Highly "Diheterotactic" Polymerization of *tert*-Butyl Crotonate

Koichi Ute, Takeshi Asada, and Koichi Hatada*

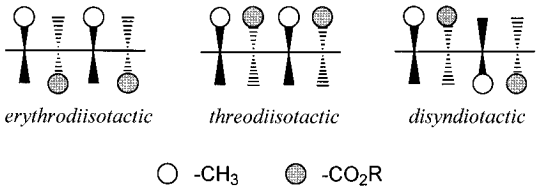
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received August 29, 1995[⊗]

ABSTRACT: The polymerization of *tert*-butyl crotonate with RMgBr or R_2Mg (R: *t*-C_4H_9, C_6H_5) in toluene gave a polymer with high stereoregularity. In particular, $(C_6H_5)_2Mg$ had high initiator efficiency and was useful for the preparation of oligomer suitable for stereostructure analysis. The oligomer of *tert*-butyl crotonate was transformed into oligo(methyl crotonate) by transesterification, and the oligo(methyl crotonate) was fractionated into the individual homologues from 1mer to 10mer by means of GPC and supercritical fluid chromatography. ^{1}H NMR spectroscopy showed that each oligomer homologue consisted essentially of two diastereomers **A** and **B**. The configurational sequences for 6mer-**A**, 7mer-**A**, 8mer-**A**, and 7mer-**B** were determined by X-ray single crystal analysis to be *et*(*ettt*)$_2$, *et*(*ettt*)$_2$*et*, *et*(*ettt*)$_3$, and (*ettt*)$_3$, respectively, where *e* and *t* denote *erythro* and *threo* diads. Accordingly, this polymerization is highly stereospecific to *ettt* structure. The *ettt* structure well explains the nonequivalence in the NMR signals due to each α-CH, *β*-CH, *β*-CH_3, and *t*-C_4H_9O group of this stereoregular poly(*tert*-butyl crotonate). The polymer chain consisting of regular repetition of an *ettt* pentad can be regarded as a double heterotactic sequence with respect to the α- and *β*-positions, and therefore this novel structure of stereoregular polymer should be termed "*diheterotactic*".

Introduction

Intense interest in the isotactic,[1,2] syndiotactic,[3,4] and heterotactic[5,6] living polymerization of methacrylates during the past 10 years has led us to examine the stereospecific polymerization of crotonates,[7−9] an isomeric family of methacrylates. The formation of stereoregular polymers of crotonates requires a higher order of stereoregulation than those for isotactic and syndiotactic polymethacrylates, because crotonates have options in that the polymer chain has two interleaved systems of nonidentical, asymmetric (*stereogenic*) carbon atoms. Generally speaking, pure *cis*- or *trans*-α,*β*-disubstituted ethylenes including crotonates can give rise to three simple stereoregular polymers; the configurations are defined as *erythrodiisotactic*, *threodiisotactic*, and *disyndiotactic*.



Recently, we have found that the polymerization of triphenylmethyl crotonate with a fluorenyllithium/diamine complex in toluene yields the highly threodiisotactic polymer.[8,9] This polymer is readily convertible into poly(methyl crotonate) by hydrolytic cleavage of the ester functions and subsequent methylation with diazomethane; an ^{1}H NMR spectrum of the poly(methyl crotonate) is shown in Figure 1a. Each resonance in the spectrum appears as a singlet of a narrow line width in contrast with those of atactic poly(methyl crotonate) (Figure 1c). Due to the high stereospecificity in the polymerization of triphenylmethyl crotonate, each individual oligomer contains a highly predominant stereoisomer. For example, the pentamer consists essentially of only one among 256 (=2^8) possible diastereomers. X-ray single crystal analysis revealed the configurational structure of this pentamer to be purely threodiisotactic.[8]

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

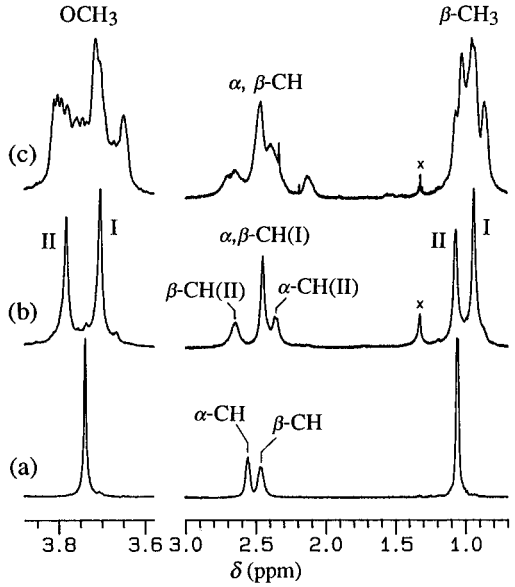


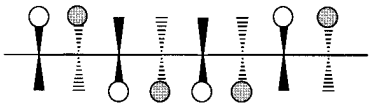
Figure 1. ^{1}H NMR spectra of poly(methyl crotonate)s with various stereoregularities measured in $(CF_3)_2CHOH/C_6D_6$ (95/5) at 55 °C and 500 MHz: (a) threodiisotactic poly(methyl crotonate) derived from poly(triphenylmethyl crotonate), (b) stereoregular poly(methyl crotonate) derived from the poly(*tert*-butyl crotonate) prepared by the polymerization with *tert*-butylmagnesium bromide in toluene, and (c) atactic poly(methyl crotonate) derived from the poly(*tert*-butyl crotonate) prepared by the polymerization with *tert*-butyllithium in THF.[8] The *β*-CH_3(I), *β*-CH(I), and α-CH(I) resonances belong to a spin system different from the *β*-CH_3(II), and *β*-CH(II), and α-CH(II) resonances, which is revealed by an ^{1}H COSY experiment on (b).[7] Reproduced with permission from the American Chemical Society.

