Feature of γ-Radiation Polymerization of Muconic Acid Derivatives in the Crystalline State

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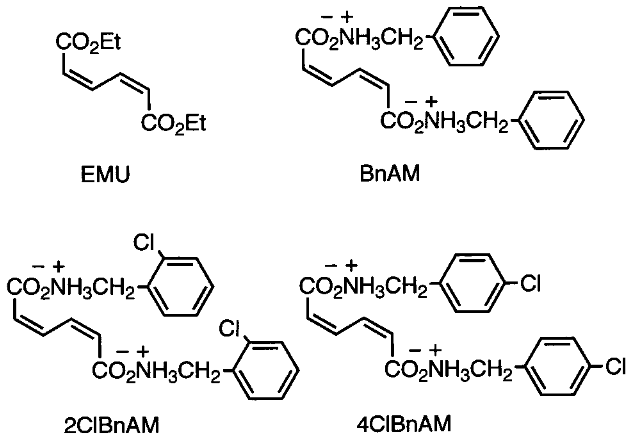
Received October 12, 1999; Revised Manuscript Received April 11, 2000

ABSTRACT: Diethyl *(Z,Z)*-muconate (EMU), di(benzylammonium) *(Z,Z)*-muconate, and its chloro-substituted derivatives are highly susceptive to γ-irradiation and polymerize in high yields in the crystalline state. γ-Radiation polymerization produces the same stereoregular polymer consisting of *meso*-diisotactic-2,5-*trans*-repeat unit, as that obtained by photopolymerization in the crystalline state. The polymer yield increases with an increase in a radiation dose, but the resulting polymer decomposes during γ-irradiation at high radiation doses. The effects of the radiation dose rate and the postpolymerization on the polymer yield were negligible for the γ-irradiation polymerization at room temperature, while the polymer yield decreased with the decrease in the crystal size and the polymerization temperature. The single-crystal structure analysis of the polymer crystal confirmed the topochemical polymerization process of the γ-radiation polymerization.

Introduction

Organic synthesis in the solid state is the most strikingly growing field of chemistry in recent years because of distinguished selectivity in the reactions, the specific morphology of the products in the solid state, and the environmental aspects of solvent-free processes.[1−5] Many examples of solid-state polymerization yielding crystalline polymers have been reported, but there are very few examples of polymerization that proceed via a topochemical reaction mechanism.[6−9] When the monomer crystals as the starting materials are converted into the polymer crystals as the products by any stimuli such as thermal or light, the symmetry of the crystal lattice of the monomers does not change during the topochemical polymerization.[10−15] Consequently, the structure of the product crystals is estimated from the structure of the starting monomer crystals. Topochemical polymerization is a convenient and unique method for the fabrication of polymer crystals, in which the polymer chains are aligned in a completely stretched conformation. In 1994, Matsumoto et al.[16] discovered that the crystals of diethyl *(Z,Z)*-muconate (EMU) are polymerized topochemically on exposure of the EMU monomer crystals to UV light, although the examples of the topochemical polymerization have been limited to some special monomers discovered in the late 1960s.[11−15] To clarify the mechanism and features of the crystalline-state polymerization of EMU, the structural change in the crystals during the polymerization process was investigated by means of time-resolved X-ray diffraction measurements, as well as infrared and Raman spectroscopies and differential thermal analysis.[17−19] Similar topochemical polymerization of other muconic acid derivatives such as di(alkylammonium) *(Z,Z)*-muconates was also found.[20−22] On the basis of the fact that the polymerization of these monomers also proceed by X-ray irradiation,[11] we started to study the γ-ray-induced polymerization of the muconic acid derivatives. A high efficiency of the solid-state polymerization was expected because of the high energy and excellent penetration properties of γ-rays.[23,24] In this paper, we report the γ-radiation polymerization of EMU, di(benzylammonium) *(Z,Z)*-muconate (BnAM), and its chloro-substituted derivatives (2ClBnAM and 4ClBnAM) in the crystalline state (Scheme 1).

Scheme 1



Experimental Section

Materials. The monomers were prepared as described previously.[17,22] EMU and the other monomers were recrystallized from hexane and methanol, respectively. The EMU microcrystals were prepared by freeze-drying with benzene.[25]

EMU: mp 54 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.89 (m, C*H*=CHCO$_2$Et, 2H), 5.97 (m, CH=C*H*CO$_2$Et, 2H), 4.21 (q, *J*

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10.1021/ma9917038 CCC: $19.00

= 7.3 Hz, CH_2, 4H), 1.31 (t, J = 7.3 Hz, CH_3, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.66 (C=O), 137.80 (CH=), 124.20 (CH=), 60.39 (CH_2), 14.17 (CH_3). IR (KBr): 1716 ($\nu_{C=O}$), 1593 cm^{-1} ($\nu_{C=C}$). UV (cyclohexane): λ_{max} 259 (ϵ = 21 300), 280 nm (sh).

