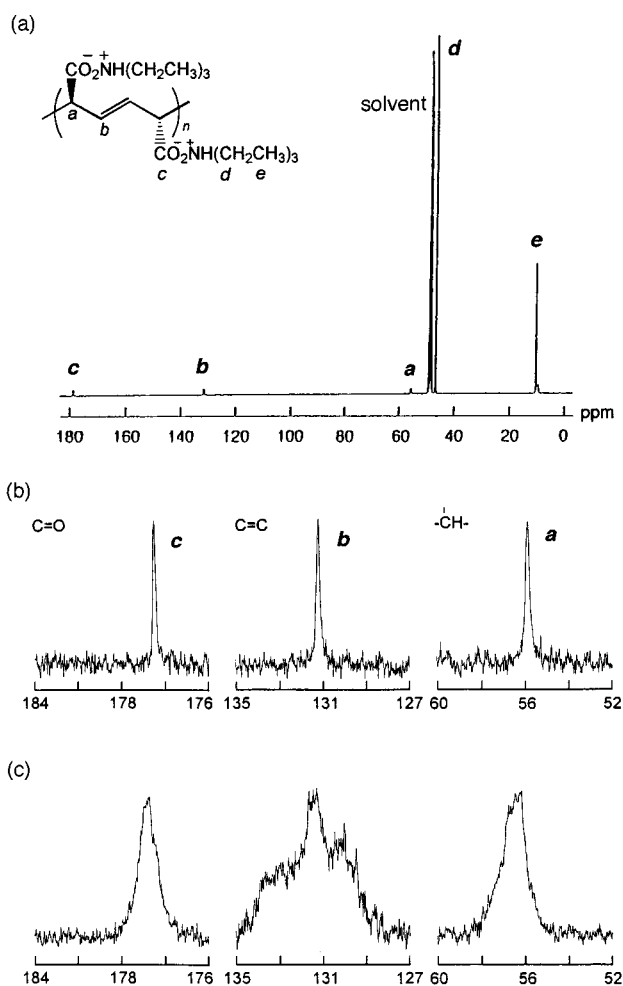
**Figure 2.** Molecular structure of **10** and **11**.**Figure 3.** Molecular structure of **12** and **13**.**Scheme 2**

n-hexane, toluene, chloroform, 1,2-dichlorobenzene, methanol, acetone, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide, fluoro-containing solvents such as trifluoroacetic acid and 1,1,1,3,3,3-hexafluoro-2-propanol, and acids or alkali, e.g., concentrated H_2SO_4 , dilute HCl, and NaOH aqueous solutions as well as water. The IR spectrum of the polymer suggests the *trans*-2,5-structure as the repeating units; the out-of-plane deformation vibration due to the *trans*-CH=CH moiety was observed at 996 cm^{-1} for the polymer of **1**, and the peak of the carbonyl stretching shifted from 1586 cm^{-1} for the monomer to 1532 cm^{-1} for the polymer. Elemental analysis also gave satisfactory results for the photopolymers. The polymer produced was confirmed to be highly crystalline by wide-angle powder X-ray diffraction; several sharp and intense peaks observed for the profile of the polymers indicate that the photopolymerization undoubtedly proceeded in the crystalline state. The chloro-substituted homologues of the polymers gave similar characteristics.

