Unusual Distribution of Degree of Polymerization Observed for Heterotactic Oligomer of Allyl Methacrylate

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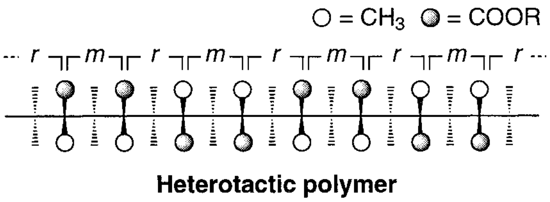
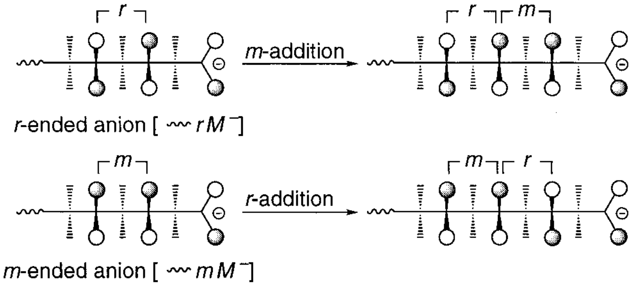
Introduction. Living polymerization is one of the promising ways for precision polymer synthesis, which provides control of molecular weight and end functionality. Even in an ideal living polymerization, however, an obtained polymer should have distribution in the degree of polymerization (DP) with a limit of polydispersity index ($\bar{M}_w/\bar{M}_n$) of $1 + 1/\text{DP}$ given by the Poisson distribution as Flory formulated.[1] Such a DP distribution of synthetic polymers with narrow molecular weight distribution has recently been well demonstrated by several analytical means such as matrix-assisted laser desorption ionization time-of-flight mass spectrometry[2] and supercritical fluid chromatography (SFC).[3]

We have reported three types of living polymerizations of methacrylates, which exhibit high stereospecificity: isotactic-,[4] syndiotactic-,[5] and heterotactic-specific living polymerizations.[6] Isotactic and syndiotactic polymers comprise contiguous meso (*m*) and racemo (*r*) diads, respectively. On the other hand, heterotactic polymer consists of an alternating sequence of *m*-diad and *r*-diad.



For the formation of a heterotactic sequence by anionic polymerization, opposite stereoselections, *m*-addition by $\sim rM^-$ forming $r\,m-$ sequence and *r*-addition by $\sim mM^-$ forming $mr-$ sequence, should take place alternatingly. Thus, it is obvious that the heterotactic propagation requires higher order stereocontrol than those for isotactic and syndiotactic propagations. In fact, there are limited number of reports on the preparation of heterotactic polymers.[7,8]

Recently, we succeeded in improving heterotactic specificity by employing allyl methacrylate (AlMA) as a monomer in the polymerization with *tert*-butyllithium (*t*-BuLi)/bis(2,6-di-*tert*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$], which gave a heterotactic polymer with *mr* triad content of 95.8%,[9] which is the highest value so far reported. We applied the SFC technique to heterotactic oligo(AlMA) for obtaining information on its DP distribution and observed peculiar distribution with respect to DP. In this communication the preliminary results of unusual DP distribution in the heterotactic oligomer are described.



Experimental Section. The oligomerization reaction was carried out in a glass ampule filled with dried nitrogen passed through Molecular Sieves 4A cooled at −78 °C. A heptane solution of *t*-BuLi (0.2 mmol) was added to MeAl(ODBP)$_2$ (1.0 mmol) in toluene (10 mL) at −95 °C. The reaction was initiated by adding AlMA (10 mmol) slowly to this mixture at −95 °C. After 2 h of the initiation, the reaction was terminated by adding methanol containing HCl at −95 °C. 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 benzene under vacuum. ^{13}C NMR spectra were measured in CDCl$_3$ at 55 °C on a Varian Unity Inova 500 spectrometer operated at 125 MHz. Molecular weights of the 8-mer and 13-mer of heterotactic oligo(AlMA), which were obtained by SFC fractionation, were confirmed by using a JEOL JMS-DX303HF mass spectrometer operated at the field-desorption (FD) mode. SFC was performed on a JASCO SUPER-200 chromatograph equipped with a 10 mm i.d. × 250 mm column packed with nonbonded silica gel (Develosil 100-5, Nomura Chemical Co., Ltd., particle size 5 μm). The SFC measurement of the heterotactic oligomer was conducted in a gradient mode both in eluent composition and in temperature as follows: flow rate of CO$_2$, 9.2−8.7 mL min^{-1} for 20 min; flow rate of methanol, 1.6−2.1 mL min^{-1} for 20 min; column temperature, 95−75 °C for 20 min; the fluid pressure, 200 kgf cm^{-2}. The chromatogram was recorded using a UV detector operated at a wavelength of 220 nm.

