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^{13}C NMR Analysis of Uniform Heterotactic Oligo(allyl methacrylate) Aiming at Understanding Even–Odd Alternation in Distribution of Degree of Polymerization

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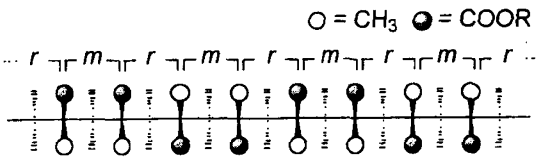
ABSTRACT : The heterotactic oligo(allyl methacrylate)s prepared with *t*-butyllithium / bis(2,6-di-*t*-butylphenoxy)-methylaluminum in toluene at −95℃ exhibit even–odd alternation in distribution of degree of polymerization (DP) except for 8 mer; oligomers with odd-number DP preferentially formed over those with even-number DP. Uniform oligomers with DPs from 5 to 11 were isolated by fractionating the oligomer with the aid of supercritical fluid chromatography (SFC), and their stereochemical structures were investigated by ^{13}C NMR spectroscopy. The NMR analysis for initiating chain-ends of the uniform oligomers revealed even–odd alternation in distribution of stereoregularity near the initiating chain-end. On the other hand, terminating chain-end analysis showed that the living anions predominantly stayed in *r*-ended anion state regardless of the DPs of living anions. The fraction of the odd–number DP oligomers (55%), calculated from the peak intensities in the SFC trace, was found to be much lower than that estimated from chain-end analysis of the original unfractionated oligomer on the assumption that propagation reaction proceeded in a completely heterotactic manner (76%). Structural analysis in the main chain of the each uniform oligomer demonstrated that even–number DP oligomers contained stereochemical defects such as *mm* sequence, while odd–number DP oligomers consist of almost perfect heterotactic sequence. These results indicate that high-level stereoregulation in the propagation process is also an important factor for the observation of evident even–odd alternation in DP distribution.

KEY WORDS Heterotactic Polymer / Oligomer / Stereospecific Living Polymerization / Supercritical Fluid Chromatography / Uniform Polymer / Polymethacrylates / End Group /

Stereospecific polymerization as well as living polymerization is of primary importance in structure control of polymer molecules *via* chain polymerization mechanism. Statistical analysis of stereostructural distribution in the main chain of obtained polymers with some analytical methods such as a nuclear magnetic resonance (NMR) method has been widely used for studies of stereospecific polymerization of vinyl monomers,[1–6] which has provided us with a way around difficulty of direct observation of active species itself with few exceptions.[7]

Besides the analysis of polymers, structural analysis of individual oligomeric species (uniform oligomers) has also brought us a lot of valuable information on polymerization reactions including initiation, propagation, and termination reactions.[8–13] Separation of oligomeric products into uniform oligomers with respect to degree of polymerization (DP) and into individual stereoisomers having the same molecular weights has been performed by chromatographic techniques such as size exclusion chromatography (SEC) and high performance liquid chromatography (HPLC). Recently, we have shown that supercritical fluid chromatography (SFC) is particularly effective for isolating uniform oligomers with higher DP.[14]

We have reported NMR analysis of heterotactic poly(ethyl methacrylate), prepared with *t*-butyllithium (*t*-BuLi)/bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$], with respect not only to main-chain stereosequence but also to that of the chain ends.[15] Heterotactic polymer is one kind of stereoregular polymers composed of an alternating sequence of meso (*m*) and racemo (*r*) diads, and limited examples have been reported.[16–24]



Heterotactic polymer

A combination of *t*-BuLi and MeAl(ODBP)$_2$ exhibits highly stereoregulating power in the polymerization of primary and secondary alkyl methacrylates in toluene at low temperatures, affording heterotactic polymers with narrow molecular weight distributions.[20,21] In particular, heterotacticity of poly(allyl methacrylate) [poly(AlMA)] obtained at −95℃ reaches to 95.8%.[24] Recently we reported unusual DP distribution observed for heterotactic oligo(AlMA) with the aid of SFC.[25] That is, odd–number DP oligomers preferentially formed over even–number DP oligomers except for 8 mer. It has been reported that living polymerization of lactide, a cyclic dimer of lactic acid, with *N,N'*-bis(salicylidene)ethylenediiminoaluminum methoxide gives preferentially even–number DP oligomers with a small amount of odd–number DP homologues as expected from the structure of the monomer.[26] However, there have been few reports on such a phenomenon for vinyl polymers. The sole exception so far reported is the polymerization of *t*-butyl croto-

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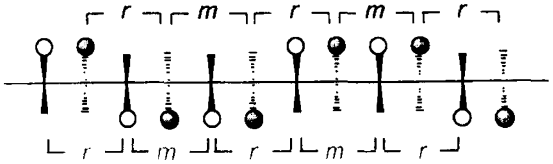
nate with diphenylmagnesium in toluene at −78℃ giving diheterotactic polymers.[27]



Diheterotactic polymer

In the present work we studied the detailed structures of a series of individual uniform oligo(AlMA)s separated by SFC whose DPs range from 5 to 11, and elucidate the mechanism of even–odd alternation in DP distribution in relation to heterotactic-specific polymerization.

EXPERIMENTAL

Materials

AlMA was purified by fractional distillation under reduced nitrogen pressure, dried over calcium dihydride and vacuum-distilled just before use. Toluene and heptane were purified in the usual manners, mixed with a small amount of *n*-butyllithium, and distilled under high vacuum. 2,6-Di-*t*-butylphenol, obtained commercially, was fractionally distilled, dried over Molecular Sieves (MS) 4 A, and used as a heptane solution. *t*-BuLi in pentane (Aldrich Co. Ltd.) was used as a heptane solution by replacing the solvent under high vacuum. The concentration was determined by titration with butan-2-ol and with *o*-phenanthroline as an indicator.[28] Trimethylaluminum in toluene (Tosoh Akzo Co.) was used for the synthesis of $MeAl(ODBP)_2$ without further purification.

Preparation of $MeAl(ODBP)_2$[29]

A solution of 2,6-di-*t*-butylphenol in heptane (2 equiv.) was added slowly to a toluene solution of trimethylaluminum (1 equiv.) at 0℃. The resulting mixture was stirred at room temperature for 20 h. The solvent was removed under vacuum, and a yellowish solid obtained was recrystallized three times by dissolving it in hot heptane and cooling gradually to −30℃. After most of the heptane was removed by a syringe and the residual heptane was evaporated under vacuum to dryness, the solid residue was dissolved in toluene and used for the polymerization reactions.

