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Stereospecific synthesis of ditactic polymers

Polymerizations of *t*-butyl crotonate and *t*-butyl isocrotonate with *t*-butylmagnesium bromide and *t*-butyllithium-trialkylaluminum and analysis of stereostructures of the polymers and oligomers

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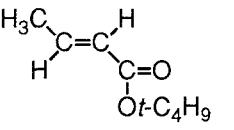
SUMMARY

Polymerizations of *t*-butyl crotonate (*E*-TBC) and *t*-butyl isocrotonate (*Z*-TBC)** were carried out in toluene at -78°C using *t*-BuMgBr as initiator. *E*-TBC gave polymers, whereas *Z*-TBC did not. The dimer of *E*-TBC isolated from the polymerization mixture by means of GPC contained predominantly one of the four possible diastereomers. X-ray crystallographic determination showed that the predominant dimer was the *erythro-diisotactic* isomer. *t*-BuLi/Et_3Al polymerized effectively both *E*-TBC and *Z*-TBC in toluene. The poly(*E*-TBC)s prepared with *t*-BuMgBr and *t*-BuLi/Et_3Al were insoluble in toluene, THF, and chloroform, but soluble in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Stereostructure of the poly(TBC)s was analyzed by the one- and two-dimensional NMR spectra measured in HFIP. The poly(*E*-TBC) prepared with *t*-BuMgBr was a 1:1 mixture of the *erythro-* and *threo-diisotactic* polymers with high stereoregularity. The poly(*E*-TBC) and poly(*Z*-TBC) obtained from the polymerizations with *t*-BuLi/Et_3Al were rich in *disyndiotactic* structure. Polymerization of TBCs with *t*-BuLi in toluene and THF was also studied.

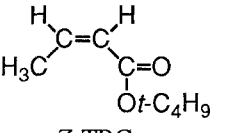
INTRODUCTION

Polymerizations of methyl methacrylate (MMA) initiated with *t*-BuMgBr and *t*-BuLi/R_3Al in toluene at -78°C are living, and give highly *isotactic* and highly *syndiotactic* polymers, respectively [1,2]. Applicability of the initiator systems to the polymerization of related *β*-substituted acrylates is of interest from the point of view of obtaining a stereochemical perspective of the reaction. In this work, *E*-TBC and *Z*-TBC were polymerized with these initiators, and the stereostructure of the resulting polymers and oligomers was investigated.

Branched alkyl crotonates are known to be polymerized effectively with anionic initiators [3-11]. Two kinds of poly(*E*-TBC) having different physical properties can be obtained by different polymerization techniques; the poly(*E*-TBC) prepared with alkyllithium in polar solvent is noncrystalline (or partly crystalline) and soluble [4,9], whereas the poly(*E*-TBC) prepared with PhMgBr in toluene is highly crystalline [3,4,9] and is insoluble in any organic solvent once it is isolated [10]. ^{13}C NMR spectra of the poly(TBC)s indicated that the polymers had different stereostructures [10] although the stereoregularities were not very high.



E-TBC



Z-TBC

On the other hand, only a limited number of papers have been published on the polymerization of isocrotonates [7,8]. Methyl, isopropyl, and *sec*-butyl isocrotonates formed polymer in very low

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**t*-Butyl (*E*)-2-butenoate and *t*-butyl (*Z*)-2-butenoate

yields under the conditions where the corresponding crotonates polymerized successfully.

Poly(TBC) can take various configurations with respect to both *t*-butyl carboxylate and *β*-methyl groups, such as *erythro-diisotactic*, *threo-diisotactic*, and *disyndiotactic*. Stereospecific synthesis of these *ditactic* polymers remains an unsettled matter in polymerization chemistry. Moreover, investigations on the *ditactic* configurations lead to understanding of the mechanism of stereoregulation, that is, the *isotactic*-like or *syndiotactic*-like addition of the monomer to the active center, and the *cis*- or *trans*-opening of the double bond. These pieces of information can not be obtained from the polymerization of (meth)acrylates unless either *β-cis* or *β-trans* position of the vinyl group is labeled with an isotope [12,13].

