SHORT COMMUNICATIONS

Remarkable Change of Stereochemistry near the Terminating Chain-End of Heterotactic Poly(ethyl methacrylate) with Conversion. Importance in Mechanistic Study of Stereospecific Polymerization with the Aid of Chain-End Analysis

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We have reported that the polymerizations of several methacrylates with a combination of *t*-butyllithium (*t*-BuLi) and bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)₂] in toluene at low temperature proceed in a living manner and give heterotactic polymers, which comprise alternating repetition of meso (*m*) and racemo (*r*) diads.^{1–4}

As depicted by the stereochemical structure of the heterotactic polymer (1), there exist two kinds of propagating anions, *m*-ended and *r*-ended anions, in the polymerization system.

In the previous paper,³ we reported ¹³C NMR analysis for the stereochemical sequences at and near the chain ends of heterotactic poly(ethyl methacrylate) [poly(EMA)]. ¹³C NMR signals of the terminal methine carbon were assigned in terms of triad sequences; $-mm$, $-mr$, $-rm$, and $-rr$ (Figure 1a). The *m*/*r* ratio of the second

diad from the terminal should correspond to the ratio of the *m*-ended and *r*-ended anions existing in the polymerization system before quenching the reaction, that is, the ratio $[\sim mM^-]/[\sim rM^-]$ can be estimated from the terminal triad fraction;

$$[\sim mM^-]/[\sim rM^-] = (-mm + -mr) / (-rm + -rr).$$

The triad analysis revealed that the ratio $[\sim mM^-]/[\sim rM^-]$ was 1/2, that is, the *r*-ended anion is more abundant than the *m*-ended one, suggesting higher stability or lower reactivity of the *r*-ended anion.

Figure 1. 125 MHz ¹³C NMR spectra of methine carbon at the terminating chain-end of heterotactic poly(EMA)s formed at (a) 100%, (b) 41%, and (c) 28% yield, respectively.

Table I. Polymerization of EMA with *t*-BuLi / MeAl(ODBP)₂ (1/5 mol/mol) in toluene at -78°C^a

Time	Yield	Tacticity ^b /%			$\bar{M}_n$ ^c	$\bar{M}_w$ ^c	$[-mm] + [-mr]$ ^d	$[-mr] + [-rr]$ ^e
h	%	<i>mm</i>	<i>mr</i>	<i>rr</i>		$\bar{M}_n$	$[-rm] + [-rr]$	$[-mm] + [-rm]$
0.3	28	4.5	90.2	5.3	2450	1.08	22/78	36/64
0.5	41	5.9	88.6	5.5	3240	1.09	22/78	33/67
24	100	7.7	87.2	5.1	5680	1.08	35/65	85/15

^a EMA 10 mmol, *t*-BuLi 0.2 mmol, MeAl(ODBP)₂ 1.0 mmol, toluene 10 ml. ^b Determined by ¹³C NMR signals of carbonyl carbon. The signals due to units at the chain ends are not calibrated. ^c Determined by GPC. ^d The *m/r* ratio of the second diad from the terminal. ^e The *r/m* ratio of the terminal diad.

Since the *mr* triad content in the main chain is close to 90%, *m* diad mostly follows *r* diad and *vice versa*. If such a high stereospecificity prevails throughout the whole process of the polymerization, most of *r*-ended anions ($\sim\sim rM^-$) should be $\sim\sim mrM^-$, and most of *m*-ended anions ($\sim\sim mM^-$) be $\sim\sim rmM^-$. Thus, the termination with protic compounds such as alcohol should produce mostly the following four types of tetrad sequences at the terminal end:

However, the methine carbon resonances show splittings due to longer stereosequence than triad level. In particular, the carbon due to $-rr$ triad shows two signals with comparable intensity at 35.39 and 35.42 ppm. This suggested the lower stereoregularity near the terminating chain-end than that in the main chain. The poly-(EMA) analyzed in the previous work (*cf.* Figure 1a) was obtained at 100% conversion and thus the chain-end structure should reflect the stereospecificity under such a condition that the monomer concentration is close to zero. This result motivated us to reexamine the chain-end structure of poly(EMA) by analyzing the polymers formed at lower conversions.

Polymerizations were carried out under the same conditions as those reported in the previous paper³ and terminated after 18 and 30 min following initiation. The polymers were obtained in 28 and 41% yields, respectively, as shown in Table I. Figures 1b and 1c show the methine carbon signals of these polymers, which are almost identical. The spectra consist of four main peaks and are simple compared with that of the polymer obtained at 100% conversion (Figure 1a). These four peaks should correspond to four types of chain-end stereosequences shown in eq 3. The results confirm that, at least in the middle of the polymerization, two types of propagating species, $\sim\sim rmM^-$ and $\sim\sim mrM^-$, exist dominantly in the system as expected from the high heterotacticity of the main chain of the polymers.

The irregularity observed at the chain end of the poly(EMA) obtained at 100% conversion (*cf.* Figure 1a) indicates that the stereospecificity of the propagating anions is affected by the monomer concentration so that the chain-end stereoregularity becomes lower at low

monomer concentration. In other words, the results suggest that the higher stereospecificity requires the existence of the monomer in sufficient amount over the propagating species.

The ratios $[\sim m M^- / \sim r M^-]$, determined from the peak intensities as $(-mm + -mr)/(-rm + -rr)$, are shown in Table I. All the values confirm the conclusion in the previous paper,³ that the *r*-ended anion is more stable or less reactive than the *m*-ended one. In addition, the ratio $[\sim m M^-] / [\sim r M^-]$ at low conversions is 22/78 while the ratio at 100% conversion is 35/65. If one follows a propagation of a single heterotactic chain, the process can be depicted as the alternation of $\sim m M^-$ and $\sim r M^-$:

The predominant existence of $\sim rM^-$ over $\sim mM^-$ in 78/22 ratio means that the propagating anion stays in $\sim rM^-$ state about four times longer than in $\sim mM^-$ state. Thus, the fractional ratio or relative stability of $\sim mM^-$ and $\sim rM^-$ is also affected by the presence of the monomer.

In the previous paper,³ we also noted that the terminal diad formed after termination is affected by the kind of alcohol used as a terminating reagent. The three poly(EMA)s examined in the present work were obtained by termination with methanol. The *r/m* ratios of terminal diad of the polymers obtained at 28, 41, and 100% conversions were 36/64, 33/67, and 85/15, respectively (*cf.* Table I). The values indicate that stereochemistry of protonation by methanol is also affected by the presence or absence of the monomer.

The effect of conversion on the chain-end stereostructure is now under examination at higher conversions in addition to the effect of non-polymerizable carbonyl compounds such as alkyl pivalates.

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