SHORT COMMUNICATIONS

Stereochemistry of the Oligomerization of Methyl Methacrylate by $t\text{-C}_4\text{H}_9\text{MgBr}$ in Toluene at -78°C

Koichi HATADA, Koichi UTE, Katsuji TANAKA,
and Tatsuki KITAYAMA

*Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan*

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Investigations on the oligomerizations of vinyl monomers provide useful and important information on the corresponding vinyl polymerization. Yoshino *et al.* studied the structures of the oligomers of isopropyl acrylate formed with phenylmagnesium bromide to elucidate the stereoregulation in the polymerization.^{1,2} Hogen-Esch and his coworkers have extensively studied the stereochemistry of anionic oligomerizations of vinylpyridines³⁻⁹ and vinyl phenyl sulfoxide^{10,11} using chromatographic and NMR spectroscopic techniques. However, little has been reported on the stereoregular oligomerization of acrylate¹² or methacrylate¹³⁻¹⁵ monomer. Wulff *et al.*¹³ and Okamoto *et al.*¹⁴ studied asymmetric oligomerizations of triphenylmethyl methacrylate with 1,1-diphenylhexyllithium- and fluorenyllithium-($-$)-sparteine complexes, respectively, in toluene at -78°C . Hogen-Esch and his coworkers carried out the anionic oligomerization of methyl methacrylate (MMA) in tetrahydrofuran (THF) by lithio or sodio salt of methyl isobutyrate followed by termination with CH_3I or $^{13}\text{CH}_3\text{I}$ and determined the structure of the symmetrical oligomers by gas chromatography and ^{13}C NMR spectroscopy.¹⁵

Recently, we found that the polymerization of MMA by $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C was a completely living and highly isotactic-specific system.^{16,17} The α - and ω -end tacticities of the PMMA were studied by 2D NMR techniques.¹⁸

In this work, isotactic oligo(MMA)s were prepared by the polymerization of MMA with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C and their configurational sequences were investigated in detail by chromatography and 2D NMR spectroscopy to gain a more detailed understanding of stereoregulation in polymerization.

The oligomers were isolated as reaction products from the early stage of the polymerization. The crude oligomers were fractionated into dimer to octamer by gel permeation chromatography. Each fraction was further separated into stereoisomers by HPLC on a silica gel column (Develosil 100-5) with mixtures of $n\text{-C}_4\text{H}_9\text{Cl}$ and CH_3CN as eluent. The stereosequence of each stereoisomer was elucidated.

Figure 1. GPC (A) and HPLC (B—E) curves of the MMA-oligomers obtained from polymerization by *t*-BuMgBr in toluene at -78°C for 15 min. Eluent, *n*-C₄H₉Cl/CH₃CN = 97.5/2.5 (B), 96/4 (C), 95/5 (D), 88/12 (E); column, Develosil 100-5, 4.6 mm (i.d.) $\times$ 250 mm; detector, RI. "x" is the peak of 2,2'-methylenebis(6-*tert*-butyl-*p*-cresol) added as an inhibitor to the reaction mixture during removal of the solvent and unreacted monomer. "*" is the peak of a diastereomer whose structure is not known yet.

ided from the 500 MHz ^1H COSY spectrum measured in nitrobenzene- d_5 at 110°C on a JNM GX500 NMR spectrometer. The meso(*m*)/racemo(*r*) assignment was carried out based on the fact that the chemical shift between the peaks of two meso methylene protons is much larger than that between the peaks of two racemo methylene protons.

Table I shows the results of oligomerization for different times. The molecular weights of oligomers were very close to the calculated values and the molecular weight distributions were very narrow, indicating that living character of the polymerization. Figure 1A shows the GPC curve of MMA oligomers obtained in the polymerization for 15 min. The oligomers

Table I. Polymerization of MMA by *t*-BuMgBr in toluene at -78°C^a

Time	Yield	$\bar{M}_n^b$		$\bar{M}_w^b$
min	%	Obsd	Calcd	$\bar{M}_n$
15	7.5	470	430	1.10
60	14.3	760	770	1.13
120	21.0	1060	1110	1.12
72 h	100 ^c	4930	5060	1.10

^a MMA 20 mmol, *t*-BuMgBr 0.4 mmol, toluene 10 ml.