EXPERIMENTAL

E-TBC and *Z*-TBC were prepared from isobutylene and the corresponding acid in the presence of sulfuric acid, and was purified by distillation. The monomers were dried over calcium dihydride and were distilled under high vacuum just before use. Isomeric purity of the *E*-TBC and *Z*-TBC was determined as >99.9 % each by ^{1}H NMR. *Z*-TBC: *b.p.* = 59.3°C / 36 mmHg, ^{1}H NMR ($CDCl_3$) δ = 1.49 (*s*), 2.09 (*dd*), 5.70 (*dq*), 6.21 (*dq*) ppm. Isocrotonic acid was synthesized by the procedure described in the literature [14]. Commercially available methyl crotonate was purified in a similar manner as above. *t*-BuMgBr and *t*-BuLi/Et_3Al (1:3) were prepared as previously described [1,2].

Polymerization was carried out in a glass ampule under a dry nitrogen atmosphere. The reaction was initiated by adding the initiator (*t*-BuMgBr or *t*-BuLi) to the solution of the monomer in toluene or in THF cooled at the reaction temperature. In the case of the *t*-BuLi/Et_3Al system, polymerization was initiated by adding the monomer with stirring to the initiator solution prepared at -78°C. The polymerization was terminated by adding a small amount of methanol at the polymerization temperature. The reaction mixture was poured into a large amount of methanol, and the precipitated polymer was collected by filtration, washed thoroughly with methanol, and dried *in vacuo* at 50°C for 3 h. The filtrate and washings were combined and evaporated to dryness to recover the methanol-soluble product.

NMR spectra were recorded on a JEOL JNM-GX500 spectrometer. GPC was performed on a JASCO TRIROTAR-II^P chromatograph equipped with Shodex GPC columns (K-806L x 2) at 40°C using chloroform as eluent and the molecular weight was calibrated with polystyrene standards. One milligram of the polymer sample for GPC was dissolved in 50 μl of HFIP, and the solution was diluted with 1.0 ml of chloroform; a 500 μl portion of the diluted solution was used for GPC analysis. X-ray data were collected with a Rigaku AFC-5R automated four-circle diffractometer using Cu-Kα radiation. The crystal structure was solved by the direct method (SHELXS-86).

RESULTS AND DISCUSSION

Polymerization of E-TBC and Z-TBC

Table 1 shows the results of polymerization of *E*-TBC. Polymerization reaction of *E*-TBC with *t*-BuMgBr in toluene at -78°C was very slow. The yield and $\overline{Mn}$ of methanol-insoluble polymer increased with time from 12 to 192 h (Figure 1), which suggested a living character of this polymerization. When the polymerization temperature was raised to -50 or -20°C 1h after the initiation at -78°C, the yield of methanol-insoluble polymer decreased as compared with the polymerization at -78°C. Initiation and polymerization at -50°C gave the polymer in a lower yield. This should be ascribed to the occurrence of side reactions such as elimination of the α-hydrogen atom from the monomer by the initiator. Therefore, initiation

reactions in this work were carried out hereinafter at -78°C irrespective of polymerization temperature.

It has been reported that the ability of polymerization of isocrotonate was very low in comparison with crotonate [7,8]. This tendency was found to be the case in the polymerizations of *E*-TBC and *Z*-TBC with *t*-BuMgBr and *t*-BuLi (Tables 1 and 2).