Oligomerization

The oligomerization reaction was carried out in a glass ampoule filled with dried nitrogen passed through MS 4 A cooled at −78℃. A heptane solution of *t*-BuLi was added to $MeAl(ODBP)_2$ in toluene at −95℃. The oligomerization reaction was initiated by adding AlMA slowly to this mixture at −95℃. The reaction was terminated by adding methanol containing HCl at −95℃. The reaction mixture was concentrated to dryness under reduced pressure, and the residue was dissolved in benzene. Insoluble materials were removed by centrifugation, and the oligomeric product was recovered from the solution by evaporating the benzene and dried under vacuum.

Table I. SFC conditions for analysis and/or isolation of heterotactic oligomers

	Oven temp.	Eluent	
		CO_2	CH_3OH
A	90→70℃ for 20 min	9.0 mL min^{-1}	1.8 mL min^{-1}
B	90→70℃ for 20 min	9.2→8.7 mL min^{-1} for 20 min	1.6→2.1 mL min^{-1} for 20 min

Measurements

^{1}H NMR, ^{1}H–^{1}H correlation spectroscopy (COSY), and heteronuclear multiple-bond correlation (HMBC) spectra and ^{13}C NMR spectra were measured in benzene-d_6 at 35℃ on a Varian Unity Inova 500 spectrometer operated at 500 MHz for ^{1}H and 125 MHz for ^{13}C NMR measurements. Molecular weight distribution of the oligomers were determined by SEC equipped with two Shodex SEC columns [KF-806 L (8 mm *i.d.* ×300 mm) × 2] using tetrahydrofuran as an eluent at 40℃. The SEC chromatograms were calibrated against standard poly (methyl methacrylate) (PMMA) samples.

SFC

SFC was performed on a JASCO SUPER-200 chromatograph equipped with a Hewlett–Packard 589 column oven. A 10 mm *i.d.* × 250 mm column packed with nonbonded silica gel (Develosil 100-5, Nomura Chemical Co., Ltd., particle size 5 μm) was used. The SFC measurement of the heterotactic oligomer was conducted under the conditions as summarized in Table I. The chromatograms were recorded using a UV detector operated at a wavelength of 220 nm. Uniform oligomers were isolated by repeated SFC fractionation for the oligomer with DP=11.2 under the conditions A (Table I). The purity of each fractionated uniform oligomers was also confirmed by SFC.

RESULTS AND DISCUSSION

Oligomerization of AlMA and Fractionation of Uniform Oligomers

Oligomerizations of AlMA were carried out with *t*-BuLi/$MeAl(ODBP)_2$ (Al/Li=3 mol/mol) in toluene at −95℃ for 4 and 8 h (Table II). Oligomers, whose average DPs were 11.2 and 15.8, were obtained at 22 and 31% yields, respectively. Figure 1 shows their SFC chromatograms measured under the conditions A or B summarized in Table I. The SFC curve (Figure 1a) of the oligomer with DP=11.2 demonstrates evident even–odd alternation in the distribution of DP except for 8 mer, whereas that (Figure 1c) with DP=15.8 shows even–odd alternation only in low DP region. Therefore, fractionation of uniform oligomers (5 mer to 11 mer) was executed for the oligomer with DP=11.2 with the aid of SFC to examine the structural difference in even–number and odd–number DP oligomers. Each fractionated oligomer exhibited a single peak in its SFC chromatogram. As an example, the chromatogram of 9 mer is shown in Figure 1b. The DP of each uniform oligomer was determined from the intensity ratios of the ^{1}H NMR signals due to the side-chain $-OCH_2-$ and that of the terminal *t*-butyl group.

Table II. Oligomerization of AlMA with t-BuLi / MeAl(ODBP)$_2$ (1/3 mol/mol) in toluene at −95℃

AlMA	t-Buli	Toluene	Time	Yield	Tacticity/% [a]			$\overline{M}_n$ [b]	$\overline{M}_w$ [c] / $\overline{M}_n$
mmol	mmol	mL	h	%	*mm*	*mr*	*rr*		
50	1.0	50	4	22	2.7	96.4	0.9	1470	1.14
10	0.2	10	8	31	3.1	95.2	1.7	2390	1.22

[a] Determined by ^{13}C NMR. [b] Determined by ^{1}H NMR. [c] Determined by SEC.

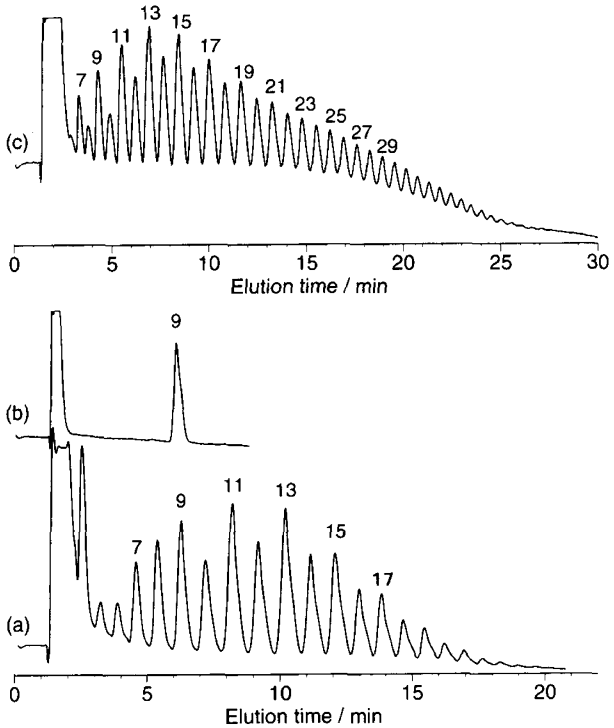
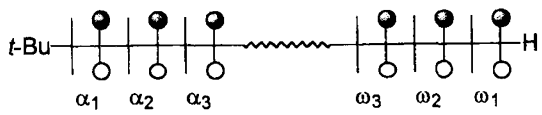


Figure 1. SFC traces of (a) heterotactic oligo(AlMA) (DP=11.2, $\overline{M}_w / \overline{M}_n$=1.14 , *mm* : *mr* : *rr*=2.7 : 96.4 : 0.9), (b) the 9 mer isolated therefrom, measured under the conditions A, and (c) heterotactic oligo(AlMA) (DP=15.8, $\overline{M}_w / \overline{M}_n$=1.22, *mm* : *mr* : *rr*=3.1 : 95.2 : 1.7), measured under the conditions B. The DPs of each peaks in (a) and (b) were determined by ^{1}H NMR spectra of the fractionated uniform oligomers and those in (c) were determined by comparison with SFC chromatogram for the oligomer containing an authentic sample of the uniform 19 mer measured under the same conditions.