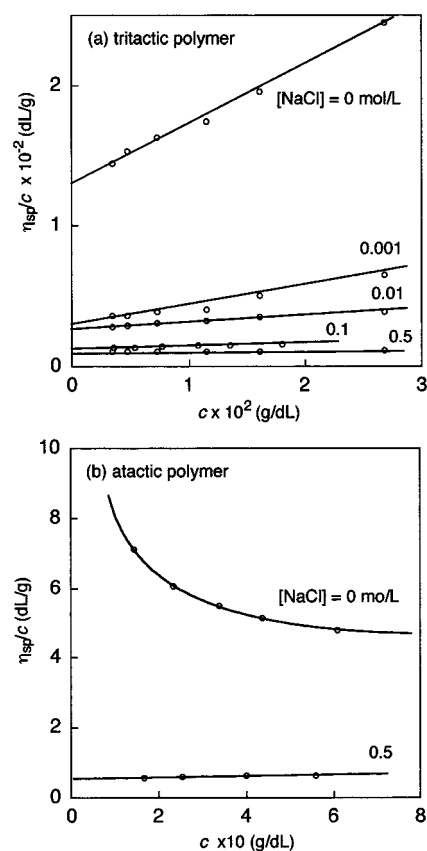
To characterize the insoluble photopolymer by some techniques in solution, we transformed them into soluble polymers by the exchange reaction of ammonium cation according to Scheme 2. It includes a heterogeneous polymer reaction process.²⁰ Namely, the benzylammonium polymer (**poly-1**) was first converted to poly(muconic acid) (**poly-12**) by immersing it in dilute HCl aqueous or methanol solution. The reaction was accomplished within several minutes with stirring at room temperature. The resulting **poly-12** was not also insoluble in any solvents including alkaline aqueous solutions. However,

Table 2. Crystallographic Data for the Crystals of Di(benzylammonium) (Z,Z)-Muconate and Its Related Derivatives

compd	1	2-Cl	3-Me	2-OMe	4-OMe	6	(S)-7
formula	C ₁₀ H ₁₂ NO ₂	C ₁₀ H ₁₁ NO ₂ Cl	C ₁₁ H ₁₄ NO ₂	C ₁₁ H ₁₄ NO ₃	C ₁₁ H ₁₄ NO ₃	C ₁₀ H ₁₀ NO ₂ Cl ₂	C ₂₄ H ₂₈ N ₂ O ₆
fw	178.21	212.66	192.24	208.24	208.24	247.10	440.49
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>a</i>	<i>C</i> 2
<i>a</i> , Å	10.98(1)	11.033(2)	8.614(2)	8.5940(6)	9.366(3)	8.842(1)	21.598(6)
<i>b</i> , Å	4.862(2)	4.9360(8)	13.731(4)	11.638(1)	10.858(4)	13.678(2)	6.139(2)
<i>c</i> , Å	17.72(1)	18.011(4)	8.795(3)	11.158(1)	5.599(3)	9.9022(9)	21.58(2)
α , deg					98.043(7)		
β , deg	97.93(9)	95.055(5)	103.06(2)	110.433(2)	98.117(6)	108.787(4)	112.02(5)
γ , deg					97.42(2)		
<i>V</i> , Å ³	936(1)	977.0(3)	1013.3(5)	1045.8(2)	551.7(4)	1133.8(2)	2652(2)
<i>Z</i>	4	4	4	4	2	4	4
<i>D</i> _c	1.264	1.446	1.260	1.323	1.253	1.447	1.103
unique reflcns	1430	1541	2327	2378	2152	2558	2323
no. obsd reflcns	1090	1301	1344	1937	1045	1718	2014
<i>R</i> , <i>R</i> _w	0.188, 0.313	0.157, 0.273	0.062, 0.126	0.081, 0.154	0.216, 0.402	0.072, 0.187	0.188, 0.297
GOF	1.23	1.15	1.16	1.13	1.72	1.05	1.25
2 θ _{max} , deg	51.2	50.1	55.0	55.0	55.0	55.0	51.2
<i>R</i> / <i>P</i>	9.24	8.13	10.58	14.24	7.68	12.63	7.96
<i>P</i> -factor	0.200	0.200	0.08	0.1220	0.200	0.15	0.200
max <i>S</i>	0.01	0.06	0.00	0.04	0.09	0.02	0.09
temp, °C	-63	23	23	23	23	23	-76
structure type	columnar	columnar	sheet(pattern 1)	sheet(pattern 1)	sheet(pattern 2)	sheet(pattern 1)	sheet(pattern 2)

**Figure 4.** ¹³C NMR spectra of poly(**13**)s in methanol-*d*₄, (a) tritactic poly(**13**), (b) tritactic poly(**13**) (expanded), and (c) atactic poly(**13**).

poly-12 was further transformed to soluble polymers by reaction with some alkylamines. Triethylamine and *n*-propylamine gave methanol-soluble poly(bis(triethylammonium) (Z,Z)-muconate) (**poly-13**) and water-soluble poly(di(*n*-propylammonium) (Z,Z)-muconate) (**poly-14**), respectively.