Table 1. Polymerizations of *E*-TBC with *t*-BuMgBr, *t*-BuLi/Et_3Al and *t*-BuLi[a]

Initiator	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)		$\overline{Mn}^c$ 10^3	$\overline{Mw}^c/\overline{Mn}$
t-BuMgBr	Toluene	-78	72	16.0	(1.9)	22.6	1.77
		-78 → -50[d]	1+72[d]	11.6[e]	(11.7)	14.6	1.62
		-78 → -20[d]	1+72[d]	5.0	(6.7)	5.9	1.71
		-50	72	4.5	(8.1)	9.7	1.56
	THF	-78	24	0	(6.4)	—	—
t-BuLi / Et_3Al	Toluene	-78	168	6.6	(6.8)	2.6	1.41
		-78 → -50[d]	1+168[d]	12.2[f]	(2.8)	2.7	1.22
		-78 → -20[d]	1+72[d]	26.0	(16.1)	4.6	1.51
t-BuLi	Toluene	-78	168	22.2	(1.8)	43.5	2.14
	THF	-78	24	93.6[g]	(6.4)	54.7	1.46

[a] *E*-TBC = 10 mmol, solvent = 5.0 ml, [*E*-TBC] / [Initiator] = 25. [b] The yield of the methanol-soluble part is given in parentheses. [c] Determined by GPC for the methanol-insoluble part. [d] The polymerization temperature was raised to the given value 1h after the initiation at -78°C. [e,f,g] The codes *E*-2, *E*-3, and *E*-1 are given to the samples e,f, and g respectively, for the NMR spectra shown in Figure 4.

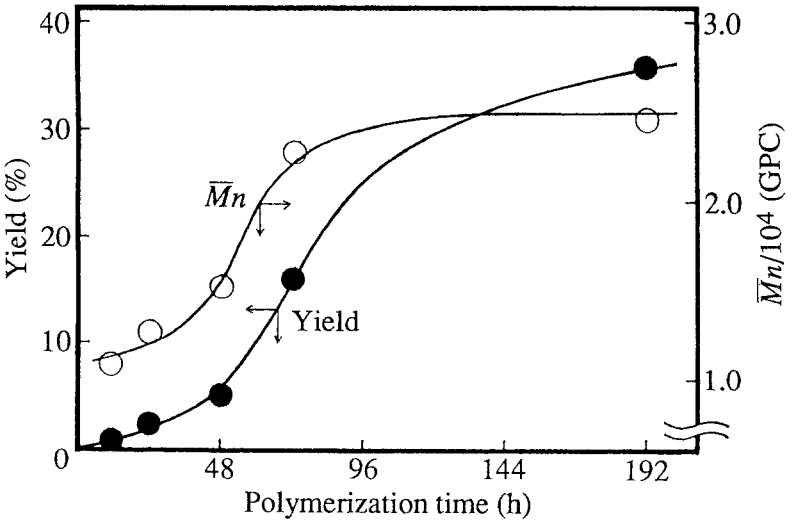


Figure 1. Variations in the yield and $\overline{Mn}$ of the poly(*E*-TBC) obtained with *t*-BuMgBr in toluene at -78°C as a function of polymerization time.

Table 2. Polymerizations of *Z*-TBC with *t*-BuMgBr, *t*-BuLi/Et_3Al and *t*-BuLi[a]

Initiator	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)	$\overline{Mn}$[c] 10^3	$\overline{Mw}$[c] / $\overline{Mn}$
t-BuMgBr	Toluene	-78	168	0 (2.3)	—	—
		-78 → -50[d,e]	1+168[d]	0 (7.0)	—	—
		-78 → -20	1+72[d]	0 (5.1)	—	—
	THF	-78	168	0 (0.8)	—	—
t-BuLi / Et_3Al	Toluene	-78	168	0 (7.8)	—	—
		-78 → -50[d,e]	1+168[d]	24.5[f] (22.1)	8.4	1.34
		-78 → -20[d,e]	1+72[d]	73.1 (16.5)	12.1	1.59
t-BuLi	Toluene	-78	168	0 (0.7)	—	—
	THF	-78	168	0 (2.9)	—	—

[a] Z-TBC = 5 mmol, solvent = 2.5 ml, [Z-TBC] / [Initiator] = 25. [b] The yield of the methanol-soluble part is given in parentheses. [c] Determined by GPC for the methanol-insoluble part. [d] The polymerization temperature was raised to the given value 1h after the initiation at -78°C. [e] Z-TBC = 10 mmol, solvent = 5.0 ml, [Z-TBC] / [Initiator] = 25. [f] The code Z-1 is given to the sample for the NMR spectrum shown in Figure 4.

