Solid-state Photopolymerization of Diacetylene-containing Carboxylates with Naphthylmethylammonium as the Countercation in a Two-dimensional Array

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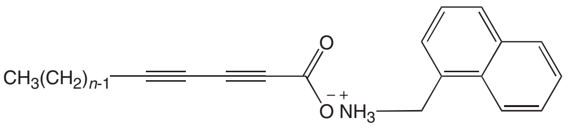
(Received October 16, 2003; CL-030979)

Naphthylmethylammonium salts of a series of diacetylene-containing carboxylic acids with various sizes of alkyl chains were photopolymerized in the crystalline state. X-ray crystal structure analyses confirmed lamellar structures characterized with the two-dimensional hydrogen networks formed between carboxylate anion and countercation layers in the crystals. The absorption properties of the resulting polymers depended on the length of alkyl substituents.

Polydiacetylenes are formed by the polymerization of diyne monomers in self-assemblies such as crystals, liquid crystals, monolayers, Langmuir–Blodgett films, and vesicles.[1] Because a change in the chain conformation of the resulting polymers can be monitored by a change in the color of the solids, polydiacetylenes are used as sensors against any stimuli using their characteristic fluorescence property to biomedical and physical applications. However, the polymerization of 3-D bulk crystals still involves difficulty to exactly predict their polymerization reactivity from the chemical structure of monomers,[2] differing from the promised polymerization of a large number of long-alkyl chain compounds as the mono- and multi-layered self-assemblies.[3] Recently, we have reported that topochemical polymerization principles and the design of the monomer stacking using supramolecular synthons for the polymerization of 1,3-diene monomers.[4–6] The most sophisticated molecules include the naphthylmethylammonium group as the countercation of diene carboxylates appropriate for the rational design and control of the arrangement of monomer molecules in the crystals. Although a stacking requirement for the monomer molecules of diacetylenes is expected to be similar to that for diene monomers during topochemical polymerization,[5] it has not been confirmed whether supramolecular synthons developed for the diene polymerization are also available for the diyne polymerization or not. To clarify this point, we synthesized variously sized linear carboxylic acids containing a diacetylene moiety (Scheme 1), and carried out the solid-state polymerization of their naphthylmethylammonium derivatives. Consequently, we have confirmed that the naphthylmethylammonium cation is useful as the supramolecular building block for the crystalline-state polymerizations of diene as well as diyne compounds through formation of the salts. The successful polymerization of not only diacetylenes with a long alkyl-chain as the substituent but also short-alkyl derivatives has revealed a change in the absorption properties of the resulting polymers, depending on the length of alkyl substituents.



1 ($n = 3$), **2** ($n = 4$), **3** ($n = 6$), **4** ($n = 8$), **5** ($n = 10$), **6** ($n = 12$), and **7** ($n = 16$)

Scheme 1.

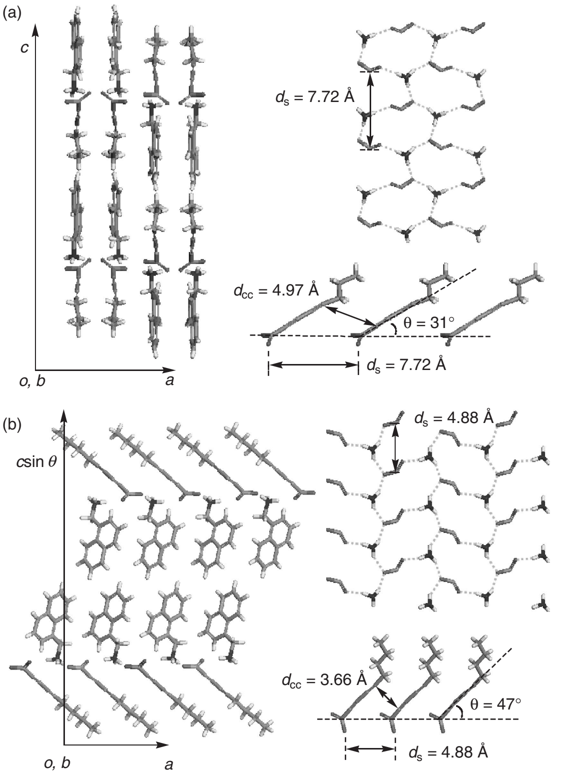


Figure 1. Views down along the *b*-axis of the crystals, hydrogen bond networks in *ab* plane, and monomer stacking structures in a column formed in a direction of the *b*-axis for **1** (a) and **2** (b).

