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Crystalline-State Polymerization of Diethyl *(Z,Z)*-2,4-Hexadienedioate via a Radical Chain Reaction Mechanism To Yield an Ultrahigh-Molecular-Weight and Stereoregular Polymer

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ABSTRACT: We have investigated the reaction mechanism of the radical polymerization of diethyl *(Z,Z)*-2,4-hexadienedioate (EMU) in the crystalline state under UV irradiation to yield a polymer of ultrahigh molecular weight with a highly regulated stereochemical structure. The molecular weight of poly(EMU) was estimated to be much higher than 10^6 by gel permeation chromatography and viscometry, irrespective of the polymerization temperature, in contrast to the polymerization rate, which significantly depended on the temperature. The crystal structural change monitored by X-ray diffraction during the polymerization has evidenced the crystal-to-crystal reaction process yielding the poly(EMU) crystals. The results of X-ray diffraction and NMR spectroscopy confirmed that the propagation proceeded under a crystal-lattice control, leading to the *meso*-diisotactic-*trans*-2,5-polymer as a completely regulated structure. The ESR measurement has revealed the radical chain mechanism and the formation of a long-lived propagating radical during the polymerization. In the initiation step of the polymerization, it is supposed that the radical formation is induced not only photochemically but also via a spontaneous process because of the crystal-lattice strain.

Introduction

The polymerization reactivity and the structure of the resulting polymers have been discussed for polymerizations in organized media such as liquid crystals, interfaces, micelles, mono- and multilayers, vesicles, inclusion compounds, and templates.[1] These organized structures offer specific polymerization media as reaction loci, which would result in a reaction rate and selectivity different from those in an isotropic state. The formation of polymers with highly controlled chain structures would be expected during the polymerization of molecular crystals consisting of the most organized structure.[2,3] Recently, the reaction mechanism and the structure of the crystals in a variety of chemical reactions in molecular crystals, especially photoreactions of organic crystals, have been intensively studied because of the developments of the static and dynamic crystal structure analyses.[4] We can expect that topochemical reactions would yield products with highly controlled structures by the crystal lattice of the reactant,[5] but few successful polymerizations in a crystalline state via a topochemical process have been actually reported: stepwise [2+2] photopolymerization of the crystals of 2,5-distyrylpyradine and its analogous diolefins[6] and thermal or radiation polymerization of diacetylenic derivatives.[7] These topochemical polymerizations were found in the late 1960s, and thereafter, many efforts were directed toward finding other monomers that polymerize via a topochemical reaction mechanism. However, the polymerization of the crystals of vinyl and cyclic monomers afforded only atactic polymers except for a few cases, for example, ring-opening polymerization of some cyclic ethers including trioxane in the solid state, yielding highly crystalline polymers.[8] The movement of the center of gravity of monomers is unavoidable during the polymerization of vinyl monomers in the solid state, resulting in collapse of the crystal structure or in lack of polymerizability. Among solid-state polymerizations, the polymerization that provides a polymer with a specific crystal structure formed under control of the crystal lattice of the monomer is distinguished as topotactic polymerization.[7a,d] The polymerization of trioxane in the solid state is a typical example of topotactic polymerization. In contrast to this, the topochemical polymerization is described as a reaction in which the crystallographic position and symmetry of the monomer as the reactant are retained in the resulting polymer as the product. In a topochemical polymerization process, the primary structure of a polymer chain, for example, regioselectivity and tacticity as well as higher order structures of chains, for example, ordering and crystallinity, is controlled, resulting in the facile formation of polymer crystals as polymerized.

In 1994, Matsumoto et al.[9] discovered that diethyl *(Z,Z)*-2,4-hexadienedioate (diethyl *cis,cis*-muconate) (EMU) yields a polymer with a regulated stereochemical chain structure and ultrahigh molecular weight by photoirradiation of the monomer crystals. As described in the previous paper,[9b] the crystalline-state polymerization of EMU is the first example of topochemical 1,4-polymerization of 1,3-diene derivatives to afford the polymer with an extremely controlled stereochemical structure, the tritactic polymer. In this article, we describe the feature of the polymerization of EMU in

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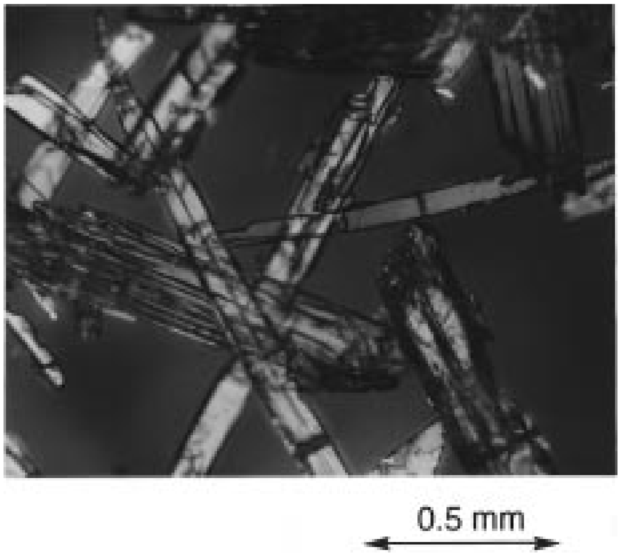


Figure 1. Polarized microphotograph of poly(EMU) crystals. The polymerization was carried out at room temperature under irradiation of sunlight for several days.

the crystalline state and the structure of the resulting polymer to propose the detailed reaction mechanism of the polymerization as a radical chain reaction.

