SHORT COMMUNICATIONS

Stereospecific Group Transfer Polymerization of Methyl Methacrylate with Lewis-Acid Catalysis— Formation of Highly Syndiotactic Poly(methyl methacrylate)

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Group transfer polymerization (GTP), disclosed in the early 1980's by Webster and co-workers,¹ is one of the versatile living polymerizations for acrylic monomers. The GTP involves ketene silvl acetals as initiators and nucleophilic or Lewis acidic catalysts and has been claimed to proceed through migration or transfer of the silvl group to maintain ketene silvl acetal units at the propagating polymer chain-ends during the polymerization. The proposed mechanism of group transfer has urged several researchers to examine the stereochemistry of GTP with the expectation of any specific effects of the ketene silvl acetal ends on the stereochemical aspect of the propagation reaction, if the associative mechanism¹⁻³ dominates the GTP. However, there had been no distinctive evidence of any special stereocontrol responsible to "group transfer",⁴⁻⁷ until we have reported a Lewisacid catalyzed GTP of methyl crotonate with HgI₂iodotrialkylsilanes (R₃SiI) as catalysts, which produces disyndiotactic poly(methyl crotonate) (Scheme 1); the stereoregularity of the polymer depends on the structure of trialkylsilyl transferring groups.^{8–11}

During the investigation of Lewis-acid mediated stereoregulation of GTP, we found a stereospecific GTP of MMA catalyzed by aluminum phenoxide with R_3SiI as a co-catalyst, which gives PMMA with a bimodal distribution of molecular weight (MW), the

high MW fraction of which had high syndiotacticity (Scheme 2). Though the overall products had a lower syndiotacticity, it is evident that there exists highly syndiotactic-specific and highly active species in this GTP system.

EXPERIMENTAL

Materials

Methyl methacrylate was purified by fractional distillation under reduced nitrogen pressure, dried over calcium CaH₂ and vacuum-distilled just before use. Dichloromethane and toluene were purified in the usual manner, dried over CaH₂, and then vacuum distilled just before use. Iodotrimethylsilane (Me₃SiI), bromotrimethylsilane (Me₃SiBr), and chlorotrimethylsilane (Me₃SiCl) purchased from Aldrich were used as received.

The ketene silyl acetal, 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS), was prepared by the previously reported procedure⁹ from methyl α lithioisobutyrate, generated from methyl isobutyrate with lithium diisopropyl amide and Me₃SiCl.

All the aluminum phenoxides were prepared from the corresponding phenols and trialkylaluminums according to the literature.¹² A typical procedure for the preparation of methylaluminum bis(2,6-di-*tert*-



Scheme 1. Disyndiotactic-specific GTP of methyl crotonate.

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Scheme 2. Stereospecific GTP of methyl methacrylate.

Table I. GTP of MMA catalyzed by alkylaluminum bisphenoxide and Me₃SiI in CH₂Cl₂ at 0 °C for 18 h^a

Run	Alkylaluminum bisphenoxide ^b	Whole polymer					Acetone-insoluble part	
		Yield	Tield M_n^c Tacticity/%		Enaction 107	mn / 07-		
		%	10 ³	mm	mr	rr	Flaction/ %	11/ %
1 ^d	EtAl(BHT) ₂	1	128.2	2.3	12.2	85.5	—	_
2	EtAl(BHT) ₂	94	33.2	1.2	15.1	83.7	13	96.2
3 ^e	EtAl(BHT) ₂	21	190	1.6	9.8	88.6	33	98.7
4	EtAl(ODBP) ₂	59	44.4	1.5	19.6	78.9	4	95.6
5	MeAl(BHT) ₂	13	20.5	1.2	13.6	85.2	21	96.9
6	MeAl(ODBP) ₂	4	22.9	1.7	10.8	87.5	36	96.6

^aMMA 10 mmol, MTS 0.2 mmol, alkylaluminum bisphenoxide 0.15 mmol, Me₃SiI 0.1 mmol, CH₂Cl₂ 4 ml. ^bSee Scheme 2 for the abbreviations. ^cThese polymers include high MW polymer whose MW exceeds a maximum porosity of the SEC columns (3×10^6). Thus, there is a possibility that the M_n values are underestimated. ^dPolymerization without Me₃SiI. ^ePolymerization at -40 ^oC for 66 h.

butylphenoxde) [MeAl(ODBP)₂] is as follows. A solution of 2,6-di-*tert*-butylphenol in toluene (2 equiv.) was added slowly to a toluene solution of trimethylaluminum (1 equiv.) at 0 °C. The resulting mixture was stirred at room temperature for 20 h. MeAl(ODBP)₂ thus formed was purified in the following procedure. The solvent was removed under vacuum to leave a yellowish solid. The product was recrystallized three times by dissolving it in hot heptane and cooling to -78 °C. After most of 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.