^{13}C NMR Analysis of Uniform Heterotactic Oligo(AlMA)s

Figure 2 shows ^{13}C NMR spectra of carbonyl and methylene carbons of the original oligomer and the uniform oligomers (5 mer to 11 mer) fractionated therefrom. The notations (α_1, α_2, ... ω_2, ω_1) of monomeric units are shown below.[30]



All the odd–number DP oligomers showed simpler spectral pattern than the even–number DP oligomers in both carbon signals. This indicates that the odd–number DP oligomers have better controlled stereostructures than those of even–number DP oligomers.

Peak assignments of the 5 mer were made based on two-dimensional NMR spectroscopy including ^{1}H–^{1}H COSY and HMBC. The five kinds of carbonyl carbons in the 5 mer are designated as α_1, α_2, ω_3, ω_2, and ω_1.[31]

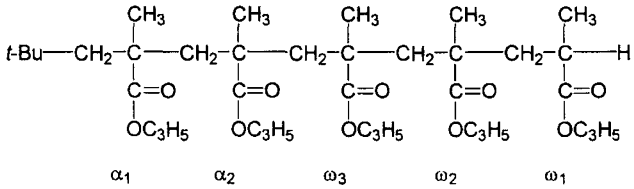


Figure 3 shows the partial HMBC spectrum of the 5 mer, which covers methylene and carbonyl carbon regions and methyl proton region. In the following, chemical shift values given are those for major components. The assignments of methylene carbons in ω_1 and ω_2 units were made by following the network of correlation peaks starting from the doublet at 1.00—1.02 ppm due to the ω-end methyl protons, which were assigned from the correlation peaks with the ω-end methine protons (*ca.* 2.58—2.64 ppm) in the H–H COSY spectrum. As expected from the structure, ω_1-CH$_2$ carbon signal at 46.98 ppm shows correlation peaks both with ω_1- and ω_2-CH_3 proton signals (1.00—1.02 ppm and 1.27 ppm). Similarly, ω_2 methylene carbon signal (49.41 ppm) also shows two correlation peaks with ω_2- and ω_3-CH_3 proton signals (1.27 and 1.45 ppm). The assignments of methylene carbons in α_1 and α_2 units were made similarly, starting from the strong peak at 0.91 ppm due to t-butyl group; t-C$_4H_9$ → α_1-CH_3 (1.40 ppm) → α_1-CH$_2$ (56.56 ppm) and α_2-CH$_2$ (52.93 ppm). α_2-CH$_2$ carbon signal (52.93 ppm) shows another correlation peak with α_2-CH_3 at 1.45 ppm in addition to that with α_1-CH_3. Thus α_2-CH_3 and ω_3-CH_3 proton signals apparently overlap with each other at 1.45 ppm.

Carbonyl carbon resonances except for those due to α_2- and ω_3-C=O carbons were assigned from the correlation peaks with methyl proton signals which were assigned to the individual monomeric units. There remained a difficulty of assigning the signals due to α_2- and ω_3-C=O carbons only by the HMBC spectrum, due to the overlapping of α_2-CH_3 and ω_3-CH_3 proton signals (1.45 ppm). The assignments shown in the figure were made based on the fact that signals due to interior units were observed at 176.37 ppm and increased with increasing DP and the shift of ω_3-C=O carbon is closer to this. An additional evidence is that the α_2-C=O carbon signal at 176.50 ppm was observed in the spectrum of 8 mer, of which methylene carbon spectrum showed the signal due to α_2 unit at the same position as that of 5 mer, while the ω_3-CH$_2$ signal was observed at higher magnetic field than that of 5 mer (*cf.* Figure 2).

As mentioned above, in the carbonyl carbon spectra of 7 mer, 9 mer, 11 mer and the original oligomer, the signals due to in-chain units are observed at 176.37 ppm, whose signal intensity increased as the DP of oligomers increased without any changes in the shape of other signals. This suggests that the in-chain units in the odd–number DP oligomers are in *mr* (heterotactic) sequence