Results

Polymerization of EMU in a Crystalline State. The crystals of EMU as the diethyl ester monomer with the *(Z,Z)*-configuration provided the polymer on exposure to sunlight or UV light. The EMU monomer was converted to the transparent polymer crystals (Figure 1) in a quantitative yield after polymerization under sunlight for several days. Here we used the EMU monomer as polycrystalline needles, which were prepared by ordinary recrystallization from hexane. In contrast to the polymerization of EMU, no polymerization proceeded for the other dialkyl esters examined, for example, methyl, octyl, dodecyl, and octadecyl esters and the *(E,Z)*- and *(E,E)*-isomers of the ethyl ester under photoirradiation at a temperature below their melting points.

The effect of the temperature was investigated for the polymerization of EMU in the crystalline state. The EMU crystals (mp 53−54 °C) afforded the polymer in the temperature region between −20 and 50 °C by photoirradiation, but the reaction hardly proceeded at a lower temperature, for example, a dry ice−methanol or liquid nitrogen temperature (Table 1). The polymerization rate depended significantly on the temperature, and the overall activation energy for the polymerization was approximately 55 kJ/mol, which was estimated from the initial slope of the curves in the time−yield relationship for the polymerization (Figure 2). The polymerizations of EMU in the melt or in solution under the photoirradiation did not give any polymer. Neither did thermal polymerization of the EMU crystals proceed in the dark below the melting point. These results confirm that the photoirradiation in a crystalline state is required for the proceeding of this polymerization.

Table 1. Crystalline-State Polymerization of EMU under UV Irradiation

temp (°C)	time (h)	yield (%)	$[\eta]^a$ ($\times 10^{-2}$ mL/g)
50	1	82.4	17.3
30	2	64.8	
0	0.5	5.1	14.1
0	2	21.0	15.6
0	4	37.2	19.4
0	4 (2)[b]	56.9	17.7
0	4 (4)[b]	51.4	19.1
0	4 (5)[b]	63.6	17.4
0	4 (8)[b]	76.8	17.0
0	4 (8)[c]	47.3	
0	8	58.0	
0	12	68.6	
0	24	95.5	19.8
−20	12	4.6	21.7
−78	8	0	
−196	8	0	

[a] In trifluoroacetic acid at 30 °C. [b] Continuous irradiation polymerization for 4 h at 0 °C, followed by postpolymerization for a given time indicated in the parentheses at 50 °C. [c] Postpolymerization at 0 °C.

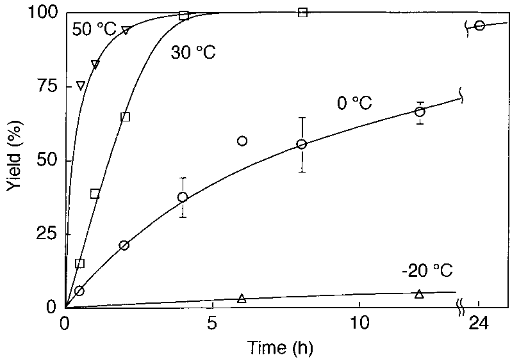


Figure 2. Time−yield curves for polymerization of EMU crystals under UV irradiation with a high-pressure Hg lamp.

Because IR irradiation resulted in no change in the EMU crystals in contrast with the polymerization induced by the UV irradiation, the polymerization process of the EMU crystals could be monitored by FT-IR spectroscopy. Figure 3 shows the change in the IR spectrum during the polymerization under UV irradiation at room temperature. The characteristic bands due to the monomer decreased, and the bands of the polymer increased with some isosbestic points. The intensity of the light efficient to polymerization was much greater compared with the conditions for the polymerizations shown in Figure 2 and Table 1, resulting in the completion of polymerization within 10 min at room temperature. From the intensity change in the absorption at 985 cm^{-1} for the out-of-plane deformation vibration due to the *trans*-CH=CH of poly(EMU) against the peak intensity at 1593 cm^{-1} for the stretching vibration due to the diene moiety of the monomer, a linear relationship was observed for the plots of the logarithm of the relative concentration of the residual monomer against the UV-irradiation time (Figure 4), indicating that this polymerization process apparently obeys the first-order reaction with respect to the monomer concentration. Detailed results for the EMU polymerization as studied by IR and Raman spectroscopies as well as X-ray diffraction will appear separately elsewhere.[10]

Molecular Weight Determination of Poly(EMU). Poly(EMU) prepared in the crystalline-state polymerization has a limited solubility because of its high stereoregularity; it is soluble in trifluoroacetic acid and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) but insoluble in any other solvent.[9] Accordingly, gel permeation chromatography (GPC) measurement was carried out using HFIP as the eluent to estimate the molecular weight of poly(EMU). The sample concentration was

