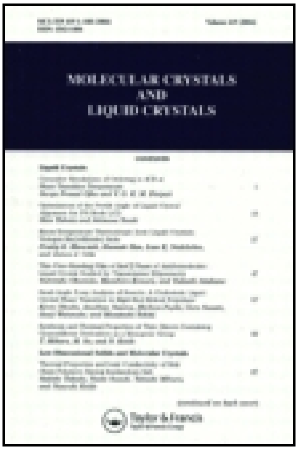

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A Role of Weak interaction between Naphthylmethyl Groups on Crystal Structure And Photopolymerization Reactivity of 1-Naphthylmethylammonium Salts of Unsaturated Carboxylic Acidsin The Crystalline State

Akikazu Matsumoto [a], Takafumi Kunisue [a], Sadamu Nagahama [a], Akikazu Matsumoto [b], Kazuki Sada [c], Katsunari Inoue [c], Tomoyuki Tanakaand [c] & Mikiji Miyata [c]

[a] Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshiku, Osaka, 558-8585, Japan

[b] PRESTO, JST

[c] Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871, Japan

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A ROLE OF WEAK INTERACTION BETWEEN NAPHTHYLMETHYL GROUPS ON CRYSTAL STRUCTURE AND PHOTOPOLYMERIZATION REACTIVITY OF 1-NAPHTHYLMETHYLAMMONIUM SALTS OF UNSATURATED CARBOXYLIC ACIDS IN THE CRYSTALLINE STATE

Akikazu Matsumoto, Takafumi Kunisue,*
and Sadamu Nagahama
Department of Applied Chemistry,
Graduate School of Engineering, Osaka City University,
Sugimoto, Sumiyoshiku, Osaka 558-8585, Japan

Akikazu Matsumoto
PRESTO-JST

Kazuki Sada, Katsunari Inoue, Tomoyuki Tanaka,
and Mikiji Miyata
Graduate School of Engineering, Osaka University
2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

We have investigated the crystal structures of several 1-naphthylmethylammonium salts of unsaturated carboxylic acids, i.e., sorbate, crotonate, tiglate, and methacrylate as the diene and vinyl monomers. In the crystals, the monomer molecules stack in a similar fashion to make a lamellar structure consisting of alternating naphthylmethylammonium cation and carboxylate anion layers. For the construction of the lamellar structure, weak intermolecular interaction such as π-π stacking and CH-π interaction is important as well as the formation of robust two-dimensional hydrogen bond network. We discuss the relationship between the molecular packing in the crystals and photopolymerization reactivity of the unsaturated carboxylic acid derivatives in the solid state.

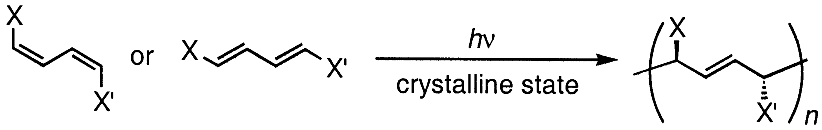
Keywords: crystal engineering; topochemical polymerization; solid-state photoreaction; supramolecular chemistry; π-π stacking; CH-π interaction; weak hydrogen bond

*Corresponding author

INTRODUCTION

Crystal engineering is the planning of syntheses in the crystalline state and the evaluation of the structure and properties of the crystalline products using pre-organized starting materials. A few single crystal-to-single crystal reactions have been reported, although it is the most suitable method for manufacturing single crystals that cannot be obtained by direct recrystallization. For example, a polymer single crystal in which polymer chains are arranged with a fully extended conformation along a specific crystallographic axis would be uniquely obtained by topochemical polymerization. Actually, however, such a successful polymerization case is seldom found because of the difficulty of the maintenance of a single crystal structure during the polymerization, despite the pioneering works on the polymerization of diolefins and diacetylenes since the 1960s [1]. In 1994, we found a new type of topochemical polymerization of diethyl (*Z,Z*)-muconate to give an ultrahigh molecular weight and stereoregular polymer [2]. The polymerization proceeds for various 1,3-diene monomers including the ester and alkylammonium derivatives of (*Z,Z*)- or (*E,E*)-muconic and sorbic acids (Scheme 1).