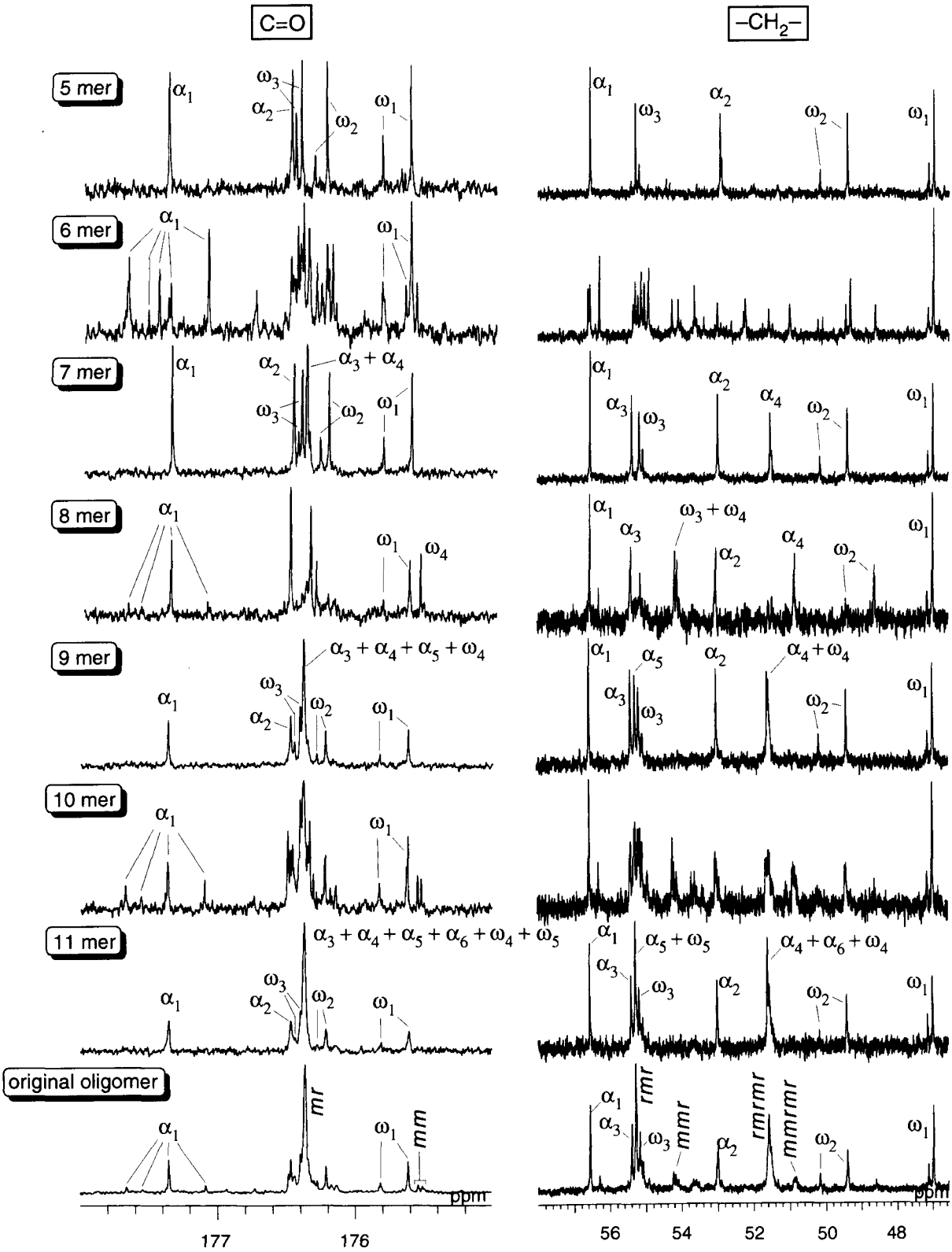


Figure 2. 125 MHz ^{13}C NMR spectra of methylene and carbonyl carbons of 5 mer to 11 mer and the original oligomer, measured in benzene-d_6 at 35℃.

and thus the predominant structures of odd–number DP living anions can be depicted as shown in Figure 4. In sharp contrast, the even–number DP oligomers, 6 mer, 8 mer, and 10 mer, show more complicate peak splittings not only in the in-chain units but also in the terminal units (α_1, ω_1). Among them the signals of 8 mer is rather simple, the structure of which is discussed later.

In the methylene carbon spectrum of the 5 mer, signals due to ω_1, ω_2, and ω_3 units are observed as pairs of major and minor signals as in the case of carbonyl carbon signals, reflecting the terminal diad stereochemistry. In addition, the methylene carbon in α_2 unit also

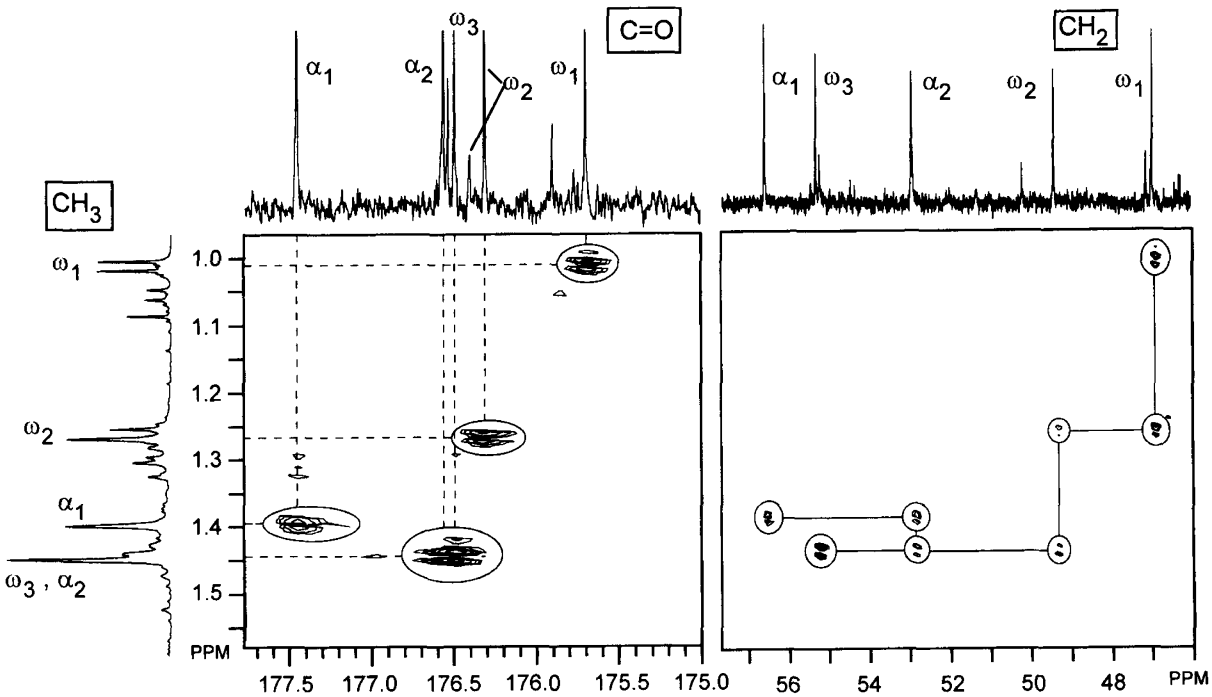


Figure 3. HMBC spectra (methylene and carbonyl carbon and methyl proton region) of the 5 mer.

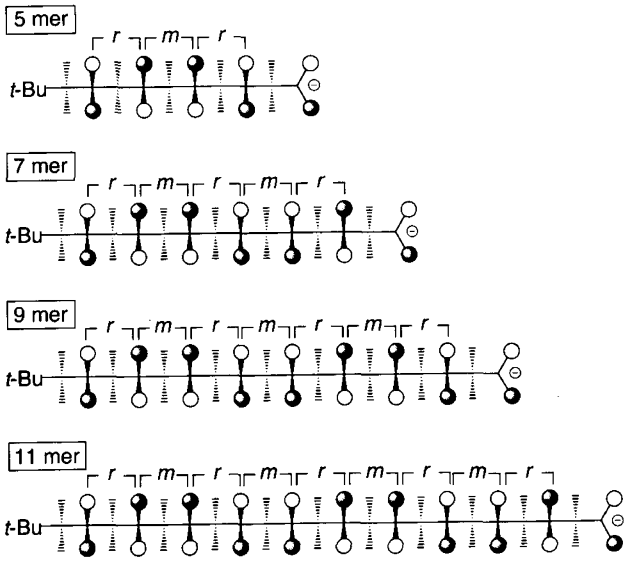


Figure 4. The structures of the predominant isomers of 5, 7, 9, and 11 mers.

shows a slight splitting. Again the series of odd-number DP oligomers (7 mer, 9 mer, and 11 mer) show rather simple spectral changes as their DP increases. In the spectrum of 7 mer, the signals at 51.54 and 55.40 ppm are newly observed in addition to those for α_1, α_2, ω_3, ω_2, and ω_1 units which are observed in the spectrum of 5 mer. This suggests that these additional peaks are assignable to in-chain units (α_3 and α_4 units). In the spectra of 9 mer and 11 mer, signal intensities in these two regions (51.6 and 55.3 ppm) increase, where *mrm* and *rmr* tetrad methylene signals appear in the spectra of the oligomer and polymer. The assignments of the *mrm* and *rmr* signals were made based on the spectral similarity between poly(AlMA) and poly(ethyl methacrylate) [poly(EMA)].[32,33] Since the odd-number DP oligomers have the initial *r* diad followed by *mrm*- sequence (for example, the major isomer of 7 mer is expected to be *rmrmrr*), the results mean that the signal at 51.54 ppm is assignable to α_4 unit in *mrm* sequence and that at 55.40 ppm to α_3 unit in ***rmr*** sequence. This in turn suggests high content of heterotactic sequence in the odd-number DP oligomers. The methylene carbon spectra of even-number DP oligomers except 8 mer show much more complicate splittings, reflecting their lower stereoregularity.