**Figure 5.** Plot of η_{sp}/c against the concentration *c* for poly(**14**) in water at 30 °C in the absence or presence of NaCl: (a) tritactic poly(**14**) and (b) atactic poly(**14**).

The high-resolution ¹³C NMR spectrum of **poly-13** in methanol-*d*₄ is shown in Figure 4, together with the spectrum of atactic **poly-13** (*at-poly-13*) as the comparison. The *at-poly-13* was prepared by the isotropic polymerization of **12** and the subsequent reaction of the resulting polymer with triethylamine, because the direct polymerization of **13** failed. The single resonances for the main chain and carbonyl carbons depicted in Figure 4b indicate the highly controlled stereochemical structure of the polymer, i.e., *meso*-2,5-*trans*-diisotactic poly-

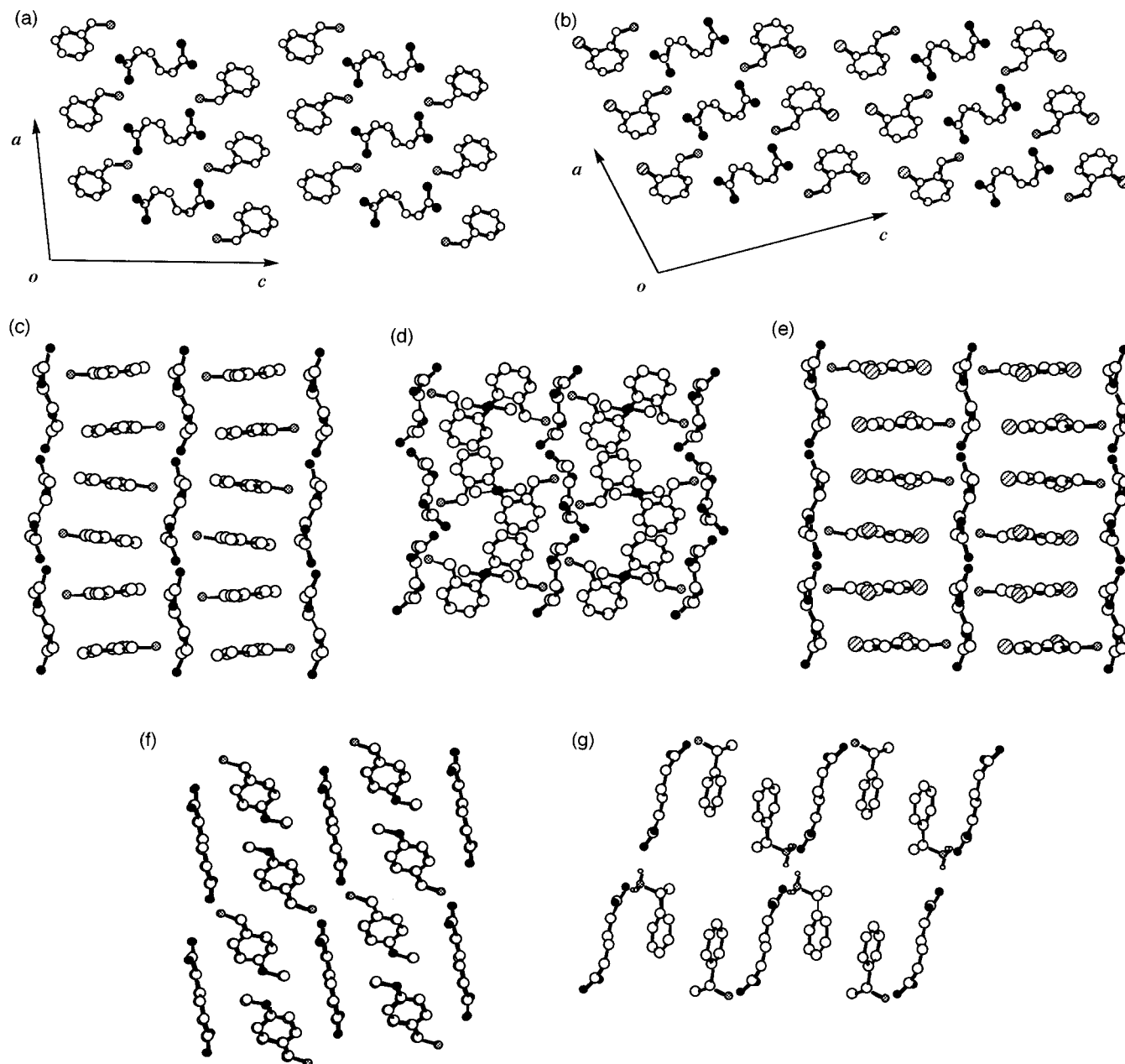


Figure 6. Crystal structures of (a) **1** viewed down along the crystallographic *b*-axis, (b) **2-Cl** viewed down along the crystallographic *b*-axis, (c) **3-Me** viewed down along the crystallographic *a*-axis, (d) **2-OMe** viewed down along the crystallographic *a*-axis, (e) **6** viewed down along the crystallographic *c*-axis, (f) **4-OMe** viewed down along the crystallographic *c*-axis, and (g) (*S*)-**7** viewed down along the crystallographic *b*-axis. The incorporated solvents are omitted. Open, shaded, and solid circles represent carbon, nitrogen, and oxygen atoms, respectively. Hydrogen atoms are omitted for clarity.

mer,^{9,10} being different from the broad and multiple resonances for the atactic polymer (Figure 4c). It was expected that the molecular packing of **10** would result in the formation of another type of stereoregular polymer, i.e., *racemo*-diisotactic polymer if a similar topochemical polymerization proceeded. However, **10** gave no polymer during photoirradiation in the crystalline state, as has already been described.

