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Enhanced Stereocontrol in Disyndiotactic-specific Group Transfer Polymerization of Methyl Crotonate—Stereochemical Evidence of Group Transfer

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ABSTRACT: Group transfer polymerization (GTP) of methyl crotonate was examined by using a ketene silyl acetal with *tert*-butyldimethylsilyl group in the presence of HgI_2 and *tert*-butyldimethylsilyl iodide as a catalyst and a co-catalyst, respectively. Under optimized conditions, the GTP produced *disyndiotactic* polymers with narrow molecular weight distribution in quantitative yields. The trialkylsilyl group in the initiator components was found to exert control over the stereochemical process of the GTP; the bulky *tert*-butyldimethylsilyl group leads to the highest disyndiotacticity. The results provide a direct evidence for the transferring silyl group to be involved in the propagation steps in the GTP. [DOI 10.1295/polymj.37.578]

KEY WORDS Ditacticity / Stereoregularity / Methyl Crotonate / Ketene Silyl Acetal / 1-Methoxy-1-(*tert*-butyldimethylsiloxy)-1-propene /

Group transfer polymerization (GTP), disclosed in early 1980's by Webster,[1] is one of the versatile living polymerizations for acrylic monomers. The GTP involves ketene silyl acetals as initiators and nucleophilic or Lewis acidic catalysts and has been claimed to proceed through migration or transfer of the silyl group to maintain ketene silyl acetal units at the propagating polymer chain-ends during the polymerization. The proposed mechanism, so-called "associative mechanism", assumes active intermediates carrying the silyl group.[1–3] On the other hand, a dissociative mechanism has also been proposed, which regards the active intermediate as an enolate as in the case of classical anionic polymerizations.[4–6]

The above mechanistical argument has urged several researchers to examine the stereochemistry of GTP with the expectation of any specific effects of the ketene silyl acetal ends on the stereochemical aspect of the propagation reaction, if the associative mechanism dominates the GTP. For example, Müller and Sticker reported that syndiotacticity of poly(methyl methacrylate) (PMMA) obtained by the GTP using nucleophilic catalyst was slightly lower than that of PMMA obtained by radical polymerization.[7] Mechanism and stereospecificity of the GTP were also discussed for cyclization polymerization of a binaphthyl dimethacrylate by Nakano and Sogah based on the results that the isotacticity of the polymer obtained by the GTP was higher (34%) than that that of the polymer obtained by radical polymerization.[8] GTP giving stereoregular polymers was reported for the polymerization of triphenylmethyl methacrylate using a nucleophilic catalyst ($mm = 91\%$).[9] Judging from the fact that radical and anionic polymerizations of this monomer also give the isotactic polymers,[10] however, the result is hardly regarded as "stereocontrol by GTP".

We have reported the GTP of methyl crotonate, a structural isomer of methyl methacrylate, using ketene silyl acetals (**1**) and (**2**) (Scheme 1), in the presence of HgI_2 and trialkylsilyl iodides (R_3SiI) as catalysts.[11] Later, the GTP of other alkyl crotonates (alkyl = ethyl, *n*-propyl, isopropyl, or *n*-butyl) was also found successful.[12] The combined catalyts HgI_2/R_3SiI has been known effective for the GTP of acrylates.[13] The predominant stereochemical structure of poly(methyl crotonate) (PMC) thus formed was found *disyndiotactic* (Scheme 2) by X-ray analysis of the oligomers and NMR spectroscopy of the polymers and oligomers.[14]

^1H NMR spectra indidated that the polymer obtained with 1-methoxy-1-(triethylsiloxy)-2-methyl-1-propene (**2**) has higher stereoregularity than that with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (**1**). The results prompted us to examine the effect of trialkylsilyl group in the GTP initiator on the stereocontrol of the GTP of the crotonate. In this paper, we chose *tert*-butyldimethylsilyl group as a bulkier silyl group in the initiator, 1-methoxy-1-(*tert*-butyldimethylsiloxy)-1-propene (**3**)[15] (Scheme 1), which formed a *disyndiotactic* PMC with much higher stereoregularity than those obtained with (**1**) and (**2**). Accordingly, the stereocontolled GTP was realized at a high level through the rational initiator design.