Another type of highly ditactic polycrotonate can be prepared by the polymerization of *tert*-butyl crotonate with *tert*-butylmagnesium bromide in toluene.[7] Figure 1b shows an ^{1}H NMR spectrum of the poly(methyl crotonate) transformed from this poly(*tert*-butyl crotonate) in a manner similar to that described above. Interestingly, each resonance due to the α-CH, *β*-CH, *β*-CH_3, and CH_3O groups splits into two peaks (I and II) of nearly equal intensity. The resonances differ from those of threodiisotactic poly(methyl crotonate) in chemical shift. Hence, the polymer was assumed to consist

0024-9297/96/2229-1904$12.00/0

of highly erythrodiisotactic and highly disyndiotactic sequences.[8] An attempt to gain further information about the stereospecificity in this polymerization by oligomer analysis was unsuccessful because of a very low yield of the oligomer.

In the present paper, we report a revised and unequivocal assignment for the configurational structure of the above-mentioned poly(*tert*-butyl crotonate). The configuration can be regarded as a double heterotactic structure with respect to the α- and *β*-positions. We will prepare a new terminology of stereoregularity, "*diheterotactic*",[10] to represent this configurational structure.



diheterotactic

The spectral feature in Figure 1b is well explained by the diheterotactic structure, because there are two magnetically nonequivalent monomer units in a diheterotactic sequence.

Experimental Section

tert-Butyl crotonate purchased from Tokyo Kasei Kogyo Co., Ltd. was purified by distillation, dried over CaH_2, and then vacuum distilled just before use. *tert*-Butylmagnesium bromide and phenylmagnesium bromide were synthesized by the reaction of magnesium turnings with *tert*-butyl bromide and bromobenzene, respectively, in diethyl ether. Solutions of *tert*-butylmagnesium bromide containing various amounts of $MgBr_2$ were prepared by the procedure described in the literature.[2,11] Diphenylmagnesium was prepared by adding 1,4-dioxane to the diethyl ether solution of phenylmagnesium bromide;[2] the precipitated adduct of 1,4-dioxane with $MgBr_2$ was removed by centrifugation. The concentration of *tert*-butyl or phenyl anion in the above-mentioned solutions was determined by acid−base titration. The concentration of total magnesium in the solutions was determined by the chelatometric titration with EDTA using Eriochrome Black T as the indicator.

Polymerization was initiated by adding the solution of the organomagnesium compound to the solution of *tert*-butyl crotonate in toluene at −78 °C under a dry nitrogen atmosphere. The reaction was terminated with a small amount of methanol, and the polymerization mixture was poured into a large amount of methanol. The precipitated polymer was collected by centrifugation, washed several times with methanol, and then dried *in vacuo* at 60 °C for 3 h. Oligomerization of *tert*-butyl crotonate was carried out in a similar manner. When the oligomerization was terminated with methanol, polymer and inorganic salts precipitated out from the oligomerization mixture. The insoluble part was removed by centrifugation, and then the soluble oligomer was recovered by evaporating the solvent.

Polymers of *tert*-butyl crotonate were converted to poly(methyl crotonate)s by the following procedure: A sample of poly(*tert*-butyl crotonate) was dissolved in trifluoroacetic acid at room temperature. After 1 h, the solution was evaporated to dryness under reduced pressure. The resultant poly(crotonic acid) was reacted with diazomethane in dry benzene. The oligomer of *tert*-butyl crotonate was transformed into oligo(methyl crotonate) in a similar manner.

The oligo(methyl crotonate) was separated into six fractions (1mer, 2mer, 3mer, 4mer, 5−11mers, and the higher oligomers) by a JASCO Trirotar-V chromatograph equipped with a column (20 × 500 mm) packed with polystyrene gel (maximum porosity: 3.0×10^3) using chloroform as the eluent. The fraction containing the oligomers from 5mer to 11mer was separated into the individual homologues by supercritical fluid chromatography (SFC). The SFC conditions are as follows: chromatograph, JASCO Super-200; column, a 10 × 250 mm column packed with nonbonded silica gel (particle size 5 μm); mobile phase, CO_2/CH_2Cl_2 = 70/30 (initial), 60/40 (15 min); temperature, 160 °C (initial), −1.2 °C/min; pressure, 20 MPa; detector, JASCO 875-UV (λ = 235 nm). The separation of diastereomers in the 5mer and 7mer fractions was performed on normal-phase HPLC using mixtures of butyl chloride and acetonitrile as the eluent.

Table 1. Polymerization of *tert*-Butyl Crotonate with RMgBr/R_2Mg/$MgBr_2$ in Toluene at − 78 °C[a]

R	[Mg]/[R]	time (h)	yield[b] (%)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	f[d]
t-C_4H_9	2.59	168	trace			
	1.91	168	5.6	11 800	1.98	0.017
	1.34	168	35.8	24 400	1.75	0.052
	1.07	168	60.1	40 400	1.60	0.053
	0.77[e]	168	86.4	72 700	1.57	0.021
C_6H_5	1.01	24	1.3	2 200	1.04	0.021
	0.54[e]	24	97.7	6 700	1.19	0.259

[a] *tert*-Butyl crotonate = 10 mmol, toluene = 5 mL, [*t*-butyl crotonate]/[R] = 25. [b] Methanol-insoluble part. [c] Determined by GPC. [d] Initiator efficiency. [e] [*tert*-Butyl crotonate]/[R] = 12.5.

