Stereospecific Polymerization of Dialkyl Muconates through Free Radical Polymerization: Isotropic Polymerization and Topochemical Polymerization

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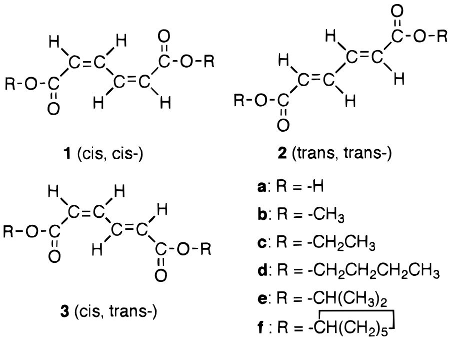
ABSTRACT: Radical polymerization of dialkyl muconates (dialkyl 2,4-hexadienoates) was investigated in an isotropic (amorphous) state, that is, solution or bulk polymerization, and in a crystalline state. In the bulk polymerization at 120 °C in the presence of a radical initiator, high molecular weight polymers of more than 10^5 were obtained in high yields, compared with those in solution polymerization. Three kinds of isomers, *cis,cis*-, *cis,trans*-, and *trans,trans*-muconates, showed similar polymerization reactivities. The microstructure in the polymers was determined by ^{1}H and ^{13}C NMR spectroscopies to be 84−91%, 6−13%, and 2−4% for *trans*-1,4-, *cis*-1,4-, and 1,2-structures, respectively, which depended on the polymerization temperature. In contrast with the bulk (in the melt) and solution polymerizations, we discovered that diethyl *cis,cis*-muconate underwent highly stereospecific polymerization in a crystalline state under UV irradiation via a topochemical polymerization mechanism. The resulting polymer was of ultrahigh molecular weight ($[\eta] = 10^3$ cm^3/g) with high stereoregularity and crystallinity. This polymer has been clarified to be a tritactic polymer, *trans*-1,4-*meso*-diisotactic or *trans*-1,4-*meso*-disyndiotactic polymer.

Introduction

A large number of polymers are produced through radical polymerization on an industrial scale, because radical polymerization is profitable compared to ionic polymerization based on the following features: application to a variety of monomers, especially polar monomers, use of water as the reaction media, and prediction and reproducibility of the reactions based on the numerous data accumulated. However, we still have some unsolved problems for the control of polymer structures, for example, molecular weight and its distribution, chain-end structure, and tacticity. Physical properties of diolefin polymers such as polybutadiene and polyisoprene intensively depend on their polymeric microstructure, that is, 1,2-, 3,4-, and *cis*- and *trans*-1,4-structures.[1] Stereoregular diolefin polymers have been synthesized with transition metal catalysts,[2] but radical polymerization yields only atactic polymers. In 1977, Bando et al.[3] investigated the radical polymerization of muconic acid (2,4-hexadienedioic acid) and its ethyl ester, which are 1,4-disubstituted butadienes, and they concluded that these monomers have low polymerization reactivity to give only oligomers by homopolymerization in solutions. Thereafter, no one has reported the radical polymerization of muconates. In an earlier period of this work, our interests were on the synthesis of high molecular weight polymers of muconates as internal diolefins and the control of the tacticity through free radical polymerization. In the first part of this article, we describe the radical polymerization of three isomers of dialkyl muconates with various ester alkyl groups, as shown in Chart 1. We found that these muconic derivatives polymerized to give high molecular weight polymers with a *trans*-1,4-repeating structure through a free radical polymerization mechanism under appropriate conditions. Both the polymerization reactivity and the polymer structure are discussed.

Chart 1



Furthermore, in the course of the work we discovered that diethyl *cis,cis*-muconate undergoes topochemical polymerization in a crystalline state to give an ultrahigh molecular weight and highly stereoregular polymer (tritactic polymer) on exposure to UV light. The preliminary results have been reported in a previous communication.[4] Here we provide the details of the topochemical polymerization process and the structure and some properties of the stereoregular polymer obtained.

Experimental Section

Monomer Synthesis. *cis,cis*-Muconic acid (**1a**) (20 g) (supplied from Mitsubishi Kagaku Co.) was reacted with excess dimethyl sulfate (126 g) in the presence of potassium carbonate (43 g) in 200 mL of acetone with stirring at room temperature for 13 days. After the acetone was evaporated from the filtrate, it was dissolved in 500 mL of benzene, washed with dilute alkali and water, and then dried over anhydrous sodium sulfate. **1b** was recrystallized from methanol. Yield: 18.3 g (76%).

1b (dimethyl (*Z,Z*)-2,4-hexadienoate): mp 74.5 °C (methanol) (lit.[5] 73.5 °C); ^{1}H NMR (CDCl$_3$) δ 7.90 (m, 2H, RO$_2$CCH=C*H*−), 5.99 (m, 2H, RO$_2$CC*H*=CH−), 3.76 (s, 6H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 166.04 (C=O), 137.95 (CH=), 123.87 (CH=), 51.49 (CH$_3$); IR (KBr) $\nu_{C=O}$ 1710, $\nu_{C=C}$ 1580 cm^{-1}.

1c was prepared with diethyl sulfate similarly to **1b**. After the potassium sulfate was filtered off, **1c** precipitated out of the solution by condensation. It was purified by recrystallization from hexane. Yield: 23%. **1c** was also synthesized from **1a** and excess ethanol in the presence of a catalytic amount

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of sulfuric acid under reflux. **1c** obtained by the latter method contained a small amount of the isomer, **3c**. It was purified by column chromatography (silica gel/hexane), followed by recrystallization. Yield: 57%.

1c (diethyl *(Z,Z)*-2,4-hexadienoate): mp 53−54 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 7.89 (m, 2H, $RO_2CCH{=}CH{-}$), 5.97 (m, 2H, $RO_2CCH{=}CH{-}$), 4.21 (q, $J = 7.3$ Hz, 4H, CH_2), 1.31 (t, $J = 7.3$ Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.66 (C=O), 137.80 (CH=), 124.20 (CH=), 60.39 (CH_2), 14.17 (CH_3); IR (KBr) $\nu_{C=O}$ 1710, $\nu_{C=C}$ 1585 cm^{-1}; UV (cyclohexane) λ_{max} 259 ($\epsilon = 21\,300$), ca. 280 nm (shoulder).

1d, **1e**, and **1f** were prepared from **1a** with the respective alcohols in the presence of an acidic catalyst by reflux in benzene for 30 h, followed by distillation under reduced pressure or recrystallization from hexane. Pure **1d** and **1f** were isolated by repeated column chromatography (silica gel/hexane). **1e** was used as a mixture of **1e** and **3e** (67/33). The yields were ca. 60%.

1d (di-*n*-butyl *(Z,Z)*-2,4-hexadienoate): bp 128 °C/1 mmHg; d^{30} 1.015; ^{1}H NMR ($CDCl_3$) δ 7.89 (m, 2H, $RO_2CCH{=}CH{-}$), 5.97 (m, 2H, $RO_2CCH{=}CH{-}$), 4.15 (t, $J = 6.5$ Hz, 4H, OCH_2), 1.65 (m, 4H, CH_2), 1.40 (m, 4H, CH_2), 0.95 (t, $J = 7.3$ Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.72 (C=O), 137.77 (CH=), 124.16 (CH=), 64.27 (OCH_2), 30.57 (CH_2), 19.11 (CH_2), 13.63 (CH_3).

1e (diisopropyl *(Z,Z)*-2,4-hexadienoate): ^{1}H NMR ($CDCl_3$) δ 7.87 (m, 2H, $RO_2CCH{=}CH{-}$), 5.94 (m, 2H, $RO_2CCH{=}CH{-}$), 5.07 (sep, $J = 6.3$ Hz, 2H, OCH), 1.28 (d, $J = 6.3$ Hz, 6H, CH_3) for the *cis,cis*-isomer; ^{13}C NMR ($CDCl_3$) δ 165.25 (C=O), 137.63 (CH=), 124.60 (CH=), 67.84 (OCH), 20.87 (CH_3) for the *cis,cis*-isomer.