Results and Discussion. Figure 1 shows an SFC trace for the heterotactic oligo(AlMA) prepared with *t*-BuLi/MeAl(ODBP)$_2$ (1/5 mol/mol) in toluene at −95 °C for 2 h, whose average DP and $\bar{M}_w/\bar{M}_n$ value are 13.8 and 1.13, respectively. The population of the oligomers with respect to DP evidently deviated from the Poisson distribution and showed even−odd alternation; the oligomers with odd-number DP formed preferentially except for the 8-mer. Such even−odd alternation in the DP distribution of vinyl polymers has scarcely been reported. The only exception is a diheterotactic polymer of *tert*-butyl crotonate prepared with diphenylmagne-

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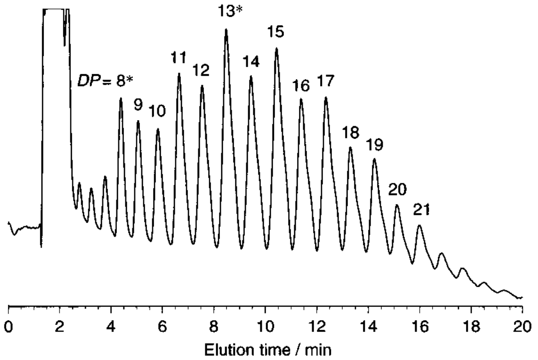


Figure 1. SFC trace of heterotactic oligo(AlMA) prepared with *t*-BuLi/MeAl(ODBP)$_2$ (1/5 mol/mol) in toluene at −95 °C for 2 h (AlMA 10 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL; yield = 19%, DP = 13.8, $\bar{M}_w/\bar{M}_n$ = 1.13, mm:mr:rr = 3.3:95.6:1.1). The DPs of the asterisked fractions were determined by FD mass spectrometry.

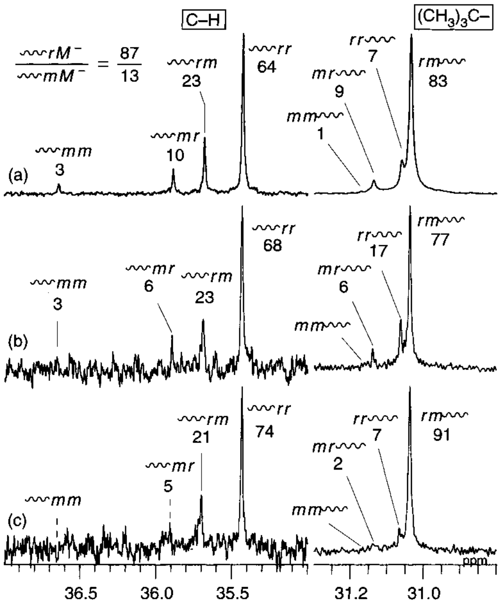
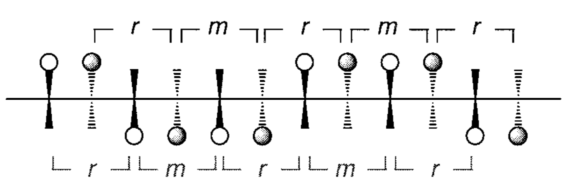


Figure 2. The 125 MHz ^{13}C NMR spectra of methine carbons at the terminating chain end and methyl carbons of the *tert*-butyl group at the initiating chain end of the unfractionated heterotactic oligo(AlMA) (a), 12-mer (b), and 13-mer (c), measured in CDCl$_3$ at 55 °C.

sium in toluene at −78 °C.[10]



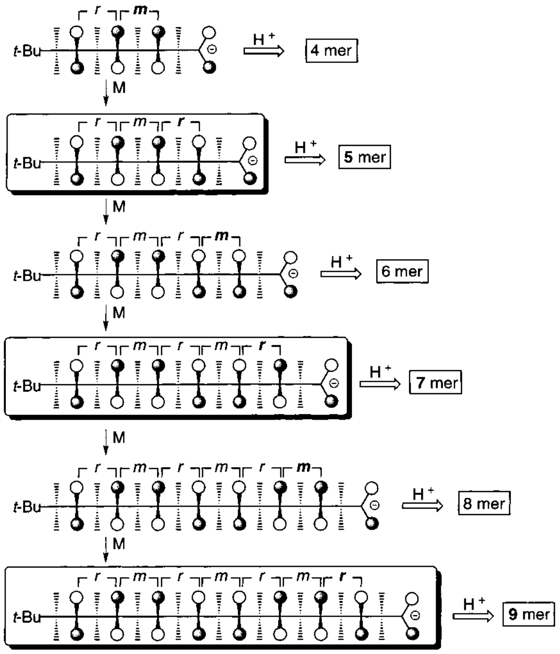
Diheterotactic polymer

In this case, oligomers with even-number DP are more abundant than those with odd-number DP. These suggest that this phenomenon of even−odd alternation in the DP distribution deeply relates to the mechanism of heterotactic-specific polymerization.