BnAM: mp 134 °C (decomposition). ^1H NMR (400 MHz, D_2O): δ 7.32 (m, Ar, 10H), 6.80 (m, C*H*=CHCO$_2$, 2H), 5.82 (m, CH=C*H*CO$_2$, 2H), 4.05 (s, CH_2, 4H). ^{13}C NMR (100 MHz, D_2O): δ 176.45 (C=O), 133.46 (Ar), 131.31 (C=C), 130.27 (Ar), 130.06 (Ar), 130.06 (C=C), 129.66 (Ar), 43.94 (CH_2). IR (KBr): 1586 ($\nu_{C=C}$), 1506 ($\nu_{C=O}$) cm^{-1}. UV (H_2O): λ_{max} 257 nm (ϵ = 16 300).

Di(2-chlorobenzylammonium) *(Z,Z)*-muconate (2ClBnAM): mp 129 °C (decomposition). ^1H NMR (400 MHz, D_2O): δ 7.28–7.46 (m, Ar, 8H), 6.82 (m, C*H*=CHCO$_2$, 2H), 5.84 (m, CH=C*H*CO$_2$, 2H), 4.22 (s, CH_2, 4H). ^{13}C NMR (100 MHz, D_2O): δ 176.51 (C=O), 131.28 (C=C), 130.21 (C=C), 132.02 (Ar), 131.95 (Ar), 131.28 (Ar), 131.03 (Ar), 130.75 (Ar), 128.61 (Ar), 41.67 (CH_2). IR (KBr): 1580 ($\nu_{C=C}$), 1500 ($\nu_{C=O}$) cm^{-1}. UV (H_2O): λ_{max} 259 nm (ϵ = 14 500).

Di(4-chlorobenzylammonium) *(Z,Z)*-muconate (4ClBnAM): mp 130 °C (decomposition). ^1H NMR (400 MHz, D_2O): δ 7.32 (m, Ar, 8H), 6.80 (m, C*H*=CHCO$_2$, 2H), 5.81 (m, CH=C*H*CO$_2$, 2H), 4.04 (s, CH_2, 4H). IR (KBr): 1580 ($\nu_{C=C}$), 1495 ($\nu_{C=O}$) cm^{-1}. UV (H_2O): λ_{max} 259 nm (ϵ = 14 300).

Polymerization. The monomer crystals (typically 50 mg) were charged in a Pyrex tube, degassed, and then sealed. Irradiation was carried out with ^{60}Co. After irradiation, the polymer was isolated by removing the unreacted monomer with chloroform or methanol. The polymer yield was determined gravimetrically as the average of 2–19 runs for each radiation condition (typically 3–5 runs). Photopolymerization was carried out at 50 or 80 °C using a high-pressure mercury lamp (Toshiba SHL-100-2, 100 W) at a distance of 10 cm under atmospheric conditions. The polymer yield was determined similarly.

Poly(EMU) (prepared by γ-radiation polymerization at a dose of 500 kGy): ^{13}C NMR (100 MHz, CF_3CO_2D): δ 176.08 (C=O), 132.25 (C=C), 65.69 (CH_2), 54.44 (CH), 14.68 (CH_3). Elemental analysis: Calcd for $(C_{10}H_{14}O_4)_n$: C, 60.59; H, 7.12. Found: C, 60.51; H, 7.10.

Measurements. The intrinsic viscosity of poly(EMU) was determined in trifluoroacetic acid at 30 °C using an Ubbelohde-type viscometer. The viscosity of poly(BnAM) was determined in 0.5 M aqueous NaCl at 30 °C after converting the polymer to poly(triethylammonium muconate).[22] NMR spectra were recorded on a JEOL JMN A-400 spectrometer. The X-ray diffraction data were collected with a thin crystal (0.15 mm × 0.02 mm × 0.02 mm) using a Kappa CCD system (Nonius) with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The index and the intensity were determined using the program DENZO, and the refinement was carried out using the program maXus.