1f (dicyclohexyl *(Z,Z)*-2,4-hexadienoate): mp 111.5−112.0 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 7.86 (m, 2H, $RO_2CCH{=}CH{-}$), 5.95 (m, 2H, $RO_2CCH{=}CH{-}$), 4.83 (m, 2H, OCH), 1.73−1.89 and 1.26−1.60 (m, 20H, CH_2); ^{13}C NMR ($CDCl_3$) δ 165.21 (C=O), 137.60 (CH=), 124.67 (CH=), 72.84 (OCH), 31.62 (CH_2), 25.35 (CH_2), and 23.72 (CH_2).

2 were prepared from muconic dichloride and the corresponding alcohol. Muconic dichloride was derived from **1a** by reflux for 5 h in thionyl chloride in the presence of a drop of pyridine. The acid chloride obtained was diluted with chloroform and allowed to react with a large amount of alcohol in the presence of triethylamine. The yield was 37−49%. **2b** has poor solubility in common organic solvents.

2b (dimethyl *(E,E)*-2,4-hexadienoate): mp 159 °C (methanol) (lit.[5] 158.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 2H, $RO_2CCH{=}CH{-}$), 6.21 (m, 2H, $RO_2CCH{=}CH{-}$), 3.79 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 166.28 (C=O), 140.95 (CH=), 128.00 (CH=), 51.91 (CH_3); IR (KBr) $\nu_{C=O}$ 1700, $\nu_{C=C}$ 1600 cm^{-1}.

2c (diethyl *(E,E)*-2,4-hexadienoate): mp 58−59 °C (hexane) (lit.[6] 64 °C); ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 2H, $RO_2CCH{=}CH{-}$), 6.20 (m, 2H, $RO_2CCH{=}CH{-}$), 4.24 (q, $J = 7.3$ Hz, 4H, CH_2), 1.32 (t, $J = 7.3$ Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.89 (C=O), 140.74 (CH=), 128.37 (CH=), 60.84 (CH_2), 14.17 (CH_3); IR (KBr) $\nu_{C=O}$ 1710, $\nu_{C=C}$ 1610 cm^{-1}.

2e (diisoproyl *(E,E)*-2,4-hexadienoate): mp 69−71 °C (methanol); ^{1}H NMR ($CDCl_3$) δ 7.29 (m, 2H, $RO_2CCH{=}CH{-}$), 6.17 (m, 2H, $RO_2CCH{=}CH{-}$), 5.10 (sep, $J = 6.3$ Hz, 2H, OCH), 1.29 (d, $J = 6.3$ Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.47 (C=O), 140.57 (CH=), 128.76 (CH=), 68.29 (OCH), 21.80 (CH_3); IR (KBr) $\nu_{C=O}$ 1700, $\nu_{C=C}$ 1600 cm^{-1}.

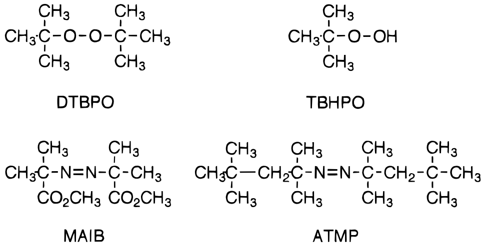
3 was prepared by the isomerization of **1** with heating and was isolated by silica gel−hexane/$CHCl_3$ column chromatography.

3c (diethyl *(E,Z)*-2,4-hexadienoate): bp 102 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 8.40 (dd, $J = 5.6$ and 11.8 Hz, 1H, *cis*-$RO_2CCH{=}CH{-}$), 6.64 (t, $J = 11.7$ Hz, 1H, *trans*-$RO_2CCH{=}CH{-}$), 6.10 (d, $J = 15.1$ Hz, 1H, *trans*-$RO_2CCH{=}CH{-}$), 5.96 (d, $J = 11.2$ Hz, 1H, *cis*-$RO_2CCH{=}CH{-}$), 4.24 (q, $J = 7.3$ Hz, 4H, CH_2), 1.329 (t, $J = 7.3$ Hz, 3H, CH_3), 1.316 (t, $J = 7.3$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 166.06 (C=O), 165.31 (C=O), 140.44 (CH=), 138.47 (CH=), 128.99 (CH=), 124.63 (CH=), 60.72 (CH_2), 60.59 (CH_2), 14.17 (CH_3).

The structure and purity of these monomers were confirmed by IR and NMR spectroscopies and HPLC.

Other Materials. Dimethyl 2,2′-azobis(isobutyrate) (MAIB) and 2,2′-azobis(2,4,4-trimethylpentane) (ATMP) were recrystallized from methanol and hexane, respectively. Commercial di-*tert*-butyl peroxide (DTBPO) and *tert*-butyl hydroperoxide (TBHPO) were used as received. The structure of the initiator used is shown in Chart 2. Other reagents and solvents were used after ordinary purifications.

Chart 2



$(CH_3)_3C{-}O{-}O{-}C(CH_3)_3$

DTBPO

$(CH_3)_3C{-}O{-}OH$

TBHPO

$CH_3C(CH_3)(CO_2CH_3){-}N{=}N{-}C(CH_3)(CO_2CH_3){-}CH_3$

MAIB

$(CH_3)_3C{-}CH_2{-}C(CH_3)_2{-}N{=}N{-}C(CH_3)_2{-}CH_2{-}C(CH_3)_3$

ATMP

Table 1. Bulk Polymerization of 1−3 with DTBPO at 120 °C

monomer no. [amt (mmol)]	monomer configuration	monomer R	amt of DTBPO (mmol)	time (h)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n
1b (7)	*cis,cis*-	methyl	0.07	4	57.6	16.4	1.71
1c (7)	*cis,cis*-	ethyl	0.07	4	25.2	30.3	1.64
1d (4)	*cis,cis*-	*n*-butyl	0.04	4	44.6	13.8	2.53
1f (5)	*cis,cis*-	cyclohexyl	0.07	3	78.9	40.9	1.85
2c (7)	*trans,trans*-	ethyl	0.07	4	60.4	10.7	2.06
2e (7)	*trans,trans*-	isopropyl	0.07	4	53.0	12.8	1.89
3c (7)	*cis,trans*-	ethyl	0.07	4	44.1	13.9	1.81

Polymerization Procedures. Polymerizations in a melt or solution were carried out in a sealed glass tube. The resulting polymers were isolated with an appropriate precipitant, for example, methanol or hexane. Polymer yield was determined gravimetrically. Stereospecific photopolymerization of **1c** was carried out in a sealed or unsealed tube and by direct irradiation of light (or through filters) on the crystals. UV light was irradiated using a Toshiba SHL-100-2. Poly(**1c**) was recovered by removing the unreacted monomer with solvents at room temperature. Purification of the polymers was carried out by reprecipitation.

Measurements. Gel permeation chromatography (GPC) was performed with a Tosoh 8000 series GPC system equipped with TSK-gel columns using tetrahydrofuran (THF) as eluent. Number- and weight-average molecular weights (M_n and M_w, respectively) were calibrated with standard polystyrenes. High-performance liquid chromatography (HPLC) was carried out by a Shimadzu LC-6A equipped with SPD-6A (ODA column; methanol as eluent). NMR spectra were recorded on a JEOL JMN A400 spectrometer in deuteriochloroform or trifluoroacetic acid-*d* at ambient temperature. ESR spectra were taken with a Bruker ESP-300 spectrometer under photoirradiation. IR spectra were recorded on a JASCO A-202 spectrometer. UV spectra were taken with a Shimadzu UV-160 spectrometer. Thermogravimetric analysis (TGA) was performed in a nitrogen stream using a Shimadzu TG-50, and the initial and maximum decomposition temperatures (T_{init} and T_{max}) were determined. Differential scanning calorimetry (DSC) was carried out with a DSC-50. Intrinsic viscosity ([η]) and the Huggins constant (k') were determined in trifluoroacetic acid at 30 °C by using the Huggins[7] and Fuoss−Mead[8] equations.

