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Structurally Controlled Polymers with Ultimate Precision – Synthesis, Characterization and Properties

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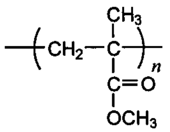
SUMMARY: The fusion of polymer synthesis and characterization and their interactive stimulation is inevitable not only for the formation of polymers with highly controlled structures but also for the development of polymer characterization, thereby bringing about the spiral progress of both fields. As a typical example of precise polymer synthesis, the preparation of uniform PMMA with 100% isotacticity is described. Stereospecific living polymerization of 1-phenyldibenzosuberyl methacrylate with methyl α-lithioisobutyrate in tetrahydrofuran at −78°C gave an isotactic polymer with narrow molecular weight distribution. The PMMA derived therefrom was found by 750 MHz ^{1}H NMR spectroscopy to consist of 89% of the PMMA which is 100% isotactic in the whole chain, and 11% of the PMMA which is 100% isotactic in the chain with only one racemo diad at the initiating chain end. The PMMA was fractionated into uniform PMMAs by supercritical fluid chromatography. The isotactic uniform PMMAs, crystallized from methanol solutions, showed the degree of crystallinity close to 100%. Highly syndiotactic PMMA was derived from poly(trimethylsilyl methacrylate) prepared with $t\text{-}C_4H_9Li$/bis(2,6-di-*t*-butylphenoxy)methylaluminum in toluene at −95℃. Stereocomplex formation of isotactic and syndiotactic uniform PMMAs were studied by on-line GPC/NMR measurements at 750 MHz and −15°C in acetone/acetone-d_6. Stereocontrol of ditactic polymers of crotonates (structural isomers of methacrylates) has been achieved for several polymerization systems, *i.e.*, *threodiisotactic, disyndiotactic*, and *diheterotactic* polymerizations, which demonstrates another state-of-the-art structural control at ultimately high level.

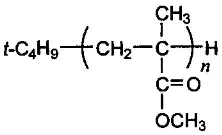
Introduction

Synthetic polymers usually consist of a mixture of macromolecules with different molecular weights and their structures are often shown, for example in the case of poly(methyl methacrylate) (PMMA), as equation 1, where the end groups are not indicated; the structures of end groups are not identified or neglected.



$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\underset{\displaystyle OCH_3}{\displaystyle C{=}O}}{C}} \right)_{\!n}\!- \qquad (1)$$

When the polymer is prepared by living polymerization, the structures of end groups are clearly known. Polymerization of methyl methacrylate (MMA) by $t\text{-}C_4H_9MgBr$ in toluene at −78°C proceeds in a living manner and the resulting polymer has the structure as depicted in equation 2, in which the structures of



$$t\text{-}C_4H_9\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\underset{\displaystyle OCH_3}{\displaystyle C{=}O}}{C}} \right)_{\!n}\!H \qquad (2)$$

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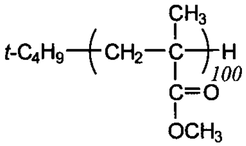
the end groups are definitely shown1). Generally, the polymer prepared by living polymerization has a definite chemical structure and a narrow molecular weight distribution (MWD), that is, the polymer is still a homologous mixture of macromolecules with a definite chemical structure.

Thus, synthetic polymers are nonuniform and not pure substances from the viewpoints of the chemistry of low molecular weight compounds, and the properties of a polymer are always observed as average values. When synthetic polymers are used as raw materials for plastics, elastomers or synthetic fibers, the existence of molecular weight distribution is not critically a deficiency. If the polymers without MWD (uniform polymers), are available, however, fundamental understanding of the structures and properties of polymers could be greatly advanced. The preparation of synthetic polymers uniform with respect to molecular weight, chemical structure and hopefully stereoregularity is an important and challenging subject in the field of polymer science.