Polymerization

Polymerization was initiated by adding a solution of initiator in CH_2Cl_2 to a stirred mixture of monomer, aluminum phenoxide, cocatalysts and CH_2Cl_2 under a dry nitrogen atmosphere. The reaction mixture was homogeneous throughout the polymerization. After predetermined period of polymerization, a small amount of HCl/CH_3OH (*ca.* 1 M) was added to the mixture, and then the solution was poured into a large amount of hexane. The precipitated polymer was collected by filtration and dried at 40 °C for 6 h.

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Measurements

Size exclusion chromatography (SEC) was performed on a JASCO PU-980 chromatograph equipped with Polymer Laboratories SEC columns PLgel Mixed-C ($7.5 \text{ mm} \times 300 \text{ mm} \times 2$, maximum porosity 3×10^6) and a JASCO RI-930 detector using CHCl₃ as the eluent at 40 °C. Molecular weight was calibrated against standard PMMA samples (Shodex).

NMR spectra were recorded on a Varian Unity-Inova 500 or 750 spectrometer in $CDCl_3$ at 55 °C. Differential scanning calorimetry (DSC) was performed on a RIGAKU DSC-8230 apparatus under nitrogen flow (100 mL/min) at a heating rate of 10 °C/min. The weight of the samples was 10 mg.

RESULTS AND DISCUSSION

GTP of MMA Catalyzed by Aluminum Phenoxide and R_3SiI

The GTP of MMA was carried out in CH_2Cl_2 with MTS in the presence of several bulky aluminum Lewis acids, such as ethylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) [EtAl(BHT)₂], and Me₃SiI at 0 °C for 18 h (MMA:MTS:aluminum Lewis acid: Me₃SiI = 100:2:1.5:1) (Table I, run 1). Without



Figure 1. SEC curves of PMMA obtained by the GTP in the presence of $EtAl(BHT)_2$ and Me_3SiI in CH_2Cl_2 at 0 °C for 18 h (solid line). The SEC curves of the high and low MW parts fractionated by SEC are also shown (dotted line). MMA, 10 mmol; MTS, 0.2 mmol; $EtAl(BHT)_2$, 0.15 mmol; Me_3SiI , 0.10 mmol.

Me₃SiI, a polymer yield was extremely low (*ca.* 1%). The polymerization with EtAl(BHT)₂ gave a predominantly syndiotactic PMMA in 94% yield. This PMMA had a bimodal distribution of MW. By means of SEC fractionation, the PMMA was separated into the high and low MW parts as shown in Figure 1. The high MW part had an apparent MW exceeding the maximum porosity of the SEC column (3×10^6) , and the rr-triad content of this part was found to be 97.5% as determined by 750 MHz ¹H NMR spectroscopy. A similar GTP at $-40 \,^{\circ}$ C for 66 h also afforded a PMMA with a bimodal MW distribution in a lower yield (21%). The high MW part isolated by SEC fractionation had an rr-content higher than 98.7% as estimated by 750 MHz ¹H NMR. This is the highest syndiotacticity reported so far for PMMA.

Figure 2 shows carbonyl ¹³C NMR signals of the high and low MW parts of the PMMA obtained at -40 °C. Very few stereochemical defect was observed for the high MW part even at heptad-level inspection. It seems evident that there exists at least two types of active sites with different activities and stereospecificities in this polymerization. Exchanging reactions of these sites must be negligible during the course of the GTP.

When EtAl(ODBP)₂, MeAl(BHT)₂ or MeAl-(ODBP)₂ was used in place of EtAl(BHT)₂, the yields of PMMA decreased in that order (Table I). All these PMMAs had bimodal MW distributions similar to that shown in Figure 1. As described in the following section, the high MW parts of the products are insoluble in acetone, and the high MW parts were isolated by precipitation into acetone and thus the ratios of the high and low MW parts in each PMMA were determined from the yields of the whole polymer and the acetone-insoluble polymer. Though the fraction of the acetone-insoluble high MW part depended on the structure of the R₁ and R₂ groups in aluminum bisphenoxides, the *rr*-contents of the high MW parts



Figure 2. Carbonyl ¹³C NMR spectra of high and low MW PMMAs obtained by $EtAl(BHT)_2$ -catalyzed GTP at -40 °C (187.5 MHz, 55 °C, CDCl₃).

were approximately 96% regardless of the structure of R_1 and R_2 . The values are slightly lower than that for the PMMA obtained by SEC fractionation probably due to less effective removal of the low MW product by solvent fractionation.