The molecular weight determination was carried out on a JASCO Trirotar-V chromatograph equipped with GPC columns (Shodex K-802.5 and K-80M) and a Shodex RI SE-61 detector using chloroform as the eluent. Though some stereoregular polycrotonates are insoluble in the organic solvents other than 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), GPC measurements are possible since the polymers become soluble in chloroform once they are dissolved in a small amount of HFIP.[7] The molecular weight was calibrated against polystyrene standards.

NMR spectra were recorded on a JEOL JNM-GX500 or a Varian Unity-plus 600 spectrometer in HFIP/C_6D_6 (95/5 v/v) at 55 °C or in $CDCl_3$ at 30 °C. X-ray data were collected with a Rigaku AFC-7R automated four-circle diffractometer using Mo Kα radiation. The crystal structures were solved by direct methods (SAPI 91).

Results and Discussion

Organomagnesium compounds are typical anionic initiators for stereospecific polymerization of methacrylates.[12] Among these, *tert*-butylmagnesium bromide is of particular interest because it initiates living and highly isotactic-specific polymerization of methyl methacrylate in toluene.[1,2] The stereospecificity in this polymerization is variable from highly isotactic to syndiotactic by shifting the Schlenk equilibrium in the initiator solution (1) from the "*t*-C_4H_9MgBr" side to the

$$2t\text{-}C_4H_9MgBr \rightleftharpoons (t\text{-}C_4H_9)_2Mg + MgBr_2 \qquad (1)$$

"$(t\text{-}C_4H_9)_2Mg$" side. The solutions of *tert*-butylmagnesium bromide containing various amounts of $MgBr_2$ can be prepared by known procedures.[2,11] In the present study, the solutions with the $[Mg^{2+}]/[t\text{-}C_4H_9]$ values ranging from 2.59 to 0.77 mol/mol have been used for the polymerization of *tert*-butyl crotonate in toluene at −78 °C. The results are shown in Table 1. The yield and $\bar{M}_n$ of poly(*tert*-butyl crotonate) increased markedly as the $[Mg^{2+}]/[t\text{-}C_4H_9]$ in the initiator decreased. However, the stereoregularity of the polymer was independent of the $[Mg^{2+}]/[t\text{-}C_4H_9]$ ratio, and all these poly(*tert*-butyl crotonate)s showed ^1H NMR spectra very similar to each other. The spectral pattern is characterized by the sharp doublet for each of the α-CH, *β*-CH, *β*-CH_3, and *t*-C_4H_9O resonances, just like a spectrum of poly(methyl crotonate) with the corresponding stereostructure (*cf.*, Figure 1b). These poly(*tert*-butyl crotonate)s were insoluble in organic solvents other than HFIP[7] unlike atactic poly(*tert*-butyl crotonate) which is soluble in aromatic and/or chlorinated hydrocarbons as well as in HFIP. The effects of $[Mg^{2+}]/[t\text{-}C_4H_9]$ on the polymerization of *tert*-butyl crotonate suggest that the active

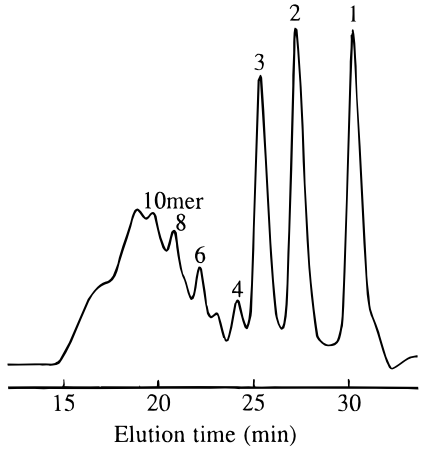


Figure 2. GPC curve of the oligo(methyl crotonate) derived from the oligo(*tert*-butyl crotonate) prepared with diphenylmagnesium in toluene at −78 °C.

species in this stereospecific polymerization should be $(t\text{-}C_4H_9)_2Mg$ rather than $t\text{-}C_4H_9MgBr$.

When phenylmagnesium bromide ($[Mg^{2+}]/[C_6H_5] = 1.01$) or diphenylmagnesium ($[Mg^{2+}]/[C_6H_5] = 0.54$) was employed as the initiator, a poly(*tert*-butyl crotonate) with the same stereoregularity as described above was obtained (Table 1). In particular, the polymerization with diphenylmagnesium proceeded rapidly to yield the polymer with a narrow molecular weight distribution almost quantitatively. The living nature and the relatively high efficiency of initiation in this polymerization with diphenylmagnesium allowed us to prepare oligomers suitable for structural analysis.

The oligomerization of *tert*-butyl crotonate with diphenylmagnesium in toluene was carried out at −78 °C for 6 h under a feed ratio of the monomer to the initiator of 5.0 mol/mol. Oligomer soluble in toluene was obtained in a 32% yield together with polymer insoluble in toluene (yield: 68%, $M_n = 4.5 \times 10^3$, $M_w/M_n = 1.24$), and this oligomer of *tert*-butyl crotonate was transformed into oligo(methyl crotonate). Figure 2 illustrates a GPC curve of the oligo(methyl crotonate). The oligomer contained relatively large amounts of the lower homologues from 1mer to 3mer. A peculiar feature of this chromatogram is that the oligomer homologues with odd numbers of repeating units (*i.e.*, 5mer, 7mer, and 9mer) are less abundant than those with even numbers of repeating units (*i.e.*, 4mer, 6mer, 8mer, and 10mer).