Results and Discussion

γ-Radiation Polymerization of Muconic Acid Derivatives. Several muconic acid derivatives were γ-irradiated with ^{60}Co in the crystalline state at room temperature to examine their γ-ray-induced polymerizability. Table 1 shows the results of the γ-radiation polymerization at a dose of 1 or 10 kGy (1 kGy = 0.1 Mrad), in comparison with the results of photopolymerization using a high-pressure mercury lamp for up to 8 h. The γ-radiation polymerization of EMU proceeded readily to give an ultrahigh molecular weight polymer in high yield. The γ-radiation polymerization of the ammonium salts of the muconic acid also provided polymers. The polymerization reactivity, deduced from the polymer yield, was in the order of EMU > BnAM ~ 2ClBnAM ≫ 4ClBnAM for both polymerizations induced by γ- and photoirradiations. Generally, halogen-containing organic compounds readily decompose upon γ-irradiation, resulting in complicated γ-radiation products by participation of the reactive halogen atoms formed.[24] However, no degradation products were detected by ^1H NMR spectroscopy after the γ-irradiation of 4ClBnAM under the conditions listed in Table 1. The facile polymerization of 2ClBnAM also suggests that the low polymer yield for 4ClBnAM is due to the lower reactivity of the 4ClBnAM crystals but is not due to the decomposition as a side reaction.

Table 1. Comparison of Yield and Intrinsic Viscosity of the Polymers Produced during γ-Radiation Polymerization and Photopolymerization of Muconic Acid Derivatives in the Crystalline State

	γ-radiation polymerization[a]			photopolymerization[b]		
monomer	dose (kGy)	yield (%)	[η] (dL/g)	time (h)	yield (%)	[η] (dL/g)
EMU	1	72	15.4[c]	1	82	17.3[c]
	10	~100	7.9[c]	4	~100	
BnAM	10	87	0.25[d]	4	84	0.12[d]
2ClBnAM	10	74		4	56	
4ClBnAM	10	8		8	6	

[a] γ-Irradiation at a dose rate of 1.0 kGy/h at room temperature. 1 kGy = 0.1 Mrad. [b] Photoirradiation with a high-pressure mercury lamp at 50 °C for EMU and 80 °C for the other monomers. [c] In trifluoroacetic acid at 30 °C. [d] In 0.5 M aqueous NaCl at 30 °C after converting polymer to poly(triethylammonium muconate).

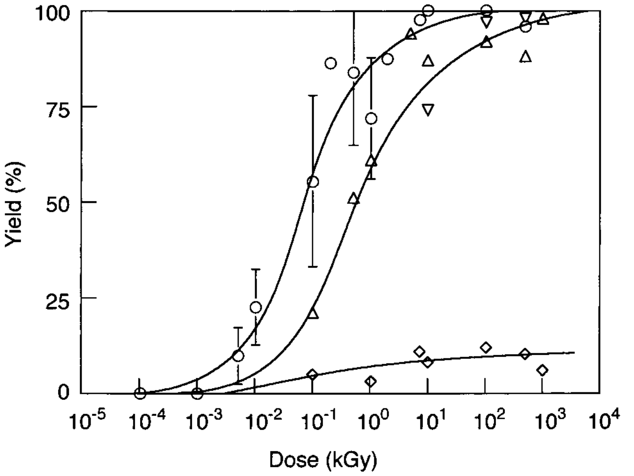

Figure 1. Relationship between irradiation dose and polymer yield during γ-radiation polymerization of several muconic acid derivatives in the crystalline state at room temperature: (○) EMU, (△) BnAM, (▽) 2ClBnAM, (◇) 4ClBnAM. 1 kGy = 0.1 Mrad. The error bars for the EMU polymerization indicate the standard deviations.

The γ-radiation polymerization of other alkyl esters of muconic acid was attempted but failed. For example, no polymer was produced after γ-irradiation of the methyl and cyclohexyl esters, which also do not polymerize in the crystalline state using UV irradiation.[17] The results of the γ-radiation and photoinduced polymerizations indicate that the polymerization reactivity of the muconic acid derivative in the crystalline state is determined by the crystal structure, irrespective of the radiation source.

The dose dependence of the polymer yield was investigated in a wide range of the radiation dose at 10^{-4}–10^3 kGy. Figure 1 shows the relationship between the radiation dose and the polymer yield. Surprisingly, a polymer was produced even upon irradiation of EMU at a small dose of less than 10^{-2} kGy. At an increasing radiation dose, the polymer yield increased and reached a quantitative yield by 10 kGy irradiation. BnAM and 2ClBnAM showed a similar polymerization reactivity, which was lower than that of EMU and much higher than that of 4ClBnAM. The less reactive 4ClBnAM gave a polymer only in ca. 10% yield at a considerably high radiation dose of 10^1-10^3 kGy.