Figure 2a shows the ^{13}C NMR signals due to end groups of the oligomer, terminal methine carbon, and initial *tert*-butyl groups. The assignments were made on the basis of those for heterotactic poly(EMA).[11] The resonances of methine carbons at the terminating chain end split into four peaks due to the terminal triad stereosequence. The *m*/*r* ratio of the second diad from the terminating chain end {([−*mm*] + [−*mr*])/([−*r m*] + [−*r r*])} corresponds to the ratio of ∿mM^- and ∿rM^- which had existed in the polymerization system before the reaction was quenched with methanol. The value (∿mM^-/∿rM^- = 13/87) indicates the predominance of ∿rM^- as in the case of the EMA polymerization.[11] In other words, the propagating anions stay in the ∿rM^- state about 6.7 times longer than in the ∿mM^- state.

The signals of methyl carbons of the *tert*-butyl group at the initiating chain end also show splittings due to initial triad stereoregularity,[11] whose relative intensities are shown in Figure 2a. The signal due to *r m*− is the strongest (83%), suggesting that *r* mM^- tetramer anions are preferentially formed among four kinds of possible tetramer anions: *r* mM^-, *r* rM^-, mmM^-, and mrM^-.

Scheme 1. Progression of Heterotactic Oligomer Anions from Tetramer to Nonamer



Scheme 1 illustrates the progression of *r* mM^- up to 9-mer anions, assuming that the propagation step proceeds in a completely heterotactic manner. Since ∿rM^- is more abundant than ∿mM^-, the odd-number DP oligomers (5-mer, 7-mer, and 9-mer in Scheme 1) should be formed predominantly.

The population of stereoisomeric active species was estimated from the stereochemical sequence distribution near the chain ends of the original oligomer with the above-mentioned assumption (Table 1). As indicated in Table 1, odd-number DP oligomers are expected to be formed from four types of stereoisomers:

r m∿rM^-, *r r*∿mM^-, *mr*∿mM^-,

and *mm*∿rM^-

and, among them, *r m*∿rM^- is the dominant species (96%). On the other hand, even-number DP oligomers are expected to be formed from other four types of stereoisomers:

r m∿mM^-, *r r*∿rM^-, *mr*∿rM^-,

and *mm*∿mM^-

The fractions of *r m*∿mM^-, *r r*∿rM^-, and *mr*∿rM^- are

Table 1. Population in Percentage of Stereoisomeric Active Species Estimated from Stereosequence Distribution near the Chain Ends of the Oligo(AlMA) Prepared with *t*-BuLi/MeAl(ODBP)$_2$ (1/5 mol/mol) in Toluene at −95 °C for 2 h

Initial triad			Stereoisomeric active species[a]	*DP* number even / odd	Population[b]		
					Total	(even)	(odd)
$r\,m\sim$	83	→	$r\,m\sim r\,M^-$	odd	72		(96)
		↘	$r\,m\sim mM^-$	even	11	(43)	
$r\,r\sim$	7	→	$r\,r\sim r\,M^-$	even	6	(25)	
		↘	$r\,r\sim mM^-$	odd	1		(1)
$mr\sim$	9	→	$mr\sim r\,M^-$	even	8	(32)	
		↘	$mr\sim mM^-$	odd	1		(2)
$mm\sim$	1	→	$mm\sim r\,M^-$	odd	1		(1)
		↘	$mm\sim mM^-$	even	0	(0)	
					even/odd = 25/75		

[a] The ratio $\sim mM^-/\sim rM^-$ is 13/87. [b] Estimated on the assumption that propagation reaction proceeds in a completely heterotactic manner. Values in parentheses are relative abundance in each of odd- or even-number DP oligomers.

estimated as 43%, 25%, and 32%, respectively, and that of $mm\sim mM^-$ is negligibly small. This suggests that even-number DP oligomers are mixtures of these three kinds of stereoisomers with comparable populations.

Figure 2b,c shows ^{13}C NMR spectra of chain ends of uniform 12-mer and 13-mer separated by SFC. In the spectrum of 13-mer, the signal due to the $r\,m-$ triad at the initiating chain end was observed with a fraction of 91% and the signals due to $-r\,m$ and $-r\,r$ triads at the terminating chain end, both derived from $\sim rM^-$, with a fraction of 95%. This indicates that almost all the oligomers with DP = 13 are formed from $r\,m\sim rM^-$ anions. This result agrees well with the estimation summarized in Table 1. On the other hand, in the spectrum of 12-mer the signals due to $r\,r-$ (17%) and $mr-$ (6%) at the initiating chain end and the signals due to $-mr$ (6%) and $-mm$ (3%) at the terminating chain end are observed more evidently than in the spectrum of 13-mer. This indicates the lower regularity of 12-mer in stereosequence at the chain ends. However, the signal intensities in the spectrum of 12-mer deviate from the estimation shown in Table 1. For example, the intensities of terminal methine signals due to $-mr$ and $-mm$, derived from $\sim mM^-$, correspond to 9% of the even-number DP oligomer, the value being much smaller than the expected value of 43% (see Table 1). Similarly, the signals due to $r\,r-$ and $mr-$ at the initiating chain end are expected to be observed with fractions of 25% and 32%, respectively, but the observed intensities correspond only to 17% and 6%. These results suggest that the simple assumption that propagation reaction proceeds in a completely heterotactic manner is inappropriate. A detailed study by structural analyses of a series of lower DP uniform oligomers is in progress.

References and Notes

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