Stereospecific Radical Polymerization of Substituted Benzyl Muconates in the Solid State Under Topochemical Control

Akikazu Matsumoto,*[a] Toshihiro Tanaka,[a,c] Kunio Oka[b]

[a] Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
Fax +81(6)66052981; E-mail: matsumoto@a-chem.eng.osaka-cu.ac.jp

[b] Research Institute for Advanced Science and Technology, Osaka Prefecture University, Gakuencho 1-2, Sakai, Osaka 599-8570, Japan

[c] Chemical Resources Laboratory, Tokyo Institute of Technology, R1-5, 4259, Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

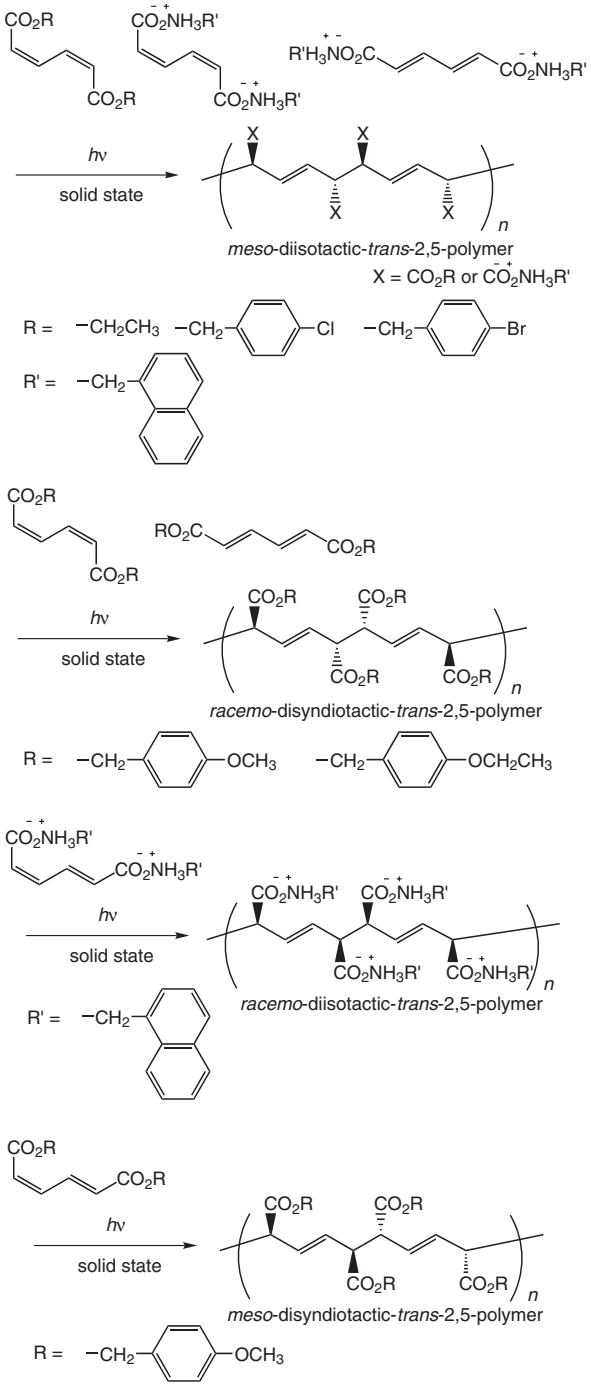
Received 15 February 2005

This paper is dedicated to Prof. B. Giese on the occasion of his 65th birthday.

Abstract: We have successfully controlled the stereochemical structure of diene polymers during radical polymerization in the solid state under UV and γ-ray radiation. The polymerization of the substituted benzyl muconates occurred via a crystal lattice controlled reaction mechanism. The polymerization is controlled by not only diisotactic and disyndiotactic, but also *meso* and *racemo* structures to afford various kinds of stereoregular polymers.

Key words: crystal engineering, controlled radical polymerization, solid-state reaction, stereoregularity, topochemical reaction

The control of stereochemical chain structures is one of the most important topics for polymer syntheses since the first discovery of stereoregular polymers in the 1950s by Natta et al.[1] The control of propagation is carried out by the coordination of a chain end and a reacting monomer to the metal center of a catalyst during the metal-catalyzed polymerization of various kinds of vinyl and diene monomers. In contrast, a radical chain-end dynamically rotates and therefore takes several preferred conformations during the free-radical polymerization,[2] leading to atactic polymer formation in most cases. In recent years, stereospecific free-radical polymerization processes in the presence of a Lewis acid[3] or template[4] was reported in addition to several successful radical polymerizations under substrate[5] and chiral-auxiliary[6] control, in which the conformation of a radical chain end and the addition of monomers are highly controlled. Polymer crystal engineering also intensively fascinates us for the control of the chain structures as well as the polymer chain assembly in the solid state.[7] During the past decade, we have demonstrated that a large number of 1,3-diene monomers proceed in the crystalline state to give polymer crystals with a highly controlled chain structure. For example, muconic and sorbic acids as well as other diene carboxylic acids as the ester, amide, and ammonium derivatives provide a stereoregular *trans*-1,4-diisotactic diene polymer during the solid-state polymerization via a topochemically controlled reaction mechanism. Topochemical polymerization is applied to many unsaturated monomers other than 1,3-diene monomers on the basis of the common to-



Scheme 1

SYNTHESIS 2005, No. 9, pp 1479–1490
Advanced online publication: 18.04.2005
DOI: 10.1055/s-2005-865320; Art ID: C00805SS

pochemical polymerization principles.[8] We have already succeeded in controlling the monomer stacking in the crystals with intermolecular interactions such as robust two-dimensional hydrogen bond networks as well as CH/π or CH/O interactions as a weak hydrogen bond to design the solid-state polymerization of 1,3-diene monomers.[9–12]

During the solid-state polymerization, an isotactic polymer is exclusively produced because monomer molecules usually tend to get arranged with a translational molecular packing in the crystals.[13] For example, the ethyl,[14] 4-chlorobenzyl,[10] or 4-bromobenzyl[10] esters of (*Z*,*Z*)-muconic acid were confirmed to stack translationally in a column in the monomer crystals, and undergo topochemical polymerization during photoirradiation leading to the formation of a diisotactic polymer (Scheme 1). The other muconic and sorbic derivatives such as the amide and ammonium derivatives also provide diisotactic polymers via the topochemically controlled propagation of translationally stacked monomers in the crystals.[7] Recently, we also found that a disyndiotactic polymer is produced by the alternate stacking of bis(4-methoxybenzyl) (*Z*,*Z*)- or (*E*,*E*)-muconate through CH/π intermolecular interactions in a column formed in the monomer crystals.[15] Furthermore, all of the four possible kinds of stereoregular diene polymers have actually been fabricated by the translational and alternate molecular stacking in the crystals in combination with the molecular symmetry of the geometric isomers of the muconic derivatives. We found that not only the (*Z*,*Z*)- and (*E*,*E*)-1,3-diene monomers, but also the (*E*,*Z*)-diene monomers undergo topochemical polymerization to provide the different kinds of stereoregular polymers.[16]

In this study, we have investigated the crystal structure and solid-state polymerization of alkoxy-substituted benzyl muconates as well as several related ester monomers, as shown in Figure 1. We report the synthesis of stereoregular diene polymers with a different stereochemical structure through the controlled radical polymerization in the solid state.

The stereospecific synthesis of muconic esters is necessary for the design and control of polymer structures because *E*/*Z*-isomerism significantly influences the photoreaction behavior in the crystalline state. In general, the *Z*,*Z*-isomers of the 1,3-diene compounds, such as the muconic derivatives, readily isomerize into the corresponding *E*,*Z*- and *E*,*E*-isomers upon heating or during photoirradiation in the absence or presence of a catalyst,[17] but the quantitative reverse reaction forming the *Z*,*Z*-isomers hardly occurred. Table 1 summarizes the results for the synthesis of benzyl muconates using (*Z*,*Z*)-muconic acid as the starting material. (*Z*,*Z*)-Muconic acid is well-known as one of the important intermediates in a natural metabolic system of aromatic compounds,[18] and a synthetic process from D-glucose using microorganisms has been developed.[19] When muconic esters were prepared by conventional methods, it was difficult to efficiently obtain *Z*,*Z*-isomers without *E*,*Z*-isomerization. For example, the dehydration of muconic acid and 4-bromobenzyl alcohol in the presence of sulfuric acid at reflux in benzene for 3 hours resulted in the formation of the *E*,*Z*-isomer as the major product; *Z*,*Z*/*E*,*Z* = 4:96. When the muconic acid chloride was prepared by the reaction with thionyl chloride in dichloromethane at reflux for one hour, and allowed to react with 4-bromobenzyl alcohol in the presence of triethylamine, the ester was isolated as the mixture of three isomers; yield: 28%, *Z*,*Z*/*E*,*Z*/*E*,*E* = 82:14:4. The esters were produced in a higher yield at a higher temperature and for a longer time, but the contents of *E*,*Z*- and *E*,*E*-isomers increased. The *Z*,*Z*-isomer was isolated by silica gel chromatography, but the *E*,*Z*- and *E*,*E*-isomers are hardly separated from each other.