The intrinsic viscosity of **poly-14** was determined in water in the absence or presence of NaCl to evaluate the molecular weight. The results of viscosity measurement are shown in Figure 5. The η_{sp}/c value increased monotonically with the decrease in the polymer concentration *c* for the solution of *at*-**poly-14** in the absence of NaCl (Figure 5b), being observed usually for polymer electrolytes in water. The $[\eta]$ value was evaluated to be 0.59 dL/g for *at*-**poly-14** in 0.5 mol/L of NaCl aqueous solution at 30 °C. In contrast, a linear relationship was

unexpectedly obtained for the solution of the tritactic **poly-14** even in the absence of NaCl (Figure 5a). This strange dilute solution property probably originates in the highly regulated stereochemical structure of the polymer. The $[\eta]$ value was dependent on the NaCl concentration: 1.20×10^2 dL/g in the absence of NaCl to 1.24×10 dL/g in the 0.5 mol/L of NaCl solution. The large $[\eta]$ value of the tritactic **poly-14** indicates the high molecular weight polymer formation during the crystalline-state polymerization of **1**. The facile formation of the high molecular weight polymer is related to the mechanism of the crystalline-state polymerization. In this system, the polymerization is initiated by radical formation under photoirradiation and proceeds in a radical chain mechanism to yield high molecular weight polymers instantaneously. This is supported by the in situ observation of the propagating species during the photopolymerization of **1** crystals by ESR spectroscopy.

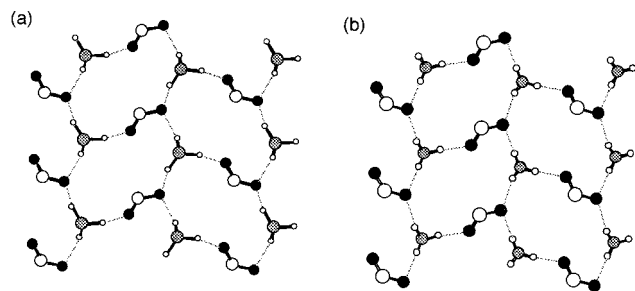


Figure 7. Hydrogen bond network of the columnar-type structure: (a) **1** and (b) **2-Cl**. Open, shadowed, and solid circles represent carbon, nitrogen, and oxygen atoms, respectively. Hydrogen atoms attached with nitrogen atoms are shown as small open circles. Dotted lines show the hydrogen bond.