Results and Discussion

1. Radical Polymerization in an Isotropic State.

Polymerization Reactivity. **1−3** were polymerized in bulk with DTBPO at 120 °C. The monomers shown in Table 1 were in a melt at this temperature. All the polymerizations proceeded homogeneously to give high molecular weight polymers ($M_n = (1{-}4) \times 10^5$) in high yields (25−79% for the 3−4 h polymerization), as shown in Table 1. The highest yield and M_n for the cyclohexyl ester are interpreted by the suppression of bimolecular termination on account of the decrease in polymer-chain

Table 2. Bulk Polymerization of 1d with DTBPO at 120 °C[a]

time (h)	yield (%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
1	15.2	13.4	24.0	1.79
2	24.3	13.9	27.4	1.96
4	44.6	13.8	34.9	2.53
6	66.3	11.3[b]	45.6[b]	4.03[b]
8	77.5	insoluble	insoluble	insoluble
12	82.4	insoluble	insoluble	insoluble

[a] **1d**, 4 mmol; DTBPO, 0.04 mmol. [b] Soluble part.

Table 3. Bulk Polymerization of 1d with ATMP at 120 °C[a]

time (h)	yield[b] (%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	composition of residual monomer[c] (%)		
					1d	**2d**	**3d**
2	54.0	7.97	11.6	1.45	98.5	0	1.5
4	73.5	8.44	12.6	1.49	96.8	0	3.2
8	76.6	7.86	11.6	1.48	88.4	0	11.6
12	84.3	8.31	12.7	1.53	82.2	0	17.8

[a] **1d**, 4 mmol; ATMP, 0.04 mmol. [b] Methanol-insoluble polymer. [c] By HPLC.

mobility due to the increasing steric bulkiness of the substituents and the increasing viscosity of the medium.[9] A similar increase in the polymerization reactivity by introduction of bulky ester alkyl groups is observed for the polymerizations of alkyl methacrylates,[10] dialkyl fumarates,[9] and dialkyl itaconates.[11] The configuration of the monomers, **1**–**3**, did not importantly influence their polymerization reactivities. Namely, three kinds of isomers, **1c**, **2c**, and **3c** gave high molecular weight polymers of more than 10^5 in high yields. These results are different from the fact that *trans* isomers show higher reactivity than *cis* isomers in the radical polymerizations of 1,2-disubstituted ethylenes; for example, fumarates give high molecular weight polymers while maleates do not yield any polymers and oligomers.[12]

When the polymerization of **1d** was carried out up to high conversions, a partly insoluble polymer was formed (Table 2); M_w and M_w/M_n increased with the conversion, and the poly(**1d**) isolated after the 8-h polymerization was swollen with chloroform and THF, but insoluble. This insoluble poly(**1d**) was a transparent elastomer, while the soluble poly(**1d**) isolated from the 4-h polymerization was a tacky mass. It is speculated that hydrogen abstraction from the allylic hydrogens of the polymer main chain by a *tert*-butoxyl radical occurred during the polymerization. The abstraction became more important in the last stage of the polymerization because the concentration of the resulting polymer increased and conversely the concentration of the unreacted monomer decreased. In the polymerization using ATMP as an azo initiator the polymer produced was soluble and the M_n, M_w, and M_w/M_n remained constant even at a high conversion of the monomer (Table 3), which was different from the polymerization with the peroxide. This indicates that the carbon-centered radical generated from ATMP and the propagating radical of poly(**1d**) do not undergo the abstraction reaction.

It was also confirmed in this experiment that isomerization of **1d** to **3d** during the polymerization is very slow, as shown in Table 3. The isomerization of **1d** or **3d** to **2d** did not proceed in this polymerization system. The reverse isomerization of a *trans* form to a *cis* form, that is, from **2d** to **1d** or **3d** and **3d** to **1d**, is not disadvantageous thermodynamically.[13] The isomerization of **1d** to **3d** hardly occurred at 120 °C in the presence of *tert*-butylcatechol, suggesting that the isomerization in Table 3 proceeded through a radical mechanism under these conditions.

Table 4. Solution Polymerization of 2b and 2c with DTBPO at 120 °C[a]

monomer	configuration	R	solvent	time (h)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n
2b	*trans*, *trans*-	methyl	*p*-xylene	25	89.5	1.54	1.85
			DMF	17	78.7	1.16	1.80
2c	*trans*, *trans*-	ethyl	DMF	20	77.3	0.71	1.73

[a] Polymerization conditions: monomer, 8 mmol; DTBPO, 0.16 mmol; solvent, 1 mL.

2 was also polymerized in *p*-xylene or dimethylformamide (DMF) at 120 °C. The results are shown in Table 4. A small part of the **2b** charged was dissolved in the solvents at the initial stage of the polymerization because of its poor solubility, and the polymerization mixture became homogeneous during the polymerization after ca. 10 h, whereas the polymerization of **2c** in DMF proceeded homogeneously throughout the polymerization. These solution polymerizations gave polymers in high yields (77–90%), but the M_n values of the polymers were lower ($M_n = (0.7-1.5) \times 10^4$) than those in the bulk polymerization owing to low monomer concentration and chain transfer to the solvents.

Table 5 shows the results of the polymerization at 60 °C. During the polymerization in benzene, **1b** gave a polymer with an M_n of less than 10^4, whereas **2b** gave hardly any polymer under similar conditions because of the low solubility. The bulk polymerization of **1c** and **1e** gave polymers with an M_n of $(1.5-3.3) \times 10^4$, but both the yield and M_n obtained during the polymerization with MAIB at 60 °C were lower than those with DTBPO at 120 °C (Table 1) despite their similar initiation rates, i.e., the decomposition rate constant (k_d) $= 8.6 \times 10^{-6}$ s^{-1} for MAIB at 60 °C[14] and $k_d = 1.4 \times 10^{-5}$ s^{-1} for DTBPO at 120 °C.[15] Therefore, the effect of the polymerization temperature was further examined for the bulk polymerization of **2c** at 70–150 °C with an appropriate initiator (1 mol %). As shown in Table 6, a high molecular weight polymer ($M_n = (5.1-10.7) \times 10^4$) was produced at a higher polymerization rate in the polymerization at 120 or 150 °C compared with the results at 70 °C. This supported the belief that the ratio of the rate constants for propagation to termination, $k_p/k_t^{0.5}$, increases with an increase in the polymerization temperature. It is speculated that the propagation of **2c** has a large activation energy based on the fact that the propagation is the reaction of a less reactive allyl radical with a sterically hindered internal diolefin.

The structure of the propagating radical from these monomers was directly investigated by ESR spectroscopy during the polymerization. Figure 1 depicts the ESR spectrum from **2c** in benzene in the presence of MAIB with UV irradiation at room temperature. The spectrum intensity decreased with an increase in the temperature because of the rapid termination. The other muconates gave similar spectra irrespectively of the monomer configuration and the ester alkyl groups. The spectra are simulated with large coupling constants due to the α- and γ-hydrogens and small constants due to the β- and δ-hydrogens; $a_1 = 13.0$ G, $a_2 = 4.4$ G, $a_3 = 13.0$ G, and $a_4 = 4.4$ G. This confirms that the propagating chain end is an allyl radical similar to the propagating radicals from isoprene and other 1,3-diene monomers.[16]

Table 5. Solution and Bulk Polymerizations of 1 and 2 with MAIB at 60 °C

monomer								
no. [amt (mmol)]	configuration	R	amt of MAIB (mmol)	solvent [amt (mL)]	time (h)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n
1b (8)	*cis,cis-*	methyl	0.16	C_6H_6 (1)	20	33.3	0.81	1.45
1c (10)	*cis,cis-*	ethyl	0.5	none	24	63.6	1.57	2.58
1e (10)[b]	*cis,cis-*	isopropyl	0.5	none	20	42.8	3.29	1.50
2b (2)	*trans,trans-*	methyl	0.06	C_6H_6 (3)	30	trace		
2c (3)[a]	*trans,trans-*	ethyl	0.04[a]	C_6H_6	20	26.7	1.36	1.52

[a] In mol/L. [b] Mixture of *cis,cis-* and *cis,trans*-isomers; *cis,cis-/cis,trans-* = 67/33.

Table 6. Bulk Polymerization of 2c at Various Temperatures

initiator[a]	temp (°C)	time (h)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n
TBHPO	150	2.5	72.6	5.10	2.25
DTBPO	120	4	60.4	10.7	2.06
MAIB	70	20	48.2	2.48	2.88

[a] 1 mol % of **2c**.