Recognizing the limitation of living polymerization that gives polymers with narrow MWD but never the uniform polymers, we have been concerned with the uniformity of synthetic polymers and devoted ourselves in developing the isolation of uniform polymers by supercritical fluid chromatography (SFC) 2-9). By using the SFC separation technique, we have isolated isotactic uniform PMMAs with the degree of polymerization (*DP*) up to100 from the polymer shown in equation 2. The structure of the 100mer of MMA can be written as in equation 3 and its molecular formula as in equation 4.



$$t\text{-}C_4H_9\text{-}\left(CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}\right)_{100}\text{-}H \quad (3)$$

$$C_{504}H_{810}O_{200} \quad (4)$$

(MW= 10069.9)

The 100mer of MMA (equation 3 or 4) is a completely pure substance whose purity is level with those of low molecular weight compounds. The polymerization of MMA with $t\text{-}C_4H_9MgBr$ in toluene gives isotactic polymers whose isotacticities are 96~97%. This means that the above-mentioned 100mer is not stereochemically pure. PMMA with 100% isotacticity was derived from the 100% isotactic poly(1-phenyldibenzosuberyl methacrylate) prepared with methyl α-lithioisobutyrate in tetrahydrofuran (THF) according to Okamoto's method10) and the stereochemically pure uniform PMMAs were isolated from the derived PMMA by SFC separation7) as mentioned in the following section.

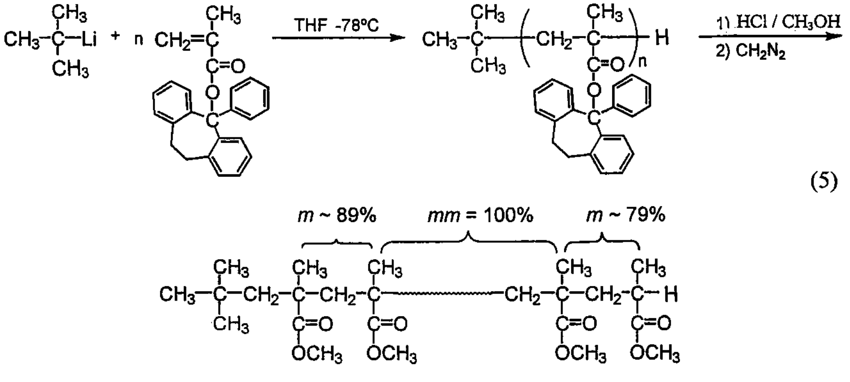
It is important to evaluate what “100% isotactic” means, in other word, what the reliability of "100% isotactic" is or what a maximum amount of irregular structure in “100% isotactic” PMMA is. This depends on the precision and accuracy of characterization technique. Quantitative determination of tacticity with high accuracy and precision can be done only by NMR spectroscopy. Tacticity determination for the “100% isotactic” PMMA was carried out by

750MHz ^{1}H NMR. From the detailed analysis by 750MHz ^{1}H NMR spectroscopy, the tacticity of the 100% isotactic PMMA was estimated to be more than 99.96 % in triad. Thus, precise synthesis of polymers needs the characterization with high precision and accuracy; the latter requires polymer samples with precisely controlled structures. In other words, the fusion of polymer synthesis and characterization and their interactive stimulation is inevitable not only for the formation of polymers with highly controlled structures but also for the development of polymer characterization, thereby bringing about the spiral progress of both fields. Precise control of polymer structure by precise synthesis needs more precise characterization technique and this raises the level of characterization technique. The characterization technique with much higher level induces much more precise method of synthesis. This is the spiral progress of synthesis and characterization.

In this paper three typical examples of our polymer syntheses with ultimate precision are described.

Preparation and properties of 100% isotactic uniform PMMAs

As mentioned above, the isotactic living polymerization of MMA by *t*-C_4H_9MgBr gives highly isotactic PMMA but never 100% isotactic polymer, that is, the isotactic PMMA is not completely pure in stereoregularity$^{1)}$. The PMMA with 100% isotacticity can be derived from the poly(1-phenyldibenzosuberyl methacrylate) prepared by *t*-C_4H_9Li at −78°C in THF$^{11)}$ as shown in equation 5.