Among the even-number DP oligomers, 8 mer shows rather simple spectra of methylene and carbonyl carbons as compared with those of other even-number DP oligomers, 6 mer and 10 mer. In the carbonyl carbon region, 8 mer shows rather simple signals due to α_1 and ω_1 units whose chemical shifts are close to those for odd-number DP oligomers, but, contrastingly, the resonance in the range from 176.1 to 176.6 ppm are quite different from each other. In particular, the signal at 176.37 ppm, due to in-chain heterotactic sequence, was not observed in the spectrum of 8 mer, indicating the existence of defective in-chain sequence. Instead, 8 mer shows additional signal at 175.56 ppm, the chemical shift of which is close to that of *mm* triad in the oligomer and polymer. These results imply that the signal at 175.56 ppm is that due to the in-chain unit included in *mm* triad. Thus 8 mer has the predominant stereosequence starting with *r* diad, followed by *m* diad, including *mm* triad within the chain, and ending with *-rr* or *-rm* triad, such as *r-m-r-m-m-r-(m/r)*.

Since the terminal diad configuration is determined by the protonation reaction and not the point of discussion here, the structure of 8 mer anion instead of 8 mer itself will be discussed in the following. The possible

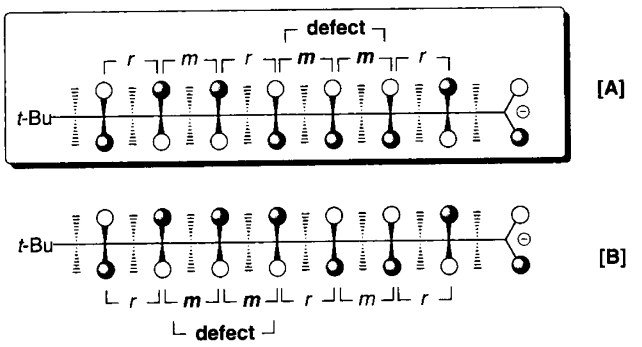


Figure 5. Two possible structures of the predominant isomers of 8 mer.

structures of $r\sim\sim\sim rM^-$ with DP=8 can be expressed by only two ways (Figure 5). The predominant structure of 8 mer anion could be depicted by structure [A] based on the comparison of methylene carbon spectra between 7 mer and 8 mer.

[1] The 8 mer shows α_1-, α_2-, and α_3-CH_2 carbon signals at almost the same chemical shifts as those of 7 mer. Thus 8 mer starts with *rm*- triad.

[2] The chemical shift of α_4-CH_2 carbon signal of 8 mer (50.85 ppm) is different from that of 7 mer (51.53 ppm). The latter (7 mer) is very close to *rmrmr* hexad signal in the spectrum of the original oligomer, and the former (8 mer) to ***mm****rmr* (*rmr****mm***) hexad. The assignments of *rmrmr* and ***mm****rmr* (*rmr****mm***) hexads are based on the spectral similarity of heterotactic poly(AlMA) and heterotactic poly(EMA).[32,33] This implies that 8 mer consists of *mm* sequence as described previously on the analysis of carbonyl carbon spectrum.

[3] Signals due to ω_3- and ω_4-CH_2 carbons of 8 mer are observed at almost the same position, whose chemical shifts are very close to that of ***mm****r* tetrad CH_2 carbon of the original oligomer.

[4] The signal due to ω_2-CH_2 of 8 mer is observed at higher magnetic field than that of 7 mer, the predominant sequence of which is *r-m-r-m-r-(m/r)*, suggesting that the difference in the stereochemical feature between 8 mer and 7 mer exists near the ω-end.

All the results indicate that the stereochemical defect (*mm* sequence) is located near the ω-end instead of α-end. Thus, the structure [A] in Figure 5 depicts the predominant 8 mer anion. The structure [A] indicates that 8 mer predominantly formed through termination reaction of *rmr****mm****rM*$^-$, suggesting the stability of $\sim\sim\sim$ ***mm****rM*$^-$. Furthermore, the peculiarly high population of 8 mer implies that hexamer anion, *rmr****m****M*$^-$, favors *m*-addition more than other even-number DP anions, which results in the formation of *rmr****mm****rM*$^-$.

Mechanism of Even–Odd Alternation in DP Distribution

As previously reported, ^{13}C NMR analysis of heterotactic oligo(AlMA), which exhibited an even–odd alternation in DP distribution, revealed that propagating anions namely start with *r* diad and preferentially stay in $\sim\sim\sim rM^-$ state rather than $\sim\sim\sim mM^-$ state.[25] Suppose that propagation reaction proceeds in a completely heterotactic manner, one should obtain the predominant structures of the living anions exemplified by eq 1 for 11 mer anion. Thus, the predominant anions should have odd-number DPs. This is consistent with the fact that odd-number DP oligomers preferentially formed.

If the propagation reaction proceeds in a completely heterotactic manner, there are two possible ways for the formation of the even-number DP oligomers; one is that an oligomer anion starts with preferred initial *r*-diad and is protonated at the less abundant $\sim\sim\sim mM^-$ state ($r\sim\sim\sim mM^-$) (eq 2), and the other is that an oligomer anion starts with minor *m* diad and is protonated at the preferred $\sim\sim\sim rM^-$ state ($m\sim\sim\sim rM^-$) (eq 3). The structure of even-number DP oligomers obtained in such two ways are exemplified by eqs 2 and 3 for 10 mer. Thus, even–odd alternation in DP distribution may depend either on the extent of stereoregulation in the beginning of polymerization or on the fraction of $\sim\sim\sim rM^-$ anions at the termination. In this regard, the analysis of the stereochemistry near the chain end is important.