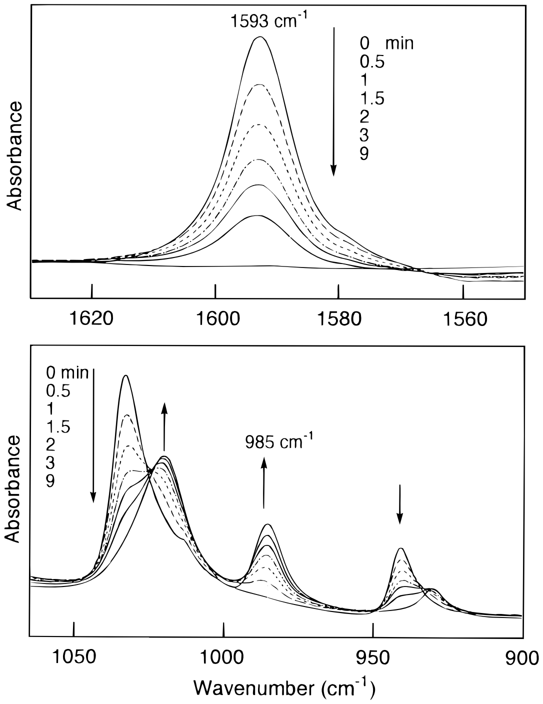


Figure 3. IR spectral change during the polymerization of EMU under UV irradiation (KBr disk).

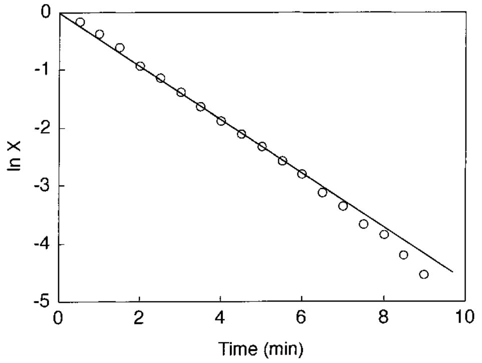


Figure 4. First-order plot for polymerization of EMU crystals under UV irradiation. *X* is the relative concentration of the residual monomer evaluated by the IR spectral data.

reduced to 0.1 mg/mL because of the extraordinary high viscosity of the solution. Standard poly(methyl methacrylate)s (poly(MMA)) with a molecular weight of 1.27 × 10^4 to 1.58 × 10^6 were used for the molecular weight calibration. The chromatogram depicted in Figure 5 indicates that poly(EMU) is of ultrahigh molecular weight, more than 10^6 at least, and no oligomer was produced during the polymerization. Thus, we could not determine the accurate molecular weight of the polymers by GPC because of the exclusion limit of the columns used.

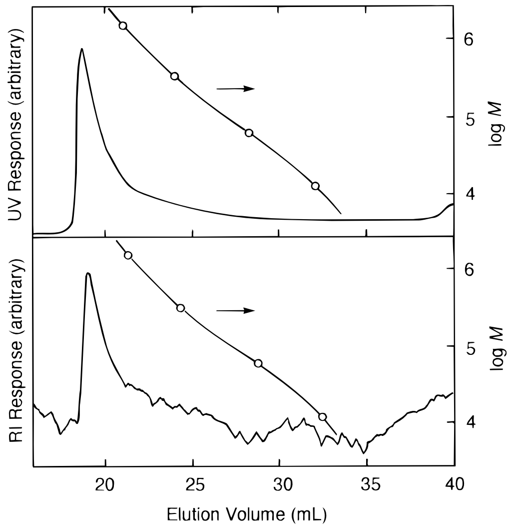


Figure 5. GPC traces of poly(EMU) with UV and RI detectors with 1,1,1,3,3,3-hexafluoro-2-propanol as the eluent at 37 °C: intrinsic viscosity of the sample polymer, $[\eta] = 939$ mL/g in trifluoroacetic acid at 30 °C; sample concentration, 0.1 mg/mL; columns, Tosoh $\mathrm{GMH_{HR}}$-H ×2; standard poly(MMA)s for calibration, $M_w = 1.58 \times 10^6$, 3.33×10^5, 6.26×10^4, and 1.27×10^4.

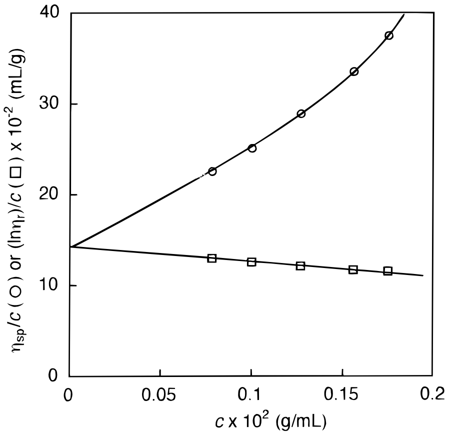


Figure 6. Huggins and Fuoss–Mead plots for determination of the intrinsic viscosity of poly(EMU): solvent, trifluoroacetic acid; temperature, 30 °C.