Structure of Polymers. The polymers of ethyl, *n*-butyl, and isopropyl esters are tacky irrespective of the polymerization conditions. The methyl and cyclohexyl derivatives were isolated as a powder and solid, respectively. The cross-linked poly(**1d**), which was formed during the polymerization under the conditions in Table 2, showed elasticity. All the polymers obtained were colorless and transparent, and they were soluble in benzene, toluene, chloroform, and THF, except for cross-linked poly(**1d**). Poly(**1d**) and poly(**1f**) were insoluble in methanol, but the others were soluble. The methyl and ethyl esters were insoluble in diethyl ether and hexane. These polymers were stable on exposure to air and UV light, resulting in no gelation during the isolation and purification of the polymers.

The polymer structure was examined by IR and NMR spectroscopies. Figure 2 shows the IR spectra of **2c** and poly(**2c**). The absorption due to the 1,3-diene at 1610 cm^{-1} in the spectrum of the monomer disappeared in that of the polymer. A peak due to the methine on a *trans* double bond was observed at 975 cm^{-1} in the spectrum of the polymer, but the characteristic peak of the *cis* double bond was not detected around 650–750 cm^{-1}. Similar results were also observed in the other polymerizations.

Figure 3 shows the ^{1}H NMR spectrum of poly(**2c**). Peaks a–d are assigned to the protons of methine on the double bond, methylene, methine adjacent to the carbonyl, and methyl, respectively. Peaks a and c are split owing to the tacticities of the asymmetric centers and *cis* and *trans* configurations of the 1,4-unit, as described later. If 1,2-propagation occurs during the polymerization, resonances due to the double bond protons in the side chain would appear. Table 7 summarizes the observed and calculated chemical shifts of alkyl crotonate and isocrotonate as model compounds for the dangling double bond in the polymer.[17,18] The α- and β-protons of the crotonate resonate at a lower magnetic field than those of the isocrotonate. These chemical shifts support that the three broad resonances at 6.3–6.8 ppm with very weak intensity in the spectrum of poly(**2c**) are assigned to the e protons shown in Figure 3. The tacticity of the chiral carbons produced by the 1,2-propagation would cause more split peaks for the e protons in the addition to the *cis* and *trans* configurations in the dangling bond. The large peaks a and c conceal the resonances due to the other protons f, g, and h.

If 2,1-propagation occurs during the polymerization, it would also give a dangling double bond similar to that in the 1,2-propagation. Here, the *cis* and *trans* configurations of the dangling double bond in the polymer should be determined by the configuration of the

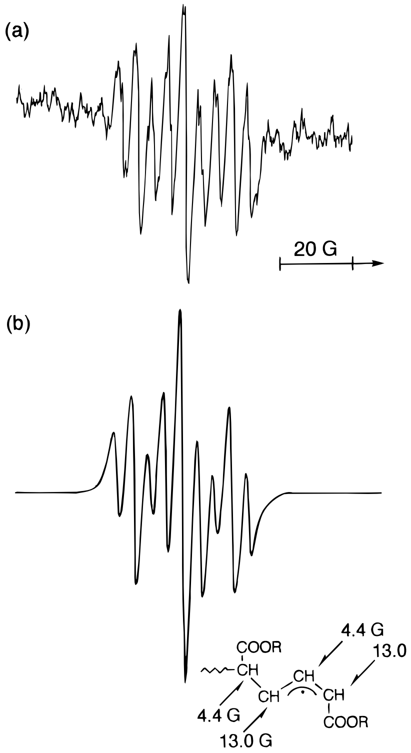


Figure 1. ESR spectrum observed for the propagating radical of **2c** in benzene under UV irradiation at room temperature: (a) observed, [monomer] = 1 mol/L, [MAIB] = 0.05 mol/L; (b) simulated, a_1 = 13.0 G, a_2 = 4.4 G, a_3 = 13.0 G, a_4 = 4.4 G.

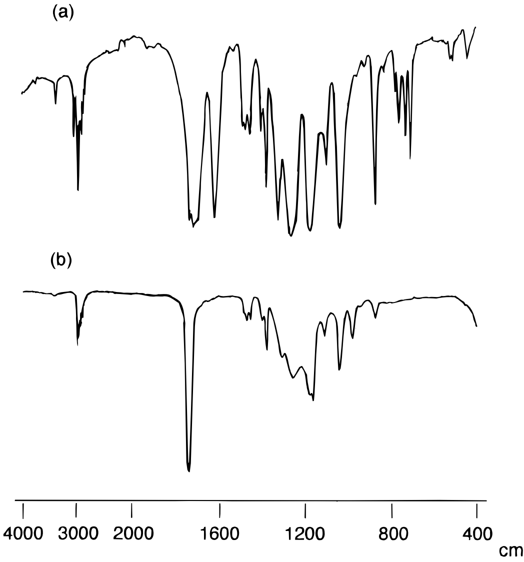


Figure 2. IR spectra of (a) **2c** and (b) poly(**2c**) prepared by bulk polymerization of **2c** (in the melt) at 70 °C.

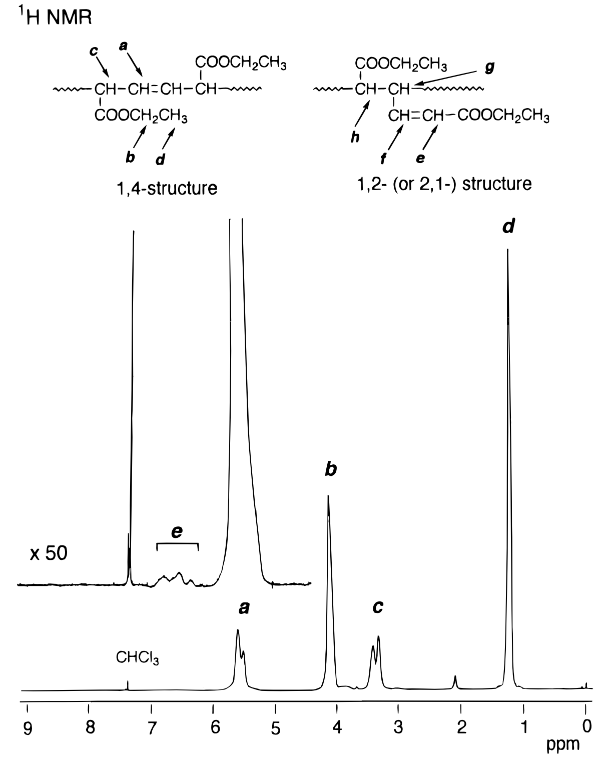
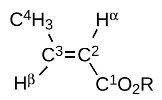
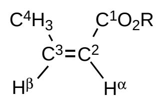


Figure 3. ^{1}H NMR spectrum of poly(**2c**) prepared by bulk polymerization of **2c** (in the melt) at 70 °C. Solvent: chloroform-*d*.