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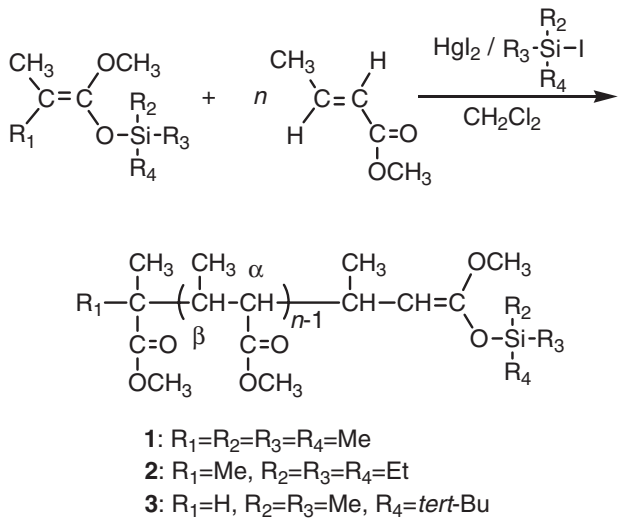
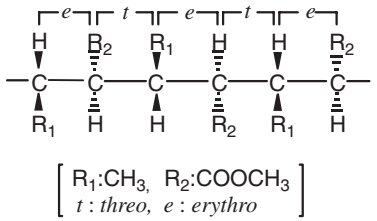


Scheme 1. Group transfer polymerization of methyl crotonate.



Scheme 2. *Disyndiotactic* poly(methyl crotonate).

EXPERIMENTAL

*Synthesis of (**3**)*[16–21]

1-Methoxy-1-(*tert*-butyldimethylsiloxy)-1-propene (**3**) was prepared by the following procedure; *tert*-butyldimethylsilyl trifluoromethanesulfonate (20 g, 0.076 mol), prepared from *tert*-butyldimethylsilyl chloride and trifluoromethanesulfonic acid, was allowed to react with methyl propionate (33.4 g, 0.379 mol) in the presence of triethylamine (38.4 g, 0.379 mol) in diethyl ether (90 mL) under a dry nitrogen atmosphere for 20 h. After the solvent was removed by evaporation, (**3**) was obtained by distilling the residue (b.p. 49.0–49.8 °C/2.2 mmHg); yield 3.0 g (19.3%).

Synthesis of tert-butyldimethylsilyl iodide (TBSI)[22]

To a mixture of *tert*-butyldimethylsilane (5.0 g, 0.043 mol) and methyl iodide (13.8 g, 0.069 mol), palladium chloride (24 mg, 0.14 mmol) was added, and the mixture was stirred at room temperature for 24 h. Excess methyl iodide was distilled off, and the residue was recrystallized from diethyl ether to give 9.3 g (90% yield) of TBSI.

Polymerization Procedure

Polymerization of methyl crotonate was carried out by a syringe technique under nitrogen in glass tubes equipped with three-way stopcock. A typical example is given below. To a stirred mixture of methyl crotonate (10 mmol), HgI_2 (0.016 mmol) and TBSI (0.048 mmol) in CH_2Cl_2 (0.6 mL), a solution of ketene silyl acetal (**3**) in CH_2Cl_2 (0.2 mmol in 3.6 mL) was added to initiate the polymerization reaction. After a predetermined period of the reaction, 0.2 mL of trifluoroacetic acid was added to the mixture, and then the volatile components were removed by evaporation under reduced pressure. The residue was dissolved in a mixture of $(CF_3)_2CHOH$ and acetone, and the solution was poured into a large amount of CH_3OH/H_2O (1/1, v/v). The precipitated polymer was collected by filtration, washed several times with CH_3OH/H_2O, and dried at 40 °C for 6 h.