(5)

The 750MHz ^{1}H NMR spectrum of the derived isotactic PMMA is shown in Figure 1 together with that of the PMMA (96% isotactic in triads) prepared with *t*-C_4H_9MgBr in toluene at −78°C. If the isotactic polymer chains contain heterotactic and/or syndiotactic triads besides isotactic one, small broad peaks would be observed around 1.19 and 1.08 ppm. Comparison of the spectra of the two PMMAs clearly indicates that the derived PMMA with 100% isotacticity contains almost no heterotactic and syndiotactic triads. In the spectrum of the PMMA with

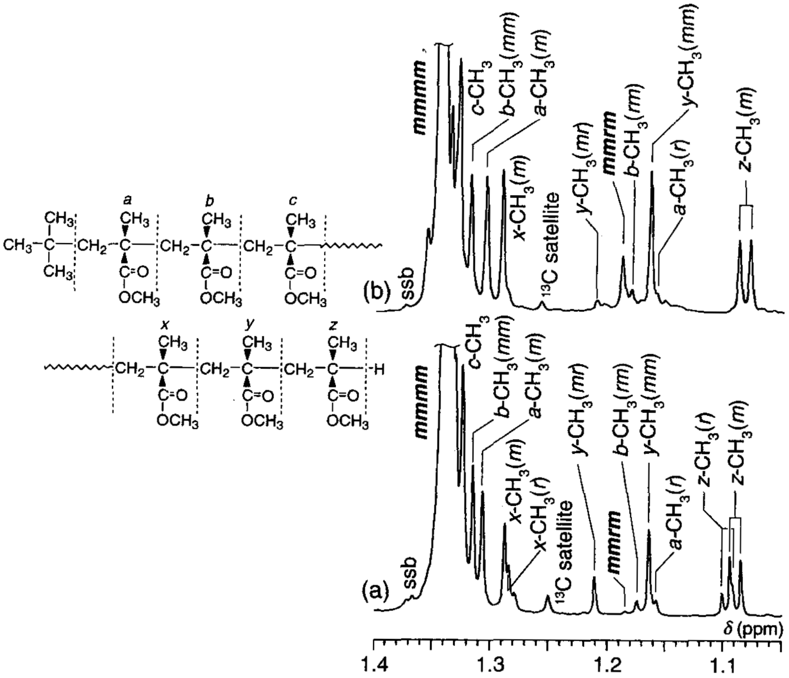
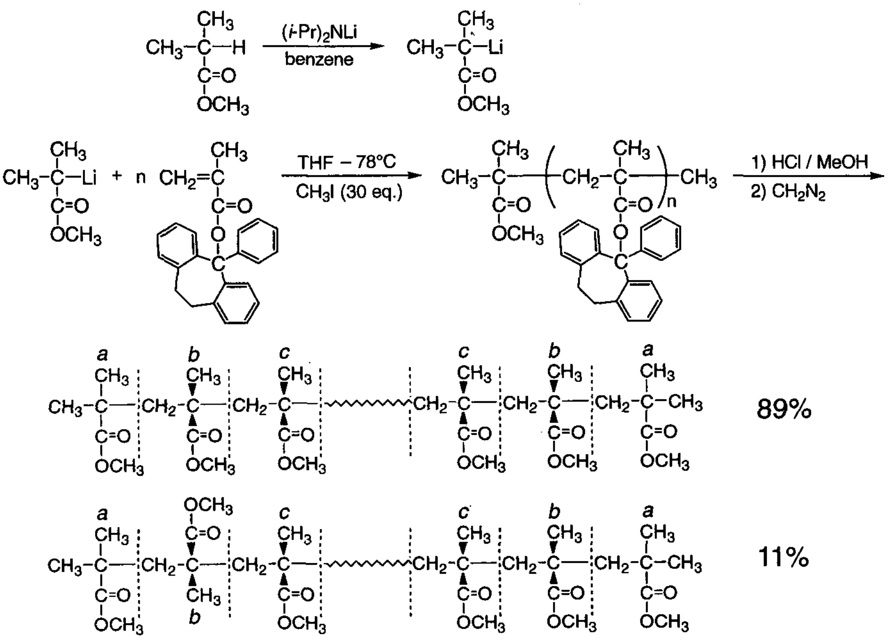


Figure 1 α-Methyl resonances in 750MHz ^{1}H NMR spectra of (a) isotactic PMMA derived from poly(1-pheyldibenzosuberyl methacrylate) prepared with by t-C_4H_9Li in THF at -78℃ and (b) PMMA prepared with t-C_4H_9MgBr in toluene at -78℃ (nitrobenzene-d_5, 110℃)