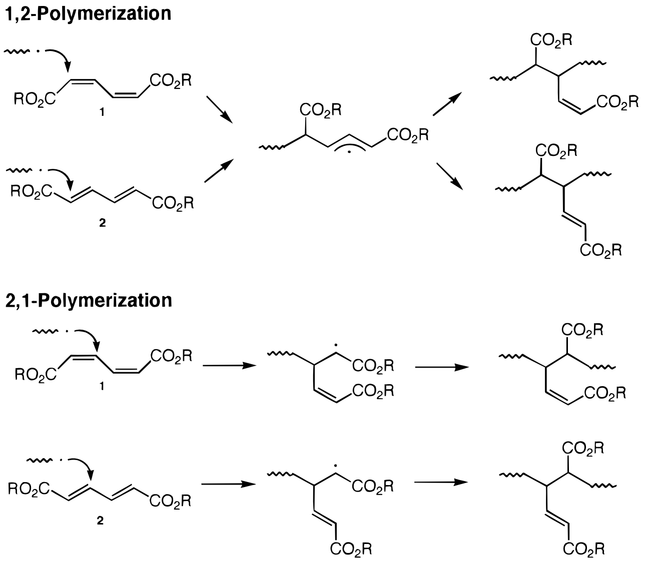
Table 7. ^{1}H and ^{13}C NMR Chemical Shifts of Alkyl Crotonate and Isocrotonate as Model Compounds for the Dangling Double Bond in the Polymer

	chemical shift, ppm			
compd	^{1}H NMR[a]		^{13}C NMR[b]	
	H$^{\alpha}$	6.85 (6.71)	C-1	166.0
	H$^{\beta}$	5.75 (5.81)	C-2	122.3
			C-3	144.1
			C-4	17.1
	H$^{\alpha}$	6.21[c] (6.16)	C-1	166.2
	H$^{\beta}$	5.70[c] (5.75)	C-2	120.4
			C-3	144.5
			C-4	15.6

[a] For *tert*-butyl ester. The values in parentheses are calculated.[17a] [b] For methyl ester.[17b] [c] Reference 18.

monomers, as represented in Scheme 1; in other words, **1** bearing a *cis,cis*-configuration would retain a *cis* double bond in the side group after the polymerization, and **2** would yield a *trans* one. Contrary to this, in the 1,2-propagation, both **1** and **2** produce allylic radicals with identical structures, resulting in dangling double bonds with both *cis* and *trans* configurations. The same structure of the propagating radicals from **1** and **2** has been confirmed by the ESR spectra as described above. In the 1,2-propagation, the ratio of *trans* to *cis* configuration of the dangling double bond is related to the conformation of the substituents around the propagating radical, irrespective of the configurational structure of the monomers. From the fact that poly(**1c**) and poly(**3c**) gave the resonances at 6.3−6.8 ppm similar to that of poly(**2c**) in the ^{1}H NMR spectra, we conclude that these resonances are due to the 1,2-propagation, but not the 2,1-propagation. The steric hindrance of the substituents in the polymer radical and in the monomer may inhibit the 2,1-propagation.

Scheme 1



Thus ^{1}H NMR spectra revealed that the contribution of the 1,2-propagation is much less (2−4%) compared to the 1,4-propagation. In the ^{13}C NMR spectrum (Figure 4), the predominant 1,4-structure of poly(**2b**) was also confirmed. Traces of the peaks based on the 1,2-unit were detectable at 165, 143, and 126 ppm for the f, h, and g carbons, respectively. These assignments are supported by the chemical shifts for the model compounds (Table 7).[17b] The methine carbon adjacent to the carbonyl (peak d) shows a well-split pattern. The peaks at 50−52 and 45−47 ppm are assigned to the *trans*-1,4- and *cis*-1,4-units, respectively (Figure 5), according to the assignments for the polymer which was prepared through group transfer polymerization by Hertler et al.[19a] The peak intensity ratio of these *cis* and *trans* units depended on the polymerization temperature; that is, the *cis*-1,4-structure increased with an increase in the temperature. The results of the determination of the microstructure of poly(**2c**) as well as the other polymers are summarized in Table 8. In the case of the isopropyl ester, the ratio of the *trans*-1,4- to *cis*-1,4-propagations is also determined by the ratio of the peaks due to the methine protons of the ester alkyl group in the ^{1}H NMR spectrum. The ratio of the *trans*-1,4-propagation to the *cis*-one agreed well with the values determined from ^{13}C NMR spectroscopy. Consequently, these polymers were revealed to consist of 84−91% of the *trans*-1,4-configuration and 6−13% of the *cis*-1,4-one.

***Trans*-1,4-Propagation Mechanism.** From the Arrhenius plots for the 1,2- to 1,4-propagations and *cis*-1,4- to *trans*-1,4-propagations, the differences in the activation energies, $E_{1,4} - E_{1,2}$ and $E_{trans\text{-}1,4} - E_{cis\text{-}1,4}$, are −5.7 and −6.5 kJ/mol, respectively, for the polymerization of **2c**. The ratio of the frequency factors is very small; $A_{1,4}/A_{1,2}$ and $A_{trans\text{-}1,4}/A_{cis\text{-}1,4}$ are 6.7 and 1.1, respectively.

The 1,2-propagation is not favored because of the increasing steric hindrance between the propagating radical and the attacking monomer. The extent of 1,2-propagation decreased depending on the configuration of the monomer in the following order: **1c** (4.3%) > **3c** (3.1%) > **2c** (2.3%) at 120 °C. A similar tendency was also observed in the polymerization at 60 °C. Because the conformations of the propagating radicals from **1c**, **2c**, and **3c** are similar, this order may reflect the more

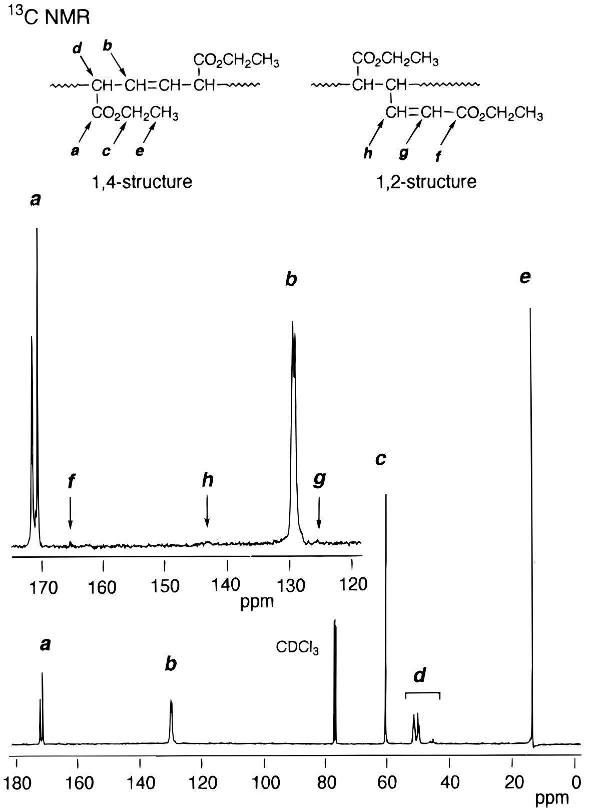


Figure 4. ^{13}C NMR spectrum of poly(**2c**) prepared by bulk polymerization of **2c** (in the melt) at 70 °C. Solvent: chloroform-*d*.

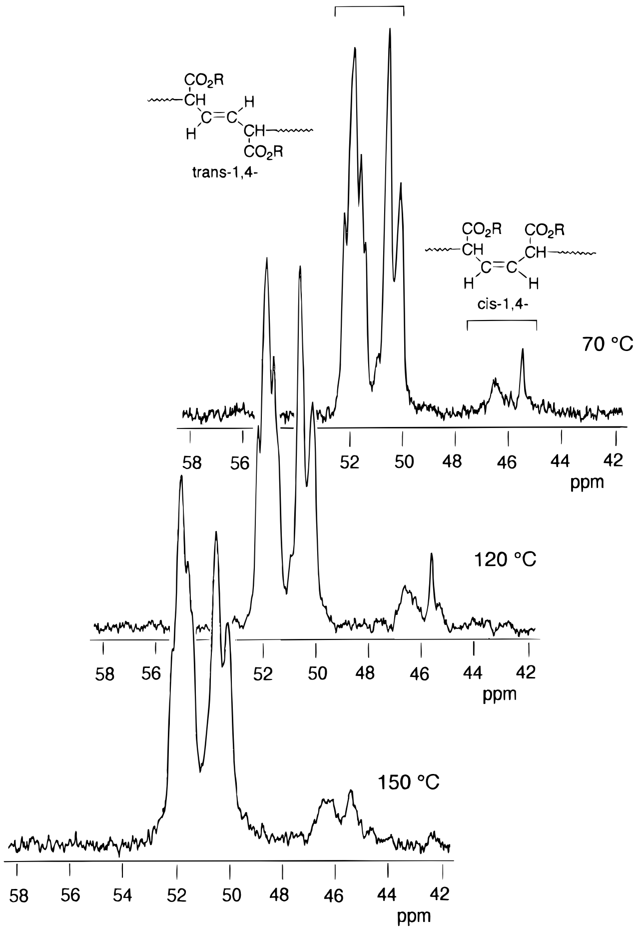


Figure 5. Expanded ^{13}C NMR spectra of poly(**2c**) prepared by bulk polymerization of **2c** (in the melt) at various temperatures.

