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Highly Threodiisotactic Polymerization of Triphenylmethyl Crotonate[1]

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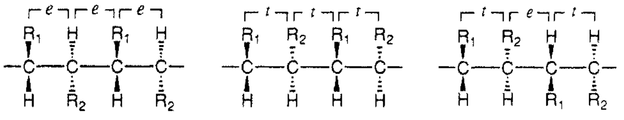
The configurational isomerism possible in polymers of α,β-disubstituted ethylenes has attracted considerable interest since the discovery of stereoregular polymers by Natta et al.[2] Generally speaking, pure *cis*- or *trans*-α,β-disubstituted ethylenes, $CHR_1{=}CHR_2$ ($R_1 \neq R_2$), can give rise to three simple stereoregular polymers; the configurations are defined as *erythrodiisotactic*, *threodiisotactic*, and *disyndiotactic*.



erythrodiisotactic *threodiisotactic* *disyndiotactic*

Polymers with a diisotactic structure were first obtained from *cis*- and *trans*-propene-*1*-d_1.[3] Several other examples of ditactic polymers of β-deuterated vinyl monomers have also been reported.[4,5] Only a limited number of papers describe the stereospecific polymerization of the α,β-disubstituted ethylenes other than β-deuterated vinyl monomers. Natta and his co-workers have shown by X-ray diffraction analysis that the cationic polymerization of isobutyl *trans*-propenyl ether yields the crystalline polymer with *threodiisotactic* structure.[6,7] It was also reported that *trans*- and *cis*-β-chlorovinyl ethers polymerize to give *threodiisotactic* and *erythrodiisotactic* polymers, respectively.[8]

Branched alkyl crotonates, such as *tert*-butyl and isopropyl crotonates, can also be polymerized in a stereospecific way by anionic initiators.[9-12] However, ditacticity of the polycrotonates is not very high, as indicated by their NMR analysis.[11,12] Recently, we found that a 1:1 blend of highly ditactic polymers is obtained by the polymerization of *tert*-butyl crotonate (TBC) with *tert*-butylmagnesium bromide in toluene.[13] In the present paper, we report the synthesis of almost perfectly (≈100%) *threodiisotactic* poly(triphenylmethyl crotonate) and its structural verification.

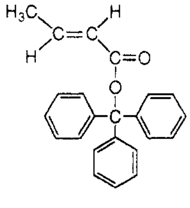
Triphenylmethyl crotonate (TrC) is a constitutional isomer of triphenylmethyl methacrylate (TrMA) which is known as the unique monomer that forms a polymer with high isotacticity regardless of the kind of polymerization systems.[14] The steric bulk of the triphenylmethyl group leads to the formation of isotactic poly(TrMA) molecules having a rigid helical conformation. When polymerized with a chiral initiator such as a 9-fluorenyllithium (FlLi)/(*S,S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane [(+)-DDB] complex, TrMA gives an optically active polymer whose optical activity derives entirely from conformational chirality (one-handed helix).[15,16]

TrC was prepared from crotonic acid and triphenylmethyl chloride in the presence of triethylamine in toluene and purified by crystallization from diethyl ether and hexane [mp 100.0–100.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.88 (dd), 5.99 (dq), 6.99 (dq), 7.28 (m)]. The procedure is similar to that described for the synthesis of TrMA.[17] Polymerization was carried out in a glass ampule under a dry nitrogen atmosphere. After the polymerization reaction was terminated by adding a small amount of methanol, the polymerization mixture was poured into a 20-fold volume of methanol. The precipitated polymer was collected by centrifugation, washed several times with methanol, and dried in vacuo at 60 °C for 3 h.