We have reported the feature and mechanism of the polymerization and the characterization of the obtained polymer crystals including application to organic intercalation reactions [3–9]. Recently, single crystal structures have been revealed for various diene monomers and a relationship between the crystal structure of monomers, that is, molecular packing in the monomer crystals and photoreactivity has been investigated [10]. During the course of the studies on the topochemical polymerization of ammonium derivatives of 1,3-diene carboxylic acids [6,7], we have found the importance of π-π stacking and CH-π interaction of aromatic rings as well as the formation of two-dimensional hydrogen bond network for the construction of molecular packing in the crystals, appropriate for the topochemical polymerization. In this paper, we describe the design of crystal structures



$X = X' = CO_2C_2H_5$, $\overset{-}{CO_2}\overset{+}{N}H_3$benzyl, $\overset{-}{CO_2}\overset{+}{N}H_3(CH_2)_{n-1}CH_3$ $(10 \leq n \leq 18)$

$X = \overset{-}{CO_2}\overset{+}{N}H_3CH_2$naphthyl, CO_2CH_3, CH_3; $X' = \overset{-}{CO_2}\overset{+}{N}H_3CH_2$naphthyl

SCHEME 1

of 1-naphthylmethylammonium salts of unsaturated carboxylic acids for topochemical polymerization. We also refer to the crystal structure and molecular packing of several vinyl monomers.

RESULTS AND DISCUSSION

We have investigated relationship between the molecular packing in the crystals and the polymerization reactivity based on the single crystal structure analysis of the diene monomers [6–8]. Figure 1 shows the crystal structure of 1-naphthylmethylammonium sorbate, as well as the stacking manner of aromatic rings in the crystal.

The sorbate anions and naphthylmethylammonium cations are arranged to make each layer structure in the crystal, as shown in (Fig. 1(a)). The layers are tightly connected each other by two-dimensional hydrogen bond network, in which the primary ammonium cations and the carboxylate anions act as the triple hydrogen bond donors and triple hydrogen bond

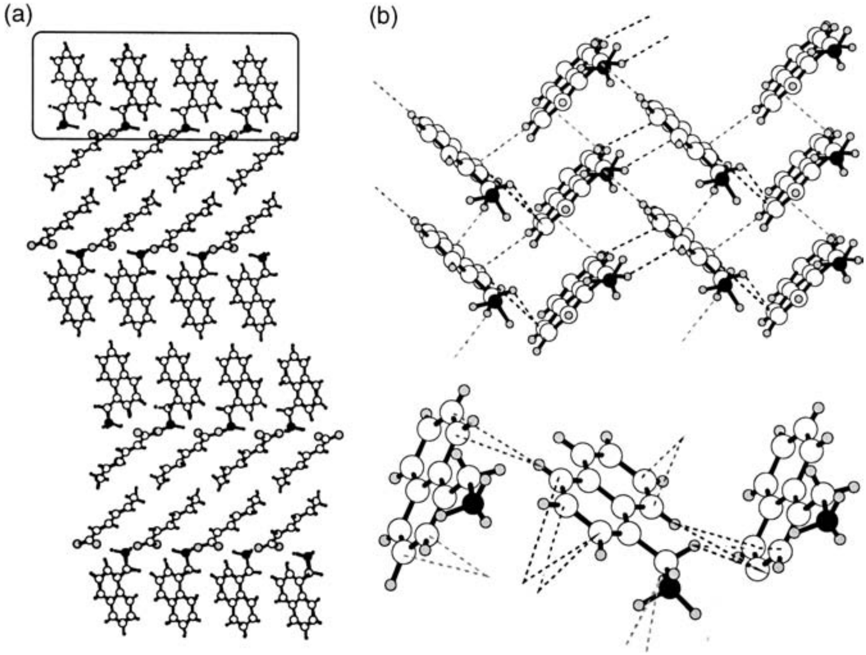


FIGURE 1 (a) Crystal structure of 1-naphthylmethylammonium sorbate viewed down along the *b* axis. (b) CH-π interaction between the naphthylmethylammonium groups in the ammonium cation layers of the crystal.

acceptors, respectively. The naphthalene rings are packed in a herringbone style with the aid of weak intermolecular interaction of π-π stacking and CH-π interaction [11,12] (Fig. 1(b)). Both aromatic and benzylic protons take a role for the CH-π interaction to the face of aromatic rings. Similar crystal structure is observed for not only the sorbate as the diene monomer but also some vinyl monomers. Figure 2 shows the crystal structure of 1-naphthylmethylammonium salts of crotonate, tiglate, and methacrylate. These unsaturated carboxylates are β-methyl-, $\alpha\beta$-dimethyl-, and α-methyl-substituted acrylic acid derivatives, respectively.