Second, we determined the intrinsic viscosities ($[\eta]$) of the polymers as the relative index of the molecular weight using the Huggins and Fuoss-Mead plots (Figure 6). We calculated the $[\eta]$ values from a linear Fuoss–Mead plot, while a Huggins plot provided the upward curvatures because of interaction between the polymer chains with an ultrahigh molecular mass even in a highly diluted solution. The values determined are summarized in Table 1. The Huggins constants were 0.42–0.43 for all the samples, slightly larger than the values for linear and flexible polymers in a good solvent. The molecular weight of the polymer remained approximately constant irrespective of the polymer yield. It was confirmed that the poly(EMU) with an ultrahigh molecular weight was produced at the initial stage of the polymerization, for example, $[\eta] = 1.4 \times 10^3$ mL/g at 5% conversion to the polymer. The polymerization temperature also has no relation to the molecular weight of the polymer, which is distinct from the great temperature dependence of the polymer yield (Figure 2).

Structure of Poly(EMU). The powder X-ray diffraction profiles were recorded to examine the difference in the crystal lattice of the polymer from that of the monomer. Figure 7 shows that poly(EMU) has a crystalline structure resembling that of the monomer; that is, this polymerization reaction evidently proceeds via a crystal-to-crystal process. Because continuous X-ray irradiation induced the polymerization of the EMU crystals, we could follow the polymerization process during the diffraction measurement. Figure 8 shows the expanded reflections in the region $2\theta = 15$–$19°$. The reflections due to the monomer crystals shifted and approached those of the polymer crystals; it has

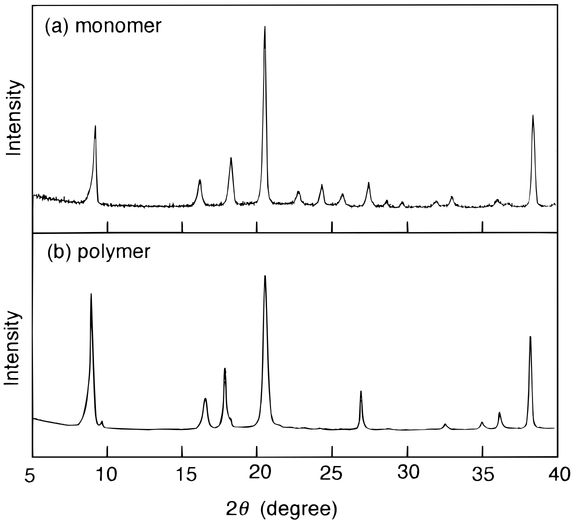


Figure 7. Powder X-ray diffraction profiles of the EMU monomer and poly(EMU).

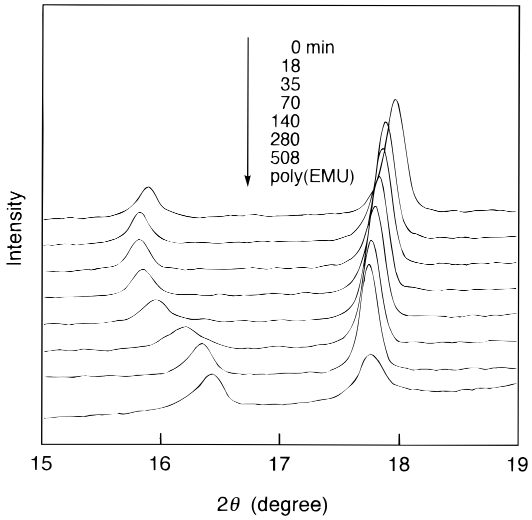


Figure 8. Change in X-ray diffraction pattern during the polymerization of EMU: Cu Kα, 40 kV, 100 mA; scan speed, 2°/min.

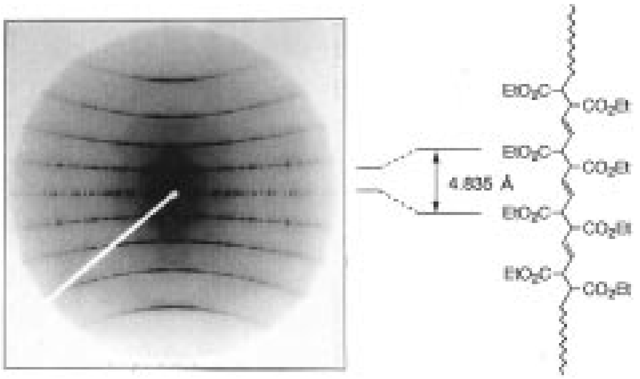


Figure 9. Full-rotation X-ray photograph of poly(EMU) with an imaging plate detector. Mo Kα, 50 kV, 200 mA; exposure time, 5400 s.