The individual oligomers from 1mer to 4mer were isolated by the fractionation with GPC. The higher homologues were separated by means of supercritical fluid chromatography (Figure 3). The stereostructure of each fraction was investigated by ^1H NMR spectroscopy. Figure 4 shows the spectral region between 3.29 and 3.79 ppm where the methoxy protons resonate. In the spectrum of the 10mer fraction, there appeared 10 singlets of equal intensities due to the 10 methoxy groups of a highly predominant diastereomer, accompanied by small resonances due to minor isomers. The spectra of the 6mer and 8mer also showed each fraction to contain a single isomer highly enriched. On the other hand, the spectra of the 5mer, 7mer, and 9mer indicated the presence of two predominant isomers with comparable abundances; these isomers can be distinguished clearly by the resonances at 3.31 (**A**) and 3.37 ppm (**B**), both of which are attributable to the methoxy group in the monomer unit next to the phenyl terminal. The resonances at 3.31 and 3.37 ppm appear in every spectrum in Figure 4. Accordingly, the oligomers are

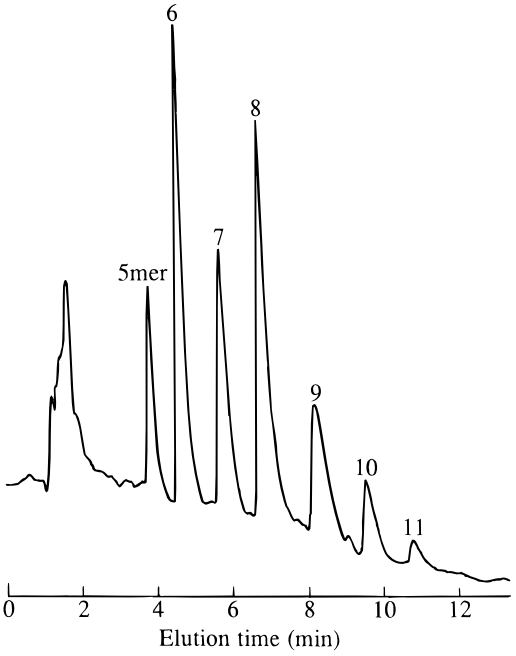


Figure 3. Supercritical fluid chromatogram of oligo(methyl crotonate).

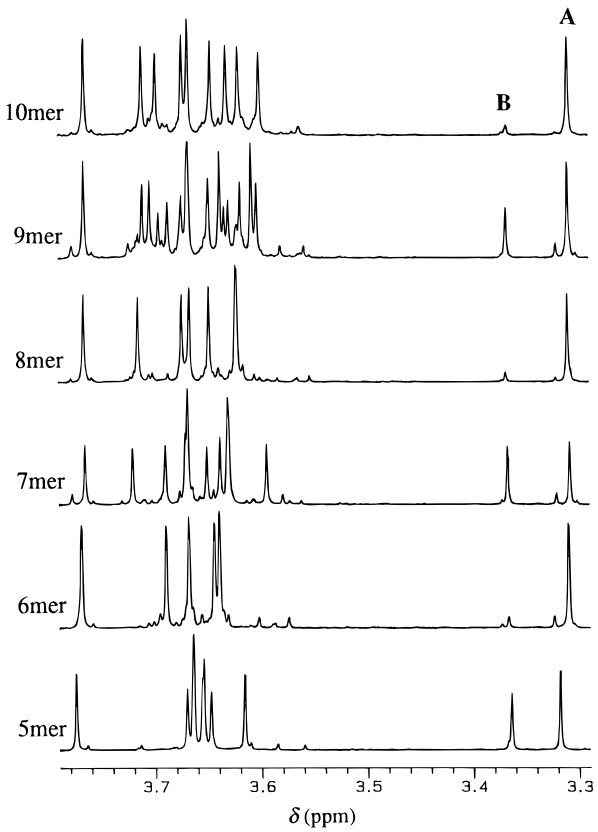


Figure 4. Methoxy proton resonances in the ^1H NMR spectra of the individual oligomers from 5mer to 10mer fractionated by supercritical fluid chromatography (*cf.* Figure 3) ($CDCl_3$, 30 °C, 500 MHz).

considered to comprise the two kinds of diastereomers **A** and **B**. The presence of only two (and a very few additional) isomers in each fraction indicates that the stereospecificity of the polymerization should be extremely high, as the number of diastereomers possible for the *N*-mer amounts to 2^{2N-2}.