Measurements

Size exclusion chromatography (SEC) was performed on a JASCO PU-980 chromatograph equipped with Polymer Laboratories SEC columns PLgel Mixed-D (7.5 mm × 300 mm × 2, maximum porosity 4×10^5) and a JASCO RI-930 detector using $CHCl_3$ as an eluent at 40 °C. Molecular weight was calibrated against standard PMMA samples (Shodex). NMR spectra were recorded on Varian Unity-Inova 750 and 500 spectrometers in $(CF_3)_3CHOH/C_6D_6$ (95/5, v/v) at 55 °C or in $CDCl_3$ at 35 °C. The strong resonances due to $(CF_3)_3CHOH$ were suppressed by the WET method.[23]

RESULTS AND DISCUSSION

Polymerization of methyl crotonate was carried out with ketene silyl acetal (**3**) in the presence of HgI_2 as a catalyst and TBSI as a co-catalyst in CH_2Cl_2. The ratio of HgI_2 and TBSI employed is close to the optimized value for the previously reported GTP of methyl crotonate.[11] The results are summarized in Table I. The polymerizations at 0 and −20 °C gave PMCs with fairly narrow molecular weight distribution (MWD) with the maximum yield, while the yield decreased and MWD became broader with decreasing polymerization temperature. The broader MWD of the polymers formed at lower temperatures could partly be ascribed to the fact that the polymer formed in the medium precipitated out below −40 °C during the polymerization. At −78 °C, the yield hardly reached completeness even when the polymerization period was extended for 600 h (65%). The polymerization at +20 °C resulted in a quite low yield (13%), probably due to self-termination by cyclization and/or *O*-to-*C*-silyl isomerization of propagating chain-ends.[14,24,25]

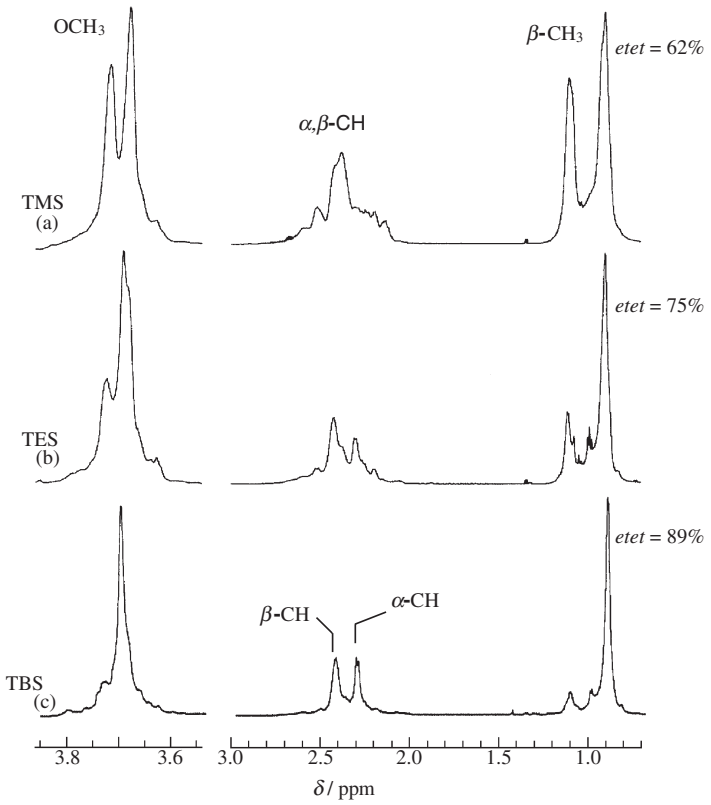


Figure 1. ^{1}H NMR spectra of PMCs prepared by the GTP with **3** (a), **2** (b) and **1** (c) ($(CF_3)_2CDOD/C_6D_6$ (95/5 v/v), 55 °C, 750 MHz).

Table I. GTP of methyl crotonate with 1-methoxy-1-(*tert*-butyldimethylsiloxy)-2-propene (**3**) in the presence of HgI_2 and TBSI in CH_2Cl_2[a]

Initiator	Temp	Time	Yield	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
mmol	°C	h	%	10^3	
0.1	20	24	13	2.4	1.28
0.1	0	24	65	9.0	1.26
0.2	0	24	99	6.7	1.16
0.2	−20	24	99	7.1	1.15
0.2	−40	24	73	6.3	1.31
0.2	−60	24	47	2.2	1.44
0.2	−78	600	65	3.2	2.16
0.1[c]	−20	168	83	32.4	1.35

[a]Monomer, 10 mmol; HgI_2, 0.016 mmol; TBSI, 0.048 mmol; CH_2Cl_2, 4 mL. [b]By SEC. [c]Monomer, 20 mmol; HgI_2, 0.032 mmol; TBDMSI, 0.096 mmol; CH_2Cl_2, 8 mL ([M]/[I] = 200).