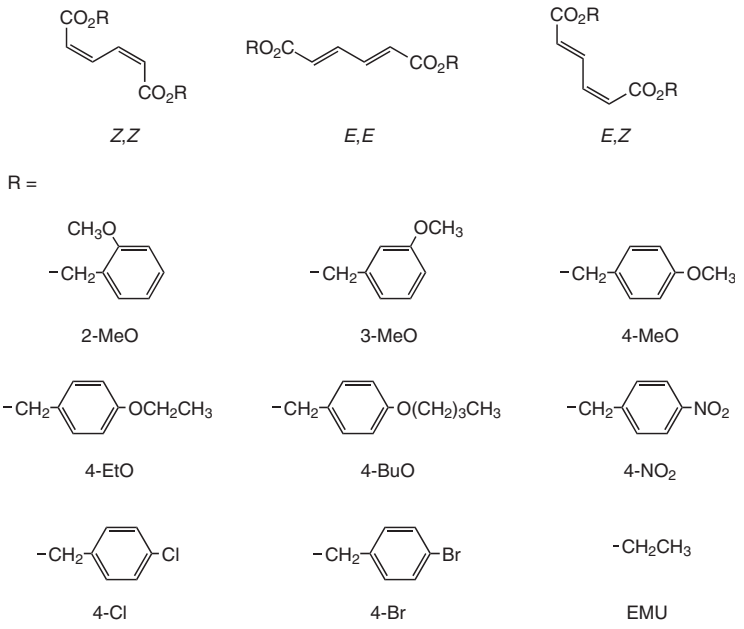


Figure 1 Chemical structure of muconates used in this study

To carry out the reactions under milder conditions for suppressing the isomerization, we first adopted a quaternary ammonium carboxylate salt as the phase-transfer catalyst in a two-phase system for the esterification. When a weak base was used, the isomerization was suppressed; *Z,Z*/*E,Z* = 82:18. Next, we tested the reaction of potassium muconate with benzyl bromides in the presence of a base in a highly polar solvent such as hexamethylphosphoramide or *N*-methylpyrrolidone. As a result, the acid was converted into the corresponding ester without any *E,Z*-isomerization. The *Z,Z*-isomers were exclusively obtained in a high yield for various kinds of substituted benzyl esters and no *E,Z*- and *E,E*-isomers were detected in the crude products (Table 1), whereas a reaction with benzyl chloride provided a mixture of *Z,Z*- and *E,Z*-isomers. Thus, the reaction of potassium muconate with benzyl bromides in a polar solvent is a convenient method for the stereoselective synthesis of *Z,Z*-derivatives, including simple processes for the synthesis and isolation of the esters (see experimental section).

The (*E,Z*)-muconates were directly prepared from (*E,Z*)-muconic acid in a method similar to that for the *Z,Z*-derivatives, or separated from a mixture of the *Z,Z*- and *E,Z*-isomers by silica gel chromatography. For the preparation of the *E,E*-monomers, the crude products as the mixture of isomers were photoirradiated at room temperature in the presence of a small amount of iodide as the isomerization catalyst.[17] All the monomers were recrystallized from chloroform or any other appropriate solvent.

Table 2 summarizes the results of the solid-state reactions for a series of substituted benzyl muconates under UV or γ-ray radiation. The reactivity and mechanism of the solid-state reactions are determined by the style of the molecular stacking in the crystals rather than the chemical nature of the reactants. Therefore, the reaction pathway of the substituted benzyl muconates in this study significantly depends on not only the substituents on a benzyl group but also the *E,Z*-configuration of the muconate. The type of a reaction for the monomers in Table 2 are divided into several groups; (i) polymerized under both UV and γ-radiation, (ii) isomerized under UV irradiation and polymerized under γ-radiation, (iii) isomerized under UV irradiation and no reaction under γ-radiation, (iv) no reaction under UV irradiation and polymerized under γ-radiation, and (v) no reaction under both UV and γ-radiation.

Some *Z,Z*-monomers underwent a solid-state polymerization and produced a polymer in a high yield under both UV and γ-ray radiation. The other *Z,Z*-derivatives isomerized to the corresponding *E,E*-isomers under UV irradiation, but they provided a different product under γ-radiation; atactic and stereoregular polymers or no reaction. Isomerization was specific to the reaction of the *Z,Z*-compounds and no isomerization occurred for the *E,E*- and *E,Z*-derivatives. Several *E,E*-monomers were polymerized under UV and γ-radiation, similar to the results of the *Z,Z*-derivatives. Two of the *E,Z*-isomers had no reaction under UV irradiation, but the γ-radiation resulted in the formation of a polymer. Interestingly, the polymerization proceeded independent of the electronic nature of the substituent on the benzyl group, the polymerization was induced by the methoxy, ethoxy, chloro, bromo, and nitro substituents at the *meta* or *para* position. Several other derivatives were inert to both the UV and γ-radiation. All the reactions of the (*E,E*)- and (*E,Z*)-muconates are classified into categories (i) or (v), and (iv) or (v), respectively. The (*Z,Z*)-muconates showed a complicated reaction behavior depending on the position and structure of the substituents due to several possible pathways, as shown in Scheme 2. The isomerization and polymerization competitively proceeds for the reaction of the *Z,Z*-isomers. Nevertheless, either an *E,E*-isomer or a polymer was obtained as the product in each reaction. Namely, the reaction occurred

Table 1 Stereospecific Synthesis of Benzyl Muconates from (*Z,Z*)-Muconic Acid[a]

RX (1.0–1.1 equiv)	Solvent[b]	K_2CO_3 (equiv)	Time (h)	Yield (%)	Isomer *Z,Z*/*E,Z*/*E,E*
4-Bromobenzyl bromide	H_2O–CH_2Cl_2[c]	2.2[d]	72	84	30:70:0
4-Bromobenzyl bromide	H_2O–CH_2Cl_2[c]	1.1	72	56	82:18:0
4-Bromobenzyl bromide	HMPA	1.5	24	79	ca. 100:0:0
4-Chlorobenzyl bromide	HMPA	1.5	48	96	ca. 100:0:0
4-Ethoxybenzyl bromide	HMPA	1.5	24	85	ca. 100:0:0
4-Nitrobenzyl bromide	HMPA	1.5	24	84	ca. 100:0:0
Benzyl bromide	NMP	2	24	63[e]	ca. 100:0:0[e]
4-Methoxybenzyl chloride	HMPA	1.5	72	78	70:30:0

[a] Reaction was carried out by stirring at room temperature.
[b] HMPA: hexamethylphosphoramide; NMP: *N*-methylpyrrolidone.
[c] With tetrabutylammonium hydrogensulfate.
[d] KOH was used.
[e] As isolated by recrystallization from MeOH.

with a high selectivity, being one of the characteristics of the solid-state reactions under a crystal-lattice control.

We previously reported that several (*Z*,*Z*)-muconic derivatives easily isomerize to the corresponding *E*,*E*-isomers in the crystalline state without any formation of *E*,*Z*-isomers as the side product, and that the reverse reaction does not occur.[20] This crystal-to-crystal one-way *E*,*Z*-isomerization is induced by the excitation of diene compounds during the UV irradiation. When the adjacent monomer molecules are situated at the position appropriate for the topochemical polymerization, the solid-state polymerization favorably proceeds via a radical chain mechanism.[21] Under γ-radiation, the formed radical species induces a similar radical chain polymerization rather than isomerization in the crystalline state. No isomerization during γ-radiation was confirmed by the NMR spectra of the recovered monomers after polymerization at a lower reaction dose.