To represent the radiation efficiency, the *G* value is defined as the number of chemical events per 100 eV of absorbed energy: $G =$ (number of formed or decomposed molecules)/(100 eV of energy absorbed).[24] Here, 1 kGy corresponds to 6.28×10^{28} eV/g. In the present case, the *G* values are calculated to be $2 \times 10^5-3 \times 10^6$ for EMU and 6×10^4 for 2ClBnAM from the polymerization results at radiation doses of 0.01–0.1 kGy, which are much higher than the values reported for radical and cationic polymerizations using γ-radiation. In general, the *G* value is known to be less than unity for nonchain reactions and $10-10^2$ for the reactions proceeding by a chain mechanism.[23] The crystalline-state polymerization of these muconate monomers in this work is initiated by radical formation induced by the irradiation and proceeds via a radical chain propagation mechanism to yield a high molecular weight polymer. Therefore, the *G* value based on the number of the polymer chains produced, but not the monomer molecules consumed, was also estimated. The polymerizations of EMU and 2ClBnAM still give large values such as $10-10^3$ when the molecular weight of the resulting polymers is assumed to be 10^5-10^7 on the basis of the intrinsic viscosity values. The absolute molecular weight and polydispersity of these polymers were difficult to determine because of the limited solubility. Poly(EMU) is soluble in trifluoroacetic acid and 1,1,1,3,3,3-hexafluoro-2-propanol but insoluble in any other solvents. Poly(2ClBnAM) is insoluble in all the solvents, being converted to the triethylammonium salt polymer soluble in methanol and water through the solid-state polymer transformation for the determination of intrinsic viscosity values.[22]

Figure 2 illustrates the ^{13}C NMR spectrum of the polymer obtained by the γ-radiation polymerization of EMU in the crystalline state at a dose of 500 kGy. The same *meso*-diisotactic-2,5-*trans* stereoregular polymer is produced, as that prepared by photopolymerization of EMU. The polymer produced by the γ-radiation polymerization at an irradiation dose higher than 10 kGy was slightly colored, but no irregular repeating units were detected in the NMR spectrum. The elemental analysis also provided satisfactory results (see Experimental Section). The coloration remained after precipitation of the polymer, indicating that it was due to chemical change in a part of the polymer chain, but not electron trapping in the crystals or formation of a small molecular byproduct.

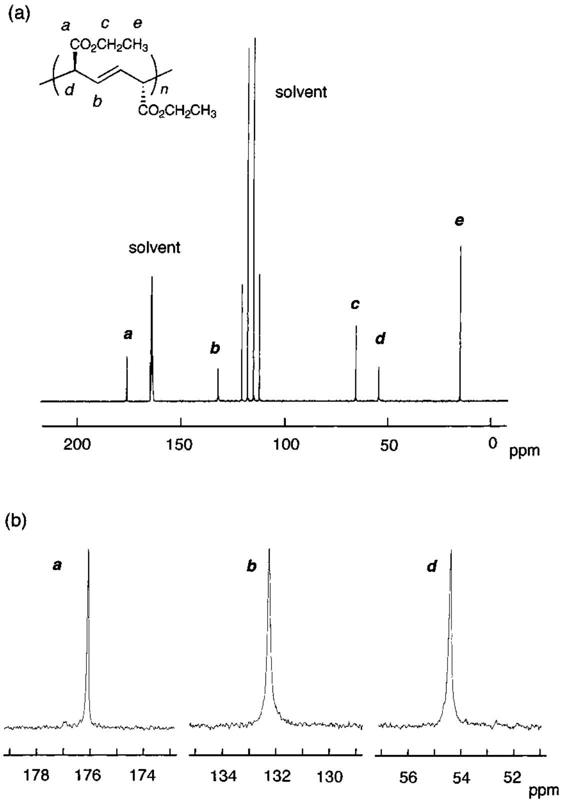

Figure 2. ^{13}C NMR spectrum of poly(EMU) prepared by γ-radiation polymerization in the crystalline state at a dose of 500 kGy. Measurement solvent: trifluoroacetic acid-*d*.

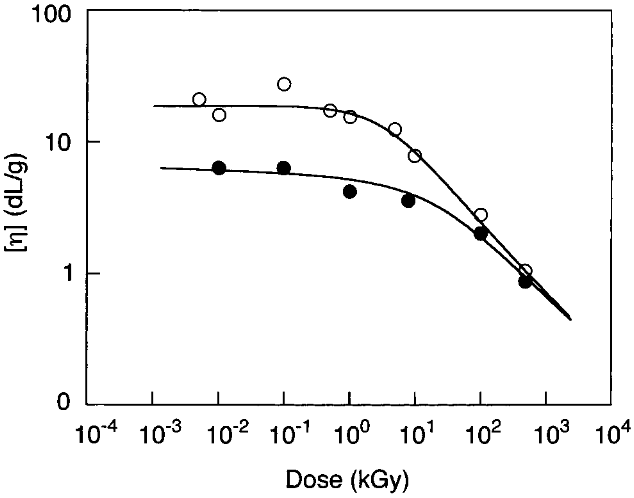

Figure 3. Effect of radiation dose on intrinsic viscosity of poly(EMU): (○) poly(EMU) obtained by γ-radiation polymerization of EMU; (●) γ-irradiation of poly(EMU) prepared by photopolymerization of EMU. $[\eta] = 6.0$ dL/g before irradiation. Measurement solvent: trifluoroacetic acid. Measurement temperature: 30 °C.