A similar temperature dependence has been observed for the GTP with (**1**) and (**2**).[14]

To obtain higher molecular weight PMC, the polymerization was conducted at $[M]_0/[initiator]_0$ ratio of 200 mol mol^{-1} for 168 h at −20 °C. The polymer was obtained in a high yield with the number-average molecular weight ($\bar{M}_n$) of 32×10^3, the value of which is the highest so far reported for PMC directly obtained by polymerizing methyl crotonate, while the GTP of other alkyl crotonates gives the polymers with $\bar{M}_n$ upto 90×10^3.[12]

Figure 1 shows ^{1}H NMR spectrum of PMC obtained with **3**/TBSI at −40 °C together with those of PMCs obtained with **1**/trimethylsilyl iodide (TMSI) and **2**/triethylsilyl iodide (TESI) at the same temperature. Peak assignments are shown in the figure according to our previous report.[14] β-CH_3 proton signals split into two principal peak groups, whose relative intensities vary depending on the initiators used. Based on NMR data of pure *disyndiotactic* oligomers, the major peak at 0.90 ppm has been assigned to *disyndiotactic* sequence or *etet* sequence (see Scheme 2), and the minor peak at 1.12 ppm to a defect sequence, which will be discussed later. At the same time, CH and OCH_3 signals of the former PMC are much simpler than those of the other two. Apparently, the PMC formed with **3**/TBSI exhibits much higher stereoregularity or higher *etet* content than the other two PMCs; bulkier the silyl group of the initiator, higher the stereoregularity of the polymer. The results clearly indicate that the stereospecificity of the GTP of methyl crotonate is affected by the silyl group of the initiator,[26] which presumably transfers in every propagation step to form the ketene silyl acetal end-group, as the original GTP concept[1] anticipates, so as to exert influence on the stereochemical aspects of the propagation reaction.

Figure 2 shows ^{1}H NMR spectra of PMCs obtained with **3**/TBSI at different polymerization temperatures. Stereoregularity of the polymer, as judged from the