copy; a broad three-line spectrum with a g -value of 2.0030 was detected, which was a close value to those due to the propagating radicals observed for radical polymerizations of diene compounds.^{8b}

Crystal Structures. To clarify the structure–photoreaction correlation, we focused on the crystal structures of some benzylammonium salts of muconates (**1**, **2-Cl**, **3-Me**, **2-OMe**, **4-OMe**, **6**, and (*S*)-**7**). Crystallographic parameters and packing diagrams are shown in Table 2 and Figure 6, respectively. They all have layer structures by two-dimensional (2D) hydrogen-bonded networks, and are classified into two types on the basis of the molecular arrangement of muconate dianions: (a) columnar-type structure and (b) sheet-type structure. In the former structure, the muconate dianions stack to make a columnar structure. The columns are sandwiched between two benzylammonium cation layers. In the latter, the muconate dianions spread to form a sheet and the substituents of the ammonium cations pillar the sheets. The crystals of **1** and **2-Cl** salts belong to the former type and the other ammonium salts form the latter.

(a) Columnar-Type Structure. The muconate anions are arranged in 1D fashion to yield a column structure. The resulting columns are linked by 2D hydrogen bond networks at both sides of the muconate dianions. Figure 7 illustrates the hydrogen bond network. The primary ammonium cations form the hydrogen bonds with three neighboring carboxylate anions and the carboxylate anions form with three neighboring ammonium cations. This 2D hydrogen bond network runs perpendicular to the molecular plane of the muconate anions. The muconate columns are sandwiched between the benzylammonium layers due to its bifunctionality. In the ammonium layer, the benzyl groups are arranged in a 2D fashion by a face-to-face interaction between aromatic rings as well as a CH– π interaction between the aromatic ring and the CH of an adjacent benzyl group.

In the muconate columns, the diene moieties are arranged in a face-to-face manner as shown in Figure 8. The tilt stacking of the muconates in the column enables its double bonds to contact individually with the double bond of different neighboring muconates along the column. The intermolecular distances between the nearest double bonds are 4.28 and 4.30 Å for the crystals of **1** and **2-Cl**, respectively, being within the distance suitable for the topochemical polymerization. Indeed, **1** and **2-Cl** that form the columnar structure in the monomer crystals yield polymers under photoirradiation. The fashion of the alignment of the monomer molecules of **1** and **2-Cl** in the crystals also supports strongly the formation of polymer of a *meso*-diisotactic-2,5-*trans*-structure during the topochemical polymerization.

(b) Sheet-Type Structure. In contrast with the columnar-type structure, the muconate anions are arranged in 2D fashion

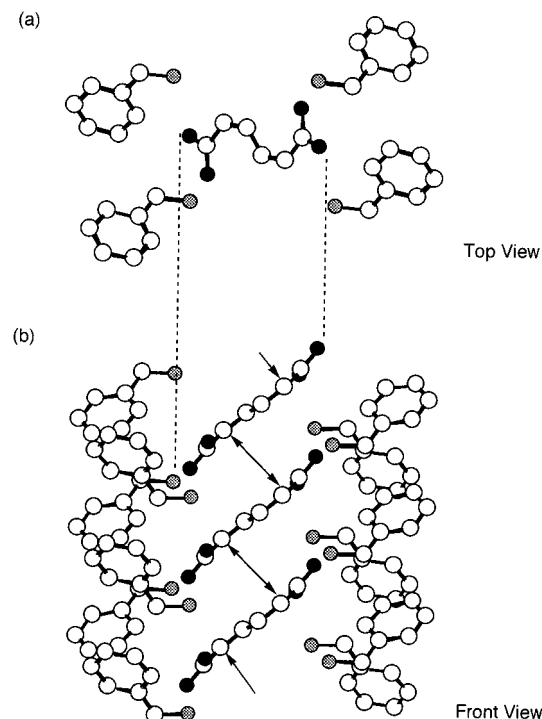


Figure 8. Molecular stacking in the column of **1**: (a) top view from the crystallographic b -axis and (b) front view from crystallographic c -axis. Open, shadowed, and solid circles represent carbon, nitrogen, and oxygen atoms, respectively.