The intrinsic viscosity of the polymers produced at various irradiation doses was determined to estimate the molecular weight of the polymers. As shown in Figure 3, an ultrahigh molecular weight polymer ($[\eta] >$ 10 dL/g) was produced during polymerization at a dose rate less than 1 kGy, and the molecular weight was independent of the dose. However, further irradiation resulted in a decrease in the molecular weight of the polymer. In comparison with the dose–yield relationship in Figure 1, it is clear that the decrease in the molecular weight starts after complete polymerization; i.e., the polymer once produced might degrade. Therefore, the polymer prepared by the UV-induced polymerization ($[\eta] = 6.0$ dL/g) was γ-irradiated at various doses in the absence of the monomer, and the intrinsic viscosity of the recovered polymers was evaluated. The $[\eta]$ value was reduced drastically when the polymer was irradiated at a dose higher than 10 kGy, similar to the results of the γ-radiation polymerization. On the basis of the fact that no defect was detected in the polymer irradiated even at a high dose of 500 kGy examined by NMR spectroscopy and elemental analysis, as already

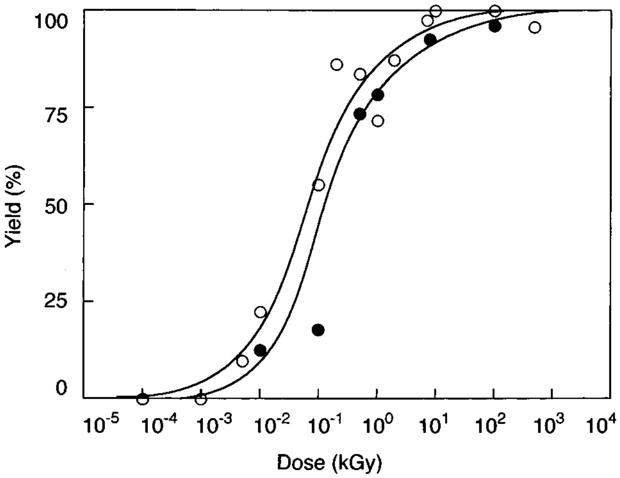

Figure 4. Relationship between radiation dose and polymer yield during γ-radiation polymerization of EMU with different crystal sizes: (●) microcrystals prepared by freeze-drying; (○) large-size crystals prepared by conventional recrystallization.

described, the excess radiation induces predominantly main chain scission, resulting in a decrease in the molecular weight rather than side-chain decomposition.

Effects of γ-Radiation Conditions and Crystal Size. In Figure 1, the error bars represent the standard deviation for the polymer yield for the dose–yield relationship of the EMU polymerization. The distribution of the experimental points was greater than expected. Similar scattered polymer yields were also observed for the UV-induced photopolymerization as previously reported.[18] In the case of the UV-induced polymerization, the incident light is absorbed near the surface of the crystals and the polymerization starts around there. The incident light reaches interior of the crystals as the polymerization proceeds because the polymer is transparent. This mechanism suggests that the crystal shape and photoirradiation conditions influence the initiation efficiency, i.e., the polymer yield. In the γ-radiation polymerization, however, the initiation should occur throughout the crystals because of the excellent penetration of γ-rays.

There are several possibilities as the reason for the distribution of the polymer yield: dose rate dependence, postpolymerization effect, and crystal size dependence of the polymerization reactivity. First, to examine the effect of the dose rate, the EMU crystals were γ-irradiated at a dose of 1.0 kGy at various dose rates of 0.2–4.0 kGy/h. The polymer yield was independent of the dose rate, indicating that the polymer yield is determined by the dose. The postpolymerization does not occur in the dark at room temperature for a given time up to 48 h in this polymerization system.