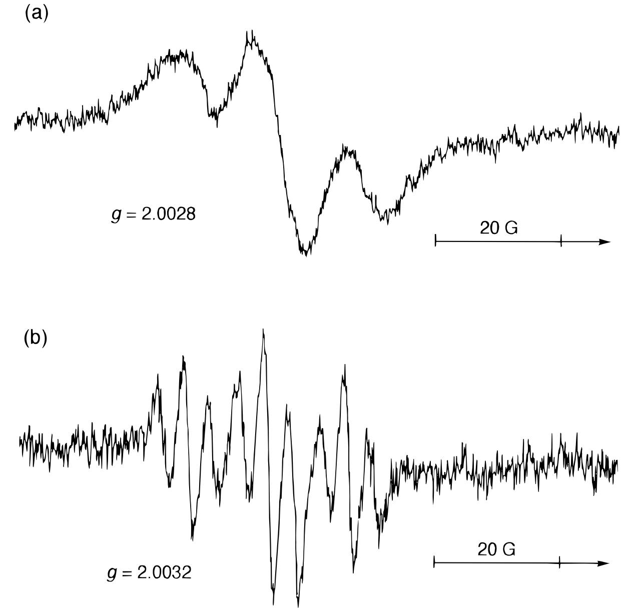


Figure 10. ESR spectra observed for propagating radicals during polymerization of EMU under UV irradiation at 5 °C: (a) crystalline-state polymerization; (b) isotropic polymerization; [EMU] = 1 M; [dimethyl azobis(isobutyrate)] = 0.05 M in benzene.

been revealed that the crystal lattice of the EMU monomer changes continuously to the lattice of the polymer. The large and continuous shift of reflections indicates the generation of mechanical strain in the monomer crystal lattice followed by the transformation to the lattice of the polymer crystal. Furthermore, we found that the polymer crystal provided a fully rotated X-ray photograph consisting of a large number of clear and spotlike reflections without any amorphous halos as represented in Figure 9, although the polymer sample was not a single crystal. This photograph proves that the polymer chains are highly oriented in the specific direction of the crystals, that is, along an axis of the needle. From the interval of the layer lines, the fiber period was determined to be 0.4835 nm.

ESR Analysis of the Polymerization Process. This crystalline-state polymerization was expected to proceed via a radical chain-reaction mechanism, judging from some features of the polymerization: initiation by photoirradiation, no formation of oligomers, and polymer formation irrespective of the medium or atmosphere. Therefore, we carried out the ESR measurement to detect the propagating radical. As shown in Figure 10, the ESR spectrum was observed during the crystalline-state polymerization of EMU at 5 °C. The spectrum observed in benzene during the isotropic polymerization by photoirradiation is also depicted as the reference. The spectrum observed in an isotropic state is characterized by two kinds of hyperfine coupling constants for the four protons: $a_\alpha = a_\gamma = 1.30$ mT and $a_\beta = a_\delta = 0.44$ mT due to the delocalized allylic radicals as the propagating species.[9] In a crystalline state, the peaks were observed as a broad triplet due to the anisotropy of the polycrystalline state of the sample. The apparent g-value was determined to be 2.0028 in the crystalline state, similar to that in an isotropic solution ($g = 2.0032$). A similar ESR spectrum due to the propagating radical was detected at −20 °C but was hardly detected below −40 °C, agreeing well with the polymerization results described above.

Subsequently, the spin density was determined as a function of the irradiation time during the polymerization. The spin density increased with the irradiation time and reached the order of 10^{15} spin/g after the 5-h irradiation (Figure 11). The decay of the radical after interruption of the irradiation was extremely slow; for example, the spectrum was observed with a half inten-

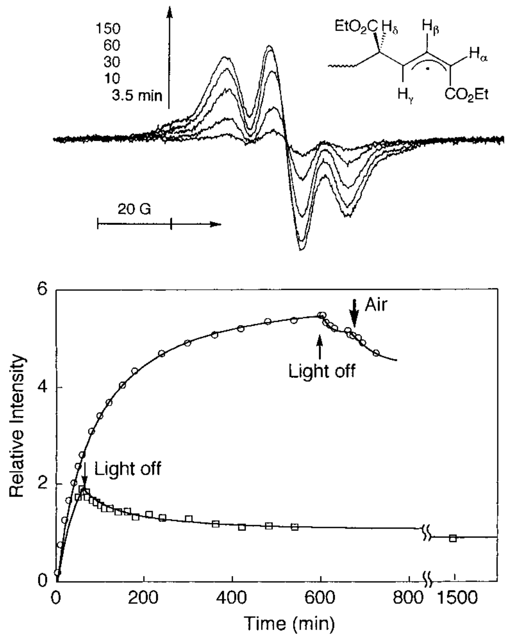


Figure 11. Change in concentration of propagating radical during crystalline-state polymerization of EMU under continuous UV irradiation and after interruption of the irradiation at 0 °C.