Table 8. Microstructure of Poly(dialkyl muconate)s Prepared by Bulk or Solution Polymerizations

polymerization conditions				microstructure[a] (%)		
monomer	configuration	R	temp (°C)	1,2-	*trans*-1,4-	*cis*-1,4-
1b	*cis,cis*-	methyl	60	2.8	(97.2)[b]	
			120	3.6	(96.4)[b]	
1c	*cis,cis*-	ethyl	60	2.6	91.3	6.1
			120	4.3	86.1	9.6
1d	*cis,cis*-	*n*-butyl	120	4.2	87.4	8.4
1e	*cis,cis*-[c]	isopropyl	60	3.2	89.5	7.3
1f	*cis,cis*-	cyclohexyl	120	4.2	83.9	11.9
2c	*trans,trans*-	ethyl	60	2.0	89.9	8.1
			70	1.9	89.9	8.2
			120	2.3	86.5	11.2
			150	3.2	84.5	12.3
2e	*trans,trans*-	isopropyl	120	2.9	84.0	13.1
					(83.2)[d]	(13.9)[d]
3c	*cis,trans*-	ethyl	120	3.1	88.0	8.9

[a] The ratios of 1,2- to 1,4-structure and of *trans*-1,4 to *cis*-1,4 were determined by ^{1}H and ^{13}C NMR, respectively. [b] Sum of *trans*-1,4 and *cis*-1,4. [c] *cis,cis*-/*cis,trans*- = 67/33. [d] By ^{1}H NMR.

significant steric hindrance in the 1,2-propagation of the monomers with the *trans* configuration. The effect of the ester alkyl group is negligible in yielding a similar microstructure. For example, the 1,2-contents were 3.6, 4.3, 4.2, and 4.2% for the polymers prepared from **1b**, **1c**, **1d**, and **1f** at 120 °C, respectively.

The Arrhenius parameters indicate that the *trans*-1,4-propagation is energetically preferred over the *cis*-1,4-propagation (−6.5 kJ/mol). The *syn*-form radicals in Scheme 2 give the *trans*-1,4-structure and the *anti*-form radicals yield the *cis*-1,4-one. The former radicals are favorable because of less steric hindrance between the polymer chain and the terminal CO_2R group.

2. Stereospecific Polymerization in a Crystalline State. Topochemical Polymerization of 1c. The results of the photoinitiated polymerization of the crystalline **1c** are shown in Table 9. The **1c** crystals polymerized on exposure to a Hg lamp, sunlight, or scattered light. This photopolymerization proceeded irrespective of the atmospheric conditions, **1c** gave a polymer in vacuo, in air, or even in water (**1c** is insoluble in water). However, **1c** gave no polymer in solutions, for example, in benzene, methanol, hexane, or toluene.

In 1964, Schmidt[20] correlated the crystal structure of several olefin derivatives with the photoreactivity and steric configuration of the products and established the topochemical principle in which the reaction tends to occur with a minimum of atom and molecular motions. Topochemical reactions yield products the structure of which is controlled by the crystal lattice of the reactant. In some cases, they give a product with a structure which is different from that of the product obtained from the reactions in a liquid or gaseous state. For example, Lahav and Schmidt et al. reported the stereospecific dehydrohalogenation[21] and vinyl-substituted cyclobutane formation[22] through topochemical reactions of some muconic derivatives. However, only two kinds of polymerizations are known as topochemical polymerization in the literature, that is, polymerizations of 2,5-distyrylpyrazine derivatives[23] and diacetylene derivatives.[24] The photopolymerization in this work also proceeds topochemically. Although the topochemical polymerization of **1b**, **2b**, **2c**, and **3c** was attempted under similar conditions, no polymer was obtained. This topochemical polymerization was unique for the **1c** crystals in the present monomer series.

Scheme 2

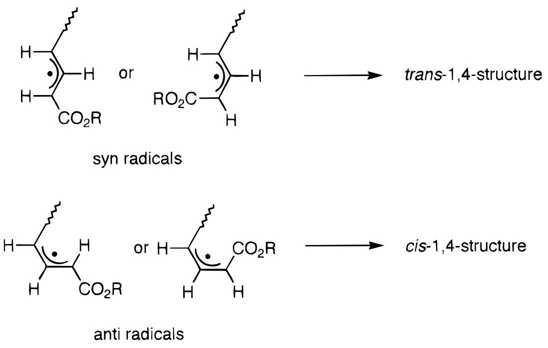


Table 9. Polymerization of the Monomer Crystals under Photoirradiation

monomer	light source	atmosphere	temp (°C)	time (h)	yield (%)
1c	Hg lamp	in degassed Pyrex tube	0	4	46.5[a]
1c	Hg lamp	in degassed quartz tube	0	4	61.5
1c	Hg lamp	in unsealed Pyrex tube	0	4	20.3
1c	sunlight	in air	rt	4	71.6
1c	sunlight	in air	rt	5[b]	88.7[c]
1c	sunlight	in water (insoluble)	rt	4	84.6
1c	scattered light	in air	rt	10[b]	>95
1c	scattered light	in benzene solution	rt	14[b]	0
1c	in dark	in air	30	48	0
1b	Hg lamp	in air	0	4	0
2b	Hg lamp	in air	0	4	0
2c	Hg lamp	in air	0	4	0
3c	Hg lamp	in air	0	4	0

[a] $[\eta] = 939$ cm^3/g, $k' = 0.56$ in CF_3COOH at 30 °C. [b] In days. [c] $[\eta] = 1170$ cm^3/g, $k' = 0.65$ in CF_3COOH at 30 °C.

The topochemical polymerization of the **1c** crystals can be directly followed with the naked eye as a morphological change during the polymerization. When light was irradiated on the crystals, the crystals were bent in the direction of the light within a few minutes after the irradiation. On subsequent polymerization, the crystals recovered their original shape except for shrinking ca. 2% in length and decreasing in transparency. As seen in the photograph of the crystals in Figure 6, an increase of the number of lines along the long axis of the crystal was observed during polymerization, probably indicating formation of cracks in the crystals. During the irradiation, the polymer chains were produced and oriented at the same time in the direction of the long axis and they formed the fibril structure, as shown in Figure 7.

Poly(**1c**) obtained by topochemical polymerization in the crystalline state was soluble in trifluoroacetic acid and 1,1,1,3,3,3-hexafluoro-2-propanol but insoluble in other common organic solvents, for example, methanol, ethanol, chloroform, benzene, hexane, THF, DMF, and dimethyl sulfoxide. This poly(**1c**) was estimated to be of very high molecular weight based on its intrinsic viscosity; the $[\eta]$ values were 939−1170 cm^3/g, corresponding to a molecular weight of more than 10^6. GPC and HPLC analyses of the chloroform-soluble part after the topochemical polymerization of **1c** showed that no oligomers were formed during the polymerization. These findings and several features of the polymerization, for example, initiation by UV irradiation and successful polymerization in water, suggest that this polymerization proceeds via a radical chain mechanism. Therefore, the photopolymerization was carried out in the ESR tube in the cavity of the spectrometer. We detected a signal with weak intensity based on the propagating radical because the concentration of the species was low.

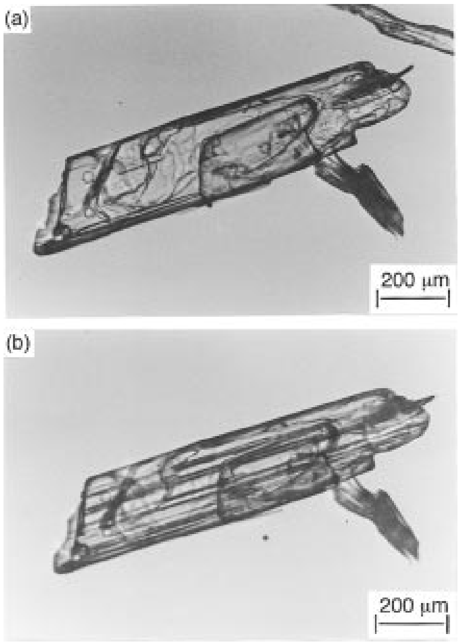


Figure 6. Photomicrographs of the crystal **1c** during topochemical polymerization: (a) 1.5 min; (b) 10 min.

