SHORT COMMUNICATIONS

Stereoregular Photopolymerization of Di(benzylammonium) Muconate in the Crystalline State

Akikazu MATSUMOTO,[†] Toru ODANI, and Shuzo AOKI

Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

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In recent years, photoreactions in organic crystals have been intensively investigated because the reaction under lattice control affords high regio- and stereoselectivities, being different from the reactions in an isotropic medium.^{1,2} Topochemical polymerization is the promising method for the synthesis of polymers with highly controlled stereochemical structures.^{3,4} However, despite many efforts, successful results have been limited to only the following two polymerizations: [2 + 2] photopolymerization of diolefin compounds such as distyrylpyradine *via* stepwise propagation mechanism⁵ and radiation or thermal polymerization of diacetylene derivatives through a chain reaction mechanism.⁶ In 1994, we discovered the crystalline-state radical polymerization of diethyl (Z,Z)-muconate (diethyl (Z,Z)-hexadienedioate),^{7,8} which would be regarded as the third example of topochemical polymerization of monomer crystals. It has already been revealed that the polymerization proceeds uniquely for diethyl (Z,Z)-muconate to give *meso*-diisotactic-*trans*-2,5-polymer, *i.e.*, the crystals of other alkyl esters of the (Z,Z)-isomer and of the ethyl esters of the (E,Z)- and (E,E)-isomers gave no polymer in contrast to the high polymerization reactivity of the diethyl ester with the (Z,Z)-configuration, suggesting that the topochemical polymerization reactivity is strictly determined by the crystal structure of the monomers.^{8,9} We started to seek the polymerizable crystals of the muconic acid derivatives other than the ester, and selected the ammonium salts as candidates because of the merits of facile monomer synthesis, the high melting point of the monomer crystals, the variety of the crystal structures of the monomers depending on the structures of the amines, and the possibility of transformation to other derivatives after polymerization. Eventually we have found that the crystal of the benzylammonium salt of (Z,Z)-muconic acid provides a crystalline polymer as the photoproduct under UV irradiation, while some derivatives underwent isomerization to the (E,E)-isomers under identical conditions. In this communication, we describe the photoreaction behavior of several di(alkylammonium) (Z,Z)-muconates and the structure and some properties of the resulting polymer from the benzyl derivative.

Di(alkylammonium) (Z,Z)-muconates were obtained from the reaction of (Z,Z)-muconic acid with the cor-

responding alkylamine in methanol at room temperature and isolated by precipitation with diethyl ether in over 95% yield.¹⁰ They were recrystallized from alcohols or acetone–water mixture to afford thin needles, which melted at 120–180°C with decomposition to the acid and the corresponding amine. When the monomer crystals were irradiated under sunlight for 3 days at room temperature, we found that these derivatives favored different reaction paths respective to the structure of the *N*-alkyl group as shown in Scheme 1. The *n*-butyl and isopropyl derivatives isomerized to (E,E)-isomers in 21 and 13% conversion, respectively, whereas the decyl, cyclohexyl, and 1-phenylethyl derivatives were inert to photoirradiation. These findings were different from the results of thermal isomerization; they were isomerized to the corresponding (E,Z)-isomers in the aqueous solution on heating. The exclusive formation of the (E,E)-isomers suggests that the isomerization of the (Z,Z)-form to the (E,E)-form occurs *via* one step during the photoirradiation in the solid state, probably with concerted intramolecular motion through 1,4-biradical formation by the photoirradiation. The photochemical *EZ*-isomerization of α,β -unsaturated acid derivatives in the solid state is also reported to depend significantly on the structure of the ammonium parts.¹¹

In the reaction of the crystals of the benzyl derivative, another product was isolated in 21% yield, which is insoluble in water, methanol, chloroform, tetrahydrofuran, toluene, dimethylformamide, dimethyl sulfoxide, trifluoroacetic acid, and hexafluoro-2-propanol as well as conc. H₂SO₄, dil. HCl, and NaOH aqueous solution. This photoproduct did not melt below its onset temperature of the decomposition. The water-soluble part was confirmed by NMR spectroscopy to be an unreacted monomer. In the IR spectrum of the insoluble product, the absorbance at 1580 cm⁻¹ due to the diene structure was not observed, and the characteristic peak due to the *trans*-CH=CH was detected at 980 cm⁻¹. The peak of the carbonyl stretching was shifted to the higher wavenumber region. These results support the formation of a polymer with *trans*-2,5-structure among possible structures as the repeating units shown in Scheme 1.

The polymerization proceeded under irradiation with a high-pressure mercury lamp as well as sunlight irrespective of the atmosphere, and the polymer yield increased with the increases in the irradiation time and the temperature (Table I). Figures 1(a) and (b) show the

[†] To whom all correspondence should be addressed.

Scheme 1.

Table I. Photopolymerization of di(benzylammonium) (*Z,Z*)-muconate with high-pressure Hg lamp

Temperature °C	Atmosphere	Time h	Yield %
0	In air	24	2
30	In air	8	19
50	In air	8	75
50	In a degassed Pyrex tube	2	18
50	In a degassed Pyrex tube	8	65
50	In a degassed Pyrex tube	12	81
80	In air	4	82

powder X-ray diffraction profiles of the monomer and the polymer, respectively, which was isolated in 81% yield by the removal of the unreacted monomer with methanol after the photoirradiation. The intensive diffractions with interplanar spacings different from those of the monomer were detected from the polymer, indicating that this polymerization proceeds *via* a crystal-to-crystal reaction process.