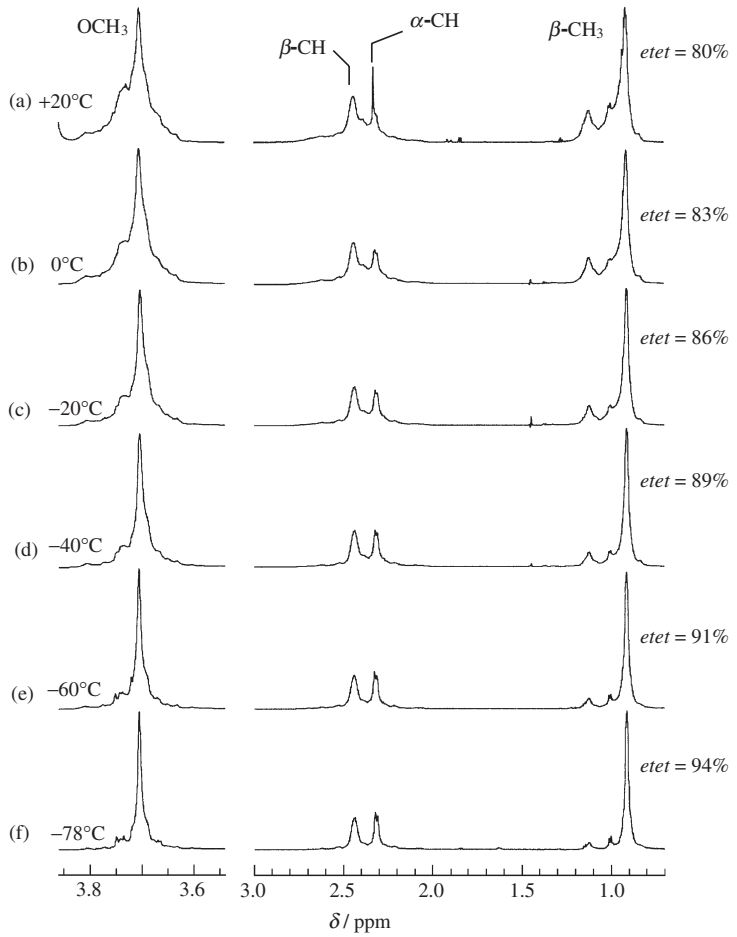


Figure 2. ^{1}H NMR spectra of PMCs prepared by the GTP with **3**/HgI_2/TBSI at +20 °C (a), 0 °C (b), −20 °C (c), −40 °C (d), −60 °C (e) and −78 °C (f) ($(CF_3)_2CDOD/C_6D_6$ (95/5 v/v), 55 °C, 750 MHz).
Letters "*e*" and "*t*" in "*etet*" denote *erythro* and *threo* configurations of the neighboring substituents (CH_3 and COOR) (see Scheme 1).

relative intensity of the peak at 0.9 ppm in the β-CH_3 region, becomes gradually higher with decreasing polymerization temperature, and reached 94% at −78 °C.

The highly *disyndiotactic* PMC still exhibits a β-CH_3 signal at 1.12 ppm as the minor component due to stereochemical defects in the chain. We have demonstrated from the stereochemical analysis of pure *disyndiotactic* oligomers, that the GTP proceeds in *trans*-opening of the double bond of the monomer, giving *erythro* configuration, and *threo* addition of the subsequent monomer addition to generate *etet* sequences.[14] It should be noted that the configurational analysis of the given polymer does not afford such information but only the repetition of *e* and *t* configurations is recognizable, while the monomeric units in the oligomer can be identified from the initial to terminal ends.

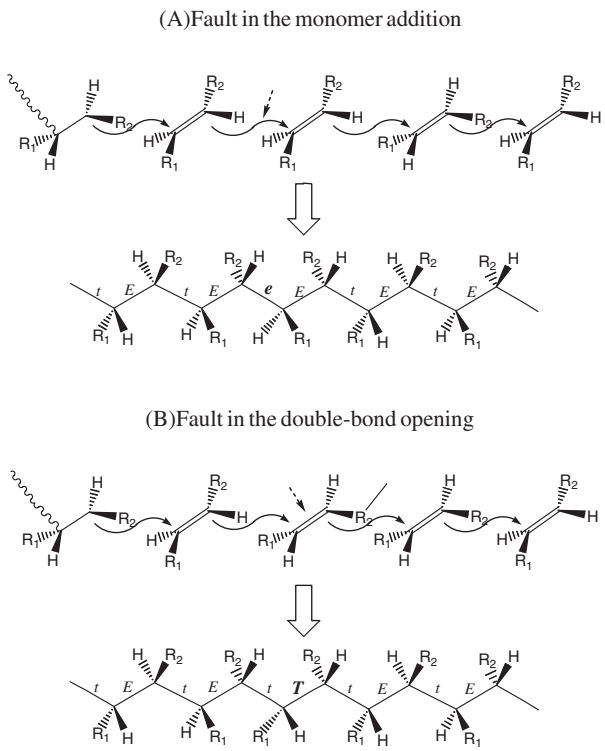
If the stereochemical fault during the propagation process happens in an isolated manner, two types of defect sequences are generated within the enough long *etet* sequence; ---*tetee*etete--- [A], and ---*tetettt*ete--- [B] (Scheme 3).