In the previous work,[25] we fabricated various sizes of the EMU crystals using several methods for the crystal preparation, i.e., recrystallization, milling, freeze-drying, and precipitation. The polymer yield depended on the crystal size during the photopolymerization of the obtained crystals. This is understandable on the basis of the following mechanism of the polymerization. The propagation proceeds very fast via a radical chain mechanism until the active site reaches the edge of the crystal or the lattice defect. Therefore, the amount of the reacting monomers per radical formed depends on the crystal size. In view of this point, the EMU microcrystals were prepared by freeze-drying to test the crystal size effects on the γ-radiation polymerization. The crystal size was approximately 1–100 μm in the length of the needles. Figure 4 compares the polymerization of the microcrystals with the large-size crystals prepared by the conventional recrystallization from hexane (crystal size is ca. 100 μm–10 mm). The polymer yield from the large-size crystals was always higher than that of the microcrystals at any radiation dose. Furthermore, we attempted to sieve the crystals into three classes in sizes of approximately 1–2, 2–5, and >5 mm in the length of the needle crystals to compare the polymerization reactivity. The polymer yield depended on the crystal sizes as summarized in Table 2, even though these crystals were not single crystals and the size is apparent. Thus, the distribution of the polymer yield described in Figure 1 is due to the presence of various sizes of crystals, which were prepared by ordinary recrystallization.

Table 2. Dependence of the γ-Radiation Polymerization on the Crystal Size of EMU[a]

preparation of crystals	approx crystal size (mm)	polymer yield (%)
recrystallized and sieved	>5	96
recrystallized and sieved	2–5	89
recrystallized and sieved	1–2	78
recrystallized	0.1–10	53
freeze-dried	0.001–0.1	18

[a] Polymerization conditions: Dose = 0.1 kGy, room temperature.

Table 3. Temperature Effect on γ-Radiation-Induced Polymerization of EMU

γ-radiation temp[a] (°C)	postpolymerization temp[b] (°C)	polymer yield (%)
−78	−78	3
−78	0	25
−78	0[c]	24
−78	r.t.	25
0	0	53
0	0[c]	58
r.t.	r.t.	53
d	−78	3

[a] Total radiation dose, 0.1 kGy. [b] Postpolymerization time, 1 h. [c] Postpolymerization time, 4 h. [d] Control experiment without γ-radiation.

In contrast with EMU, the size effect of the ammonium salts of muconic acid could not be examined, because of the difficulty of crystal growth to large-size crystals; i.e., the recrystallization of BnAM and 2ClBnAM always provided thin crystals. The difference in the polymerization reactivity between EMU and the ammonium salts in Figure 1 and Table 1 includes the size effects in addition to the substantial difference in the reactivities of each crystal.

The γ-radiation polymerization depends strongly on the temperature. The results are shown in Table 3. When the crystals were γ-irradiated at −78 °C, followed by postpolymerization at the same temperature, a trace amount of the polymer was produced. From the results of a control experiment without γ-irradiation, a small amount of the polymer was formed during the procedures for the crystal preparation and the workup. The γ-radiation at 0 °C increased the polymer yield to 55%, which is similar to the yield obtained at room temperature. When postpolymerization was carried out at 0 °C or room temperature after γ-irradiation at −78 °C, the polymer was obtained in a greater amount (25%), independent of the temperature and time of the post-

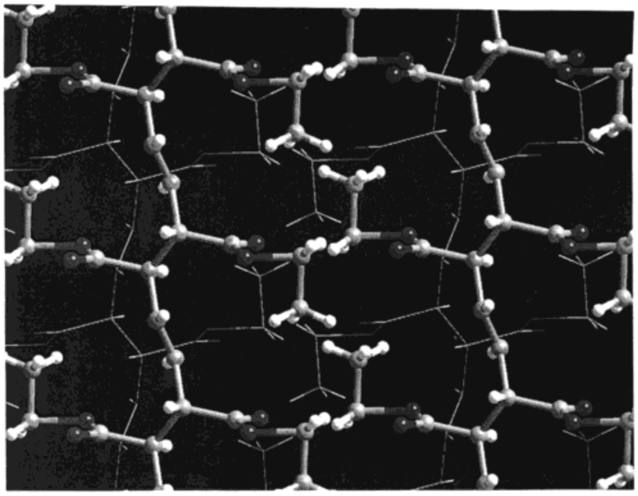

Figure 5. Crystal structure of poly(EMU). Poly(EMU) single crystal was prepared by γ-radiation polymerization at a dose of 2 kGy.

polymerization. γ-Radiation polymerization does not proceed at −78 °C, but the elevated temperature induces postpolymerization. We have already pointed out a possibility of the structural change in the EMU crystals at a low temperature.[19] In the DSC thermogram, a very small endothermic peak ($\Delta H = 8.5$ J/g) due to a crystal-to-crystal transition was detected at −45 °C. This was also supported by the X-ray diffraction measurement of the powdered EMU crystal at various temperatures. Very recently, Tashiro et al. revealed the change in the single-crystal structure of EMU depending on the temperature.[26,27] The EMU crystals above 0 °C are polymerized, while the crystal structure below −45 °C cannot induce the polymerization, because of the difference of the molecular packing in the crystals. On the basis of these results, the radical species that was formed at −78 °C by the γ-irradiation cannot initiate polymerization at −78 °C, but the crystal structural change due to the increasing temperature allows the radicals to be initiated and the subsequent propagation results in a high molecular weight polymer. The polymer yield after the postpolymerization is determined by the number of the radicals trapped in the crystals during the γ-irradiation at −78 °C.