The X-ray crystallographic analyses of the monomer and the polymer single-crystals reveal a relationship between the molecular stacking in the monomer crystals and the stereochemical structure of polymers as well as the solid-

Table 2 Products for UV and γ-Radiation of Substituted Benzyl Muconates in the Crystalline State[a]

Monomer	Ar substituent	UV Irradiation		γ-Radiation		Reaction
		Product	Yield (%)	Product	Yield (%)	type[b]
(*Z*,*Z*)-2-MeO	2-Methoxy	*E*,*E*-Isomer	18	No reaction	–	iii
(*Z*,*Z*)-3-MeO	3-Methoxy	*E*,*E*-Isomer	4	Polymer[c,d]	55	ii
(*Z*,*Z*)-4-MeO	4-Methoxy	Polymer	93	Polymer	ca. 100	i
(*Z*,*Z*)-4-EtO	4-Ethoxy	Polymer	95	Polymer	ca. 100	i
(*Z*,*Z*)-4-BuO	4-*n*-Butoxy	*E*,*E*-Isomer	57	Polymer	ca. 100	ii
(*Z*,*Z*)-4-NO_2	4-Nitro	Polymer	31	Polymer	ca. 100	i
(*Z*,*Z*)-4-Cl[e]	4-Chloro	Polymer	97	Polymer	ca. 100	i
(*Z*,*Z*)-4-Br[e]	4-Bromo	Polymer	87	Polymer	ca. 100	i
(*E*,*E*)-2-MeO	2-Methoxy	No reaction	–	No reaction	–	v
(*E*,*E*)-3-MeO	3-Methoxy	Polymer	67	Polymer	ca. 100	i
(*E*,*E*)-4-MeO	4-Methoxy	Polymer	81	Polymer	ca. 100	i
(*E*,*E*)-4-EtO	4-Ethoxy	Polymer	63	Polymer	ca. 100	i
(*E*,*E*)-4-BuO	4-*n*-Butoxy	No reaction	–	No reaction	–	v
(*E*,*E*)-4-NO_2	4-Nitro	No reaction	–	No reaction	–	v
(*E*,*E*)-4-Cl	4-Chloro	No reaction	–	No reaction	–	v
(*E*,*E*)-4-Br	4-Bromo	No reaction	–	No reaction	–	v
(*E*,*Z*)-4-MeO	4-Methoxy	No reaction	–	Polymer[c]	96	iv
(*E*,*Z*)-4-EtO	4-Ethoxy	No reaction	–	No reaction	–	v
(*E*,*Z*)-4-BuO	4-*n*-Butoxy	No reaction	–	Polymer[c,d]	80	iv
(*E*,*Z*)-4-NO_2	4-Nitro	No reaction	–	No reaction	–	v
(*E*,*Z*)-4-Cl	4-Chloro	No reaction	–	No reaction	–	v
(*E*,*Z*)-4-Br	4-Bromo	No reaction	–	No reaction	–	v

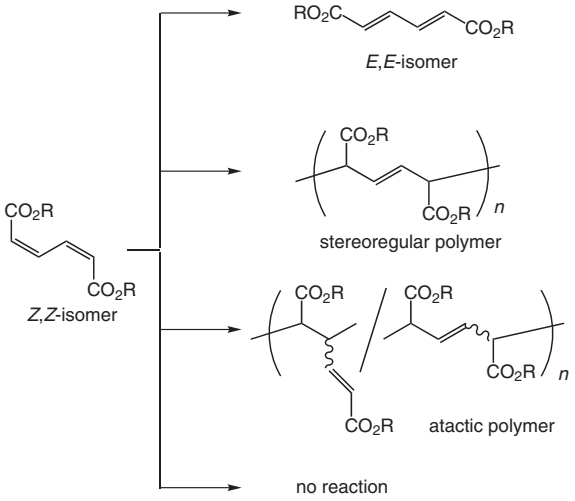
[a] Benzyl muconates were recrystallized from $CHCl_3$. UV irradiation was carried out using a high-pressure Hg lamp (100 W) at a distance of 10 cm for 8 h at r.t. γ-Radiation was carried out with ^{60}Co at r.t. at a dose of 200 kGy. Polymers were isolated as insoluble products. The isomerization conversion was determined by ^1H NMR spectroscopy.

[b] i: polymerized under both UV and γ-radiation; ii: isomerized under UV irradiation and polymerized under γ-radiation; iii: isomerized under UV irradiation and no reaction under γ-radiation; iv: no reaction under UV irradiation and polymerized under γ-radiation; v: no reaction under both UV and γ-radiation.

[c] The product was soluble in $CHCl_3$. The yield was determined from the integration ratio of benzyl methylene protons in the ^1H NMR spectra.

[d] Atactic polymer was obatined after the γ-radiation polymerization at a dose of 200 kGy.

[e] Ref.[10]



Scheme 2

state polymerization reactivity. The crystal structures of the monomers were determined at –70 °C to avoid the effect of the polymerization during X-ray measurements. A comparison of the crystallographic data for the monomer and polymer single crystals provides much information regarding the solid-state polymerization mechanism.

The crystallographic results confirm a topochemical process during the polymerization of the muconates in the solid state. As a typical example, the crystal structures of (*Z*,*Z*)-NO_2 and poly[(*Z*,*Z*)-NO_2] are shown in Figure 2, which indicates translational monomer packing leading to diisotactic polymer formation. Figure 3 shows the alternate stacking resulting in a disyndiotactic polymer for (*Z*,*Z*)-4-MeO and poly[(*Z*,*Z*)-4-MeO].[15]

Figure 4 shows intermolecular interaction forming the translational and alternate molecular stacking in a columnar structure in the crystals. In the alternate stacking structure, the CH/π interaction[22] is important between the methoxy methyl and the phenyl carbons of the benzyl group. The zig-zag chain of the interaction is formed along a monomer column, and it supports the alternate stacking. A similar interaction is observed in the polymer crystals. The weak intermolecular interactions are capable of a variety of crystal structure formations by inducing a different molecular stacking leading to the different tacticity of the polymers. This is contrast to the formation of exclusive translational molecular stacking for the ammonium derivatives supported by a strong hydrogen bond network, which has a robust and credible but inflexible structure.[23] Disyndiotactic polymers are obtained from the 4-methoxy and ethoxy derivatives by the alternate stacking, and all the other polymers have a diisotactic structure due to the translational stacking of the monomers. For example, the 3-methoxy, 4-chloro-, 4-bromo-, and *n*-butoxy derivatives translationally stack as well as the nitro-substituted one shown in Figure 2, resulting in the formation of the diisotactic polymers.

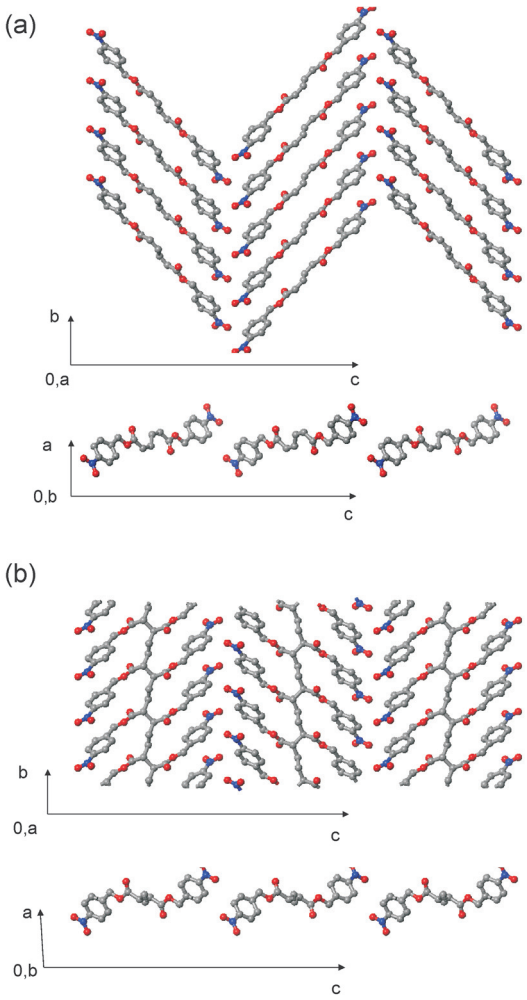


Figure 2 Single-crystal structures of (*Z*,*Z*)-NO_2 and poly[(*Z*,*Z*)-NO_2]; The monomer molecules are translationally stacked along the crystallographic *b* axis of the crystal of *Z*,*Z*-NO_2. Diisotactic polymer chains are formed along the same axis during the polymerization.

The relationship between the molecular stacking in the monomer crystals and the polymerization reactivity has already been examined in detail in our previous study.[7] The monomer stacking structures of the monomers used in this study were also checked according to a general rule for the polymerization of 1,3-diene monomers.[8,24] We determined the stacking distance (d_s), the distance between the reacting C_2 and C_5' carbons (d_{cc}), and the tilt angles of the molecular plane (θ_1 and θ_2) to estimate the polymerization reactivity[7] (Figure 5). These results are summarized in Table 3. For all the polymerizable monomers, the stacking distance was 4.7–5.5 Å, and the carbon-to-carbon distance for the reaction was 3.3–4.2 Å. In the monomer crystal of (*Z*,*Z*)-3-MeO, the largest d_s value (5.54 Å) and d_{cc} value (4.16 Å) were observed. Due to the structure consisting of a poor molecular stacking in the monomer crystals, no polymer was formed during the UV irradiation. Even under γ-radiation, the polymer formation possibly collapsed the crystal structure during the initial stage of the polymerization, leading to the atactic polymer formation.