96% isotacticity (Figure 1b), the heterotactic signal (*mmrm*) is evidently observed at 1.185 ppm. The 100% isotactic PMMA shows a very small signal at the same chemical shift (Figure 1a), the intensity of which is 7.8% of the ^{13}C satellite signal (1.25 ppm) of the strong isotactic signal. This peak with very small intensity can be assigned to the heterotactic sequence. Then the isotacticity in the main chain could be estimated to be 99.96%, since the intensity of the ^{13}C satellite signal is 0.555% of the main signal.

Most of the small but sharp peaks in the range from 1.06 to 1.34 ppm are assigned to the protons of the α-methyl groups at both chain ends (Figure 1). The assignments were made with the aid of ^{1}H COSY$^{12)}$. There are observed the signals due to the α-methyl groups at the initiating and terminating chain ends in meso and racemo placements, as indicated in Figure 1. The spectra clearly show that the tacticities at both ends are not 100% isotactic; small but detectable amounts of racemo diads exist at both ends even in the case of the PMMA derived from poly(1-phenyldibenzosuberyl methacrylate). The isotacticity at the terminating chain end depends strongly on the terminating reagents but the attempts to enhance it to 100% was unsuccessful$^{13)}$. When the polymerization reaction with methyl α-lithioisobutyrate in THF at −78°C was terminated with CH_3I to introduce methyl group at the chain end, the chain-end carbon becomes nonasymmetric (non-chiral) and the ultimate diad is completely isotactic.



(6)

Termination reaction with CH3I also results in the same structures at both chain ends, leading to the enhanced precision of the quantitative determination of the tacticity defects. Now, it is clear that 100% isotactic poly(1-phenyldibenzosuberyl methacrylate) was prepared by the procedure and 100% isotactic PMMA was derived therefrom. The polymer consists of 89% of the PMMA which is 100% isotactic in the whole chain, and 11% of the PMMA which is 100% isotactic in the chain with only one racemo diad at the initiating chain end. The evidence for 100% isotacticity of the PMMA thus obtained is shown in Figure 2[11].

Uniform PMMAs with 100% isotacticity were obtained by SFC fractionation of the completely isotactic PMMA, and their crystallization behaviors were compared with those of uniform isotactic PMMAs with the corresponding *DP*s but with a small amount of in-chain

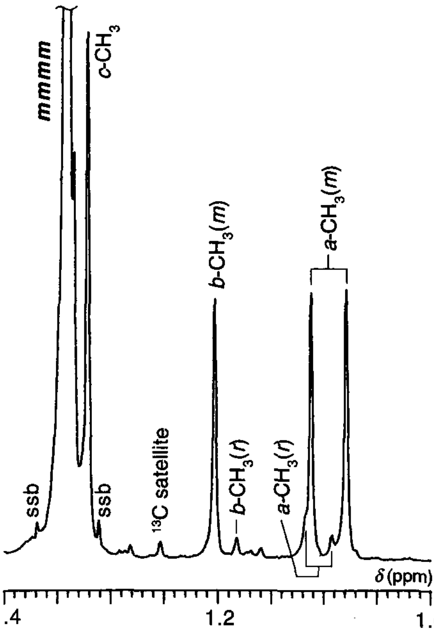


Figure 2 750MHz ^{1}H NMR spectrum of the PMMA derived from the poly(1-phenyldibenzosuberyl methacrylate) prepared with methyl α-lithioisobutyrate in THF at −78°C (nitrobenzene-d_5, 110°C, 750MHz) stereochemical defects7). Figure 3 shows melting endotherms of 41mers and 44mers of the two kinds of uniform isotactic PMMAs crystallized from methanol by solvent evaporation. In each *DP*, the uniform PMMA with 100% isotacticity had higher melting point (*T*m) and larger heat of fusion per repeating unit (*ΔH*), clearly indicating that the crystallinity and *T*m of the uniform isotactic PMMA was increased significantly by the enhancement in in-chain tacticity from 96.1 to 100%. Kusy14) reported that *ΔH* value for completely isotactic PMMA with infinite chain length is expected to be 1.20±0.08 kcal/mol. The value indicates that the crystallinities of the completely isotactic uniform PMMAs described in Figure 3 are, at least, almost 90%.