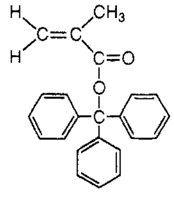
Table I. Polymerization of Triphenylmethyl Crotonate (TrC)[a]

initiator	solvent	temp (°C)	time (h)	yield[b] (%)	$\bar{M}_n{}^c \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^c$
AIBN[d]	toluene	60	24	0		
t-BuMgBr	toluene	−78	168	0		
FlLi	THF	−78	24	0		
FlLi	toluene	−78	24	35.5	60.6	2.32
FlLi/TMEDA	toluene	−78	168	82.5	2.2	1.30
FlLi/(+)-DDB	toluene	−78	24	100	17.9	1.94

[a] TrC, 2.0 g; solvent, 10 mL; [TrC]/[initiator] = 25. [b] Methanol-insoluble part. [c] The data of the poly(methyl crotonate) derived from the poly(TrC). Determined by GPC calibrated with standard polystyrene samples. [d] TrC, 1.0 g; toluene, 5 mL; [TrC]/[AIBN] = 100.



TrC



TrMA

TrC gave no polymer by the radical polymerization initiated with AIBN in toluene at 60 °C. Attempts to polymerize TrC with *t*-BuMgBr in toluene were unsuccessful. On the other hand, polymerization of TrC with FlLi in toluene at −78 °C for 24 h afforded methanol-insoluble polymer in a substantial yield. When the FlLi/(+)-DDB complex was used as the initiator, the polymerization proceeded very rapidly to give poly(TrC) quantitatively. The FlLi/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) complex was also effective for polymerization of TrC, and the molecular weight distribution of the resulting polymer was fairly narrow. The results are summarized in Table I.

All the poly(TrC)s were transformed to poly(methyl crotonate)s [poly(MeC)s] by hydrolytic cleavage of the triphenylmethyl groups (in 5% HCl/methanol, reflux 2 h) and subsequent methylation with diazomethane in dry benzene. Figure 1a shows the 500-MHz ^{1}H NMR spectrum of the poly(MeC) which was derived from the poly(TrC) obtained with FlLi/(+)-DDB. The signals due to the CH_3O, β-CH_3, α-CH, and β-CH protons appeared at 3.74, 1.07, 2.56, and 2.47 ppm, respectively. The β-CH_3 resonance exhibited small splitting due to the vicinal coupling with the β-CH proton. The spectrum in Figure 1a differs markedly from the spectrum of the atactic poly(MeC) derived from the poly(TBC)[13,18] obtained by the polymerization of TBC with *t*-BuLi in THF at −78 °C (Figure 1c). The relatively narrow line width of the resonances in Figure 1a clearly indicates extremely high stereoregularity of the poly(MeC) derived from poly(TrC). The poly(MeC)s derived from the poly(TrC)s prepared with FlLi and FlLi/TMEDA showed spectra similar to Figure 1a.

In the preceding paper, we demonstrated that polymerization of TBC with *t*-BuMgBr in toluene gives a 1:1 blend of highly ditactic polymers. The ditactic components in the poly(TBC) were determined to be *erythrodiisotactic* and *threodiisotactic* sequences by two-dimensional NMR analysis.[13] The poly(MeC) derived from the poly(TBC)[18] showed two sets of NMR signals with nearly

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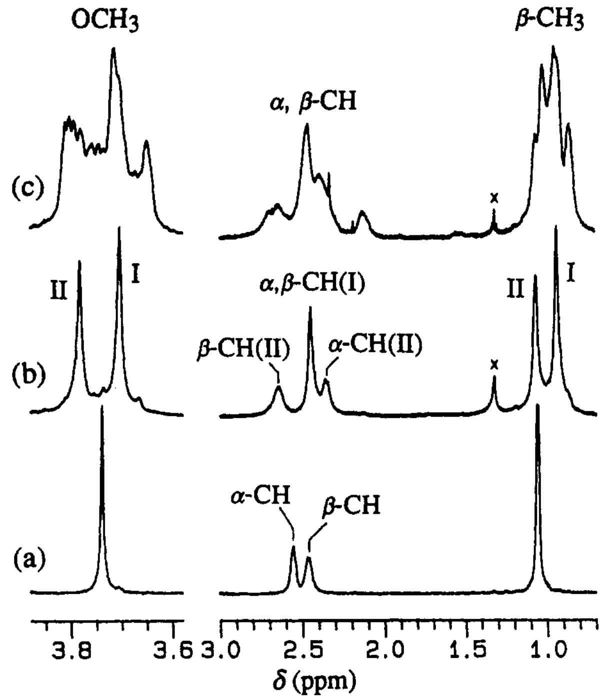