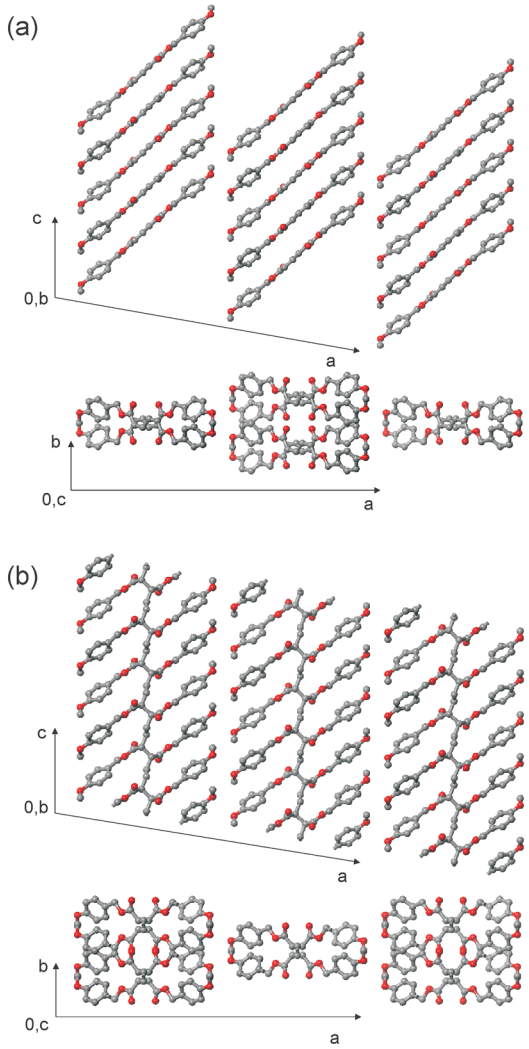


Figure 3 Single-crystal structures of (*Z*,*Z*)-4-MeO and poly[(*Z*,*Z*)-4-MeO]; The monomer molecules are alternately stacked along the crystallographic *b* axis of the crystal of (*Z*,*Z*)-4-MeO (Ref.[15]). Disyndiotactic polymer chains are formed along the same axis during the polymerization.

The polymers were highly crystalline and insoluble in organic solvents after they were isolated as the polymer crystals by removing the unreacted monomer with any organic solvent. When the polymer crystals were once heated over their melting point in the bulk, or in a polar solvent with a high boiling point, they were recovered as the amorphous or partly crystalline polymers for the alkoxy-substituted benzyl ester polymers. In contrast, the chloro- and bromo-substituted polymers were insoluble after heating because of their high melting temperature and strong intermolecular interaction. The polymer crystals are uniquely obtained by the solid-state polymerization, while partly crystalline polymers are prepared by the crystallization of preformed polymers by a conventional method. They show physical properties different from each other.

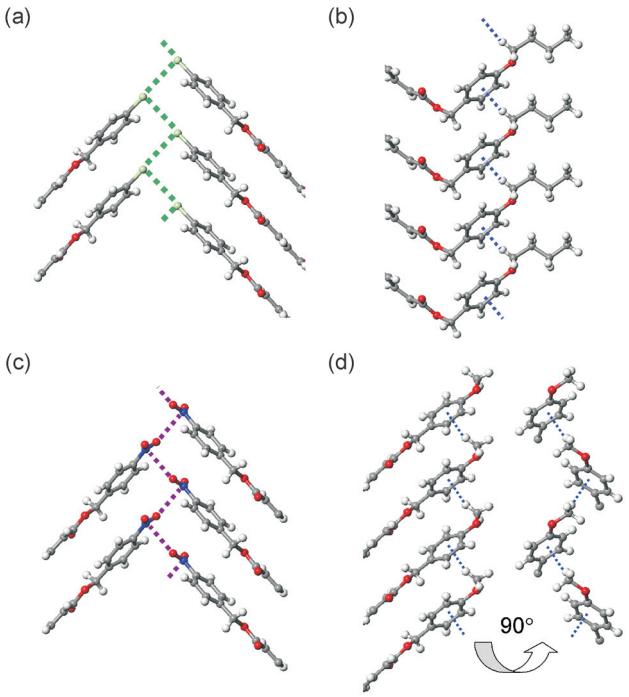


Figure 4 Intermolecular interaction forming the translational molecular stacking in the crystals: (a) (*Z*,*Z*)-4-Cl, (b) (*Z*,*Z*)-4-BuO, (c) (*Z*,*Z*)-4-NO_2; Intermolecular interaction forming the alternate molecular stacking in the crystals: (d) (*Z*,*Z*)-4-MeO

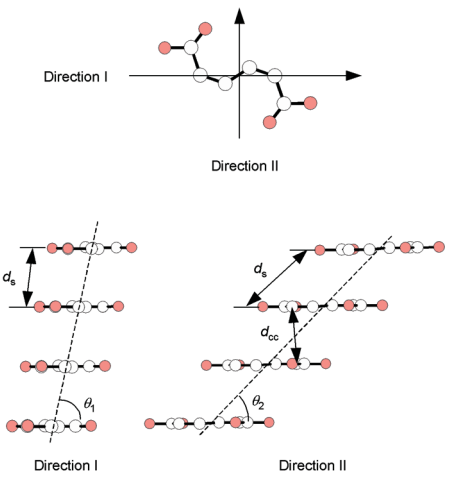


Figure 5 Stacking model for the muconate derivatives in the crystalline state and the definition of stacking parameters used for the prediction of the topochemical polymerization reactivity. d_{cc} is the intermolecular distance between the 2- and 5′-carbons. d_s is the stacking distance between the adjacent monomers in a column. θ_1 and θ_2 are the angles between the stacking direction and the molecular plane in orthogonally different directions. The view from direction I is parallel to a vector through the 2- and 5-carbons of the diene moieties (Ref.[7]).

The narrow and single peaks for each carbon observed in ^{13}C NMR spectra for the polymers obtained by the γ-radiation polymerization of substituted benzyl muconates and the subsequent treatment by heating. This indicates the formation of a stereoregular polymer during the polymer-

ization, except for the polymerization of (*Z*,*Z*)-3-MeO and (*E*,*Z*)-4-BuO. These two monomers provided no polymer under UV-irradiation and an amorphous polymer during γ-radiation polymerization due to the poor molecular stacking in the monomer crystals.

There are four types of possible stereoregular structures for each *trans*-1,4-polymer of 1,4-disubstituted butadiene[10] (Scheme 1). In general, the stereochemistry of polymers is represented by two kinds of relationships as follows: one is the relative configuration between the two repeating monomer units, diisotactic and disyndiotactic polymers, and the other is the relative configuration between the vicinal carbon centers, being represented by the *meso* and *racemo*. The stereochemical structure of the polymers produced during the topochemical polymerization is designed on the basis of the *E*,*Z*-configuration and the stacking of the monomers. When the corresponding *E*,*Z*-monomers with a different symmetrical structure undergo topochemical polymerization, the produced polymer has a stereoregular structure different from that obtained from the *Z*,*Z*- and *E*,*E*-monomers. Actually, the alternate stacking of bis(4-methoxybenzyl) (*E*,*Z*)-muconate resulted in the formation of a *meso*-disyndiotactic polymer.

Table 4 summarizes the comparison and the chemical shifts for the stereoregular polymers obtained from various muconic esters. The *meso* and *racemo* structure can be determined based on the absolute value of the chemical shift; 170.2–170.5 and 170.9–171.3 ppm for the C=O carbons, 129.6–129.9 and 129.3–129.4 ppm for the CH=CH carbons, 51.3–52.0 and 50.7–50.9 ppm for the CH carbons, respectively, independent of the kind of ester groups and diisotactic or disyndiotactic structures. A difference in a chemical shift depending on the *meso* and *racemo* structures was also observed for polyfumarates with alkoxycarbonyl substituents on the vicinal carbons in the polymer main chain, as was previously reported.[25] The stereochemical structure of the polymers can directly be determined by a single crystal structure analysis in some cases. However, NMR spectroscopy is a convenient method for determining the stereochemical structure of the polymers, because polymer single crystals with a high quality for an X-ray experiment are not always successfully obtained.