Single crystals suitable for X-ray structural determination were grown from the heptane/chloroform solutions of the 6mer and 8mer fractions. The individual

Table 2. Crystal Data and Experimental Parameters for X-ray Structure Determination of Hexakis-, Heptakis-, and Octakis(methyl crotonate) Obtained by the Oligomerization of *t*-Butyl Crotonate with $(C_6H_5)_2Mg$ in Toluene at −78 °C[a]

	6mer-**A**	7mer -**A**	7mer-**B**	8mer-**A**
molecular formula	$C_{35}H_{54}O_{12}$	$C_{41}H_{62}O_{14}$	$C_{41}H_{62}O_{14}$	$C_{46}H_{70}O_{16}$
mol wt	678.82	778.93	778.93	879.05
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
cryst size/mm	0.50 × 0.33 × 0.05	0.53 × 0.23 × 0.1	0.88 × 0.13 × 0.05	1.30 × 0.53 × 0.15
a/Å	13.859(3)	14.162(4)	14.341(5)	28.749(4)
b/Å	17.626(3)	18.704(6)	18.138(8)	8.826(4)
c/Å	8.170(6)	8.560(6)	8.588(4)	19.622(5)
α	94.42(3)	100.90(4)	93.54(4)	90
β	104.76(3)	101.18(4)	98.15(3)	91.03(2)
γ	86.43(2)	97.63(2)	76.40(3)	90
V/Å^3	1922(1)	2150(1)	2148(1)	4977(2)
Z	2	2	2	4
D_{calcd}/g cm^{-3}	1.173	1.203	1.204	1.173
scan width/deg	1.26 + 0.30 tan *θ*	1.10 + 0.30 tan *θ*	0.84 + 0.30 tan *θ*	0.94 + 0.30 tan *θ*
2*θ* range	6.0 < *θ* < 50.0	6.0 < *θ* < 55.0	6.0 < *θ* < 45.0	6.0 < *θ* < 50.0
total no. of unique data	5262	9891	5623	9396
no. of obsd data	2365 ($I > 3\sigma(I)$)	3556 ($I > 3\sigma(I)$)	1791 ($I > 5\sigma(I)$)	3887 ($I > 3\sigma(I)$)
no. of variables	434	496	496	559
R	0.162	0.063	0.073	0.063
R_w	0.088	0.038	0.055	0.041
goodness of fit	6.95	2.42	3.22	3.44

[a] Scan type *ω*−2*θ*, scan rate 16.0 deg/min.

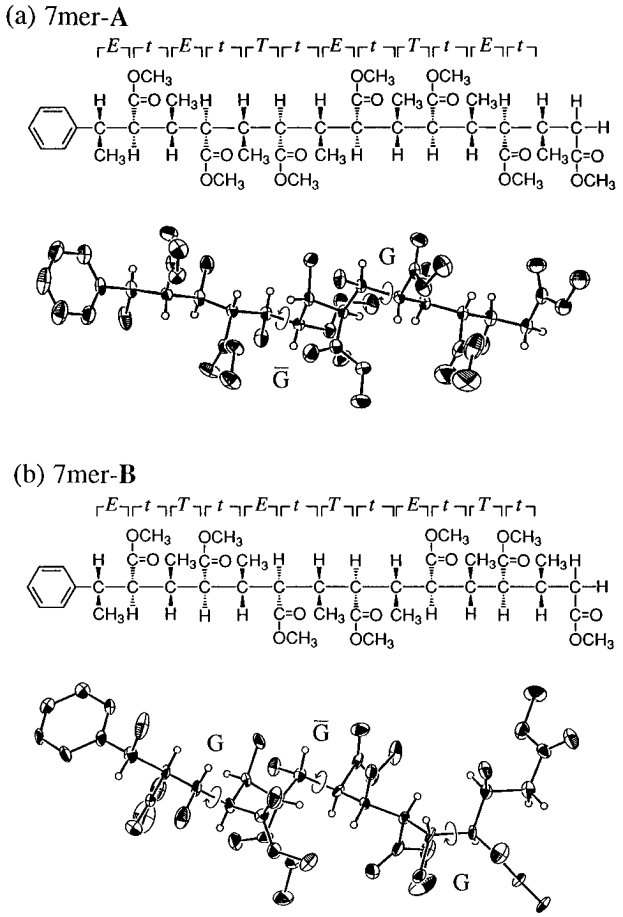


Figure 5. Structures of diheterotactic heptakis(methyl crotonate)s [(a) 7mer-**A** and (b) 7mer-**B**]. Methyl and ring hydrogen atoms are omitted for clarity.

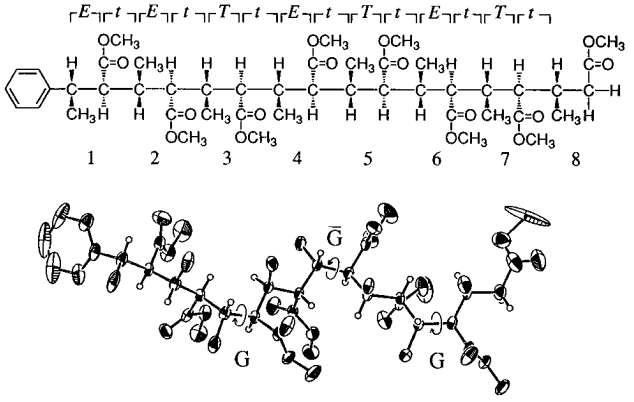
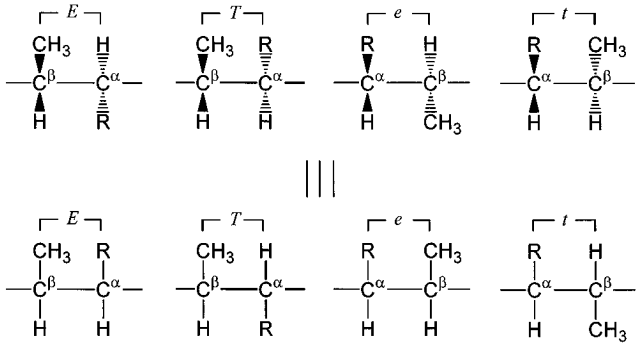


Figure 6. Structure of diheterotactic octakis(methyl crotonate) (8mer-**A**). Methyl and ring hydrogen atoms are omitted for clarity.