Table 3. Intermolecular Center-to-Center Distances between the Nearest Double Bonds in the Crystals

crystal	distance (Å)	
	face-to-face contact	edge-to-edge contact
1	4.278 (in column)	4.785 (inter-column)
2-Cl	4.298 (in column)	4.776 (inter-column)
2-OMe	10.99 (inter-sheet)	5.456 (in sheet)
3-Me	8.348 (inter-sheet)	6.272 (in sheet)
4-OMe	9.366 (inter-sheet)	4.338 (in sheet)
6	9.902 (inter-sheet)	6.315 (in sheet)
(<i>S</i>)- 7	10.90 (inter-sheet)	4.858 (in sheet)

to yield a sheet structure. The sheet runs parallel to the molecular plane of the muconates. Namely, the muconate anions lay in the hydrogen bond sheet. The hydrogen bond networks are depicted in Figure 9 and are divided into two patterns: pattern 1 for **3-Me**, **2-OMe**, and **6**, and pattern 2 for **4-OMe** and (*S*)-**7**. In the former pattern, two carboxylate anions and two ammonium cations form an eight-membered cyclic hydrogen bond network and are further cross-linked with the neighboring cyclic hydrogen bond networks to form a 2D-sheet structure. In the latter, the primary ammonium cations and the carboxylate anions form a typical 1D ladder-type hydrogen bond network. The dicarboxylate moiety of the muconate dianions enables the 1D network at both sides to yield a 2D hydrogen-bonded layer. In both cases, the primary ammonium cations and the carboxylate anions act as triple hydrogen bond donors and triple hydrogen bond acceptors, respectively. The hydrogen bond networks spread in two-dimensional directions to form the sheet structures because of the bifunctionality of muconic acid. The substituents of the ammonium cations protrude out of the sheet and act as the pillar. Offset and distances between the sheets change according to the shape and size of the substituents.

The intermolecular distances of the double bonds are summarized in Table 3. There are nearest couples of double bonds in the inner the sheet in each crystal of pattern 2 (4.34 and 4.86