We further tried to synthesize stereoregular polymers with different tacticities but the same ester alkyl group. The monomer stacking structure and the tacticity of the obtained polymers by topochemical polymerization significantly depended on the structure of the ester alkyl groups. As a result, it is very hard to obtain different stereoregular polymers from the same monomer by polymerization. Therefore, we adopted the polymer transformation from the various benzyl ester polymers to the ethyl ester polymers with different tacticities. The benzyl esters were readily hydrolyzed and produced poly(muconic acid)s, which were dissolved in ethanol as the triethylammonium salt and then reacted with ethanol, leading to the quantitative transformation as ethyl esters. Consequently, the

Table 3 Monomer Stacking Parameters for Topochemically Polymerizable Substituted Benzyl Muconates in the Monomer Crystals[a]

Monomer	Polymerization reactivity		d_s	d_{cc}	θ_1	θ_2
	UV	γ-Ray	(Å)	(Å)	(degree)	(degree)
Translational Stacking Monomers						
(*Z*,*Z*)-4-BuO	no	yes	4.86	3.78	88	52
(*Z*,*Z*)-4-Cl[c]	yes	yes	5.06	3.48	78	43
(*E*,*E*)-3-MeO	yes	yes	5.14	3.38	78	40
(*Z*,*Z*)-4-Br[c]	yes	yes	5.21	3.89	72	49
(*Z*,*Z*)-4-NO_2	yes	yes	5.24	3.61	75	44
(*Z*,*Z*)-3-MeO	no	yes[b]	5.54	4.16	65	46
Alternate Stacking Monomers						
(*Z*,*Z*)-4-MeO	yes	yes	4.74	3.44	–[d]	–[d]
(*Z*,*Z*)-4-EtO	yes	yes	4.83	3.25	–[d]	–[d]
(*E*,*E*)-4-MeO	yes	yes	4.87	3.32	–[d]	–[d]
(*E*,*E*)-4-EtO	yes	yes	4.82	3.25	–[d]	–[d]
(*E*,*Z*)-4-MeO	no	yes	5.39	3.90	–[d]	–[d]

[a] d_{cc}: Distance between the reacting C_2 and C_5' carbons, d_s: stacking distance, θ_1, θ_2: tilt angles of the molecular plane.
[b] Crystals collapsed during the polymerization.
[c] Ref.[10]
[d] Not determined because of alternate stacking.

Table 4 ^{13}C NMR Chemical Shifts for Stereoregular Muconate Polymers with Different Tacticities

Polymer	Tacticity	Chemical shift, δ ($CDCl_3$) at r.t.		
		C=O	CH=	CH
Poly[(*Z*,*Z*)-4-BuO]	*meso*-Diisotactic	170.28	129.74	51.27
Poly[(*E*,*E*)-3-MeO]	*meso*-Diisotactic	170.20	129.71	51.74
Poly[(*E*,*Z*)-4-MeO]	*meso*-Disyndiotactic	170.16	129.85	51.61
Poly[(*Z*,*Z*)-4-MeO]	*racemo*-Disyndiotactic	170.95	129.31	50.74
Poly[(*E*,*E*)-4-MeO]	*racemo*-Disyndiotactic	170.94	129.38	50.71
Poly[(*Z*,*Z*)-4-EtO]	*racemo*-Disyndiotactic	170.87	129.31	50.85
Poly[(*E*,*E*)-4-EtO]	*racemo*-Disyndiotactic	170.89	129.30	50.85
Poly(EMU)	*meso*-Diisotactic	170.48	129.59	52.04
	meso-Disyndiotactic[a]	170.46	129.71	51.45
	racemo-Disyndiotactic[b]	171.32	129.37	50.61

[a] Derived from poly[(*E*,*Z*)-4-MeO] by polymer transformation.
[b] Derived from poly[(*E*,*E*)-4-MeO] by polymer transformation.

chemical shifts for the poly(EMU)s with various tacticities also supported the same conclusion (Table 4). The physical properties of the substitiuted benzyl and ethyl esters with different tacticities are now under investigation. The results will be reported elsewhere in the future together with details for the transesterification of the polymers.

Historically, the isotactic polymerization of vinyl monomers was followed by syndiotactic one, as seen in the development of the stereospecific polymerization of styrene,[26] propylene,[27] methacrylates,[28] and crotonates.[29] More sophisticated catalysts are required for the control of the syndiotactic propagation during a catalytically controlled polymerization. For diene polymerization with a catalytic control, Takasu et al.[30] recently reported the synthesis of a predominantly disyndiotactic poly(alkyl sorbate) by anionic polymerization. However, the synthesis of diene polymers with a highly controlled stereochemical structure has been still one of the challenging topics, including polymuconates and polysorbates.[31] We have successfully demonstrated the stereochemical control of diene polymers, the control of not only diisotactic and disyndiotactic but also *meso* and *racemo* structures, during the solid-state polymerization under crystal-lattice control, which has a feature different from those for the controlled polymerization in solution.

Esterification of (*Z*,*Z*)-Muconic Acid; Bis(4-bromobenzyl) Muconate; Typical Procedures

Method A;Using a Phase-Transfer Catalyst: (*Z*,*Z*)-Muconic acid (711 mg, 5.0 mmol), Bu_4NHSO_4 (3.73 g, 11 mmol), and KOH (1.23 g, 22 mmol) were dissolved in 1,2-dichloroethane (20 mL) and H_2O (20 mL) in a 100 mL flask. 4-Bromobenzyl bromide (2.75 g, 11 mmol) was added and the mixture stirred at r.t. for 3 d. The reaction mixture was poured into H_2O (100 mL), and the crude product was extracted with $CHCl_3$ (2 × 100 mL). The combined $CHCl_3$ extracts were washed with H_2O, dried (Na_2SO_4), and evaporated under reduced pressure to provide a crude white solid. The solid was subjected to short-path silica gel column chromatography with $CHCl_3$, to provide bis(4-bromobenzyl)muconate; yield: 20.1 g (84%); isomer ratio: *Z*,*Z*/*E*,*Z* = 30:70 (determined by ^1H NMR spectroscopy).

Method B; Using Hexamethylphosphoramide: To (*Z*,*Z*)-muconic acid (2.1 g, 15 mmol) in hexamethylphosphoramide (20 mL) in a 100-mL flask equipped with a $CaCl_2$ tube were added 4-ethoxybenzyl bromide (6.6 g, 33 mmol) and K_2CO_3 (4.4 g, 32 mmol) and stirred at r.t. for 1 d. The reaction mixture was poured into H_2O (300 mL), and the crude product was extracted with $CHCl_3$ (2 × 150 mL). The combined $CHCl_3$ extracts were washed with H_2O, dried (Na_2SO_4), and evaporated under reduced pressure. To precipitate the 4-ethoxybenzyl esters, H_2O and MeOH were added to the residual liquid. The precipitated white solid was filtered and dried under reduced pressure; yield: 5.23 g (85%).

Bis(2-methoxybenzyl) (*Z*,*Z*)-Muconate [(*Z*,*Z*)-2-MeO]

Colorless plates; mp 87.3–88.0 °C ($CHCl_3$).

IR (KBr): 1589 (C=C), 1713 cm^{-1} (C=O).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (m, C*H*=CHCO$_2$R, 2 H), 7.29–7.35 (m, C_6H_4, 4 H), 6.88–6.98 (m, C_6H_4, 4 H), 6.03 (m, CH=C*H*CO$_2$R, 2 H), 5.24 (s, CH_2, 4 H), 3.85 (s, CH_3, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.58 (C=O), 157.58 (C_6H_4), 138.10 (CH=), 129.91, 129.74, 124.18, 123.93, 120.43, and 110.46 (C_6H_4 and CH=), 61.82 (CH_2), 55.42 (CH_3).

UV (MeCN): λ_{max} = 266 nm (ε = 26800).

Bis(3-methoxybenzyl) (*Z*,*Z*)-Muconate [(*Z*,*Z*)-3-MeO]

Colorless prisms; mp 57.1–57.9 °C ($CHCl_3$).

IR (KBr): 1588 (C=C), 1718 (C=O).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (m, C*H*=CHCO$_2$R, 2 H), 7.24–7.31 (m, C_6H_4, 4 H), 6.85–6.97 (m, C_6H_4, 4 H), 6.03 (m, CH=C*H*CO$_2$R, 2 H), 5.16 (s, CH_2, 4 H), 3.81 (s, CH_3, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.32 (C=O), 159.77, 138.37, 137.18, 129.68, 124.02, 120.41, 113.83 and 113.68 (C_6H_4 and CH=), 66.16 (CH_2), 55.25 (CH_3).

UV (MeCN): λ_{max} = 267 nm (ε = 25600).

Bis(4-methoxybenzyl) (*Z*,*Z*)-Muconate [(*Z*,*Z*)-4-MeO]
Colorless plates; mp 82.9–83.2 °C ($CHCl_3$).

IR (KBr): 1584 (C=C), 1717 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (m, C*H*=$CHCO_2R$, 2 H), 7.30–7.35 (m, C_6H_4, 4 H), 6.88–6.93 (m, C_6H_4, 4 H), 6.00 (m, CH=C*H*CO_2R, 2 H), 5.13 (s, CH_2, 4 H), 3.82 (s, CH_3, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.48 (C = O), 159.70 (C_6H_4), 138.21 (CH =), 130.18, 127.80, and 124.11 (C_6H_4), 114.00 (CH =), 66.13 (CH_2), 55.30 (CH_3).

UV (MeCN): λ_{max} = 264 nm (ε = 261000).

Bis(4-ethoxybenzyl) (*Z*,*Z*)-Muconate [(*Z*,*Z*)-4-EtO]
Colorless plates; mp 91.9–92.5 °C ($CHCl_3$).