Figure 1. ^{1}H NMR spectrum of poly(MeC) derived from poly(TrC) which was obtained by polymerization with FlLi/(+)-DDB (a). The spectra of the ditactic-blend poly(MeC) (b) and atactic poly(MeC) (c) derived from the poly(TBC)s[13] obtained by the polymerization of TBC initiated with *t*-BuMgBr in toluene and *t*-BuLi in THF, respectively, are also shown [$(CF_3)_2CHOH/C_6D_6$ (95/5), 55 °C, 500 MHz]. (×) Signals due to impurities.

equal intensity (I and II) for the CH_3O, β-CH_3, α-CH, and β-CH protons each (Figure 1b). It is clear that neither the signal set I nor II fits the resonances in Figure 1a. Hence, the configuration of the poly(TrC) was expected to be different from those of the two diisotactic structures.

In order to determine the configurational structure of the poly(TrC)s, the stereostructure of the oligomeric product was investigated. The oligomerization of TrC was carried out using FlLi/TMEDA as initiator in toluene at −78 °C for 24 h ([TrC]/[FlLi] = 5). The methanol-soluble oligomer (yield 65%) was converted to oligo(MeC) and then fractionated by means of preparative GPC into the individual homologues from the dimer to pentamer (dimer:trimer:tetramer:pentamer = 13:50:26:11, in weight). The trimer fraction contained two diastereomers in a ratio of 75:25 as determined by ^{1}H NMR. The tetramer fraction consisted of three diastereomers, and the relative abundance was 71:17:12. On the other hand, the pentamer fraction consisted essentially of a single diastereomer (>99%) although 256 (=2^8) diastereomers are theoretically possible for this pentamer. The results suggest that the propagation reaction of the oligo(TrC) anion over the tetramer step should be highly stereospecific.

Single crystals were grown from an ethanol/chloroform solution of the pentamer fraction and subjected to X-ray crystallographic determination.[19] Figure 2 shows the molecular structure of the predominant pentamer. The relative configuration for the nine asymmetric carbon atoms is ($S^*,R^*,S^*,R^*,R^*,S^*,R^*,S^*,R^*$) from the fluorenyl terminal to the hydrogen terminal as formulated in Figure 2, the configurational sequence of the pentamer therefore being purely *threodiisotactic*. The backbone of the pentamer molecule assumes the structure of a 3/1 helix consisting of a repeated *trans–gauche* conformation, $(TG)_3$, except the fifth monomeric unit from the fluorenyl end group (Figure 3). The helical structure is essentially identical with that of isotactic polypropylene.[20]

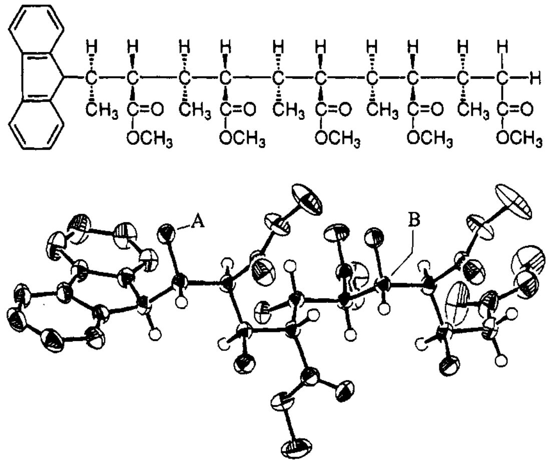


Figure 2. Structure of the *threodiisotactic* pentamer of methyl crotonate. Methyl and ring hydrogen atoms are omitted for clarity. See also Figure 3.

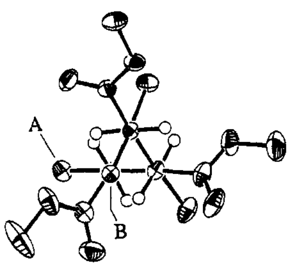
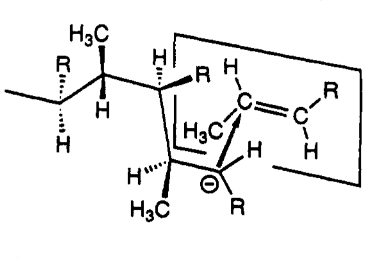


Figure 3. 3/1 helix formed by the three monomeric units embedded in the *threodiisotactic* pentamer of methyl crotonate. See Figure 2 for the notation (A and B) of the carbon atoms.