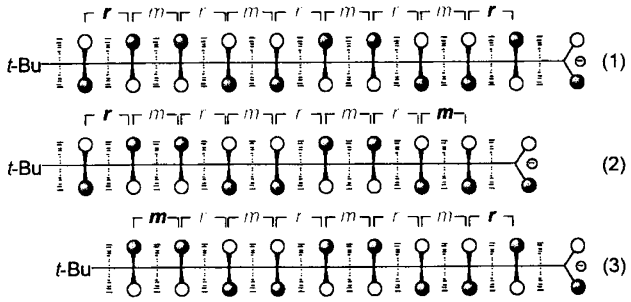


Figure 6 illustrates the ^{13}C NMR resonances due to methyl carbons of *t*-butyl group at the initiating chain-end and those due to methine carbons at the terminating chain-end of 5 mer to 11 mer and the original unfractionated oligomer. Both the signals principally split into four peaks reflecting triad stereosequences near the chain-ends. The assignments were made based on the similarity of the spectra with those for heterotactic poly(EMA) having the same end groups.[15] In Figure 7 are plotted the triad tacticity distribution at the initiating chain-ends of 5 mer to 11 mer and the original oligomer. This evidently indicates that odd-number DP oligomers have better controlled stereostructure near the initiating chain-end than even-number DP oligomers. However, the signal due to *rm*-initial triad is observed with the strongest intensity in all the cases. On the other hand, terminating chain-end analysis showed that the living anions predominantly stay in $\sim\sim\sim rM^-$ anion state regardless of the DP of living anions (Figure 8). These results suggest that the stereoregulation at the beginning of the polymerization is more important cause for the even–odd alternation in DP distribution of the oligomer obtained.

From the distribution of stereostructures near the chain ends, that is, triad fractions at the initiating end and diad fractions at the penultimate diad, the populations of 8 possible stereoisomeric active species were estimated for each oligomer as shown in Table III. Table III also includes the values estimated from the chain-end analysis of the unfractionated (original) oligomer by assuming the completely heterotactic sequence in the inner chain. As far as the in-chain sequence is perfectly

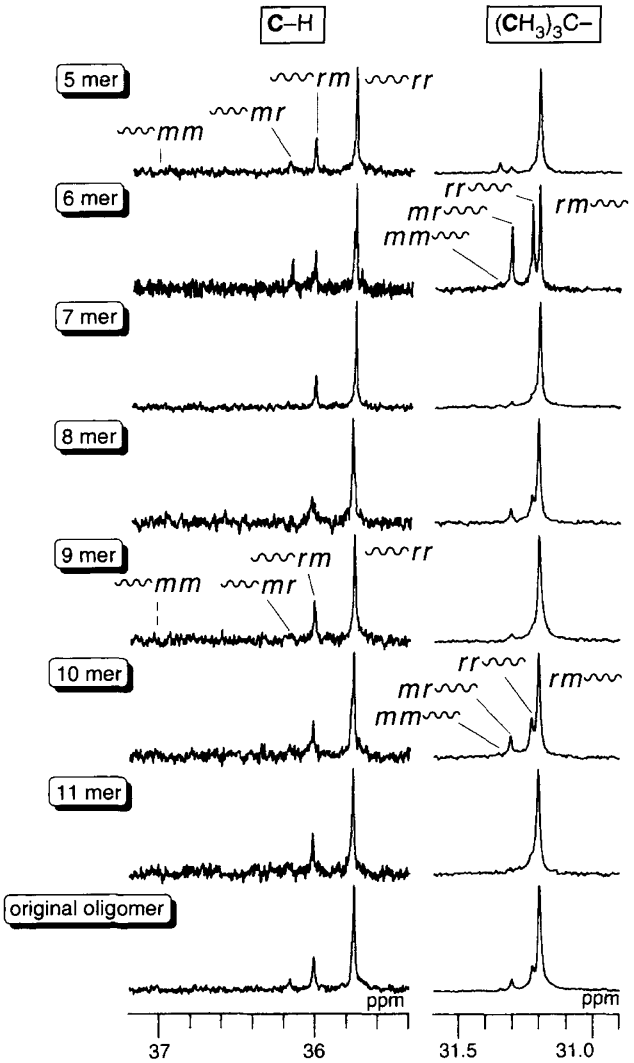


Figure 6. 125 MHz ^{13}C NMR spectra of methyl carbons of *t*-butyl group at the initiating chain-end and methine carbons at the terminating chain-end of 5 mer to 11 mer fractionated by SFC and the original oligomer, measured in benzene-d_6 at 35℃.

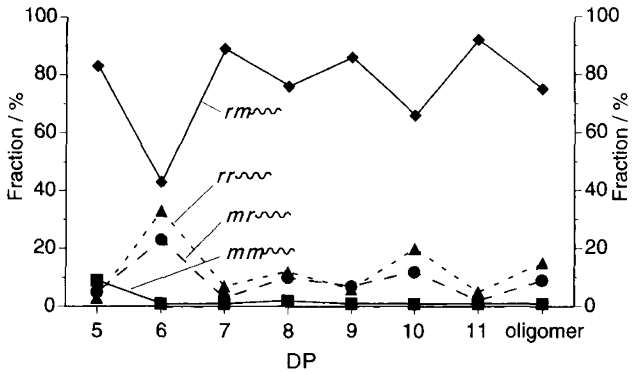


Figure 7. Triad tacticity distribution at the initiating chain-end of 5 mer to 11 mer and the original oligomer.

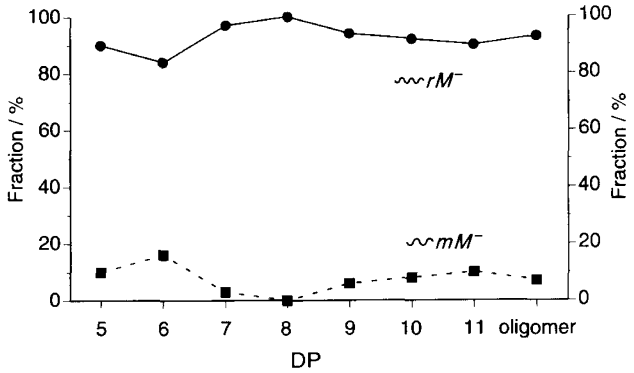


Figure 8. Fractions of $\sim\sim\sim mM^-$ and $\sim\sim\sim rM^-$, which formed 5 mer to 11 mer and the original oligomer ($\sim\sim\sim mM^- = [-mm] + [-mr]$, $\sim\sim\sim rM^- = [-rm] + [-rr]$).

heterotactic, four kinds of active species,

$rm\sim\sim\sim rM^-$, $mm\sim\sim\sim rM^-$, $rr\sim\sim\sim mM^-$, and $mr\sim\sim\sim mM^-$ (*group A*)

should be odd-number DP oligomers, and other four,

$rm\sim\sim\sim mM^-$, $mm\sim\sim\sim mM^-$, $rr\sim\sim\sim rM^-$, and $mr\sim\sim\sim rM^-$ (*group B*)