The precursor unsaturated carboxylic acids are oily when the alkyl substituent chain is short ($n = 3$–10), but all the naphthylmethylammonium salts are isolated as the colorless crystals. Recrystallization of **1** and **2** from methanol provided single crystals as the plate or needle forms,[7] respectively, but the longer alkyl derivatives **3**–**7** were isolated as the crystalline powders. Figure 1 shows the crystal structures of **1** and **2**. The molecular packing and the structure of 2-D hydrogen bond network for **2** are similar to those for the crystals of diene carboxylic ammoni-

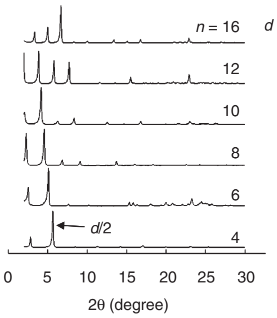


Figure 2. Powder X-ray diffraction profiles of **2**–**7** ($n = 4$–16) [Cu K_α].

ums previously reported.[6] In the crystal of **2**, the monomer molecules are arranged in a column with a stacking distance and angle of 4.88 and 47°, respectively, which are appropriate values for the polymerization of diyne compounds. In contrast, the monomer stacking structure for **1** has been revealed to differ from those for not only **2** but also the other alkylammonium salts of muconic and sorbic acids. In the previous work, we classified the pattern of the hydrogen bond networks into several kinds of ladder or sheet structures for sorbates and muconates.[6c] The monomer stacking structure of **1** was not suitable to the polymerization ($d_s = 7.72$ Å and $\theta = 31°$).

The stacking structure of the monomers **2**–**7** was estimated from interlayer distance (d) in the powder X-ray diffraction (Figure 2). The d-values linearly increased with an increase in the alkyl-chain length. A linear relationship between the n and d values suggests that an alkyl chain structure inclined to lamellar sheets with a tilt angle of ca. 45°, based on an increment along with an increase in the n number (0.89 Å per a carbon). This value is similar to the other layered crystals of saturated and unsaturated carboxylic acids coupled with the naphthylmethylammonium,[8,9] indicating the intense power of this countercation as well as the alkyl-chain packing for molecular arrangement on the 2-D grid of hydrogen bond networks.

The crystals of **2**–**7** colored to red, purple, or blue on UV- and γ-ray irradiation, as was expected from the crystal structure, while **1** was inert. The polymerization reactivity was deduced from a reduction in the intensity of the peak due to the stretching of asymmetric diyne moiety at 2243 cm^{-1}. The conversion was 18–48% for 2 h UV irradiation and independent of the length of the alkyl substituents. The wavelength of maximum absorption observed at an initial stage of the polymerization depended on the n value (Figure 3). When the n value decreased, the absorption was observed at a shorter wavelength region for the crystals of the short alkyl-chain derivatives ($n < 10$). We further confirmed that the absorption property of polydiacetylenes was dependent on the length of alkyl spacers inserted between the diyne moiety and carboxylate group. We are continuing further investigation on the control of polymerization reactivity and polymer properties of diacetylene-containing carboxylic acid with naphthylmethylammonium as the countercation. The 2-D molecular array would be also applied to the design of solid-state polymerization in any other systems including self-assemblies such as LB film and vesicles.

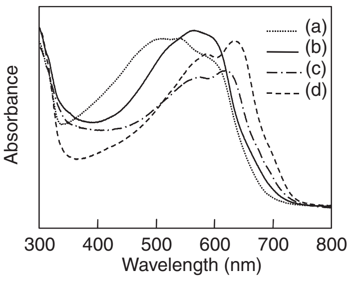


Figure 3. UV and visible absorption spectra of the polydiacetylenes obtained from (a) **2** ($\lambda_{\max} = 537$ nm), (b) **3** ($\lambda_{\max} = 565$ nm), (c) **5** ($\lambda_{\max} = 618$ nm), and (d) **7** ($\lambda_{\max} = 634$ nm). The spectra were recorded by the diffusion reflectance method.

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7 **1**: $C_{19}H_{19}NO_2$, 293.36, orthorhombic, *Pbca*, $a = 14.13(5)$ Å, $b = 7.72(3)$ Å, $c = 30.4(1)$ Å, $V = 3320.2(2)$ Å^3, $Z = 8$, $D_{\text{calcd}} = 1.174$ g cm^{-3}, unique reflns 3825, no obsd ($I > 2\theta(I)$) 385, $R = 0.065$, $R_w = 0.122$, GOF = 0.994, 23 °C. **2**: $C_{20}H_{21}NO_2$, 307.39, monoclinic, $P2_1/a$, $a = 11.231(5)$ Å, $b = 4.881(2)$ Å, $c = 31.21(1)$ Å, $\beta = 90.50(2)°$, $V = 1710(1)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.193$ g cm^{-3}, unique reflns 3076, no obsd ($I > 2\theta(I)$) 935, $R = 0.142$, $R_w = 0.322$, GOF = 2.999, 23 °C.

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Published on the web (Advance View) December 27, 2003; DOI 10.1246/cl.2004.96