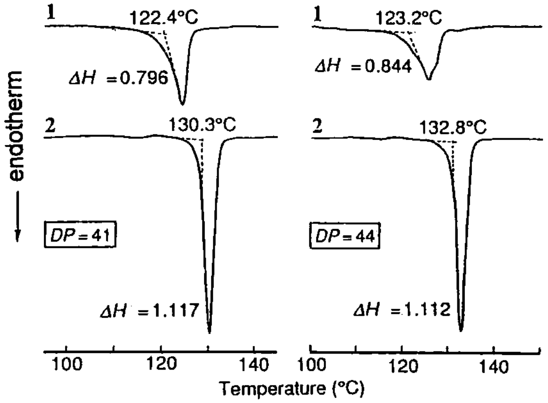


Figure 3 Melting endotherms of uniform 41mers and 44mers of highly isotactic PMMA 1 (*mm*=96.1%) and 100% isotactic PMMA 2 (heating rate; 5℃/min)
ΔH values are given in kcal/mol.

Studies on the stereocomplex formation between isotactic and syndiotactic PMMAs using highly stereoregular uniform PMMAs

It is well known that mixing of solutions of isotactic and syndiotactic PMMAs in a certain solvent such as THF or acetone leads to the formation of stereocomplex. However, the process of the complex formation is still unclear and the studies using polymers with MWD can not give unambiguous results because of the difficulty of differentiating the associated and unassociated species.

Using uniform isotactic and syndiotactic PMMAs, we could observe stereocomplex formation process precisely using conventional GPC by appreciating extreme narrowness of the GPC peaks of the uniform PMMAs with unambiguously defined molecular weight 4,15). GPC measurements of a THF solution of a 1:1 mixture of the isotactic 50mer and syndiotactic 50mer stored at −15℃ for 32hr showed a small peak (7.8 % to the whole peak) due to the stereocomplex besides the large peaks due to the original PMMAs; the elution volume of the small peak was close to that of the 100mer. The initial stage of the stereocomplex formation includes the association of a single molecule of isotactic PMMA and a single molecule of syndiotactic PMMA4). By similar experiments the minimum length of the isotactic and syndiotactic sequences for the complex formation was determined as 40mer~42mer8,16). Uniform stereoblock PMMA comprising isotactic PMMA (*DP* = 46) and syndiotactic PMMA (*DP* = 46) blocks was found by GPC to form intra- and intermolecularly associated stereocomplexes in acetone[17]. In this paper the results of the studies in acetone using the uniform PMMAs with higher tacticities will be described; acetone is a stronger complexing solvent than THF.

The 100% isotactic uniform PMMAs mentioned above are used as isotactic species. Highly syndiotactic PMMAs were derived from the highly syndiotactic poly(trimethylsilyl methacrylate) prepared with *t*-C_4H_9Li/methylaluminum 2,6-di-*t*-butylphenoxide in toluene at −78°C and the syndiotacticities are about 98% in triad.

A 1:1 mixture of 47mers of the isotactic and syndiotactic uniform PMMAs in acetone was allowed to stand at −15°C for 24 h and subjected to GPC at −15°C (Fig. 4). Besides the elution peak due to non-complexed 47mers, a peak due to stereocomplex was observed at a high molecular weight region in the chromatogram. The stereocomplex peak had a relative intensity of 66%, and showed an apparent *M*n of 6.37×10^3 (*M*w/*M*n = 1.02). The fact that the *M*n of the stereocomplex formed is less than twice of the original species may be due to the conformation or molecular shape of the complex. When a similar experiment was carried out for a blend of 47mers of isotactic (*mm* = 95.9%) and syndiotactic (*rr*=92.8%) PMMAs with lower tacticities, the intensity of stereocomplex peak decreased to 39.5%. The intensity and apparent *M*n of stereocomplex decreased with decreasing molecular weight of uniform PMMA components. The stereocomplex peak was hardly observed in the chromatogram of a 1:1 blend of isotactic and syndiotactic 37mers with higher tacticities.