On the basis of the X-ray analysis of the predominant pentamer, it is reasonably assumed that the poly(TrC) obtained by the same polymerization system (FlLi/TMEDA) has likewise *threodiisotactic* structure. The configuration of the poly(TrC)s prepared with FlLi and FlLi/(+)-DDB should also be *threodiisotactic* because of the similarity in the ^{1}H NMR spectra of all the poly(MeC)s derived from poly(TrC)s. This conclusion requires revision of the configurational assignment for the ditactic-blend poly(TBC) prepared with *t*-BuMgBr (cf. Figure 1b); the blend ditactic sequences are now attributable to *erythrodiisotactic* and *disyndiotactic* sequences.

The absolute information of the ditactic structure leads to a mechanistic conclusion about the stereoregulation processes in the polymerization.[2–8,11–13] In the case of *trans*-α,β-disubstituted ethylenes including crotonates, the *threodiisotactic* polymer chain is the product of the stereospecific processes in which the mode of double-bond opening is *cis* and the direction of monomer placement to the active center is syndiotactic-like. In other words, the α-*si** face of the β-(R^*)-poly(TrC) enolate attacks the β-*re** face of the TrC monomer as illustrated in the following scheme in which the 3/1 helix conformation similar to the pentamer of MeC (cf. Figure 2) is assumed for the polymer anion. Taking the steric repulsion among the methyl and



triphenylmethyl groups in the monomer and polymer anion into consideration, this scheme seems to be quite reasonable for the explanation of the high *threodiisotactic* specificity of the polymerization.

In analogy with isotactic poly(TrMA),[15,16] it may be possible for *threodiisotactic* poly(TrC) to be prepared in an optically active form based on stable one-handed helical conformation when an appropriate chiral initiator is used. The specific rotation of the poly(TrC) prepared with FlLi/(+)-DDB was measured in chloroform (c = 1.0 g·dL) at 25 °C. The $[\alpha]_D$'s were 5.6° and 7.4° for the poly(TrC) samples with an average degree of polymerization (DP) of 15 and 36, respectively. The poly(TrC) having a DP larger than *ca.* 50 was insoluble in any solvent examined. Although the optical rotation of the poly(TrC) samples was much smaller than that of the poly(TrMA) obtained under similar conditions (344°, DP = 47),[16] the one-handed helix stabilized by the bulky triphenylmethyl groups is suggested to contribute the small optical activity of the poly(TrC)s since the optical activity was lost when the poly(TrC)s were converted to poly(MeC)s. The stability of the helical conformation of poly(TrC) in solution is interesting in connection with the other examples of optically active helical polymers,[15,16,21-26] and further studies will be published elsewhere.

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(18) The poly(TBC) was converted to poly(MeC) by cleavage of the *t*-butyl groups (in CF_3CO_2H, at room temperature) and subsequent methylation with CH_2N_2.

(19) The pentamer ($C_{38}H_{50}O_{10}$ = 666.81; mp = 157.9–158.7 °C) crystallized in the triclinic system of space group $P\bar{1}$. The lattice constants were as follows: $a = 15.1834\ (16)$ Å, $b = 15.3033\ (13)$ Å, $c = 8.3251\ (17)$ Å, $\alpha = 102.012\ (10)°$, $\beta = 95.674\ (12)°$, $\gamma = 79.531\ (8)°$, $V = 1856.8\ (5)$ Å^3, $Z = 2$, $D_{calc} = 1.1927$ g·cm^{-3}. X-ray data were collected with a Rigaku AFC-5R automated four-circle diffractometer using Cu $K\alpha$ radiation (λ = 1.5418 Å, 40 kV, 200 mA). The reflection data were empirically corrected for absorption. The structure was solved by the direct method (SHELXS-86). Positions of all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions. The final R value was 6.13% for the structure refined by the least-squares method using 5054 unique reflections with $|F_0| > 3\sigma(F_0)$.

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