Table 1 summarizes the C-C distance for the close contacts between the naphthalene rings each other or the naphthalene ring and methylene group through CH-π interaction in the crystals of the naphthylmethylammonium salts of unsaturated carboxylic acids. The vinyl and diene groups are arranged in a similar fashion in the lamellar crystals due to the similar fashion of two-dimensional hydrogen bond network and naphthyl packing. The methylene protons contact to the 2- and 3-carbons of the naphthalene

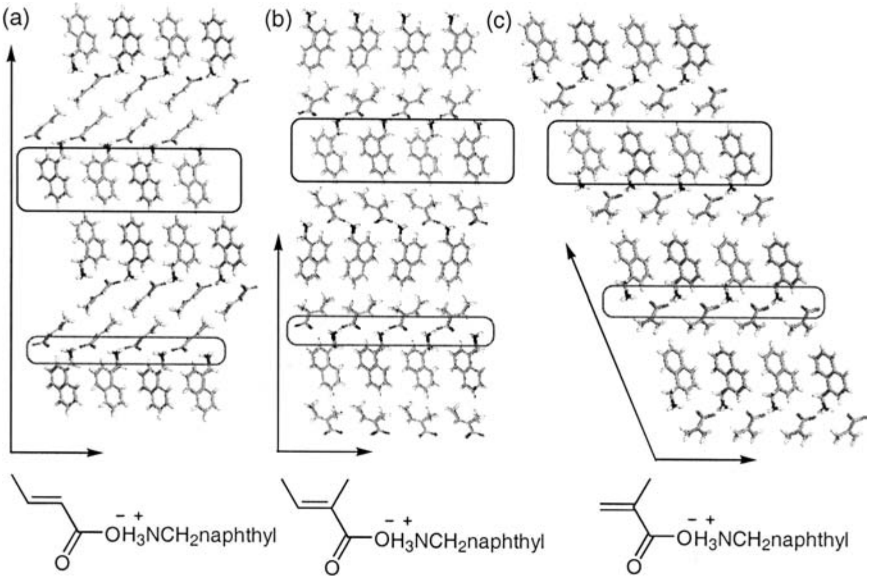


FIGURE 2 Crystal structure of 1-naphthylmethylammonium salts of α- and β-methyl-substituted acrylic acids: (a) crotonate, (b) tiglate, (c) methacrylate. In the crystals, similar interlayer two-dimensional hydrogen bond network and the stacking of naphthyl groups in the cationic layers are observed independent of the number and position of the methyl substituent on the double bond.

TABLE 1 Close C(sp_2)-HC Contacts for Structural Units Regarding CH-π Interaction in the Crystals of 1-Naphthylmethylammonium Salts of Unsaturated Carboxylic Acids

	C-C Distance for $C_{naphthyl} \cdots H\text{-}C_{naphthyl}$ (Å)			
Monomer	C(7)-HC(4)	C(8)-HC(4)	C(3)-HC(8)	C(4)-HC(8)
Sorbate	>4.0	3.90	4.00	3.74
Crotonate	>4.0	3.80	3.90	3.67
Tiglate	>4.0	3.84	>4.0	3.81
Methacrylate	3.79	3.66	3.94	3.81
	C-C Distance for $C_{naphthyl} \cdots H\text{-}C_{methylene}$ (Å)			
Monomer	C(2)-HC(m)	C(3)-HC(m)	C(2)-HC(m′)	C(3)-HC(m′)
Sorbate	3.70	3.61	3.89	3.70
Crotonate	3.64	3.55	3.88	3.72
Tiglate	3.61	3.59	4.01	3.74
Methacrylate	3.59	3.51	3.96	3.76

ring in forming a stable aromatic stacking. The 4- and 8-carbons and protons also closely contact to each other.

Recently, Sada *et al.* [13] pointed out the prominent ability of the arrangement of various aliphatic carboxylic acids into lamellar sheet structures, of which the thickness is determined by the combination of several carboxylic acids with different alkyl chains lengths. The hydrogen bond network, the stacking of the naphthalene rings, and the alkyl chain packing support the robust lamellar structure. It would be very useful for the design of organic and crystalline materials with a layer structure.