^b Determined by GPC.^c $mm/rm/rr = 96.5/3.2/0.3$.

mostly contained dimer to octamer and no unimer. The nonexistence of unimer suggests that the unimer anion is much more reactive

Figure 2. *meso/racemo* ratios at the α - and ω -ends of the MMA-oligomers obtained from the polymerization by *t*-BuMgBr in toluene at -78°C for 15 min. The m/r ratios for the PMMA of $\overline{\text{DP}}=25$ are cited from ref 16.

than the dimer anion. A similar trend was observed in the anionic asymmetric polymerization of triphenylmethyl methacrylate.^{13,14}

Each oligomer was separated into stereoisomers by HPLC (Figure 1 B–E) and the stereosequence of each isomer was determined by ^1H COSY as indicated in the figure. The peak intensities for *m*- and *r*-dimers indicate that the addition of a proton to the dimer anion is non-stereospecific. The addition is almost non-stereospecific for the trimer anion ($(mm+rm)/(mr+rr)=1.20$) and for higher oligomer up to octamer (Figure 2). The addition of a proton to the polymer anion was also found to be non-stereospecific.¹⁸ Polymerization of MMA by *t*-C₄H₉MgBr in toluene at -78°C is highly isotactic-specific^{16,17} ($m/r > 50$) and in-chain tacticity of the oligomers is highly isotactic as easily realized from Figure 1. It is not surprising but should be noted in studies on the stereochemistry of oligomerization that the addition of a proton to the propagating chain end is not stereospecific while the addition of monomer is

highly stereospecific. The addition of a proton to the oligomer anion of isopropyl acrylate formed with phenylmagnesium bromide has been reported to be highly stereospecific.^{1,2} The reason for the difference between the polymerizations of the acrylate and the methacrylate is not clear at present.

The m/r ratio of the trimers at the α -end was 18.6 ($= (mm+rm)/(rm+rr)$) and values between 10 and 20 were obtained for higher oligomers (Figure 2), indicating that the addition of MMA to the unimer anion is less isotactic-specific than that to the higher propagating anion. Accordingly, a rather bulkier group may be needed for the highly isotactic-specific stereoregulation at the propagating chain end.

It should be noted that, in general, the elution time for the stereoisomer with more *r* dyad is smaller than that for the stereoisomer with more *m* dyad. The same trend was observed for the oligo (MMA) derived from oligo (triphenylmethyl methacrylate) prepared by fluorenyllithium-(–)-sparteine complex (silica gel, *n*-C₄H₉Cl–CH₃CN)¹⁴ and for styrene oligomer (polystyrene gel, diisopropyl ether)^{19,20} (silica gel, hexane–CH₂Cl₂).²¹ For heterotactic trimers, *mr* trimer eluted faster than the *rm* trimer. This indicates that the *m* dyad sequence at ω -end is more adsorptive than that at the α -end, probably due to the bulky and nonpolar *t*-butyl group at the α -end. The same elution profiles were observed for pairs of higher stereoisomers such as *mmr*–*rmm*, *mmmr*–*rmmm*, *mmmmr*–*rmmmm*, and *mmmmmr*–*rrmmmm*. On the other hand, the *rr* trimer had practically identical retention time with that of *mr* trimer. Furthermore, the *rrr* tetramer was retained more than the *rmr* tetramer even though the former contained more *r* dyad than the latter.

These *rr* and *rrr* oligomers contain the ϵ -isotactic²² sequence as shown above. By assuming that the pair of ester groups functioning in the ϵ -isotactic configuration is as effective for cooperative adsorption as that in the *m* dyad (γ -isotactic²²) sequence, the slower elution of the *rr* trimer or *rrr* tetramer may be reasonably explained. By taking these factors into consideration, the elution order of the stereoisomers of oligo(MMA)s can be predicted, and hence usable for determining the stereochemical structure of an oligomer. A detailed investigation of this is now under way.

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