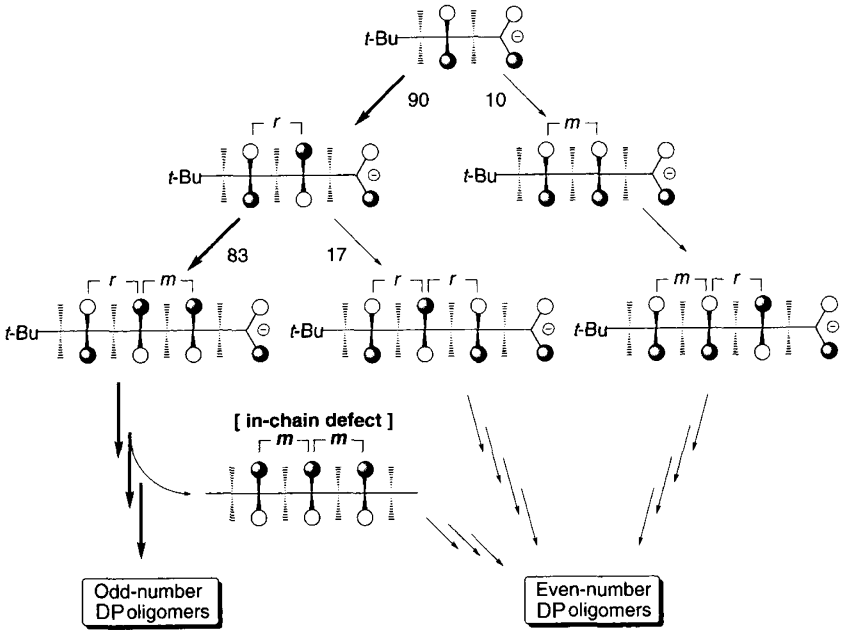
be even-number DP oligomers. The populations of stereoisomers for individual odd-number DP oligomers, 5, 7, 9, and 11 mers, fit well with those estimated for unfractionated odd-number DP oligomer, $rm\sim\sim\sim rM^-$ being the predominant species. This confirms the high stereoregularity of these odd-number DP oligomers. On the contrary, the populations for 6 mer, 8 mer, and 10 mer deviate from the estimated values for even-number DP oligomers from the analysis of the unfractionated oligomer. In particular, $rm\sim\sim\sim rM^-$ is a main fraction in all the even-number DP oligomers, which is not likely an even-number DP oligomer if the in-chain sequence is completely heterotactic.

The ratio of odd-number and even-number DP oligomers to be formed was estimated to be 0.73 : 0.27 from the stereoregularity distribution near the chain ends of the unfractionated oligomer on the assumption that tacticity of the oligomer is perfectly heterotactic (*cf.* Table III). However, the ratio observed in the SFC chromatogram (*cf.* Figure 1a) was 0.55 : 0.45 from the peak intensities from 6 mer to 21 mers. The tacticity of the unfractionated oligomer was determined from carbonyl carbon NMR signals with neglect of the resonances due to α_1 and ω_1 units; $mm : mr : rr = 2.7 : 96.4 : 0.9$ (*cf.* the bottom in Figure 2). The high stereoregularity of the oligomer is seemingly inconsistent with the difference between the observed and expected fractions of odd-number and even-number DP oligomers. The triad value of the defective sequences ($mm + rr$) is 3.6%. If the defect locates randomly within the ensemble of the oligomer molecules with the average DP of 11.2, one would expect 0.4 defect in a chain in average; that is, in a rough estimate, 40% of the oligomer molecules contain one defect and the rest of 60% are completely heterotactic. If such stereochemical defects exist in the heterotactic oligomer anions with the predominant chain-end structure, $rm\sim\sim\sim rM^-$, it should have even-number DP, such as $rmrmmrM^-$ (8 mer). This means that even-number DP oligomers may be derived from $rm\sim\sim\sim rM^-$ anions which contain one defect per chain. Then the simple estimation of the odd/even ratio of 0.73/0.27 should be corrected for the probability of the formation of the stereochemical defects. If the defects exist randomly irrespective of the stereosequence at the initiating chain-end, the fractions of odd-number and even-number DP oligomers are calculated as follows by assuming that 40%

Table III. Population of stereoisomeric active species estimated from stereosequence distribution near the chain ends [a]

	Odd-number oligomer				Even-number oligomer			Unfractionated oligomer [b]	
	5 mer	7 mer	9 mer	11 mer	6 mer	8 mer	10 mer		
Group **A**									
rm~~~*rM*⁻	0.76	0.87	0.82	0.83	0.36	0.74	0.61	(Odd)	0.70 (0.96)
mm~~~*rM*⁻	0.08	0.01	0.01	0.01	0.01	0.02	0.01		0.01 (0.01)
rr~~~*mM*⁻	0.00	0.00	0.00	0.01	0.05	0.00	0.02		0.01 (0.02)
mr~~~*mM*⁻	0.00	0.00	0.01	0.00	0.04	0.00	0.01		0.01 (0.01)
Group **B**									
rm~~~*mM*⁻	0.09	0.03	0.05	0.09	0.07	0.02	0.06	(Even)	0.05 (0.19)
mm~~~*mM*⁻	0.01	0.00	0.00	0.00	0.00	0.00	0.00		0.00 (0.00)
rr~~~*rM*⁻	0.02	0.06	0.05	0.04	0.28	0.13	0.19		0.14 (0.51)
mr~~~*rM*⁻	0.04	0.03	0.06	0.02	0.19	0.09	0.11		0.08 (0.30)

[a] Calculated as the product of fractions of the stereosequences at the initiating chain-end and the propagating chain-end, *e. g.*, *rm*~~~*rM*⁻ (0.76) for 5 mer was calculated from *rm*-(0.84)×~~~*rM*⁻ (0.90). [b] Estimated on the assumption that propagating reaction proceeds in a completely heterotactic manner. Values in parentheses are relative abundance in each of odd- or even-number DP oligomers.



Scheme 1. Mechanism of even-odd alternation in DP distribution of heterotactic oligo(AlMA).

of oligomer molecules in average have one defect.

i) For odd-number DP oligomer;
odd-number DP oligomer without defect having *group A* end group: 0.73×0.60,
odd-number DP oligomer with one defect having *group B* end group: 0.27×0.40,
and thus in total : 0.73×0.60+0.27×0.40=0.44+0.11=0.55.

ii) For even-number DP oligomer;
even-number DP oligomer without defect having *group B* end group: 0.27×0.60,
even-number DP oligomer with one defect having *group A* end group: 0.73×0.40,
and thus in total : 0.27×0.60+0.73×0.40=0.16+0.29=0.45.