Methanol-insoluble polymer was not obtained from the polymerization of Z-TBC with *t*-BuMgBr in toluene, although the polymerization mixture exhibited deep orange-yellow color on initiation. The coloration was also observed for the polymerizations of *E*-TBC and MMA with *t*-BuMgBr, which is a sign of successful initiation in this polymerization system. Polymerizations of *E*-TBC with *t*-BuLi in toluene and in THF at -78°C afforded polymers in 22 and 94 % yields, respectively, whereas those of Z-TBC gave no polymer.

On the other hand, Z-TBC formed polymer in a higher yield than *E*-TBC in the polymerization initiated with *t*-BuLi/Et_3Al in toluene. The yield increased with increasing polymerization temperature, and at -20°C, the total yield reached to 89.6 %; this is the first example of isocrotonate polymerization giving a substantial yield.

The poly(Z-TBC) obtained with *t*-BuLi/Et_3Al was soluble in toluene, chloroform and THF, whereas the poly(*E*-TBC)s obtained with *t*-BuLi/Et_3Al and with *t*-BuMgBr in toluene were insoluble in the solvents once they were isolated from the polymerization mixture by precipitation in methanol. The insolubility coincides with that of the poly(*E*-TBC) prepared with PhMgBr in toluene [10]. However, we have found that HFIP dissolves the poly(*E*-TBC)s readily at room temperature. Mixing the HFIP solutions with toluene, chloroform or THF caused no precipitation over the entire range of compositions.

Methyl crotonate did not polymerize with any of the initiator systems described above.

Stereostructure of the predominant dimer obtained by the polymerization of E-TBC with t-BuMgBr in toluene

In the polymerization of *E*-TBC with *t*-BuMgBr in toluene at -78°C, most (*c.a.* 80% by GPC) of the methanol-soluble product was the linear dimer of *E*-TBC. The dimer was fractionated by means of GPC from the methanol-soluble part. ^1H NMR spectrum of the dimer fraction showed that the fraction contained predominantly one of the four possible diastereomers (Figure 2a). X-ray crystallographic determination demonstrated that the dimer (*m.p.* = 70.2 ~ 70.5°C, *monoclinic*, $P2_1$, a = 19.065 Å, b = 11.434 Å, c = 10.340 Å, β = 101.2°, Z = 4, *Dcalcd* = 1.034 g/cm^3) was the *erythro-diisotactic* isomer (Figure 3). When

the polymerization was terminated with CD_3OD instead of CH_3OH, the resulting dimer gave the spectrum shown in Figure 2b. The geminal coupling between H^d and H^e disappeared, and the intensities of the signals due to H^d and H^e became 30 and 70 %, respectively, of those in Figure 2a. This indicates that the dimer exists as a living but dormant anion in the reaction mixture and that the protonation (deuteration) reaction of the dimer anion with CH_3OH (CD_3OD) was *isotactic*-specific. Recently, we reported that protonation of the living PMMA anion prepared with *t*-BuMgBr in toluene with phenol was highly *isotactic*-specific (95%) [15].