Table 4. X-ray Crystal Structure Analysis of Poly(EMU)s Prepared by γ- and X-ray Radiation Polymerization and EMU Monomer

	polymer crystals		monomer crystal[b]
	γ-radiation[a]	X-ray[b]	
chemical formula	$(C_{10}H_{14}O_4)_n$	$(C_{10}H_{14}O_4)_n$	$C_{10}H_{14}O_4$
shape of crystal	needle	needle	needle
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.3910(8)	10.4030(12)	10.2320(24)
b (Å)	4.8390(7)	4.8410(3)	4.9310(6)
c (Å)	10.9620(15)	10.9920(13)	11.4970(28)
β (deg)	107.6240(10)	107.627(10)	107.146(10)
unit cell vol (Å^3)	525.30(21)	529.8(2)	554.29(2)
Z	2	2	2
D	1.254	1.243	1.188
no. of reflections	1012	990	1067
unique reflections	370	465	402
R	0.071	0.081	0.043
R_w	0.081	0.091	0.120

[a] Prepared by γ-radiation polymerization in this work. [b] Reference 26.

Polymer Single-Crystal Structure. Because of the excellent penetration of the γ-rays into the crystals and the topochemical process of the polymerization, the polymerization should proceed throughout the crystals and there should be fewer defects in the crystals than in the UV polymerization. Therefore, we attempted the X-ray crystal structure analysis of the polymer crystals. The γ-radiation of single crystals of the EMU monomer prepared by recrystallization from hexane was carried out at a dose of 2 kGy at room temperature. We selected polymer crystals with a quality sufficient for crystal structure analysis from a mixture of the polymer crystals, which were prepared by polymerization of the needle-shaped single crystals of the monomer with various sizes and qualities. While large-size crystals of which the length is greater than ca. 1 mm contained cracks or defects after the γ-radiation polymerization, we found transparent and thinner crystals suitable for analysis of the crystal structure. The crystal structure determined is shown in Figure 5. The parameters for the crystal structure analysis are summarized in Table 4 in comparison with the results of poly(EMU) prepared by X-ray irradiation and the EMU monomer.[26] The polymer crystal structure is very similar to that of the EMU monomer crystal, which was recently determined by rapid structure analysis using a CCD camera system as a two-dimensional detector.[26] Both crystals have an identical crystal system and a space group, monoclinic and $P2_1/c$, and both lattice parameters were very similar, evidencing that the γ-radiation polymerization proceeds via the topochemical polymerization mechanism. The crystal lattice parameters determined for the polymer crystals prepared by γ-radiation polymerization in this work also agreed with those for the polymer crystal produced during X-ray irradiation.

Polymerization Mechanism in the Crystalline State. The crystalline-state polymerization of EMU presumably starts by the formation of a radical species, irrespective of the kind of light or ray. In γ-irradiation, an evolved electron can produce a radical anion by reaction with diene moiety. In addition, bond cleavage by the γ-rays results in the formation of carbon or oxygen-centered radicals. These radicals would be formed throughout the crystals during the γ-radiation polymerization, in contrast with the fact that a diradical is formed at a local area near the surface of the crystals by excitation of the monomer at the initial stage of the UV polymerization. Two types of mechanisms have been proposed for the topochemical polymerization in the solid state: heterogeneous and homogeneous reactions.[11−14] In the former, the polymerization starts preferentially at specific positions and proceeds with the nucleation of the product phase. This is often accompanied by subsequent macroscopic phase separation. In the homogeneous reaction, the product polymer is randomly distributed in the crystals, resulting in a solid solution during the reaction. The product is isomorphous throughout the crystals. The excellent penetration property of γ-ray seems to induce a homogeneous polymerization at the initial stage of the polymerization. Actually, however, the polymer was isolated as the polymer crystals after removing an unreacted monomer even at a low conversion (Figure 6), differing from the expectation of the random formation of polymer chains in the crystals. The formation of a polymer chain possibly accelerates further polymerization of the monomer molecules adjacent to it. The large G value for this polymerization also supports a belief of the spontaneous