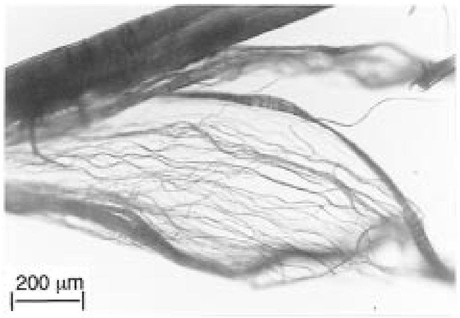


Figure 7. Fibril structure of poly(**1c**) prepared by topochemical polymerization of the **1c** crystal.

Table 10. Effect of Wavelength of Irradiation Light on Polymerization of 1c Crystals

light source	wavelength (nm)	atmosphere	temp (°C)	time	yield (%)
Hg lamp	>250	in vacuo	0	4 h	38.3
	>280	in vacuo	0	4 h	41.6
	>360	in vacuo	0	4 h	10.5
	>390	in vacuo	0	4 h	1.3
	>670	in vacuo	0	4 h	0
sunlight	>250	in air	rt	3 days	89.7
	>280	in air	rt	3 days	91.9
	>360	in air	rt	3 days	54.2
	>390	in air	rt	3 days	46.2
	>670	in air	rt	3 days	0
	310−410	in air	rt	5 days	90.8
	300−500	in air	rt	5 days	77.2
	390−590	in air	rt	5 days	27.9
	460−590	in air	rt	5 days	8.9

Further ESR study of this topochemical polymerization is now in progress. From the experiments with photoirradiation of selected wavelength as shown in Table 10, it has been clarified that light of ca. 300 nm is effective for this polymerization. **1c** has a maximum absorption due to a $\pi-\pi^*$ transition at 260 nm and a weak absorption at 280 nm due to an $n-\pi^*$ transition. A radical species seems to be produced from the excited **1c**, but the mechanism for radical formation and initiation of the polymerization is still ambiguous.

Structure of Stereoregular Poly(1c). The polymer obtained by the topochemical polymerization of the **1c**

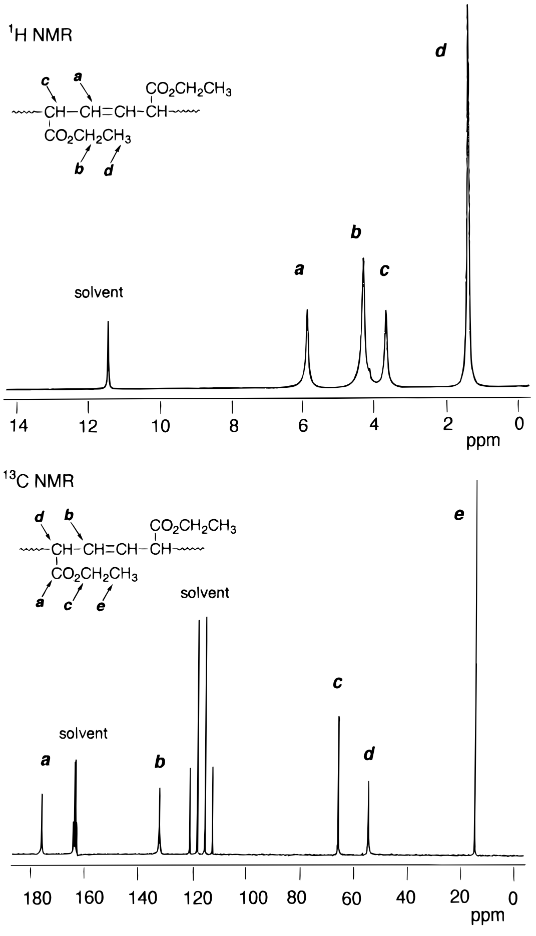


Figure 8. ^{1}H and ^{13}C NMR spectra of poly(**1c**) prepared by topochemical polymerization of the **1c** crystals. Solvent: trifluoroacetic acid-*d*.

crystals has been revealed to be of excellent stereoregularity. The ^{1}H and ^{13}C NMR spectra of the poly(**1c**) are shown in Figure 8, which were measured in trifluoroacetic acid-*d* at ambient temperature. In these spectra, the peaks due to the 1,2- and *cis*-1,4-structures are not observed. The comparison of the expanded ^{13}C NMR spectra of the stereoregular poly(**1c**) prepared by topochemical polymerization with those of the poly(**1c**) prepared by ordinary radical polymerization in the melt at 70 °C is shown in Figure 9. All resonances of the stereoregular poly(**1c**) are single peaks with a narrow line width, compared to the complicated splitting of the peaks for the predominantly *trans*-1,4-poly(**1c**) prepared by the isotropic polymerization described in section 1. This indicates that this stereoregular polymer is a highly regulated tritactic polymer; that is, the tacticities of the double bond and the two methine carbons are highly regulated. Four possible structures of the repeating units of the tritactic polymers are illustrated in Figure 10, which are produced by combination of the ordering manner of the monomer molecules with the opening mode of the diene unit. These possibilities are dominated by the crystal structure. Rätzsch et al.[19b] and Wang et al.[19c] reported the ^{13}C NMR chemical shifts of *meso*- and *d,l*-2,3-dialkylsuccinic acid and its ester. The carbonyl and methine carbons of the *meso* compound resonate at a higher and lower magnetic field than those of the *d,l*-compound, respectively (Table 11). The carbonyl and methine carbon resonances at 176.0 and 54.3 ppm suggest that the topochemically-prepared polymer is of *meso*-diisotactic or *meso*-disyndiotactic structure.[19a] Further studies of the tacticity of this stereoregular polymer are continuing.

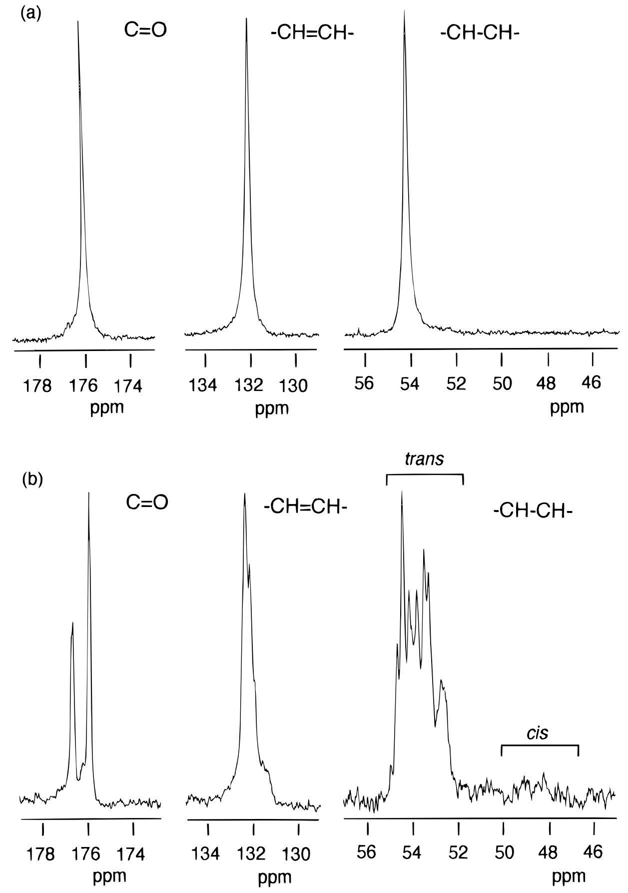


Figure 9. Expanded ^{13}C NMR spectra of poly(**1c**)s prepared by (a) topochemical polymerization of the **1c** crystals and (b) isotropic polymerization of **1c** in the melt. Solvent: trifluoroacetic acid-*d*.