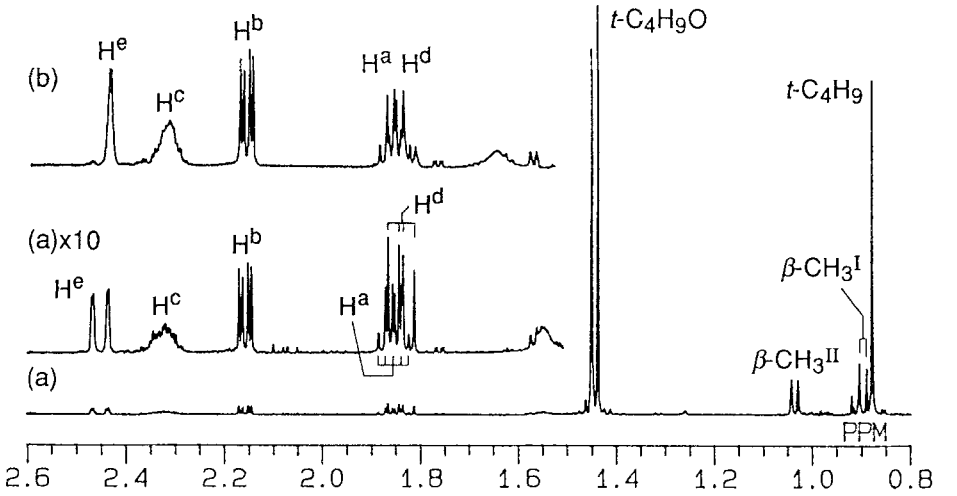


Figure 2. ^1H NMR spectra of the dimer fractions of the oligo(*E*-TBC)s obtained by the polymerizations initiated with *t*-BuMgBr in toluene at -50°C (initiation at -78°C) and terminated with CH_3OH (a) or CD_3OD (b) (500MHz, $CDCl_3$, 30°C). $^3J(H^a\text{-}H^b)$ = 9.40Hz, $^3J(H^b\text{-}H^c)$ = 3.61Hz, $^3J(H^c\text{-}H^d)$ = 11.4Hz, $^3J(H^c\text{-}H^e)$ = 1.89Hz, $^2J(H^d\text{-}H^e)$ = 15.8Hz. See Figure 3 for the notations of H^a~H^e and $CH_3^{I,II}$.

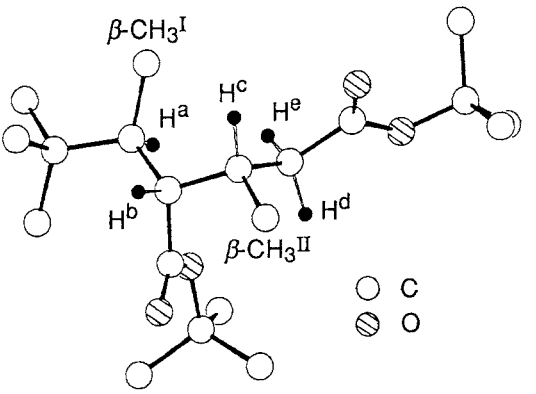
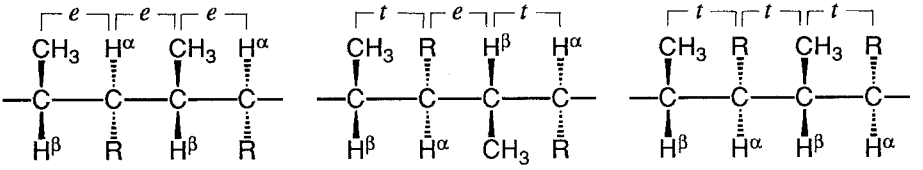


Figure 3. X-ray molecular structure of the *erythro-diisotactic* dimer of *E*-TBC (methyl hydrogen atoms are omitted for clarity).