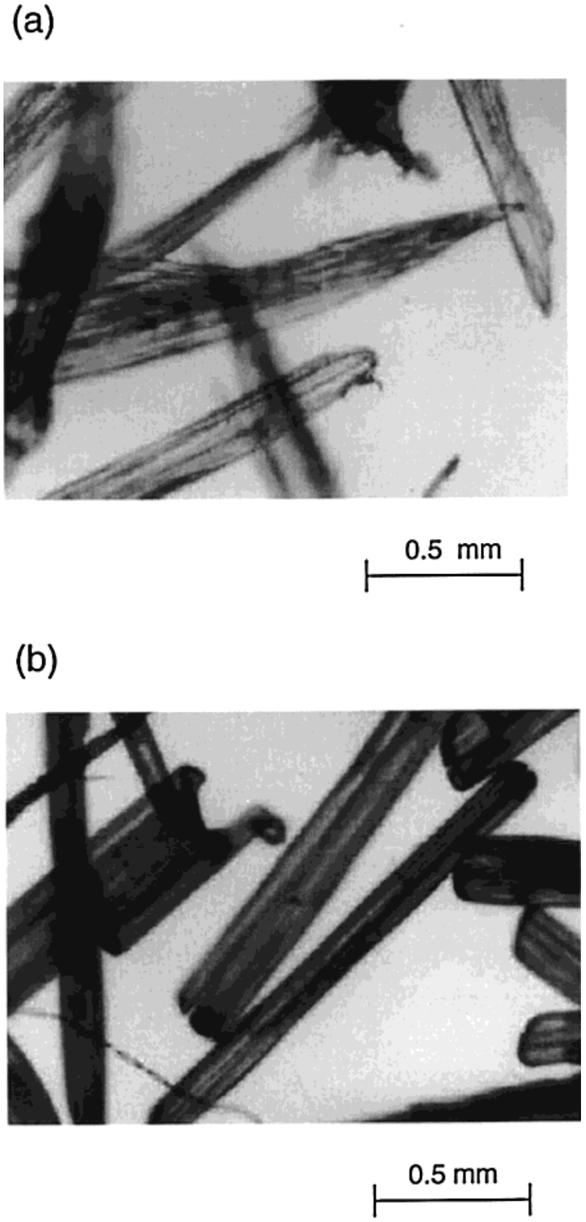

Figure 6. Microphotograph of poly(EMU) crystals obtained by γ-radiation polymerization: (a) conversion 10% and (b) conversion 75%.

initiation due to the crystal lattice strain formed in the monomer crystal domain during the polymerization. The polymer crystal lattice is not the same as the monomer crystal lattice, and the crystal-lattice strain was confirmed by the continuous shift of the peak in the powder X-ray diffraction.[19] The polymerization accelerated by the crystal strain results in the formation of polymer crystal domains that exist heterogeneously in the crystals at the intermediate conversion. At the last stage of the polymerization, the crystal lattice is close to that of the complete polymer crystal. During most cases of polymerizations in the solid state, when considerable strain in the crystal lattice is generated due to the mismatching of the lattices of the monomer and the polymer, this may result in the formation of structural defects in the crystals, e.g., cracking or collapse of the crystals. A nonsignificant change in lattice parameters during polymerization is expected to induce a single crystal-to-single crystal transition from a monomer crystal to a polymer crystal. A change in the lattice parameters during the polymerization of EMU is 1.6, 1.9, and 4.7% for the *a*-, *b*, and *c*-axes, respectively. Slight but nonnegligible shrinkage in the direction of *b*-axis is important for the successful polymerization in the crystalline state, because new covalent bonds are formed between the monomers aligned along this axis. γ-Radiation polymerization is convenient for the production of a large amount of crystals at a time, and the fabrication of polymer single crystals in a larger size would make it possible to study the physical and optical properties of the polymer crystals as new organic materials.

Conclusions. We have investigated the γ-radiation polymerization of EMU and related derivatives under various conditions. These diene monomers are very susceptive to irradiation to give a high molecular weight polymer in a high yield. The effects of the radiation dose rate and the postpolymerization on the polymer yield are negligible for the γ-radiation polymerization at room temperature, whereas the polymer yield depends on the temperature of the γ-irradiation and postpolymerization. The crystal size also significantly influences the polymerization reactivity. A tritactic stereoregular polymer is produced during the γ-radiation polymerization, identical to that prepared by the photopolymerization. The poly(EMU) single crystal obtained under the appropriate γ-radiation conditions verified the process of topochemical polymerization under γ-radiation.

Acknowledgment. This work was partly supported by the Grant-in-Aid for Scientific Research (No. 11650911) from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Crystallographic data of poly(EMU). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA9917038