The corrected values agree well with the observed value obtained from the SFC analysis (*cf.* Figure 1a). The results mean that existence of a small fraction of the defective sequence evidently deteriorates the clear observation of the even-odd alternation in DP distribution. Therefore, in addition to the high stereoselectivity at the beginning of the polymerization, extremely high stereoregularity in the propagation process is also important factor for the even-odd alternation in DP.

In Scheme 1 is described the simplified flowchart for the formation of odd-number and even-number DP oligomers. This means that even-number DP oligomers form by several different routes; (1) the oligomerization starts with *m*-addition, (2) *r*-addition consecutively occurs after the oligomerization starts with *r*-addition, and (3) one defective sequence such as *mm* forms in the inner chain during the propagation process after the oligomerization starts regularly with *rm*- initial sequence. The omnifarious routes of the formation of even-number DP oligomers result in the complicated splittings in their NMR spectra, *i.e.*, the lower stereoregularity as compared with odd-number DP oligomers.

In conclusion, the heterotactic oligomers, which exhibit even-odd alternation in DP distribution, were fractionated into uniform oligomers with respect to DP by SFC, and the stereostructures of uniform oligomers were investigated by ^{13}C NMR spectroscopy. ^{13}C NMR analy-

sis revealed for the first time that odd– and even–number DP oligomers have different stereochemical structures, the former having better controlled structure from the initiating to the terminating chain-ends than the latter. Among even–number DP oligomers, however, 8 mer also showed exceptionally simple spectral pattern as compared with the others, 6 mer and 10 mer. The predominant structure of 8 mer anion was found to be $rmr\boldsymbol{mm}rM^-$, suggesting the stability of $\sim\sim\sim\boldsymbol{mm}rM^-$. Furthermore, the peculiarity of 8 mer population implies that $rmr\boldsymbol{m}M^-$ favors m-addition more than other even–number DP anions. The chain-end analysis demonstrated that the stereospecificity in the beginning of the polymerization is very important for the even–odd alternation in DP distribution. Furthermore, the in-chain stereochemical analysis indicated that a small amount of the stereochemical defect in the main chain, such as *mm* sequence, drastically affects even–odd alternation in DP distribution. This means that high stereospecificity in the propagation process is inevitable for the clear observation of even–odd alternation in DP distribution, and thus the unusual DP distribution may be a good measure for judgment of high stereoregularity of heterotactic polymers obtained.

REFERENCES

1. C. Wolfsgruber, G. Zannoni, E. Rigamonti, and A. Zambelli, *Makromol. Chem.*, **176**, 2765 (1975).
2. W. Kaminsky, K. Külper, H. H. Brintzinger, and F. R. W. P. Wild, *Angew. Chem. Int. Ed.*, **24**, 507 (1985).
3. J. A. Ewen, *J. Am. Chem. Soc.*, **106**, 6355 (1984).
4. Y. Doi, S. Ueki, and T. Keii, *Macromolecules*, **12**, 814 (1979).
5. H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).
6. B. D. Coleman and T. G Fox, *J. Chem. Phys.*, **38**, 1065 (1963).
7. H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, Y. Kai, and N. Kanehisa, *Macromolecules*, **26**, 7134 (1993).
8. Ch. B. Tsvetanov, A. H. E. Müller, and G. V. Schulz, *Macromolecules*, **18**, 863 (1985).
9. K. Hatada, K. Ute, K. Tanaka, and T. Kitayama, *Polym. J.*, **19**, 1328 (1987).
10. K. Ute, T. Nishimura, and K. Hatada, *Polym. J.*, **21**, 1027 (1989).
11. H. Schlaad and A. H. E. Müller, *Macromol. Rapid Commun.*, **16**, 399 (1995).
12. T. Nakano, Y. Okamoto, and K. Hatada, *Polym. J.*, **27**, 882 (1995).
13. T. Nakano, Y. Okamoto, and K. Hatada, *Polym. J.*, **27**, 892 (1995).
14. K. Hatada, *J. Polym. Sci. Part A. Polym. Chem.*, **37**, 245 (1999), and references therein.
15. T. Kitayama, T. Hirano, and K. Hatada, *Polym. J.*, **28**, 61 (1996).
16. M. Goodman and J. Brandrup, *J. Polym. Sci., A*, **3**, 327 (1965).
17. S. Nozakura, S. Ishihara, Y. Inaba, K. Matsumura, and S. Murahashi, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1053 (1973).
18. K. Hatada, Y. Okamoto, H. Ise, S. Yamaguchi, and H. Yuki, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 731 (1975).
19. K. Hatada, H. Sugino, H. Ise, T. Kitayama, Y. Okamoto, and H. Yuki, *Polym. J.*, **12**, 55 (1980).
20. T. Kitayama, Y. Zhang, and K. Hatada, *Polym. Bull.*, **32**, 439 (1994).
21. T. Kitayama, Y. Zhang, and K. Hatada, *Polym. J.*, **26**, 868 (1994).
22. S. Nakahama, M. Kobayashi, T. Ishizone, A. Hirao, and M. Kobayashi, *Polym. Mater. Sci. Eng.*, **76**, 11 (1997).
23. K. Yamada, T. Nakano, and Y. Okamoto, *Macromolecules*, **31**, 7598 (1998).
24. T. Hirano, H. Yamaguchi, T. Kitayama, and K. Hatada, *Polym. J.*, **30**, 767 (1998).
25. T. Hirano, T. Kitayama, J. Cao, and K. Hatada, *Macromolecules*, **33**, 1926 (2000).
26. K. Ute and K. Hatada, *Preprints of 5th SPSJ International Polymer Conference*, 269 (1994).
27. K. Ute, T. Asada, and K. Hatada, *Macromolecules*, **29**, 1904 (1996).
28. S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 195 (1965).
29. A. P. Shreve, R. Mullhaupt, W. Fultz, J. Calabrese, W. Robbins, and S. D. Ittel, *Organometallics*, **7**, 409 (1988).
30. The initiating end group of the chain (the *t*-Bu group side) and the terminating end (the methine hydrogen side) are designated as α-end and ω-end, respectively.
31. Usually the monomeric unit of the middle of 5 mer are represented as α_3 unit. However, the signal assigned to ω_3 unit in the spectrum of 5 mer appears as the doublet signals due to ω_3 unit in the spectra of odd–number DP oligomers with higher DPs. Thus, the representation of ω_3 unit was used here.
32. T. Kitayama, T. Hirano, Y. Zhang, and K. Hatada, *Macromol. Symp.*, **107**, 297 (1996).
33. T. Kitayama, T. Hirano, and K. Hatada, *Tetrahedron*, **53**, 15263 (1997).