NMR spectroscopy of the Poly(E-TBC) and Poly(Z-TBC)

Figure 4 shows the carbonyl and β-methyl ^{13}C NMR spectra of the poly(*E*-TBC)s prepared with *t*-BuLi in THF (Sample *E*-1), *t*-BuMgBr in toluene (Sample *E*-2), and *t*-BuLi/Et_3Al in toluene (Sample *E*-3), and of the poly(*Z*-TBC) prepared with *t*-BuLi/Et_3Al in toluene (Sample *Z*-1) (*cf.* Tables 1 and 2). All the spectra were measured in HFIP containing 5vol-% C_6D_6 at 50°C. The configurational diads in the *ditactic* polymers are denoted as "*erythro* (*e*)" and "*threo* (*t*)" according to the IUPAC recommendation [16].*** Then the configurational triads in the *erythro-diisotactic*, *disyndiotactic*, and *threo-diisotactic* sequences can be represented as *ee*, *et*, and *tt* respectively.



erythro-diisotactic *disyndiotactic* *threo-diisotactic*

The signal due to the carbonyl carbon of Sample *E*-1 (Figure 4a) consisted of three broad peaks, and the signal due to the β–methyl group appeared as two peaks. These splitings should be attributed essentially to configurational triads. Sample *E*-1 is considered to be *atactic* because the polymerization with *t*-BuLi in THF is expected to proceed in a free anionic mechanism.

Sample *E*-2 gave two peaks with nearly equal intensity for every kind of carbons including the carbonyl and β–methyl groups (Figure 4b). The narrow line widths of the signals were in contrast to the broad ones observed for Sample *E*-1. These features of the NMR signals suggest that Sample *E*-2 is a binary mixture of highly stereoregular sequences. One of them is reasonably assumed as the *ee* sequence because the predominant dimer formed in the polymerization mixture was the *ee* isomer. The other is attributed to the *tt* sequence on the basis of the two-dimensional NMR

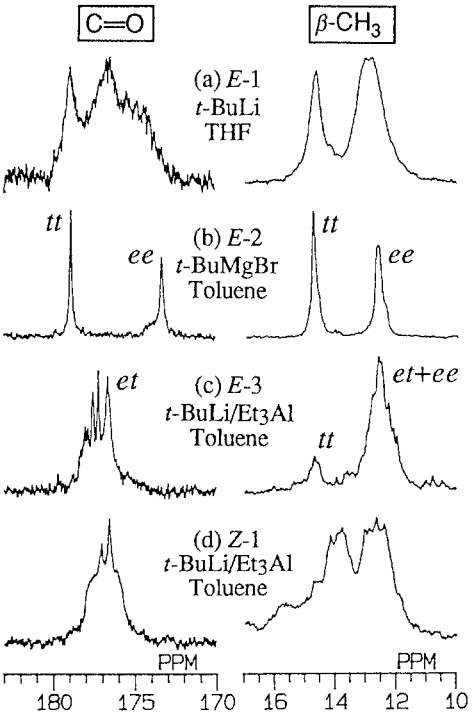


Figure 4. ^{13}C NMR spectra of poly(*E*-TBC)s (Samples *E*-1~*E*-3) (a~c) and poly(*Z*-TBC) (Sample *Z*-1) (d) (125MHz, HFIP/C_6D_6 = 95/5, 50°C).

*** The "*meso*" and "*racemic*" notations have been conventionally used for *ditactic* polymers [17] as well as (mono)*tactic* polymers. However, the notations for *ditactic* polymers are inconsistent to the IUPAC definitions of the "*meso*" and "*racemo*" stereosequences.

spectroscopy as described below.

The carbonyl carbon signals of Samples *E*-3 and *Z*-1 appeared as broad multiplets (Figures 4c and 4d) in between the two peaks due to the carbonyl groups in the *ee* and *tt* sequences of Sample *E*-2. The broad multiplets were assigned to the carbonyl group in the *et* sequence because the magnetic environments around the carbonyl group in the *et* sequence lie in the intermediate between *ee* and *tt* sequences. This assignment is consistent with the fact that the PMMA obtained under similar conditions is highly *syndiotactic* [2].