IR (KBr): 1585 (C=C), 1717 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (m, C*H*=$CHCO_2R$, 2 H), 7.28–7.32 (m, C_6H_4, 4 H), 6.86–6.90 (m, C_6H_4, 4 H), 5.99 (m, CH=C*H*CO_2R, 2 H), 5.11 (s, OCH_2, 4 H), 4.03 (q, 4 H, C*H*$_2$$CH_3$), 1.41 (t, CH_2CH_3, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.50 (C=O), 159.06, 138.19, 130.17, 127.58, 124.11, and 114.49 (C_6H_4 and CH=), 66.16 (OCH_2), 63.46 (*C*H_2CH_3), 14.79 (CH_2CH_3).

UV (MeCN): λ_{max} = 266 nm (ε = 28500).

Bis(4-butoxybenzyl) (*Z*,*Z*)-Muconate [(*Z*,*Z*)-4-BuO]
Colorless plates; mp 82.7–83.2 °C ($CHCl_3$).

IR (KBr): 1593 (C=C), 1718 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (m, C*H*=$CHCO_2R$, 2 H), 7.28–7.31 (m, C_6H_4, 4 H), 6.86–6.89 (m, C_6H_4, 4 H), 5.99 (m, CH=C*H*CO_2R, 2 H), 5.11 (s, OCH_2, 4 H), 3.96 (t, 4 H, C*H*$_2$$CH_2CH_2CH_3$), 1.72–1.80 (m, 4 H, $CH_2CH_2CH_2CH_3$), 1.43–1.54 (m, 4 H, $CH_2CH_2CH_2CH_3$), 0.97 (t, 6 H, $CH_2CH_2CH_2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.50 (C=O), 159.29, 138.18, 130.15, 127.52, 124.13, and 114.52 (C_6H_4 and CH=), 67.71 and 66.18 (OCH_2 and $CH_2CH_2CH_2CH_3$), 31.26 ($CH_2CH_2CH_2CH_3$), 19.22 ($CH_2CH_2CH_2CH_3$), 13.84 ($CH_2CH_2CH_2CH_3$).

UV (MeCN): λ_{max} = 266 nm (ε = 28900).

Bis(4-nitrobenzyl) (*Z*,*Z*)-Muconate [(*Z*,*Z*)-4-NO_2]
Pale yellow plates; mp 174.1–175.2 °C ($CHCl_3$).

IR (KBr): 1587 (C=C), 1712 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.26 (m, C_6H_4, 4 H), 7.96 (m, C*H*=$CHCO_2R$, 2 H), 7.52–7.56 (m, C_6H_4, 4 H), 6.09 (m, CH=C*H*CO_2R, 2 H), 5.29 (s, OCH_2, 4 H).

UV (MeCN): λ_{max} = 271 nm (ε = 43100).

Bis(2-methoxybenzyl) (*E*,*E*)-Muconate [(*E*,*E*)-2-MeO]
Colorless plates; mp 140.9–141.3 °C ($CHCl_3$).

IR (KBr): 1614 (C=C), 1703 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.36 (m, C*H*=$CHCO_2R$ and C_6H_4, 6 H), 6.88–7.00 (m, C_6H_4, 4 H), 6.25 (m, CH=C*H*CO_2R, 2 H), 5.27 (s, CH_2, 4 H), 3.85 (s, CH_3, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.89 (C=O), 157.60 (C_6H_4), 141.05 (CH=), 129.89, 129.79, 128.37, 123.88, 120.45, and 110.51 (C_6H_4 and CH=), 62.20 (CH_2), 55.45 (CH_3).

UV (MeCN): λ_{max} = 266 nm (ε = 35400).

Bis(3-methoxybenzyl) (*E*,*E*)-Muconate [(*E*,*E*)-3-MeO]
Colorless plates; mp 75.3–75.7 °C ($CHCl_3$).

IR (KBr): 1605 (C=C), 1716 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.34 (m, C*H*=$CHCO_2R$ and C_6H_4, 6 H), 6.86–6.97 (m, C_6H_4, 4 H), 6.24 (m, CH=C*H*CO_2R, 2 H), 5.19 (s, CH_2, 4 H), 3.81 (s, CH_3, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.61 (C=O), 159.75 (C_6H_4), 141.21 (CH=), 137.08, 129.69, 128.87, 128.23, 120.48, and 113.78 (C_6H_4 and CH=), 66.56 (CH_2), 55.25 (CH_3).

UV (MeCN): λ_{max} = 266 nm (ε = 35400).

Bis(4-methoxybenzyl) (*E*,*E*)-Muconate [(*E*,*E*)-4-MeO]
Colorless plates; mp 119.8–121.8 °C ($CHCl_3$).

IR (KBr): 1612 (C=C), 1713 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.34 (m, C*H*=$CHCO_2R$ and C_6H_4, 6 H), 6.92–6.88 (m, C_6H_4, 4 H), 6.20 (m, CH=C*H*CO_2R, 2 H), 5.14 (s, CH_2, 4 H), 3.81 (s, CH_3, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.76 (C=O), 159.77 (C_6H_4), 141.08 (CH=), 130.27, 128.31, and 127.70 (C_6H_4), 114.00 (CH=), 65.56 (CH_2), 55.30 (CH_3).

UV (MeCN): λ_{max} = 263 nm (ε = 28000).

Bis(4-ethoxybenzyl) (*E*,*E*)-Muconate [(*E*,*E*)-4-EtO]
Colorless plates; mp 126.5–127.2 °C ($CHCl_3$).

IR (KBr): 1613 (C=C), 1713 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.37 (m, C*H*=$CHCO_2R$ and C_6H_4, 6 H), 6.89–6.93 (m, C_6H_4, 4 H), 6.22 (m, CH=C*H*CO_2R, 2 H), 5.16 (s, OCH_2, 4 H), 4.05 (q, C*H*$_2$$CH_3$, 4 H), 1.43 (s, CH_2CH_3, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.79 (C=O), 159.15, 141.08, 130.27, 128.33, 127.50, and 114.52 (CH= and C_6H_4), 66.61 and 63.48 (OCH_2 and *C*H_2CH_3), 14.81 (CH_2CH_3).

UV (MeCN): λ_{max} = 266 nm (ε = 37000).

Bis(4-butoxybenzyl) (*E*,*E*)-Muconate [(*E*,*E*)-4-BuO]
Colorless plates; mp 108.0–108.8 °C ($CHCl_3$).

IR (KBr): 1613 (C=C), 1706 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.33 (m, C*H*=$CHCO_2R$ and C_6H_4, 6 H), 6.87–6.90 (m, C_6H_4, 4 H), 6.19 (m, CH=C*H*CO_2R, 2 H), 5.14 (s, OCH_2, 4 H), 3.96 (q, C*H*$_2$$CH_2CH_2CH_3$, 4 H), 1.72–1.79 (m, 4 H, $CH_2CH_2CH_2CH_3$), 1.43–1.54 (m, 4 H, $CH_2CH_2CH_2CH_3$), 0.97 (t, 6 H, $CH_2CH_2CH_2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.79 (C=O), 159.38, 141.06, 130.25, 128.33, 127.44, and 114.54 (CH= and C_6H_4), 67.73 and 66.62 (OCH_2 and $CH_2CH_2CH_2CH_3$), 31.26 ($CH_2CH_2CH_2CH_3$), 19.24 ($CH_2CH_2CH_2CH_3$), 13.85 ($CH_2CH_2CH_2CH_3$).

UV (MeCN): λ_{max} = 266 nm (ε = 37900).

Bis(4-nitrobenzyl) (*E*,*E*)-Muconate [(*E*,*E*)-4-NO_2]
Pale yellow powder; mp 191.9–193.3 °C ($CHCl_3$).

IR (KBr): 1616 (C=C), 1716 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.26 (m, C_6H_4, 4 H), 7.53–7.56 (m, C_6H_4, 4 H), 7.40 (m, 2 H, C*H*=$CHCO_2R$), 6.31 (m, CH=C*H*CO_2R, 2 H), 5.32 (s, OCH_2, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.20 (C=O), 142.72, 141.60, 128.49, 127.93, and 123.88 (CH= and C_6H_4), 65.19 (OCH_2).

UV (MeCN): λ_{max} = 269 nm (ε = 51200).

Bis(3-methoxybenzyl) (*E*,*Z*)-Muconate [(*E*,*Z*)-3-MeO]
Colorless liquid.