isomers **A** and **B** in the 7mer fraction, which were resolved by normal-phase HPLC, also gave single crystals in a similar manner. The crystallographic data are summarized in Table 2. Figures 5 and 6 show the crystal structures of the 7mers and 8mer-**A**, respectively. Prior to the discussion of their stereostructures, it is convenient to define the following notations of stereochemistry. If the direction of the propagation in a growing chain is considered, there are four kinds of configurational diad:



The capital letters *E* and *T* denote the *erythro* and *threo* diads, respectively, in a monomer unit. The small letters *e* and *t* stand for the *erythro* and *threo* diads between adjacent monomer units. By the use of the notations, the configurational structures of 6mer-**A**, 7mer-**A**, and 8mer-**A** can be expressed as $Et(EtTt)_2$, $Et(EtTt)_2Et$, and $Et(EtTt)_3$, respectively. All of them comprise the configurational repeating unit *EtTt* with the first two diads being an extra *Et* sequence. Fur-

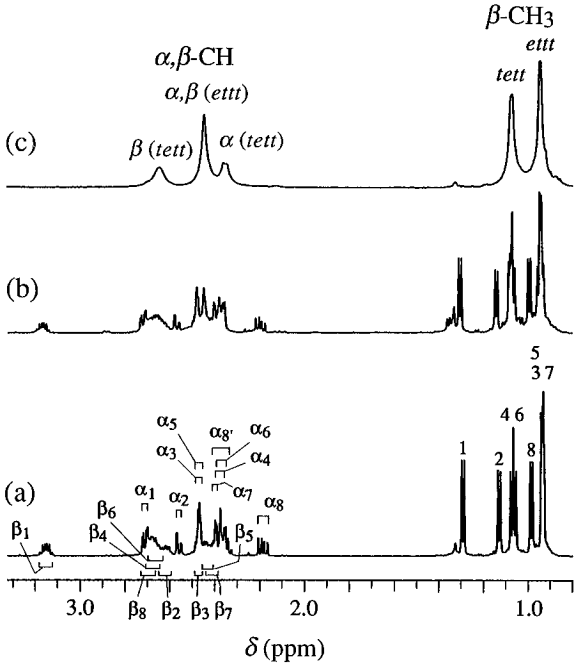


Figure 7. ^{1}H NMR spectra of diheterotactic 8mer-**A** (a) and 10mer-**A** (b) of methyl crotonate and of diheterotactic poly(methyl crotonate) (c) measured in $(CF_3)_2CDOD/C_6D_6$ (95/5) at 55 °C and 600 MHz. See Figure 6 for the numbering system of the methyl and methine groups in 8mer-**A**.

thermore, 7mer-**B** has a configurational sequence represented by $(EtTt)_3$. Therefore, the polymerization yielding these oligomers is strongly suggested to be stereospecific to the *EtTt* structure, and the configurational structure of the poly(methyl crotonate) in Figure 1b should be assigned to the "diheterotactic" structure consisting of regular repetition of an *EtTt* sequence, as defined in an introductory paragraph.

Figure 7a shows an ^{1}H NMR spectrum of 8mer-**A**. The assignment of the methyl and methine proton resonances was made on the basis of ^{1}H COSY experiments at 600 MHz.[13] The resonance at 0.93 ppm is due to the *β*-methyl protons in the third, fifth, and seventh monomer units from the phenyl terminal. The *β*-methyl protons in the fourth and sixth units resonate at 1.06 ppm. The presence of two distinct resonance groups for the *β*-methyl protons in the interior monomer units is associated with the configurational structure of 8mer-**A**. The *β*-methyl groups in the third, fifth, and seventh units are located in *EtTt* sequences while those in the fourth and sixth units are located in *TtEt* sequences (*cf.*, Figure 6), and thus the two kinds are magnetically nonequivalent. The *β*-methyl resonances at 0.93 and 1.06 ppm also appear in the spectra of 10mer-**A** (Figure 7b) and diheterotactic poly(methyl crotonate) (Figure 7c). For a long polymer chain where chain ends are immaterial, the relative configurations in a monomer unit (*E* and *T*) cannot be observationally distinguished from those between adjacent monomer units (*e* and *t*), and the written direction of the sequences is entirely arbitrary. Hence, the configurational sequence for the resonance at 0.93 ppm may be expressed as *ettt* and that at 1.06 ppm as *tett* (Figure 7c). In a manner similar to that described above, comparison of the spectra in Figure 7 allows the configurational assignments for the α- and *β*-CH resonances in diheterotactic poly(methyl crotonate).

X-ray crystallographic analysis of the oligomers in Table 2 gives not only configurational information but also conformational information about the diheterotactic

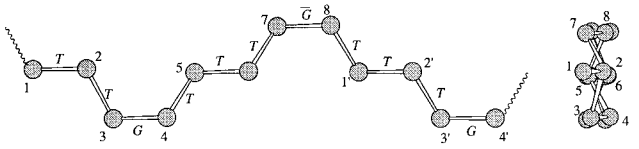
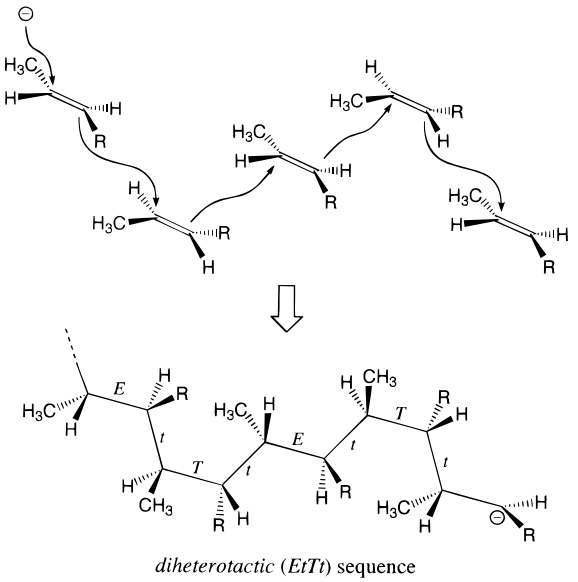