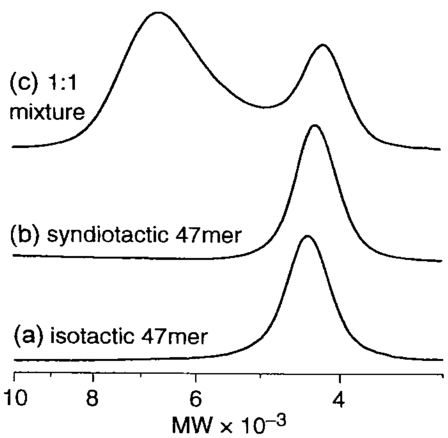


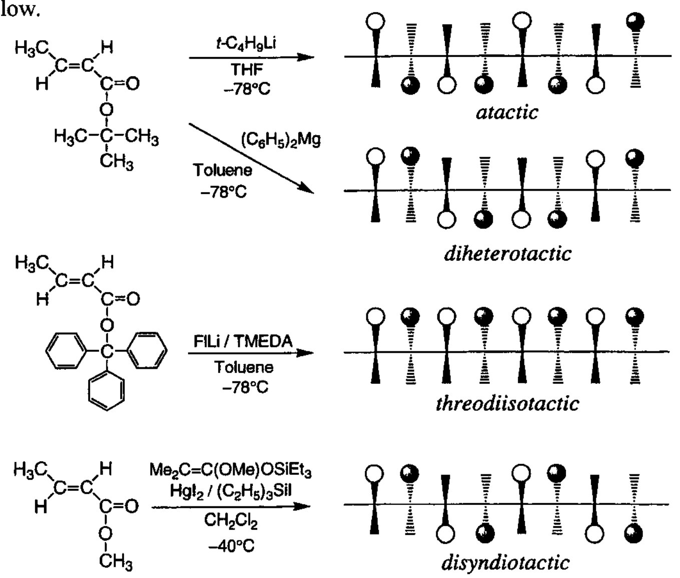
Figure 4 GPC curves of the isotactic 47mer (a) and syndiotactic 47mer (b) of MMA and their 1:1 mixture (c)

The 1:1 blend of isotactic and syndiotactic uniform PMMAs (46mers) was subjected to the on-line GPC/NMR measurements at 750MHz and −15°C in acetone/acetone-d_6. The measurement was made 24 h after mixing of the solutions. The ^{1}H NMR spectrum of the fraction from the GPC peak with larger elution time showed that the peak was due to the mixture of isotactic 46mer and a small amount of syndiotactic one. The NMR spectrum from the smaller elution time showed broad resonances due to the complex formation[18].

The blends of syndiotactic and isotactic 46mers at several ratios (*st*-/*it*- ratios of 0.5, 1.0 and 2.0) were also analyzed by on-line GPC/NMR at −15°C. Only the NMR probe was kept at 45°C so as to observe the NMR resonances with high precision. The composition of the blend (*st*-/*it*- ratio) was determined as a function of elution time by monitoring OCH_3 proton resonances in syndiotactic and isotactic triads. The non-complexed fraction was found to be a mixture of syndiotactic and isotactic 46mers, the *st-/it*-ratios increased with increasing feed ratio of syndiotactic and isotactic polymers. The *st-/it*-ratios in the stereocomplex parts increased between 1.5 and 2.0 with increasing feed ratio of syndiotactic and isotactic polymers. This indicates that the stereocomplex formed in acetone is a mixture of 1:1 and 2:1 (*st-* : *it-*) complexes with different hydrodynamic volumes. It should be noted that a 2:1 complex forms even in the case of 1:2 feed ratio of syndiotactic and isotactic 46mers[15,18].

Preparation of highly ditactic polycrotonates

Stereospecific polymerization of α,β-disubstituted ethylenes has attracted considerable interest because stereostructures of the resulting polymers give us the detailed information about the mechanism of stereoregulation in the polymerizations. We have successfully studied the isotactic[1], syndiotactic[19] and heterotactic[20] living polymerizations of methacrylates during these 10 years. This led us to examine the stereospecific polymerization of crotonates. Pure *cis-* or *trans*-α,β-disubstituted ethylene can give three types of stereoregular polymers; *erythrodiisotactic, threodiisotactic* and *disyndiotactic* polymers. Recently we have succeeded in preparing *threodiisotactic*[21], *disyndiotactic*[22,23] and *diheterotactic*[24] polymers from several crotonates as shown below.