IR (KBr): 1601 (C=C), 1722 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (dd, *J* = 15.6, 11.6 Hz, *trans*-C*H*=CHCO$_2$R, 1 H), 7.30–7.33 (m, C_6H_4, 4 H), 6.88–7.00 (m, C_6H_4, 4 H), 6.69 (t, *J* = 11.6 Hz, *cis*-C*H*=CHCO$_2$R, 1 H), 6.18 (d, *J* = 15.6 Hz, *trans*-CH=C*H*CO$_2$R, 1 H), 6.02 (d, *J* = 11.6 Hz, *cis*-CH=C*H*CO$_2$R, 1 H), 5.22 (s, OCH_2, 2 H), 5.21 (s, OCH_2, 2 H), 3.82 (s, OCH_3, 3 H), 3.81 (s, OCH_3, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.76 and 164.94 (C=O), 159.72 and 159.57, 140.98, 138.96, 137.31, 137.10, 129.69, 129.63, 128.85, 113.90, 113.70, and 113.47 (CH= and C_6H_4), 66.34 and 66.29 (OCH_2), 55.23 (CH_3).

UV (MeCN): λ_{max} = 267 nm (ε = 29700).

Bis(4-methoxybenzyl) (*E*,*Z*)-Muconate [(*E*,*Z*)-4-MeO]
Colorless plates; mp 83.8–84.8 °C ($CHCl_3$).

IR (KBr): 1595 (C=C), 1711 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (dd, *J* = 15.6, 11.6 Hz, *trans*-C*H*=CHCO$_2$R, 1 H), 7.20–7.35 (m, C_6H_4, 4 H), 6.87–6.91 (m, C_6H_4, 4 H), 6.62 (t, *J* = 11.6 Hz, *cis*-C*H*=CHCO$_2$R, 1 H), 6.11 (d, *J* = 15.6 Hz, *trans*-CH=C*H*CO$_2$R, 1 H), 5.96 (d, *J* = 11.6 Hz, *cis*-CH=C*H*CO$_2$R, 1 H), 5.16 (s, OCH_2, 2 H), 5.14 (s, OCH_2, 2 H), 3.81 (s, OCH_3, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.91, and 165.07 (C=O), 159.67 (C_6H_4), 140.78 and 138.82 (CH=), 130.28, 130.19, 128.97, 127.97, 127.75, and 124.54 (C_6H_4), 114.00 and 113.96 (CH=), 63.34 and 66.26 (CH_2), 55.30 (CH_3).

UV (MeCN): λ_{max} = 266 nm (ε = 27100).

Bis(4-ethoxybenzyl) (*E*,*Z*)-Muconate [(*E*,*Z*)-4-EtO]
Colorless prisms; mp 78.5–79.1 °C ($CHCl_3$).

IR (KBr): 1600 (C=C), 1715 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (dd, *J* = 15.6, 11.6 Hz, *trans*-C*H*=CHCO$_2$R, 1 H), 7.29–7.33 (m, C_6H_4, 4 H), 6.86–6.88 (m, C_6H_4, 4 H), 6.62 (t, *J* = 11.6 Hz, *cis*-C*H*=CHCO$_2$R, 1 H), 6.13 (d, *J* = 15.6 Hz, *trans*-CH=C*H*CO$_2$R, 1 H), 5.97 (d, *J* = 11.6 Hz, *cis*-CH=C*H*CO$_2$R, 1 H), 5.15 (s, OCH_2, 2 H), 5.14 (s, OCH_2, 2 H), 4.00–4.06 (m, C*H*$_2$CH$_3$, 4 H), 1.39–1.42 (m, CH$_2$C*H*$_3$, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.93 and 165.09 (C=O), 159.11 and 159.05 (C_6H_4), 140.75 and 138.82 (CH=), 130.24, 130.15, 128.97, 127.80, 127.59, 124.56, 114.54, and 114.51 (C_6H_4 and CH=), 66.38 and 66.29 (OCH_2), 63.48 (*C*H$_2$CH$_3$), 14.81 (CH$_2$*C*H$_3$).

UV (MeCN): λ_{max} = 266 nm (ε = 29800).

Bis(4-butoxybenzyl) (*E*,*Z*)-Muconate [(*E*,*Z*)-4-BuO]
Colorless plates; mp 78.5–79.1 °C ($CHCl_3$).

IR (KBr): 1598 (C=C), 1715 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (dd, *J* = 15.6, 11.6 Hz, *trans*-C*H*=CHCO$_2$R, 1 H), 7.29–7.33 (m, C_6H_4, 4 H), 6.87–6.89 (m, C_6H_4, 4 H), 6.62 (t, *J* = 11.6 Hz, *cis*-C*H*=CHCO$_2$R, 1 H), 6.11 (d, *J* = 15.6 Hz, *trans*-CH=C*H*CO$_2$R, 1 H), 5.97 (d, *J* = 11.6 Hz, *cis*-CH=C*H*CO$_2$R, 1 H), 5.15 (s, OCH_2, 2 H), 5.13 (s, OCH_2, 2 H), 3.93–3.98 (m, 4 H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.72–1.80 (m, 4 H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.43–1.54 (m, 4 H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.97 (t, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.93 and 165.07 (C=O), 159.31 (C_6H_4), 140.75 and 138.81 (CH=), 130.24, 130.15, 128.97, 127.69, 127.47, 124.54, and 114.52 (C_6H_4 and CH=), 67.69 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 66.39 and 66.29 (OCH_2), 31.26 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 19.22 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.84 (CH$_2$CH$_2$CH$_2$*C*H$_3$).

UV (MeCN): λ_{max} = 266 nm (ε = 31800).

Polymerization; General Procedure
The monomer crystals were photoirradiated using a high-pressure mercury lamp (Toshiba SHL-100-2, 100W, Pyrex filter) at a distance of 10 cm under atmospheric conditions at r.t. After irradiation, the polymers were isolated by removal of the unreacted monomer with $CHCl_3$. For γ-radiation polymerization, monomer crystals were charged in a Pyrex tube, degassed, and then sealed. γ-Radiation was carried out with ^{60}Co at r.t. The irradiation dose was 200 kGy. After irradiation, quantitative polymer formation was checked by IR and NMR spectra.

Poly[(*Z*,*Z*)-4-MeO]
Mp 199 °C.

IR (KBr): 974 (C=C), 1736 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.14 (m, C_6H_4, 4 H), 6.74–6.77 (m, C_6H_4, 4 H), 5.36 (br s, CH=CH, 2 H), 4.84 (q, OCH_2, 4 H), 3.67 (s, 6 H, OCH_3), 3.39 (br s, CH, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.98 (C=O), 159.54, 130.20, 129.38, 127.70, and 113.86 (C_6H_4 and CH=), 66.61 (CH_2), 55.14 (OCH_3), 50.76 (CH).

Poly[(*Z*,*Z*)-4-EtO]
Colorless plates; mp 187 °C.

IR (KBr): 974 (C=C), 1735 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.12 (m, C_6H_4, 4 H), 6.72–6.75 (m, C_6H_4, 4 H), 5.40 (s, CH=, 2 H), 4.82 (q, 4 H, CH_2), 3.88 (q, 4 H, C*H*$_2$CH$_3$), 3.43 (s, 2 H, CH), 1.32 (t, 6 H, CH$_2$C*H*$_3$);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.87 (C=O), 158.88, 130.16, 129.31, 127.46, and 114.30 (C_6H_4 and CH=), 66.62 (CH_2), 63.24 (*C*H$_2$CH$_3$), 50.85 (CH), 14.75 (CH$_2$*C*H$_3$).

Poly[(*Z*,*Z*)-4-BuO]
Colorless plates.

IR (KBr): 975 (C=C), 1736 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08–7.12 (m, C_6H_4, 4 H), 6.74–6.77 (m, C_6H_4, 4 H), 5.59 (br s, CH=CH, 2 H), 4.73 (q, OCH_2, 4 H), 3.82 (s, 4 H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 3.31 (br s, CH, 2 H), 1.67–1.74 (m, 4 H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.38–1.48 (m, 4 H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.99 (t, 6 H, CH$_2$CH$_2$CH$_2$C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.28 (C=O), 159.19, 130.21, 129.74, 127.05, and 114.40 (C_6H_4 and CH=), 67.54 and 66.73 (OCH_2 and *C*H$_2$CH$_2$CH$_2$CH$_3$), 52.27 (CH), 31.27 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 19.21 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.85 (CH$_2$CH$_2$*C*H$_2$*C*H$_3$).

Poly[(*E*,*E*)-3-MeO]
Mp 193 °C.

IR (KBr): 984 (C=C), 1733 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.15 (m, C_6H_4, 2 H), 6.75–6.80 (m, C_6H_4, 6 H), 5.59 (br s, CH=CH, 2 H), 4.81 (q, OCH_2, 4 H), 3.69 (s, 6 H, OCH_3), 3.35 (br s, CH, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.22 (C=O), 159.61, 136.80, 129.71, 129.59, 120.46, 113.81, and 113.73 (C_6H_4 and CH=), 66.72 (CH_2), 55.11 (OCH_3), 50.77 (CH).

Poly[(*E*,*E*)-4-MeO]
Colorless plates; mp 195 °C.