A stacking structure in the monomer crystals is evaluated with the following four parameters; the intermolecular carbon-to-carbon distance between the double bonds that react during the topochemical polymerization (d_{cc}) and the stacking distance (d_s), as well as the angles between the stacking direction and the molecular plane. We have revealed the importance of the d_s values for the process of the topochemical polymerization for several diene monomers including the ester and ammonium derivatives of muconic and sorbic acids. Namely, when the d_s value is close to the length of the repeating unit of polymer chains, i.e., a fiber period with a fully stretched conformation, topochemical polymerization would proceed successfully with less strain in the crystals.

Table 2 shows the results of the photoreaction of the diene and vinyl monomers in the crystalline state under UV irradiation together with the molecular stacking parameters. The d_{cc} value is 4.99, 4.63, 4.83, and 3.91 Å

TABLE 2 Photoreaction Products and Stacking Parameters for Naphthylmethylammonium Salts of Unsaturated Carboxylic Acid Monomers in the Crystalline State

Monomer	Photoproduct[a] (Yield, %)	d_s (Å)	d_{cc} (Å)
Sorbate	Tritactic polymer (98)[b]	4.99	5.37
Crotonate	No reaction	4.92	4.63
Tiglate	No reaction	4.76	4.83
Methacrylate	No reaction	4.82	3.91

[a] Photoirradiation conditions: With a high-pressure mercury lamp (100 W) in a distance of 10 cm at room temperature. The polymer was isolated as the insoluble product in methanol. The structure and conversion of the produced geometrical isomer were determined by ^{1}H NMR spectroscopy.

[b] Ref. 7.

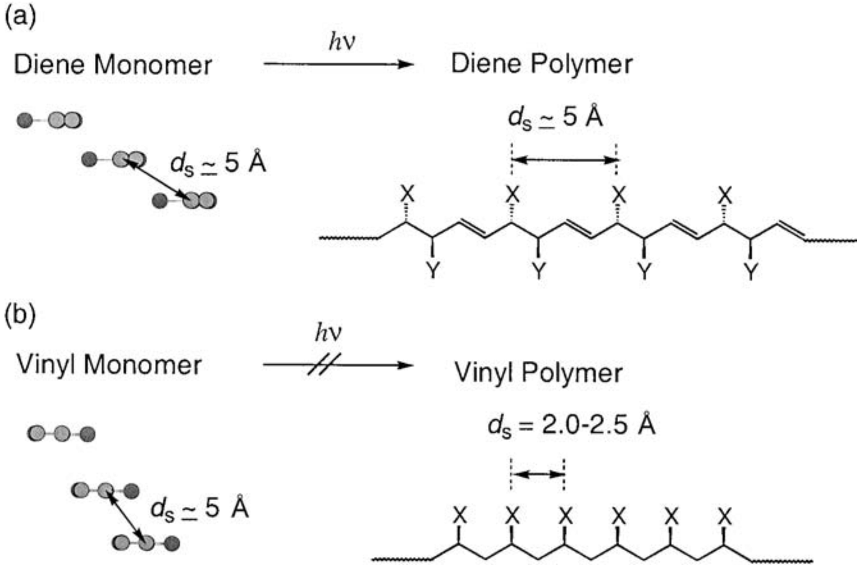


FIGURE 3 A model of molecular stacking and topochemical polymerization reactivity for (a) diene and (b) vinyl monomers. When the stacking distance of monomers in the crystal is equal to the fiber period of the produced polymer, polymerization proceeds to give a high molecular weight polymer via a topochemical reaction mechanism without any movement of the molecular mass of monomer molecules.

for the sorbate, crotonate, tiglate, and methacrylate derivatives, respectively, while the d_s value is 4.8–5.0 Å independent of the structure of unsaturated moieties. No photopolymerization ability of the vinyl compounds is different from the high polymerization reactivity of the diene monomer, despite the similar stacking structure in the crystals and a shorter C-C distance rather than that for the sorbate. This result is consistent well with the consideration from the characteristics of topochemical polymerization in the crystalline state. When the stacking distance of monomer molecules in the crystal is equal to the fiber period of the produced polymer, polymerization readily proceeds with the minimum movement of the molecular mass of monomer molecules. Because a fiber period for vinyl polymers is shorter than that for diene polymers (Fig. 3), closer stacking is required for molecular packing to achieve the topochemical polymerization of vinyl monomers. Unfortunately, however, such a closer molecular stacking is not obtained according to the present strategy using aromatic stacking and hydrogen bond network formation. An alternating strategy using any other supramolecular synthon would possibly realize the topochemical polymerization of vinyl monomers in future.

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