(7)

(8)

(9)

t-Butyl crotonate gave an atactic polymer with *t*-C_4H_9Li in THF at -78°C but a diheterotactic polymer with $(C_6H_5)_2Mg$ in toluene at -78°C. Diheterotactic polymer is a new type of ditactic polymer, which has not been obtained so far. Triphenylmethyl crotonate afforded a threodiisotactic polymer with fluorenyllithium (FlLi) in toluene at -78°C in the presence of tetramethylethylenediamine (TMEDA). Group transfer polymerization of methyl crotonate gave a disyndiotactic polymer when a ketene silyl acetal, 1-methoxy-1-(triethylsiloxy)-2-methyl-1-propene, HgI_2, and $(C_2H_5)_3SiI$ were used as an initiator, a catalyst and a cocatalyst, respectively. The polymers of *t*-butyl and triphenylmethyl crotonates were easily converted into the poly(methyl crotonate)s with the corresponding stereoregularities by transesterification. 750 MHz ^1H NMR spectra of the derived poly(methyl crotonate)s are shown in Figure 5. Comparison of the spectra of the three ditactic poly(methyl crotonate)s with that of the atactic one clearly indicates that the ditactic polymers, particularly the diheterotactic and threodiisotactic ones, are very highly stereoregular.

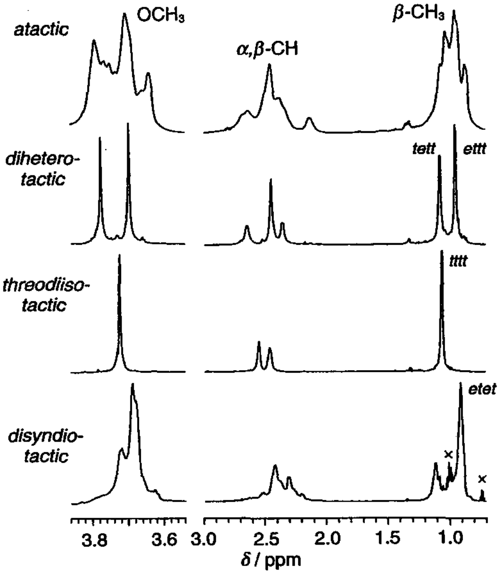


Figure 5 750MHz ^1H NMR spectra of poly(methyl crotonate)s with various stereostructures [$(CF_3)_2CHOH/C_6D_6$ (95/5), 55℃]

Tacticity assignment was made through the X-ray crystallographic analyses of the derived oligo(methyl crotonate)s since it was difficult only by NMR spectroscopy. For example, the methanol-soluble oligomer from the polymerization of *t*-butyl crotonate with FlLi in toluene in the presence of TMEDA was converted to the oligo(methyl crotonate), which was fractionated by GPC into individual homologues from dimer to pentamer. The dimer, trimer and tetramer contained several diastereomers. The pentamer consisted essentially of a single diastereomer (> 99%) although 256 (=2^8) diastereomers are theoretically possible. X-ray analysis of the single crystal of the pentamer indicated that the configurational sequence of the pentamer backbone was purely threodiisotactic. The results suggest that the propagation reaction over the tetramer anion step is threodiisotactic-specific. The tacticity assignments for the other two ditactic polymers were carried out similarly.

Stereospecific polymerization of crotonates requires a higher order of stereoregulation than that for methacrylate polymerization since polycrotonate chains have two types of asymmetric carbons in the constitutional repeating units. Particularly, in the diheterotactic polymerization of *t*-butyl crotonate, stereoregulation at the pentad level is required; the configurational repeating unit at the pentad level is *ettt* (*e*: erythro, *t*: threo). So the highly ditactic polymerizations of crotonates mentioned here is one of the typical examples of precisely controlled polymer syntheses.

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