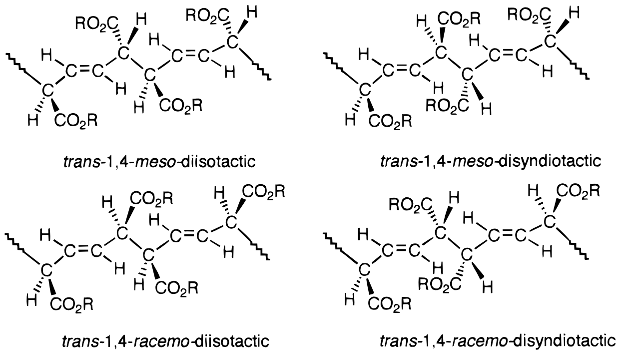


Figure 10. Four possible configurations for the stereoregular sequence of the *trans*-1,4-polymer of dialkyl muconate.

The thermal properties of the stereoregular poly(**1c**) were subsequently examined by DSC with the sample which was prepared as follows: after the photopolymerization of the **1c** crystals, the unreacted monomer was extracted with chloroform at room temperature. The remaining polymer was dried in vacuo and used for the DSC measurement without further treatment, for example, dissolving in solvents, melting, or annealing. In the DSC thermogram (Figure 11), no transition was observed below the onset temperature of decomposition ($T_{\text{init}} = 253$ °C, Figure 12) in the first heating cycle without any preheating. In the second run after preheating to 250 °C, an endothermic peak was observed at 239 °C. This transition is due to the melting of the

Table 11. ^{13}C NMR Chemical Shifts for Poly(1c) Prepared by Topochemical and Isotropic Polymerizations and Several Model Compounds

	chemical shift, ppm		
compd	C═O	CH	solvent[a]
poly(**1c**) prepared by topochemical polymerization	175.98	54.33	A
poly(**1c**) prepared by isotropic polymerization	176.78	54.90	A
	176.05	54.65	
		54.36	
		54.08	
		53.75	
		53.43	
		53.21	
		52.70	
d,l-2,3-diethylsuccinic acid	176.0	47.9	B
meso-2,3-diethylsuccinic acid	175.7	50.2	B
diisopropyl *d,l*-2,3-dimethylsuccinate	175.7	42.9	C
diisopropyl *meso*-2,3-dimethylsuccinate	175.1	43.9	C

[a] A, trifluoroacetic acid-*d*; B, THF-d_8;[19b] C, chloroform-*d*.[19c]

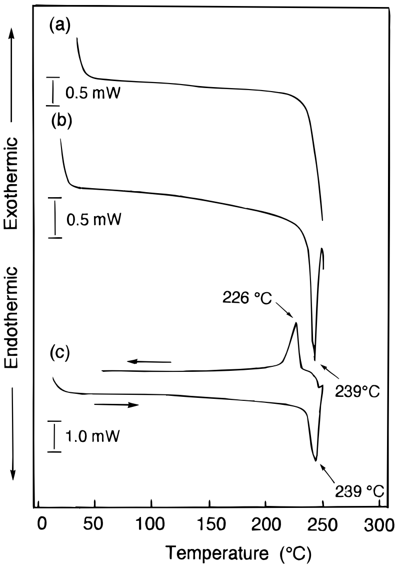


Figure 11. DSC traces for poly(**1c**) prepared by topochemical polymerization of the **1c** crystals: (a) first run without preheating; (b) second run after preheating to 250 °C and subsequent quenching; (c) heating and cooling process. Heating and cooling rate of 10 °C/min.

crystalline part of the polymer. In the cooling cycle, the exothermic peak due to the crystallization was clearly observed at 226 °C and the formation of spherulite was also confirmed. The TGA thermograms in Figure 12 indicate that the stereoregular poly(**1c**) has a higher T_{init} and the subsequent decomposition is completed below 350 °C. This is due to the high tacticity of poly(**1c**) prepared by topochemical polymerization, i.e., the homogeneity of the chemical structure of the repeating units in the polymer.

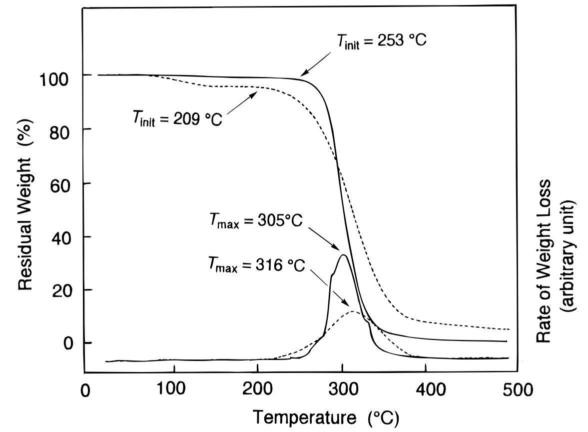
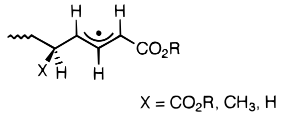


Figure 12. TGA curves of poly(**1c**)s prepared by (a) topochemical polymerization of the **1c** crystals (—) and (b) isotropic polymerization of **1c** in the melt (- - -). Heating rate of 10 °C/min. In a nitrogen stream.

Chart 3



3. Stereospecific Polymerization of Substituted Butadienes. The *trans*-1,4-polymerizations through radical polymerization in isotropic media have also been reported for several other butadiene derivatives, for example, 2,4-pentadienoic acid and its esters[25−28] and 2,4-hexadienoates (alkyl sorbates).[28] The preferred *trans*-1,4-propagation of these diene monomers is accounted for by similar conformations of the propagating radicals depicted in Chart 3, where X is CO_2R, CH_3, or H. Thus the stereoselectivity is determined by the conformation of the propagating chain end during the free radical polymerization of the muconates and other related substituted butadienes. In these polymerizations in isotropic media, however, the *trans*-1,4-selectivity is incomplete and the tacticities with respect to the two chiral carbon centers are atactic. On the other hand, in the inclusion polymerization, complete *trans*-1,4-polymerization is achieved.[29,30] Furthermore, the topochemical polymerization in this work provided a tritactic polymer on account of the strictly limited stereochemical requirement of the crystal lattice. In anionic polymerization with alkyllithium in a nonpolar solvent, stereospecific polymerization of muconates has been reported. In 1965, the synthesis of tritactic poly(diisopropyl muconate) by anionic polymerization with *n*-butyllithium in toluene at −40 °C was first reported[31] as well as the polymerization of alkyl sorbates by Natta and co-workers.[32,33] However, the structure of their tritactic poly(diisopropyl muconate) prepared by anionic polymerization has not been examined by NMR spectroscopy.

Conclusions. It has been revealed that dialkyl muconates give high molecular weight polymers in bulk polymerization at 120 °C with a radical initiator, despite the internal diolefin structure. Because the propagation is a reaction between the less reactive allyl radical and the sterically hindered internal diolefin, the activation energy for the propagation is probably larger than that in the propagation of less-hindered ordinary vinyl monomers, resulting in the lower polymerization reactivity of the muconates at a lower temperature. The resulting polymer consists predominantly of the 1,4-structure and the ratio of *trans*-1,4 to *cis*-1,4 is 6.9−15.0, depending on the polymerization temperature. The *trans*-1,4-polymers from the muconates can be utilized as a plastic or rubber with excellent transparency and stabilities to oxidation and light as a new type of diene and acrylate polymer.

In contrast to solution and bulk polymerizations in an isotropic state, the photopolymerization of the crystals of **1c** uniquely proceeds to give a polymer of ultrahigh molecular weight with a highly regulated structure (tritactic polymer). From the interesting features of the polymerization and high stereoregularity of the polymer obtained, we have revealed that the polymerization of the crystalline **1c** on exposure to a light proceeds through a topochemical polymerization mechanism. Our topochemical polymerization of muconate is the first evidence of the synthesis of tritactic polymers of a diene polymer with a highly regulated structure through topochemical polymerization. The polymerizations of monomers with an organized structure show a different reactivity and mechanism in the reactions compared to those in an isotropic solution or a melt. Molecular crystals as well as micelles, mono- or multilayers, vesicles, liquid crystals, and inclusion compounds can provide specific polymerization media as reaction loci.[34] As a next step in the study on the topochemical polymerization of muconates, the clarification of the detailed features and mechanism and the crystallographic analysis are now in progress.

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