The sequence [B] is comprised of *diheterotactic* sequences, *ettt* and ***t***t*et*, which are found in a *diheterotactic* PMC (Scheme 4) derived from poly(*tert*-butyl crotonate) prepared with diphenylmagnesium in toluene.[27]

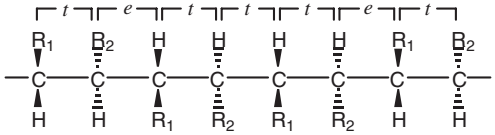
Figure 3 illustrates ^{1}H NMR spectra of three types of stereoregular PMCs so far reported, *disyndiotactic*, *threodiisotactic*, and *diheterotactic* PMCs, together with that of *atactic*-like one. The chemical shifts of the β-methyl signals of the *diheterotactic* PMC (*ettt*; 0.93 ppm, ***t****tet*; 1.04 ppm) are different from that of the minor β-methyl signal (1.12 ppm) (see Figure 3). Thus the defect in the *disyndiotactic* PMC is not likely the type [B] but the type [A], the latter of which might be generated through the fault not in the mode of double-bond opening but in the direction of monomer addition.

CONCLUSIONS

The present work demonstrates that highly *disyndiotactic* PMC can be obtained by the GTP using 1-methoxy-1-(*tert*-butyldimethylsiloxy)-1-propene (**3**),



Scheme 3. Possible mechanisms of defect formation in the *disyndiotactic* sequence of PMC. Capital letters "*E*" and "*T*" are used to denote the relative configurations formed through the double-bond opening, while the lower-case letters indicate those formed through monomer addition process.



diheterotactic

$$\left[\begin{array}{l} R_1{:}CH_3,\ R_2{:}COOCH_3 \\ t : threo,\ e : erythro \end{array}\right]$$

Scheme 4. *Diheterotactic* poly(methyl crotonate).

where stereoregularity of PMCs could be controlled most probably through the steric demand of the bulky R_3Si- group of the initiator which transfers in every propagation step to stay at the ketene silyl acetal terminal, as the original GTP concept[1] anticipates, so as to exert influence on the stereochemical process of the propagation reaction. Higher stereoregularity of the polymer also facilitates the stereochemical assignment of the minor configulational component in the polymer to be the sequence ---*etetee*etet---, which in turn reveals the stereochemical fault during the propagation. In conclusion, high level of stereocontrol is now realized by the GTP process with rational design of the transferring group of the initiator.

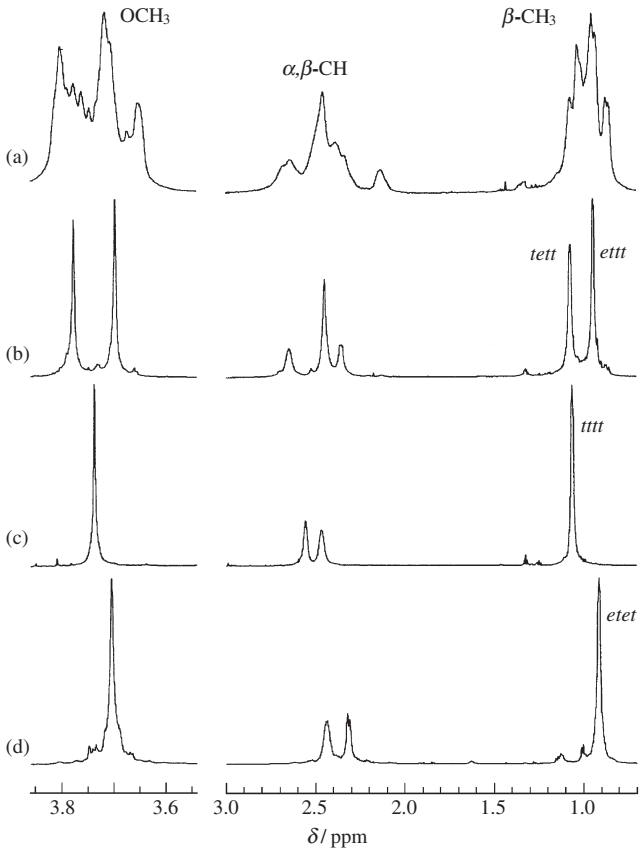


Figure 3. ^{1}H NMR spectra of *atactic* (a), *diheterotactic* (b), *threodiisotactic* (c), and *disyndiotactic* PMCs ($(CF_3)_2CDOD/C_6D_6$ (95/5 v/v), 55 °C, 750 MHz).

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