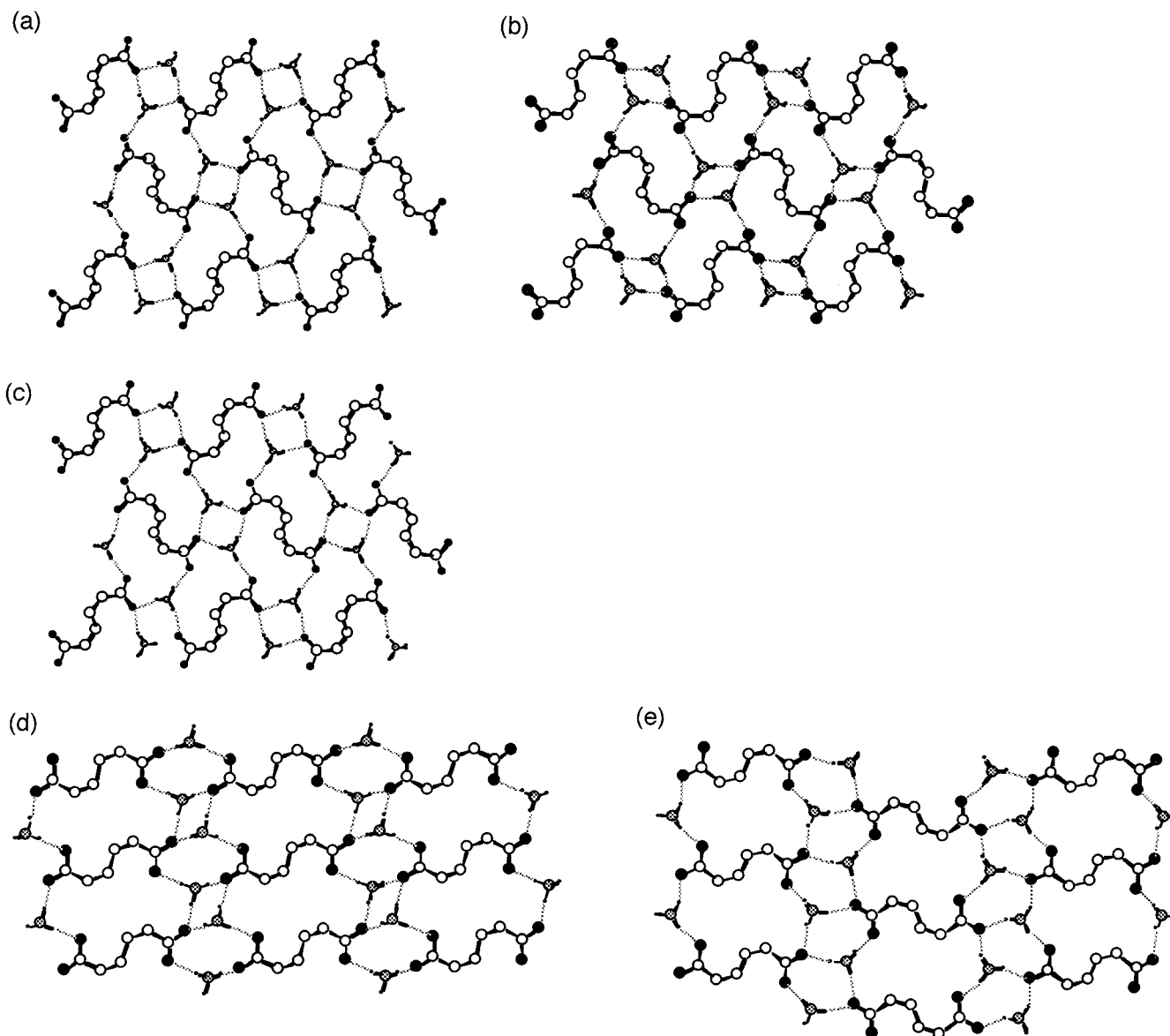


Figure 9. Hydrogen bond network of the sheet-type structures: (a) **3-Me**, (b) **2-OMe**, (c) **6**, (d) **4-OMe**, and (e) (*S*)-**7**. Open, shadowed, and solid circles represent carbon, nitrogen, and oxygen atoms, respectively. Hydrogen atoms attached with nitrogen atoms are shown as small open circles. Dotted lines show the hydrogen bond.

for **4-MeO** and (*S*)-**7**, respectively), but they are arranged as an edge-to-edge type. The distance and the orientation of the inter-sheet couples are far from the criteria of the intermolecular photoreactions, being not suitable for photopolymerization. Indeed, the derivatives that belong to this form have no photopolymerization reactivities. They favor photoisomerization as a unimolecular reaction or no reactions.

Conclusion

We have demonstrated the photoreactivities and crystal structures of a series of benzylammonium muconates. X-ray structure analysis has revealed that molecular packing in the crystalline state controls the pathway of the photoreaction, that is, the mode of the reaction and the stereochemistry of the photoproducts. The columnar-type structure formed by the appropriate stacking of the muconate anions is indispensable for the process of topochemical polymerization. Namely, the photopolymerizable columnar structure implies the face-to-face arrangement of the muconates in a suitable distance of the double bonds, as seen in the crystals of **1** and **2-Cl**. The

minimum movement of the diene groups yield polymers. The stereoregularity of the resulting polymers is in good agreement with that expected from the crystal structure. These results indicate that the photopolymerization of the benzylammonium muconates belongs to the crystal lattice-controlling reaction, i.e., topochemical polymerization.