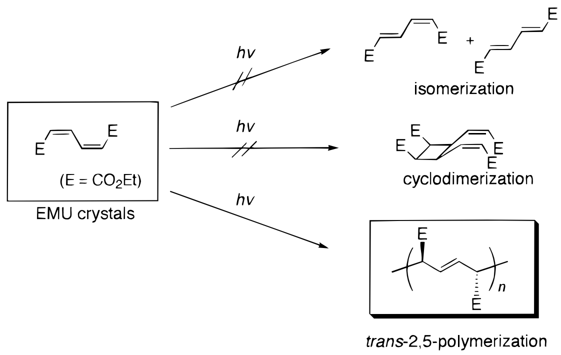
sity of the original one even after 1 day, indicating that the termination process of the propagating radical occurs less frequently. This is distinguished from the solution polymerization in an isotropic state, in which the propagating radicals terminate immediately. When air was injected into the tube during the ESR measurement, the radical reacted with oxygen at a very low rate because of the slow diffusion of oxygen into the crystals.

The postpolymerization was carried out using the long-lived propagating radicals. The prepolymerization by the photoirradiation was performed at 0 °C for 4 h (polymer yield 37.2%); then the irradiation was interrupted, and the crystals were kept at 50 °C in the dark. The results are shown in Table 1. The postpolymerization proceeded, and the increment of the yield was observed clearly at 50 °C, whereas the postpolymerization proceeded slowly at 0 °C. The increase in the [η] values of the polymer was not observed, suggesting an increase in the number of polymer chains produced during the postpolymerization.

Discussion

Characteristic Polymerization of EMU. The polymerization of EMU proceeds uniquely by photoirradiation in the crystalline state through a radical mechanism. Other dialkyl 2,4-hexadienedioates examined in this work provided no polymer during the crystalline-state photoirradiation irrespective of their configuration and the ester alkyl groups. It has been confirmed that neither isomerization nor dimerization occurs during the EMU polymerization (Scheme 1), whereas the *(Z,Z)*-2,4-hexadienedioic derivatives including the acids and esters isomerize to the *(E,Z)*-isomers in solutions on heating and to the *(E,E)*-isomers by photoirradiation in a solution in the presence of an isomerization catalyst such as iodine and it has been reported that the acid and the monomethyl ester afford cyclobutane dimers on UV irradiation.[5b] When bulk polymerization in the melt was carried out at 120 °C in the presence of a radical initiator to examine the chemical reactivity of these monomers, the polymerization proceeded to give high-molecular-weight polymers in 25–88% yield for the 4-h polymerization,[9] indicating that these monomers had no distinct difference in polymerization reactivity in an isotropic state. The uniquely successful crystalline-state polymerization of EMU would be ascribed to the difference in the crystal structure but not the difference in the chemical reactivity of the double bond of the monomers.

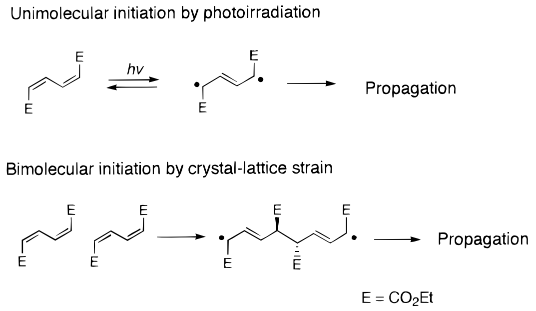
Scheme 1



Initiation Mechanism. A radical species from EMU excited by photoirradiation probably initiates the polymerization. The UV absorption band of EMU (λ_{max} (π–π^*) = 259 nm, ϵ = 21 300 in cyclohexane) is consistent with the dependence of the wavelength of the irradiation light on the polymerization reactivity; the polymerization proceeds when UV light of approximately 300 nm or less is irradiated. In the crystals, the diradical produced by the irradiation immediately reacts with neighboring monomers, whereas it prefers to return to the ground state in solution. Other possibilities for the radical formation, for example, a defect in the crystal lattice or the crystal surface or impurities adsorbed on the surface, would decline with quantitative conversion of the monomer to the polymer after irradiation for a long time. When an EMU crystal was photoirradiated, the crystal first bent in the direction of the incident light and then it recovered the original linear shape except for an approximately 2% shrinkage in the length of the needle. This morphology change in the crystal during the reaction is interpreted as the polymerization starting by excitation of the monomer near the surface on irradiation and the incident light reaching inside the crystals because of the transparency of the polymer produced around the approximately 300-nm region. This is supported by the UV absorptions (λ_{max}-(n–π^*) = 224 nm, ϵ = 1850 in acetonitrile) of the atactic poly(EMU) with the microstructure of *trans*-2,5-/*cis*-2,5-/2,3- = 85/12/3, which was prepared by bulk polymerization of EMU in the melt at 120 °C in the presence of di-*tert*-butyl peroxide. The atactic poly(EMU) is soluble in many organic solvents used for the UV–visible absorption measurement, while the stereoregular poly(EMU) prepared by crystalline-state polymerization is insoluble in the appropriate solvents.