Figure 5 shows the ^{1}H COSY spectrum of Sample *E*-2. The attached one-dimensional spectrum shows that each signal due to the β-methyl, *t*-butoxy, and the α- and β-methine (H^α and H^β) protons consists of the two peaks arising from the *ee* and *tt* sequences with nearly equal abundance. The assignment of the signals due to H^α and H^β in each sequence was made on the basis of the correlation peaks between H^α and H^β, and between H^β and β-methyl. Absence of correlation peaks between the *ee* and *tt* sequences clearly indicates that the polymer is a 1:1 mixture of *erythro-* and *threo-diisotactic* polymers. The *ee*/*tt* assignment was based on a consideration of the chemical shift difference between H^α and H^β in each sequence; the chemical shift difference in the *ee* sequence should be larger than that in the *tt* sequence because H^α and H^β in the *ee* sequence are flanked by two methyl and two carbonyl groups, respectively, whereas both H^α and H^β in the *tt* sequence are flanked by a methyl group and a carbonyl group if an extended zigzag form is assumed for the polymer backbone (*cf.* the scheme above). The assignment for the configurational triads for the ^{13}C NMR signals could be directly made by the ^{13}C-^{1}H COSY experiment.

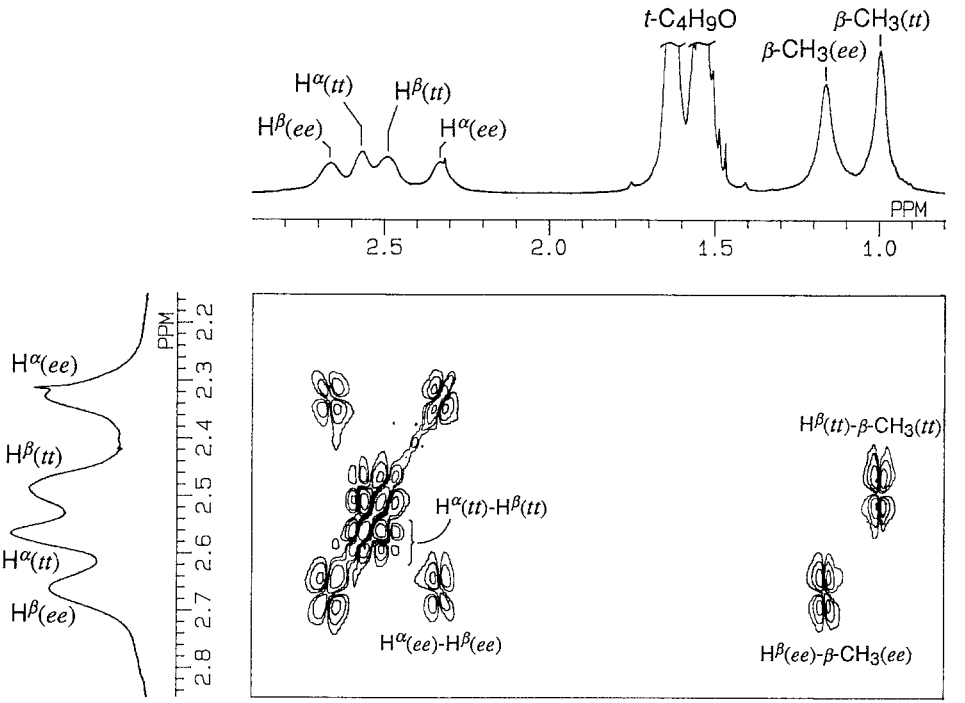


Figure 5. ^{1}H COSY of the poly(*E*-TBC) prepared with *t*-BuMgBr in toluene (Sample *E*-2, 500 MHz, $(CF_3)_2CDOD/C_6D_6$ = 95/5, 50°C).

Taking into account the steric effects of the side groups, the *erythro-diisotactic* polymer chain is considered to exist predominantly in stable zigzag conformation whereas the *threo-diisotactic* chain is expected to deviate slightly from zigzag structure to take helical conformation. The broader line width of the ^{1}H and ^{13}C NMR signals due to the *ee* sequence as compared with the narrower one of the corresponding signals due to the *tt* sequence suggests that the *erythro-diisotactic* polymer is less flexible than the *threo-diisotactic* polymer because of the rigid zigzag conformation.