Moreover, we have confirmed that primary ammonium cations and carboxylate anions act as triple hydrogen bond donors and triple hydrogen bond acceptors, respectively. The bifunctionality of the muconate dianions enables the layer structure with the 2D hydrogen bond network to form. This indicates that bis(primary ammonium) salts of rigid-structure dicarboxylates can be an important supramolecular synthon in the design of the organic materials with various types of layer structures.

Experimental Section

General Methods. (*Z,Z*)-Muconic acid (**12**) was supplied from Mitsubishi Chemical Co. Ltd., Tokyo. Other commercial chemicals were used as received without further purification. NMR and IR spectra were

recorded on a JEOL JMN A400 and a JASCO Herschel FTIR-430 spectrometer, respectively. Intrinsic viscosity was determined at 30 °C with an Ubbelohde-type viscometer. The powder X-ray diffraction profile was recorded on a Shimadzu XD-610 diffractometer or RINT-2000. The ESR spectrum was taken with a Bruker ESP-300 spectrometer under photoirradiation with a 1-kW xenon lamp.

X-ray Crystallography. Experimental details of the X-ray analysis are provided in Table 2. All single-crystal X-ray data were collected on a Rigaku R-AXIS-IV or R-AXIS RAPID diffractometer equipped with an imaging plate area detector at Osaka University and a Rigaku AFC7R four-circle diffractometer or a Rigaku R-AXIS RAPID diffractometer at Osaka City University, using Mo K α radiation monochromated by graphite. The structures were solved by the direct method with the programs SHELXS86 and SIR92 and refined by full-matrix least-squares procedures. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

Preparation of the Salts. All the benzylammonium (Z,Z)-muconates were prepared from **12** with the corresponding benzylamines in methanol at room temperature and quantitatively isolated by precipitation with a large amount of diethyl ether. They were recrystallized from an acetone/water mixture in 5/1 v/v, except for **9** and (*S*)-**7** which were recrystallized from an acetone/2-propanol mixture in 5/1 v/v and methanol, respectively. All the obtained crystals were colorless thin needles. **10** and **11** were prepared by a similar procedure with (*E,Z*)- and (*E,E*)-muconic acids as the starting materials. These acids were obtained by isomerization of **12** thermally and photochemically in the presence of iodine, respectively. See the Supporting Information for the spectral data of the compounds.

Photoreaction. Photoirradiation was carried out using a high-pressure mercury lamp (Toshiba SHL-100-2, 100 W, Pyrex filter) at a

distance of 10 cm under atmospheric conditions. After irradiation, the polymer was isolated by removal of the unreacted monomer with methanol. Photoisomerization products were determined by ¹H NMR spectroscopy. **Poly-1:** IR(KBr) 1532($\nu_{\text{C=O}}$), 996($\delta_{\text{trans-CH=CH}}$) cm⁻¹. Anal. Calcd for (C₂₀H₂₄N₂O₄)_n: C, 67.40; H, 6.79; N, 7.86. Found: C, 67.15; H, 6.78; N, 7.74.

Transformation of Polymers. The benzylammonium polymer was immersed in HCl methanol (ca. 1 mol/L) at room temperature for 10 mins, filtered, and washed with methanol to yield **poly-12** quantitatively. **Poly-12:** IR (KBr) $\nu_{\text{C=O}}$ 1714 cm⁻¹. Anal. Calcd for (C₆H₆O₄)_n: C, 50.71; H, 4.26. Found: C, 50.42; H, 4.29. **Poly-12** (10 mg), a large excess of *n*-propylamine (1 mL), and methanol (5 mL) were stirred in a sample tube at room temperature for 1 h to yield **poly-14**. The transformed polymer was filtered, washed, and dried in vacuo. The transformation to **poly-13** was carried out with triethylamine and methanol-*d*₄ in an NMR tube without isolating the polymer. **Poly-13:** ¹³C NMR (100 MHz, CD₃OD) δ 178.46 (C=O), 131.17 (C=C), 55.85 (CH), 46.99 (CH₂), 10.73 (CH₃).

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Supporting Information Available: Spectral data of the compounds, ESR spectrum, and crystallographic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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