The GTP of MMA was also investigated using Me₃SiCl, Me₃SiBr, or Me₃SiOTf (OTf:CF₃SO₃) in place of Me₃SiI as a co-catalyst of EtAl(BHT)₂ under the conditions described in Table I. The polymer yields decreased in the order, Me₃SiI (94%) > Me₃SiBr (41%) > Me₃SiCl (8%), and Me₃SiOTf did not afford polymeric products.

Properties of Highly Syndiotactic PMMA

The high MW part showed different solubility from the low MW part. While the whole polymer was soluble in CHCl₃, the high MW part was insoluble in acetone, THF and toluene, and the low MW part was soluble in these solvents. Thus, the high MW part could be isolated simply by pouring a CHCl₃ solution of the bimodal PMMA into a large amount of these solvents. Figure 3 shows SEC curves of the resultant PMMAs before and after fractionation with toluene. The *rr*-content of the toluene-insoluble high MW part was slightly lower than that of the SEC-fractionated high MW part, probably due to less effective removal of the low MW product.



Figure 3. SEC curves of the PMMA obtained with MTS catalyzed by MeAl(BHT)₂ and Me₃SiI in CH₂Cl₂ at -40 °C, and the fractionated PMMAs with toluene.

The toluene-insoluble high MW PMMA showed glass transition temperature (T_g) at 131.2 °C by DSC analysis. This value is consistent with the T_g expected for highly syndiotactic PMMA: according to the literature,¹³ T_g of PMMA with $M_n > 30,000$ increased with increasing syndiotacticity and can be extrapolated to be 131 °C for 100% syndiotactic PMMA.

To examine whether the unusual solubility of the highly syndiotactic PMMA arises from high tacticity or high MW, the toluene-insoluble high MW PMMA was subjected to thermal degradation to obtain lower MW PMMA, since PMMA is known to undergo unzipping degradation upon thermal treatment.^{14,15} The thermal degradation of the PMMA ($M_n \ge 507,000$) was conducted at 340 °C for 10 min under high vacuum, leaving the residual polymer with M_n of 52,000 in 15% yield, while the rr-triad content did not change (Figure 4). In spite of the much lower $M_{\rm n}$, the resultant syndiotactic PMMA was also insoluble in acetone, THF and toluene, indicating that the low solubility of the highly syndiotactic PMMA in various solvents is not due to the high MW but to its high stereoregularity.

CONCLUSION

Among the bulky aluminum Lewis acids and trimethylsilyl halides examined, the combination of EtAl(BHT)₂ as the catalyst and Me₃SiI as the co-catalyst gave the highest activity in the GTP of MMA with MTS in CH₂Cl₂. Though the whole products showed moderate syndiotacticity as well as a bimodal distribution of MW, the high MW fractions were found to be highly syndiotactic, whose *rr*-triad content reached 98.7% after careful fractionation by SEC. The highly syndiotactic PMMA was also isolated more easily by solvent fractionation with acetone or toluene according to the distinct difference in solubility as compared with the low MW fraction, although the incomplete separation resulted in lower



Figure 4. SEC curves of the highly syndiotactic PMMA (the toluene-insoluble fraction of the PMMA obtained by MeAl- $(BHT)_2$ -Me₃SiI catalyzed GTP in CH₂Cl₂ at -40 °C) before (a) and after (b) thermal degradation. The degradation of the PMMA (60 mg) was carried out *in vacuo* at 340 °C for 10 min to leave 9 mg of the residual PMMA.

value of rr-triad content (95–96%). Since the number of active species responsible for the formation of the high MW polymers is expected to be extremely small, the identification of the putative initiating species to be generated in the system is still a challenge. As a preliminary experiment, the GTP with $B(C_6F_5)_3$, an effective Lewis acid for the GTP of acrylates,¹⁶ as an alternative to the aluminum phenoxides was carried out under otherwise same conditions, which gave PMMA with low syndiotacticity (rr = 70% at 0 °C, rr = 86% at -40 °C) and narrow distribution of MW $(M_{\rm w}/M_{\rm n} = 1.08 - 1.10)$. Thus, the aluminum phenoxide is expected to play a principal role in this high level of stereoregulation, possibly through coordination to the carbonyl group of MMA and the propagating species. On the other hand, the silvl iodide co-catalyst has been supposed to activate both initiator and growing chain-ends in the GTP.^{17,18}

With our proceeding finding of stereospecific GTP of crotonates,^{10,11} the present GTP of MMA extends the possibility of stereocontrol in GTP through the use of appropriate Lewis-acid catalysts, though the highly syndiotactic PMMA is formed as a part of the whole product and, as a consequence, the fractionation process is inevitable as in the case of the early stage of isotactic-specific polymerization of propylene invented by Natta.¹⁹

However, distinctively different properties that the PMMA exhibits, such as high solvent-resistance, should be attractive both industrial and scientific viewpoints.

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