Muroga and coworkers observed three peaks for the carbonyl ^{13}C NMR signals of the poly(*E*-TBC) prepared with PhMgBr in toluene at room temperature, and assigned them to the *ee*, *et* and *tt* sequences, respectively, from the lowest-field peak to the highest one, on the basis of a propagation mechanism of a reversible double-Markovian process [10]. They also made assignment for the two broad peaks at 14 (I) and 12 ppm (II) due to the β-methyl group as (I) = *ee* + *et* and (II) = *tt*. Our assignment is different from theirs in regard to both carbonyl and β-methyl signals (*cf.* Figure 4) although they mentioned that their assignment was interchangeable.

The formation of the 1:1 mixture of *erythro-* and *threo-diisotactic* polymers leads to the somewhat curious conclusion that the two completely opposite processes of stereoregulation (*i.e.* the *trans*-opening/*isotactic*-like addition and the *cis*-opening/*syndiotactic*-like addition processes) take place independently and simultaneously in the polymerization system. According to Yoshino et al., when isopropyl acrylate-β-*d* was polymerized in toluene at -78°C with PhMgBr as initiator, the configuration of the polymer obtained was a mixture of *eeee* and *tttt* sequences [18,19]. It is interesting that our result about the poly(*E*-TBC) obtained by *t*-BuMgBr in toluene coincides with their result.

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REFERENCES

1. K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, T. Kitayama, *Polym. J.*, **18**, 1037 (1986).
2. T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto, K. Hatada, *Makromol. Chem., Suppl.*, **15**, 167 (1989).
3. G. Natta, M. Peraldo, M. Farina, *Belg. Pat.*, 599,833 (1961).
4. M. L. Miller, J. Skogman, *J. Polym. Sci., Part A*, **2**, 4551 (1964).
5. T. Tsuruta, T. Makimoto, T. Miyazako, *Makromol. Chem.*, **103**, 128 (1967).
6. R. K. Graham, J. E. Moore, J. A. Powell, *J. Appl. Polym. Sci.*, **11**, 1797 (1967).
7. Y. Kobuke, T. Fueno, J. Furukawa, *J. Polym. Sci., A-1*, **5**, 2701 (1967).
8. T. Tsuruta, T. Makimoto, K. Tanabe, *Makromol. Chem.*, **114**, 182 (1968).
9. T. Kitano, T. Fujimoto, M. Nagasawa, *Macromolecules*, **7**, 719 (1974).
10. Y. Muroga, I. Noda, M. Nagasawa, *Macromolecules*, **13**, 1081 (1980).
11. A. Matsumoto, A. Horie, T. Otsu, *Polym. J.*, **23**, 211 (1991).
12. C. Schuerch, W. Fowells, A. Yamada, F. A. Bovey, F. P. Hood, E. W. Anderson, *J. Am. Chem. Soc.*, **86**, 4481 (1964).
13. T. Yoshino, J. Komiyama, M. Shinomiya, *J. Am. Chem. Soc.*, **86**, 4482 (1964).
14. C. Rappe, *Org. Synth., Coll. Vol.*, **6**, 711 (1988).
15. K. Ute, T. Asada, N. Miyatake, K. Hatada, *Makromol. Chem., Macromol. Symp.*, in press.
16. IUPAC, Stereochemical Definitions and Notations Relating to Polymers, *Pure Appl. Chem.*, **53**, 733 (1981).
17. R. Chûjô, M. Kamei, A. Nishioka, *Polym. J.*, **3**, 289 (1972).
18. T. Yoshino, K. Kuno, *J. Am. Chem. Soc.*, **87**, 4404 (1965).
19. T. Yoshino, J. Komiyama, *J. Am. Chem. Soc.*, **88**, 176 (1966).

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