The overall activation energy of the polymerization is considerably large, 55 kJ/mol, in this crystalline-state polymerization. The photoinitiation rate is independent of the temperature, and the activation energy for the initiation step is regarded as zero. The propagation step also might imply a small activation energy because the propagation occurs very fast to yield a constant and high molecular weight of the polymer independent of

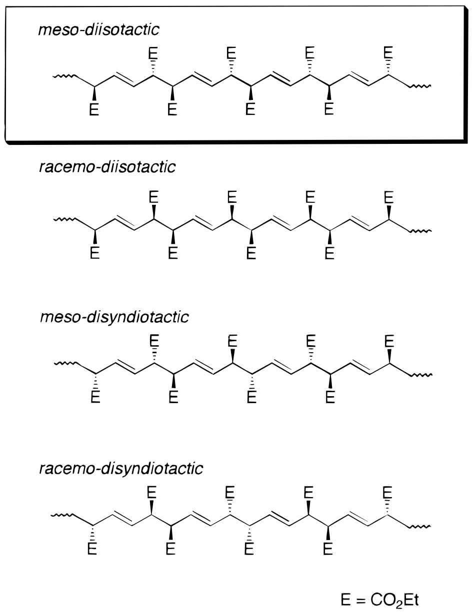
Scheme 2



the polymerization temperature. These results suggest another type of initiation in addition to photochemical initiation. In the change of the X-ray diffraction pattern during the polymerization (Figure 6), a continuous shift of the diffraction peaks was observed, but not as a simple superposition of the diffractions due to the monomer and the polymer crystals, indicating the continuous transformation of the monomer lattice to the polymer lattice via generation of lattice strain during the polymerization process. This crystal-lattice strain would induce further initiation; namely, a diradical is produced by the combination of two monomer molecules with strain in the lattice (Scheme 2). The large activation energy for the overall polymerization would correspond to this initiation process. This mechanism accounts for the formation of isolable polymer crystals even at low conversion, because the polymer chain produced could particularly accelerate the polymerization (initiation) around the preformed polymer chain. The first-order reaction with respect to the monomer concentration observed by the IR technique during the polymerization of EMU means first-order initiations, because the propagation is very fast and the propagating radical is long-lived; that is, the polymerization rate is determined by the initiation step. The crystal-lattice strain-induced initiation is also supported by the results of the postpolymerization, that is, the temperature dependence and the constant molecular weight of the resulting polymers.

Stereoregular Propagation. The diradical propagation proceeds in the crystal lattice to give a polymer of extremely regulated stereochemical structure at a considerably great rate. The fast propagation is supported by the formation of an ultrahigh-molecular-weight polymer in the initial stage of the polymerization. The NMR chemical shifts suggested the *meso*-diisotactic-*trans*-2,5- or *meso*-disyndiotactic-*trans*-2,5-structure of poly(EMU), as has been described in the previous work.[9] The fiber period for the poly(EMU) crystal, 0.4835 nm determined in this work, is equal to the 0.483 nm predicted for poly(*trans*-1,4-butadiene) with the *trans*STS^{-1} conformation and much shorter than the 0.860 nm calculated for poly(*cis*-1,4-butadiene) with the TT′*cis*T′ conformation,[11] where S and T represent skew and trans conformations, respectively. This fiber period indicates the possibility of the polymer configuration of the *meso*-diisotactic-*trans*-2,5- or *racemo*-diisotactic-*trans*-2,5-structure of the polymer. Combination of the X-ray results with the NMR data has confirmed the *meso*-diisotactic-*trans*-2,5-structure as the most plausible configuration of the polymer (Chart 1).

Chart 1



Thus, the propagation in the crystalline-state polymerization of EMU has been revealed to proceed under complete stereochemical control. In the field of radical reactions a high stereoselectivity has been achieved in radical reactions by substrate or chiral auxiliary control.[12] Substrate-controlled diastereoselection is observed for intramolecular radical additions to multiple bonds, that is, radical cyclization and the reactions of cyclic radicals as well as acyclic systems which are controlled by the allylic strain effects. In addition reactions, the configurations of new stereogenetic centers may be controlled by chiral groups attached to the radical or the alkene. In radical polymerization, triarylmethyl methacrylates[13] and a derivative of acrylamide,[14] which afford a highly isotactic polymer, are typical examples according to these reaction control principles. The crystalline-state radical polymerization in this work is regarded as another type of controlled reaction to provide highly regulated stereochemistry of polymers by the aid of the crystal lattice, that is, under the reaction-locus control.

Long-Lived Propagating Radicals. As shown in the ESR work, the propagating radical is long-lived in the crystalline state. Because the polymer chain produced cannot diffuse in the crystal, the radicals might terminate by combination only when they come in contact during the propagation of the aligning monomers in the crystals. The slow decay of the radical after interception of the irradiation in Figure 11 may be ascribed to the bimolecular termination. The long-lived radicals which result in unimolecular termination are formed by a change in the distance between the radical and the monomer or by the absence of the reacting monomers at the edge of the crystals. Such long-lived radicals are accumulated during the long irradiation and are readily detectable by ESR spectroscopy. The spin concentration estimated by ESR spectroscopy is consistent with that calculated from the assumption that long-lived diradicals of the polymer with a molecular weight of the order 10^7 to 10^8 are formed. In this work, the polymerization was carried out with a mixture of needles of various lengths of approximately 0.1−10 mm, the polymers are supposed to be a mixture of polymers with various molecular weights. When we can control the crystal size, that is, the length of the needles, the molecular weight of the polymers produced would also be regulated. In our preliminary work, the [η]

values of poly(EMU) decreased by one or two orders by means of other methods for the preparation of the monomer crystals, for example, reprecipitation, freeze-drying, and milling.[15]