IR (KBr): 974 (C=C), 1735 cm^{-1} (C=O).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.14 (m, C_6H_4, 4 H), 6.74–6.77 (m, C_6H_4, 4 H), 5.36 (br s, CH=CH, 2 H), 4.84 (q, OCH_2, 4 H), 3.67 (s, 6 H, OCH_3), 3.39 (br s, CH, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.98 (C=O), 159.54, 130.20, 129.38, 127.72, and 113.86 (C_6H_4 and CH=), 66.61 (CH_2), 55.14 (OCH_3), 50.76 (CH).

Poly[(*E*,*E*)-4-EtO]
Colorless plates; mp 181 °C.

IR (KBr): 973 (C=C), 1735 cm^{-1} (C=O).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.11 (m, C_6H_4, 4 H), 6.71–6.74 (m, C_6H_4, 4 H), 5.39 (br s, CH=, 2 H), 4.82 (s, OCH_2, 4 H), 3.88 (t, 4 H, CH_2CH_3), 3.42 (br s, CH, 2 H), 1.32 (t, 6 H, CH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.89 (C=O), 158.88, 130.18, 129.80, 127.50, and 114.32 (C_6H_4 and CH=), 66.63 (CH_2), 63.26 (CH_2CH_3), 50.85 (CH), 14.75 (CH_2CH_3).

Poly(EMU) (*meso*-Diisotactic-*trans*-2,5-polymer)
Colorless needles.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.56 (br s, CH=CH, 2 H), 4.02 (q, CH_2, 4 H), 3.27 (br s, CH, 2 H), 1.19 (t, CH_3, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.48 (C=O), 129.59 (CH=), 60.89 (CH_2), 52.04 (CH), 14.01 (CH_3).

X-ray Crystallography
Single crystal X-ray data were collected on a Rigaku R-AXIS RAPID Imaging Plate diffractometer using Mo-K_α radiation monochromated by graphite. The structures were solved by a direct method with the program SIR92 and refined using full-matrix least-squares procedures. All calculations were performed using the CrystalStructure crystallographic software package from the Molecular Structure Corporation.

References

(1) (a) Odian, G. *Principles of Polymerization*, 4th ed.; Wiley: New York, **2004**. (b) Pino, P.; Suter, U. W. *Polymer* **1976**, *17*, 977. (c) Farina, M. *Top. Stereochem.* **1987**, *17*, 1. (d) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.

(2) (a) Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*; VCH: Weinheim, **1996**. (b) *Radicals in Organic Synthesis*, Vol. 1 & 2; Renaud, P.; Sibi, M. P., Eds.; Wiley-VCH: Weinheim, **2001**. (c) Matsumoto, A. In *Handbook of Radical Polymerization*; Matyjaszewski, K.; Davis, T. P., Eds.; Wiley: New York, **2002**, 691. (d) Matsumoto, A.; Giese, B. *Macromolecules* **1996**, *29*, 3758. (e) Spichty, M.; Giese, B.; Matsumoto, A.; Fischer, H.; Gescheidt, G. *Macromolecules* **2001**, *34*, 723.

(3) (a) Yamada, K.; Nakano, T.; Okamoto, Y. *Macromolecules* **1998**, *31*, 7598. (b) Matsumoto, A.; Nakamura, S. *J. Appl. Polym. Sci.* **1999**, *74*, 290. (c) Isobe, Y.; Fujioka, D.; Habaue, S.; Okamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 7180. (d) Ray, B.; Isobe, Y.; Morioka, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2003**, *36*, 543. (e) Lutz, J. F.; Neugebauer, D.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6986.

(4) (a) Feldman, K. S.; Porter, N. A.; Allen, J. R. *Templated Organic Synthesis*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH: Weinheim, **2000**, 219. (b) Serizawa, T.; Hamada, K.; Akashi, M. *Nature* **2004**, *429*, 52.

(5) (a) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349. (b) Nakano, T.; Shikisai, Y.; Okamoto, Y. *Polym. J.* **1996**, *28*, 51. (c) Hoshikawa, N.; Hotta, Y.; Okamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12380.

(6) Porter, N. A.; Allen, T. R.; Breyer, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 7676.

(7) (a) Matsumoto, A.; Odani, T. *Macromol. Rapid Commun.* **2001**, *22*, 1195. (b) Matsumoto, A. *Polym. J.* **2003**, *35*, 93. (c) Matsumoto, A. *Top. Curr. Chem.* **2005**, *254*, 263.

(8) Matsumoto, A.; Tashiro, K.; Miyata, M.; Tsubouchi, T.; Tanaka, T.; Odani, T.; Nagahama, S.; Tanaka, T.; Inoue, K.; Saragai, S.; Nkamoto, S. *Angew. Chem. Int. Ed.* **2002**, *41*, 2502.

(9) Matsumoto, A.; Odani, T.; Chikada, M.; Sada, K.; Miyata, M. *J. Am. Chem. Soc.* **1999**, *121*, 11122.

(10) Matsumoto, A.; Nagahama, S.; Odani, T. *J. Am. Chem. Soc.* **2000**, *122*, 9109.

(11) Matsumoto, A.; Tanaka, T.; Tsubouchi, T.; Tashiro, K.; Saragai, S.; Nakamoto, S. *J. Am. Chem. Soc.* **2002**, *124*, 8891.

(12) Nagahama, S.; Inoue, K.; Sada, K.; Miyata, M.; Matsumoto, A. *Cryst. Growth Des.* **2003**, *3*, 247.

(13) Tieke, B. *Adv. Polym. Sci.* **1985**, *71*, 79.

(14) Tashiro, K.; Zadorin, A. N.; Saragai, S.; Kamae, T.; Matsumoto, A.; Yokoi, K.; Aoki, S. *Macromolecules* **1999**, *32*, 7946.

(15) Tanaka, T.; Matsumoto, A. *J. Am. Chem. Soc.* **2002**, *124*, 9676.

(16) Nagahama, S.; Tanaka, T.; Matsumoto, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 3811.

(17) Elvidge, J. A.; Linstead, R. P.; Sims, P.; Orkin, B. A. *J. Chem. Soc.* **1950**, 2235.

(18) Hayashi, O.; Katagiri, M.; Rothberg, S. *J. Am. Chem. Soc.* **1955**, *77*, 5450.

(19) Draths, K. M.; Frost, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 9630.

(20) Odani, T.; Matsumoto, A.; Sada, K.; Miyata, M. *Chem. Commun.* **2001**, 2004.

(21) Matsumoto, A.; Yokoi, K.; Aoki, S.; Tashiro, K.; Kamae, T.; Kobayashi, M. *Macromolecules* **1998**, *31*, 2129.

(22) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π Interaction: Evidence, Nature, and Consequences*; Wiley: New York, **1998**.

(23) Sada, K.; Inoue, K.; Tanaka, T.; Tanaka, A.; Epergyes, A.; Nagahama, S.; Matsumoto, A.; Miyata, M. *J. Am. Chem. Soc.* **2004**, *126*, 1764.

(24) (a) Xiao, J.; Yang, M.; Lauher, J. W.; Fowler, F. W. *Angew. Chem. Int. Ed.* **2000**, *39*, 2132. (b) Hoang, T.; Lauher, J. W.; Fowler, F. W. *J. Am. Chem. Soc.* **2002**, *124*, 10656. (c) Nomura, S.; Itoh, T.; Nakasho, H.; Uno, T.; Kubo, M.; Sada, K.; Inoue, K.; Miyata, M. *J. Am. Chem. Soc.* **2004**, *126*, 2035.

(25) (a) Yoshioka, M.; Matsumoto, A.; Otsu, T.; Ando, I. *Polymer* **1991**, *32*, 2741. (b) Yoshioka, M.; Matsumoto, A.; Otsu, T. *Polym. J.* **1991**, *23*, 1191. (c) Matsumoto, A.; Otsu, T. *Macromol. Symp.* **1995**, *98*, 139.

(26) Ishihara, N.; Seimiya, M.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2465.

(27) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255.

(28) (a) Kitayama, T.; Masuda, E.; Yamaguchi, M.; Nishiura, T.; Hatada, K. *Polym. J.* **1992**, *24*, 817. (b) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134.

(29) (a) Ute, K.; Asada, T.; Nabeshima, Y.; Hatada, K. *Polym. Bull.* **1993**, *30*, 171. (b) Ute, K.; Tarao, T.; Honjo, S.; Ohnuma, H.; Hatada, K.; Kitayama, T. *Polym. J.* **1999**, *31*, 177.

(30) Takasu, A.; Ishii, M.; Inai, Y.; Hirabayashi, T.; Inomata, K. *Macromolecules* **2003**, *36*, 7055.

(31) (a) Natta, G.; Farina, M.; Donati, M. *Makromol. Chem.* **1961**, *43*, 251. (b) Donati, M.; Perego, G.; Farina, M. *Makromol. Chem.* **1965**, *85*, 301.