Figure 8. Skeletal conformation of a diheterotactic polycrotonate with $T_3GT_3\bar{G}$ geometry [T, *trans*; G, *gauche*-(+); $\bar{G}$, *gauche*-(−)].

Scheme 1



diheterotactic (*EtTt*) sequence

polymer chain. The carbon skeleton of the $Et(EtTt)_3$ sequence in 8mer-**A** (Figure 6) adopts $T(T_3GT_3\bar{G}T_3G)T$ conformation where T, G, and $\bar{G}$ denote *trans*, *gauche*-(+), and *gauche*-(−) geometries, respectively. It should be noted that G and $\bar{G}$ geometries occur alternately at *tTt* tetrads in the configurational sequence. This is also the case for the skeletal conformations of 7mer-**A** (Figure 5a), 7mer-**B** (Figure 5b), and 6mer-**A**. Consequently, the backbone of diheterotactic poly(methyl crotonate) is considered to take $T_3GT_3\bar{G}$ conformation in the crystalline state (Figure 8). The $T_3GT_3\bar{G}$ structure is one of the possible conformations of a single-bonded carbon chain proposed by Bunn[14] and found in the crystal structures of poly(oxacyclobutane),[15] poly(ethylene succinate),[16] poly(ethylene-*alt*-2-butene),[17] and poly(ethylene-*alt*-cyclopentene).[17]

From the point of view of polymerization mechanism, *E* and *T* diads relate to the mode of double bond opening (*trans* opening and *cis* opening) while *e* and *t* diads relate to the way in which successive monomer molecules approach the growing chain. The two ways of monomer approach forming *e* and *t* diads are defined as "*erythro* addition" and "*threo* addition", respectively.[18] The absence of an *e* diad in the configurational sequences of the oligomers indicates that the *si** face of a growing chain end should always attack the *re** face of the prochiral center at the *β*-position of a monomer molecule (*threo* addition) in this diheterotactic polymerization. The *si** face at the α-position and the *re** face at the *β*-position are the same enantiotopic face of a crotonate molecule. Along with repeated *threo* additions, *trans* opening and *cis* opening of the monomer double bond take place alternately to produce an *EtTt* sequence (Scheme 1). The only exception is at the initial stage of the polymerization. The first steric triad is produced when the 1mer anion adds to the second monomer molecule; this step proceeds in a *trans* open-

Table 3. Relative Abundance of Diastereomers in the Oligo(*tert*-butyl crotonate) Prepared with $(C_6H_5)_2Mg$ in Toluene at −78 °C[a]

	isomer **A**		isomer **B**		other	total
DP	configuration	%	configuration	%	isomers (%)	(%)
5	*EtEtTtEt*	5.2	$(EtTt)_2$	4.0	∼0	9.2
6	$Et(EtTt)_2$[b]	19.7	$(EtTt)_2Et$	2.0	3.2	24.9
7	$Et(EtTt)_2Et$[b]	8.0	$(EtTt)_3$[b]	6.4	2.4	16.8
8	$Et(EtTt)_3$[b]	23.8	$(EtTt)_3Et$	3.2	1.2	28.2
9	$Et(EtTt)_3Et$	7.5	$(EtTt)_4$	4.1	1.6	13.2
10	$Et(EtTt)_4$	6.4	$(EtTt)_4Et$	0.9	0.4	7.7
total		70.6		20.6	8.8	100

[a] Determined from the ^{1}H NMR spectra of the oligo(methyl crotonate) derived from the oligo(*t*-butyl crotonate). *E* and *T* denote the *erythro* and *threo* sequences in a repeating unit, and *t* denotes the *threo* sequence between repeating units. [b] Configurational structure determined by X-ray single crystal analysis.

ing−*threo* addition mechanism leading to the formation of the 2mer anion with an *Et* structure. A major part of the 2mer anions also undergoes a *trans* opening−*threo* addition to the third monomer molecule rather than a *cis* opening−*threo* addition, and thus the 3mer anion with an *EtEt* structure is produced. The formation of an *EtTt* sequence from this 3mer anion begins in the subsequent (fourth) monomer addition, which yields the oligomers and polymers with the isomer **A** type structure, $Et(EtTt)_n$.

The alternate occurrence of *trans* opening and *cis* opening in the diheterotactic polymerization may be responsible for the differences between the odd and even oligomers in their relative abundance (Figure 2) and diastereomeric purity (Figure 4). Table 3 shows the dependence of the relative abundance of the oligomers from 5mer to 10mer on their configurational structure.[19] It will be noted from Table 3 that there are two types of oligomer chains ended with *Et* and *Tt* sequences. In the homologues of isomer **A**, odd oligomers have configurational sequences ended with *Et*, whereas even oligomers have the *Et*-ended sequences in the homologues of isomer **B**. For both **A** and **B** homologues, the amount of *Et*-ended oligomers is smaller than that of *Tt*-ended oligomers. This suggests that *Et*-ended oligomer anions should be more reactive for chain propagation than *Tt*-ended oligomer anions. In other words, the rate of a *cis* opening−*threo* addition process should be faster than the rate of a *trans* opening−*threo* addition process.