Conclusions. We have demonstrated that the crystalline-state polymerization of EMU proceeds in a radical chain mechanism by the UV irradiation to yield ultrahigh-molecular-weight with a *meso*-diisotactic-*trans*-2,5-polymer. The crystal structural change during the photoirradiation evidenced the crystal-to-crystal process of the polymerization. Thus, crystalline-state polymerization would be useful for control of the polymerization reactivities and the structures of the resulting polymers, especially the control of the stereoregularity and the molecular weight of the polymers. The success of the crystalline-state polymerization of EMU as one of the 1,3-diene derivatives may extend the kinds of monomers that are provided for topochemical polymerization.[16] The determination of the crystal structures of the EMU monomer and poly(EMU) is under investigation to establish the position of the EMU polymerization in a crystalline state as the third example of topochemical polymerization following distyrylpyradines and diacetylenes.

Experimental Section

Materials. EMU was prepared from *(Z,Z)*-2,4-hexadienedioic acid (*cis,cis*-muconic acid), supplied from Mitsubishi Chemical Co., Ltd., Japan, by the method described in the previous paper.[9b] EMU was recrystallized from hexane to provide needle crystals with a melting point of 53−54 °C. IR (KBr): 1716 ($\nu_{C=O}$), 1593 cm^{-1} ($\nu_{C=C}$). ^{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 = 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$_3$). UV(cyclohexane): λ_{max} 259 (ϵ = 21 300), 280 nm (shoulder).

The other esters were also synthesized similarly. Commercial di-*tert*-butyl peroxide was used as received. Dimethyl 2,2′-azobis(isobutyrate) was recrystallized from methanol.

Photopolymerization. Photopolymerization of the crystals was carried out in a sealed Pyrex ampule under irradiation of UV light using a high-pressure mercury lamp (Toshiba SHL-100-2, 100 W) at a distance of 10 cm. A typical polymerization procedure is described below. Monomer EMU (200 mg, 1.0 mmol) was placed in an ampule, which was then evacuated on a vacuum line. After irradiation, polymer was isolated by removal of the unreacted monomer with chloroform (20 mL) for 5−10 h at room temperature. Photopolymerization was also carried out by direct exposure to sunlight. Postpolymerization was performed in a thermostated bath in the dark after continuous photoirradiation for a given time.

Spectroscopic Data of Poly(EMU). IR(KBr): 1730 ($\nu_{C=O}$), 1288 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR (400 MHz, CF$_3$CO$_2$D): δ 5.85 (broad, CH=, 2H), 4.29 (broad, OCH$_2$, 4H), 3.64 (broad, CHCO$_2$, 2H), 1.35 (broad, CH$_3$, 6H). ^{13}C NMR (100 MHz, CF$_3$CO$_2$D): δ 175.98 (C=O), 132.17 (CH=), 65.57 (CH$_2$), 54.33 (*C*HCO$_2$), 14.58 (CH$_3$). Anal. Calcd for $(C_{10}H_{14}O_4)_n$: C, 60.59; H, 7.12. Found: C, 60.66; H, 7.04.

Measurements. GPC was performed with a Tosoh HPL-8020 instrument equipped with Shimadzu SPD-6AV (220 nm) and GMH$_{HR}$-H (×2) columns using HFIP as eluent at a flow rate of 0.5 mL/min. The sample concentration was 0.1 mg/mL. Molecular weights were calibrated with standard poly(MMA)s ($M_w = 1.577 \times 10^6$, 3.33×10^5, 6.26×10^4, and 1.27×10^4). Viscosity was measured in trifluoroacetic acid at 30 °C using an Ubbelohde viscometer. The [η] values were determined using the Huggins and Fuoss−Mead equations. IR spectra were recorded on a JASCO 8300 FT-IR spectrometer for the sample in a KBr disk. UV irradiation was carried out using a middle-pressure mercury lamp for the pursuit of the polymerization monitored by IR spectroscopy. UV−visible spectra were taken with a Shimadzu UV-160 photometer. ESR spectra were taken with a Bruker ESP-300 spectrometer under temperature control. Photoirradiation was carried out with a 1-kW xenon lamp. The *g*-value was determined using an NMR field meter (Echo Electronics, Co., Ltd.) and a microwave counter (Advantest, R5372). The X-ray powder pattern was measured using a RIGAKU RAD-ROC diffractometer with a graphite-monochromatized Cu Kα line (40 kV, 100 mA, 5−40°, scan speed 2°/min). The full-rotation X-ray diagrams were measured with a DIP 1000 (MAC Science, Mo Kα line, graphite monochromator, 50 kV, 200 mA, rotation, exposure time 5400 s).

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