When the polymer was immersed in dil. HCl aqueous solution at room temperature, it was quantitatively converted to poly(muconic acid) despite the heterogeneous reaction, *i.e.*, the polymer was throughout insoluble during the reaction. The resulting polyacid was also insoluble in any organic or aqueous solvents, whereas atactic poly(muconic acid) is soluble in alkaline solution as well as in some polar organic solvents.¹² The poly(muconic acid) thus obtained was further transformed to the ammonium salts again by immersion in the methanol solution of the corresponding amines, although the esterification with diazomethane failed. The benzyl ammonium polymer obtained after the polymer reaction was revealed to remain the crystalline structure, as shown in Figure 1(c), and show the solubility similar to the original polymer. We also succeeded in the preparation of soluble polymers as the other alkyl-ammonium salts by the transformation. The single and sharp resonances in the ¹³C NMR spectrum of poly-(bis(triethylammonium) muconate) indicate the highly

Figure 1. Powder X-ray diffraction profiles of (a) di(benzylammonium) (*Z,Z*)-muconate monomer, (b) its polymer after removal of the unreacted monomer (conversion 81%), and (c) poly(di(benzylammonium) (*Z,Z*)-muconate) derived through the polymer reaction (see the text). Cu-*K*_α, 30 kV, 20 mA, scan speed 1 deg min⁻¹. **Figure 2.** ¹³C NMR spectrum of poly(bis(triethylammonium) (*Z,Z*)-muconate) prepared by the solid-state polymer reaction of poly((*Z,Z*)-muconic acid) with triethylamine in methanol at room temperature. Measurement solvent: methanol-*d*.

controlled stereochemical structure of the repeating units of the polymer (Figure 2), *i.e.*, *meso*-2,5-*trans*-structure similar to poly(diethyl (*Z,Z*)-muconate).^{8,9} The viscosity measurement of the soluble polymers confirmed the ultra-high molecular weight polymer formation; for example, $[\eta] = 1.27 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$ in 0.5 mol L⁻¹ NaCl aqueous solution at 30°C for the *n*-propylammonium polymer. The details of the reversible transformation between the ammonium salts and the acid are now under investigation.

The transformation to the acid was also achieved by thermal process. When the polymer as the ammonium salt was subjected to thermogravimetric analysis in a nitrogen atmosphere with a heating rate of 10°C min⁻¹, the weight loss started at *ca.* 150°C and the residual weight at 260°C was 52%, which agrees with the cal-

culated value for the elimination of benzylamine. The ammonium polymer was transformed to the acid by heating at 200°C for 1 h *in vacuo*, being confirmed by IR spectroscopy. The resulting poly(muconic acid) decomposed over 350°C.

In conclusion, we discovered the novel photopolymerization of di(benzylammonium) muconate in the crystalline state to yield a crystalline polymer which has a highly regulated stereochemical structure. The polymer as the crystals obtained in this work would be useful as starting materials to design the various functional polymer crystals through polymer reaction.

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REFERENCES AND NOTES

1. Y. Ohashi, "Reactivity in Molecular Crystals," Ed., Kodansha-VCH, Tokyo, 1993.
2. V. Ramamurthy, "Photochemistry in Organized and Constrained Media," Ed., VCH, New York, N.Y., 1991.
3. G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971).
4. G. Wegner, *Pure Appl. Chem.*, **49**, 443 (1977).
5. M. Hasegawa, *Adv. Phys. Org. Chem.*, **30**, 117 (1995); *Adv. Polym. Sci.*, **42**, 1 (1982).
6. H. Bässler, *Adv. Polym. Sci.*, **63**, 1 (1984); H. Sixl, *ibid.*, **63**, 49 (1984); V. Enkelman, *ibid.*, **63**, 91 (1984).
7. A. Matsumoto, T. Matsumura, and S. Aoki, *J. Chem. Soc., Chem. Commun.*, 1389 (1994).
8. A. Matsumoto, T. Matsumura, and S. Aoki, *Macromolecules*, **29**, 423 (1996).
9. A. Matsumoto, K. Yokoi, S. Aoki, K. Tashiro, T. Kamae, and M. Kobayashi, *Macromolecules*, in press.
10. Di(benzylammonium) (Z,Z)-muconate: mp 140–143°C with decomposition (acetone/H₂O = 5/1 in vol.); ¹H NMR (D₂O, 400 MHz) δ 7.34 (m, 10H, Ar), 6.79 (m, 2H, CH=CH-CH=CH), 5.82 (m, 2H, CH=CH-CH=CH), 4.05 (m, 4H, CH₂); ¹³C NMR (D₂O, 100 MHz) δ 176.41 (C=O), 131.31 (CH=CH-CH=CH), 130.06 (CH=CH-CH=CH), 133.46, 130.27, 130.06, 129.66 (Ar), 43.94 (CH₂); IR (KBr) $\nu_{C=O}$ 1500, $\nu_{C=C=C}$ 1580 cm⁻¹; UV (H₂O) λ 257 nm (ϵ 16,300); *Anal.* Calcd for C₂₀H₂₄N₂O₄ (356.42): C, 67.40%; H, 6.79%; N, 7.86%. Found: C, 67.37%; H, 6.76%; N, 7.77%. Poly(di(benzylammonium) (Z,Z)-muconate): IR (KBr) $\nu_{C=O}$ 1515, $\delta_{trans-CH=CH}$ 980 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%.
11. K. Kinbara, A. Kai, Y. Maekawa, Y. Hashimoto, S. Naruse, M. Hasegawa, and K. Saigo, *Mol. Cryst. Liq. Cryst.*, **276**, 141 (1996).
12. Y. Bando, T. Dodou, and Y. Minoura, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1917 (1977).