The configurational structure of the diheterotactic polycrotonates seems to be essentially identical with that of the "crystalline" poly(*tert*-butyl crotonate)s prepared formerly by Natta *et al.*[20] and Miller *et al.*[21] using phenylmagnesium bromide as the initiator of polymerization and by Graham *et al.*[22] using dibutylmagnesium, because the polymerization conditions are similar to those in the present paper. Muroga and his co-workers have prepared the poly(*tert*-butyl crotonate) according to Miller's method and studied its configurational structure by 25.2 MHz ^{13}C NMR spectroscopy in toluene-d_8; they carried out the stereochemical assignment of the resonances on the basis of configurational statistics and reported the poly(*tert*-butyl crotonate) chains to consist of *eeee*, *eett*, and *tttt* pentads.[23] The spectral pattern of their poly(*tert*-butyl crotonate) resembles that of our diheterotactic poly(*tert*-butyl crotonate) recorded at 125 MHz in HFIP/C_6D_6,[7] except that some extra peaks are observed in the former spectrum.

In conclusion, the polymerization of *tert*-butyl crotonate with organomagnesium compounds such as *tert*-butylmagnesium bromide, di-*tert*-butylmagnesium, phenylmagnesium bromide, and diphenylmagnesium in toluene at −78 °C has been found to be highly stereospecific to the diheterotactic structure. The discovery of the new stereoregular polycrotonate with a configurational repeating unit at the pentad level (*ettt*) was entirely unexpected, since neither erythrodiisotactic nor disyndiotactic polycrotonate with a configurational repeating unit at the triad level (*ee* or *et*) has been proved to be prepared yet.

Acknowledgment. A part of this work was supported by the Grant-in-Aid for Scientific Research (No. 07750976) from the Ministry of Education, Science, Sports, and Culture of Japan and by the Ogasawara Foundation for the Promotion of Science & Engineering.

Supporting Information Available: Listings of positional and thermal parameters for 6mer-**A**, 7mer-**A**, 7mer-**B**, and 8mer-**A** crystals (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Hatada, K.; Ute, K.; Tanaka, K.; Kitayama, T.; Okamoto, Y. *Polym. J.* **1985**, *17*, 977.
(2) Hatada, K.; Ute, K.; Tanaka, K.; Okamoto, Y.; Kitayama, T. *Polym. J.* **1986**, *18*, 1037.
(3) Kitayama, T.; Shinozaki, T.; Masuda, E.; Yamamoto, M.; Hatada, K. *Polym. Bull.* **1988**, *20*, 505.
(4) Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Makromol. Chem., Suppl.* **1989**, *15*, 167.
(5) Kitayama, T.; Zhang, Y.; Hatada, K. *Polym. Bull.* **1994**, *32*, 439.
(6) Kitayama, T.; Zhang, Y.; Hatada, K. *Polym. J.* **1994**, *26*, 868.
(7) Ute, K.; Asada, T.; Nabeshima, Y.; Hatada, K. *Polym. Bull.* **1993**, *30*, 171.
(8) Ute, K.; Asada, T.; Nabeshima, Y.; Hatada, K. *Macromolecules* **1993**, *26*, 7086.
(9) Ute, K.; Asada, T.; Nabeshima, Y.; Hatada, K. *Acta Polym.* **1995**, *46*, 458.
(10) There are two configurational sequences, $(ettt)_n$ and $(eeet)_n$, both of which should be termed *diheterotactic* in the sense of the word. In the present paper, however, the term diheterotactic refers to the $(ettt)_n$ structure.
(11) Schlenk, W.; Schlenk, W., Jr., *Chem. Ber.* **1929**, *62*, 920.
(12) Hatada, K.; Kitayama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *13*, 189.
(13) Asada, T. Doctoral Thesis, Osaka University, 1996.
(14) Bunn, C. W. *Proc. R. Soc.* **1942**, *A180*, 67.
(15) Tadokoro, H.; Takahashi, Y.; Chatani, Y.; Kakida, H. *Makromol. Chem.* **1967**, *109*, 96.
(16) Ueda, A. S.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1971**, *2*, 387.
(17) Natta, G.; Alleda, G.; Bassi, I. W.; Corradini, P.; Ganis, P. *Makromol. Chem.* **1962**, *58*, 242.
(18) The *erythro* and *threo* additions do not correspond to the constant and alternating steric attacks defined in the literature: Natta, G.; Peraldo, M.; Farina, M.; Bressan, G. *Makromol. Chem.* **1962**, *55*, 139.
(19) Although the ratios of two predominant isomers and the other isomers in the 2mer, 3mer, and 4mer fractions were determined by ^{1}H NMR spectroscopy to be 51:49:0, 66:17:17, and 77:6:17, respectively, it was difficult to make their configurational assignments by chemical shifts of the resonances.
(20) Natta, G.; Peraldo, M.; Farina, M. Belg. Patent 599,833, 1961.
(21) Miller, M. L.; Skogman, J. *J. Polym. Sci., Part A* **1964**, *2*, 4551.
(22) Graham, R. K.; Moore, J. E.; Powell, J. A. *J. Appl. Polym. Sci.* **1967**, *11*, 1797.
(23) Muroga, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1980**, *13*, 1081.

MA951275F