

Anionic polymerization of methyl methacrylate in the presence of chromium carbonyl [Cr(CO)₆]

Effect of the new initiating systems [nBuLi/Cr(CO)₆ and nBuLi/Cr(CO)₆/tBuOK] on the polymerization behavior

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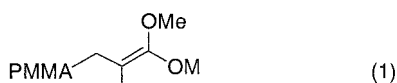
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Summary

The presence of Cr(CO)₆ in nBuLi-initiated anionic polymerization of methyl methacrylates (MMA) was found to effectively enhance stereoselectivity of the polymerization in toluene at 0°C. nBuLi/Cr(CO)₆ afforded an isotactic PMMA with 86 % of *mm* triad, and the polymers obtained with nBuLi/Cr(CO)₆/tBuOK were rich in heterotactic structures (*mr* = ca. 54%). In both cases, the selectivity was improved in ca. 10% compared to those of the polymerization conducted under the similar conditions without Cr(CO)₆.

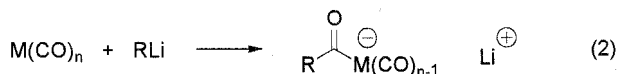
Introduction

Controlling the anionic polymerization of MMA has been one of the most challenging objectives in polymer synthesis. Both iso- and syndiospecific living polymerizations of MMA have been achieved by using Grignard reagent or alkyllithium/alkylaluminum as an initiator at low temperature [1-4]. On the other hand, the polymerizations initiated with silyl enolate (Group Transfer Polymerization, GTP) [5], aluminum porphyrin [6], and samarocene [7] have been reported to proceed in a living manner even at room temperature, owing to the highly stable propagating species consisting of Si, Al, and Sm metals, respectively. In particular, highly syndiotactic PMMAs can be obtained by the samarocene initiator [7]. Based on these successful examples, the use of propagating species including various main group or transition metals other than Li, Na, K, or Mg would be promising to control the polymerization [Eq. (1)], although the number of reports along such a strategy has been limited so far [8,9].

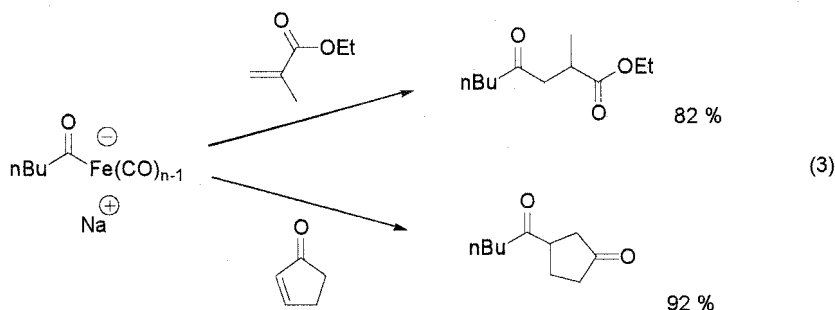


M: Li, Na, K, Mg → Si, Al, Sm, etc.

We have assumed that if transition metal ate complexes with an anionic charge on the metal center can initiate the anionic polymerization of acrylate monomers, it will be possible to incorporate diverse transition metals into the propagating species. Actually, we have already reported that transition metal ate complexes of Mo, W, and Mn generated by the reaction of the corresponding metal halides (MX_n) with $n+1$ equiv. of organolithium are effective initiators for the MMA polymerization [10,11]. As another general method for generating transition metal ate complexes, we chose here the reaction of metal carbonyls with alkyllithium reagents, which has been established in organometallic chemistry to provide ate complexes bearing an acyl anion on the metal center [12,13] [Eq. (2)].



Although one of this type of ate complexes has been shown to perform 1,4-addition effectively in the reaction with α,β -unsaturated carbonyl compounds [14] [Eq. (3)], to the best of our knowledge, there has been no report on the application of the ate complexes as an initiator for acrylate monomers.



In this study, we examined the initiating ability of the acyl carbonyl ate complex for the anionic polymerization of MMA. As a starting metal carbonyl compound, we selected chromium carbonyl $Cr(CO)_6$, whose reaction with organolithium reagents has been utilized to generate the ate complexes which can serve as precursors for preparation of chromium carbene complexes [15,16]. Although the precursors could exist in a tautomeric form in which the anionic charge is located at the acyl oxygen, we assume that they can be regarded as Cr analogues of the Fe ate complex in Eq. (1), at least with respect to the nucleophilic reactivity.

Experimental

Materials

MMA was distilled from CaH_2 before use. Toluene was distilled from Na before use. $nBuLi$ was purchased from Kanto Chemical Co., Inc. as a n -hexane solution (1.6 M) and it was diluted with n -hexane distilled from CaH_2 . The diluted solution of $nBuLi$

was titrated with 0.1 N HCl and 0.1 N NaOH aqueous solutions using phenolphthalein as an indicator. tBuOK was purchased from Kanto Chemical Co., Inc. and used as received. Cr(CO)₆ was purchased from Strem Chemicals, Inc. and used as received.

General polymerization procedure

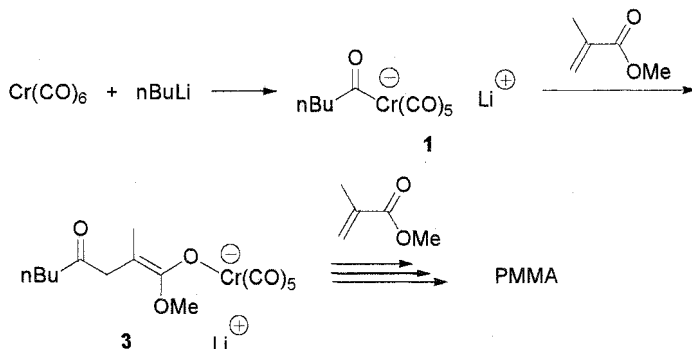
Under N₂ atmosphere, Cr(CO)₆ (20 ~ 30 mg) was dissolved in 10 ml of toluene to form a colorless solution in a Schlenk tube. After the solution was cooled to 0°C, hexane solution of nBuLi [0.16 M in n-hexane, 0.9 equiv. to Cr(CO)₆] was added dropwise and the mixture was stirred for 3 h at 0°C to give a light brown solution of [nBuC(=O)Cr(CO)₅]⁻Li⁺ (**1**). For the initiation with [nBuC(=O)Cr(CO)₅]⁻K⁺ (**2**), 3 equiv. of tBuOK was added to the solution of **1** at 0°C and the mixture was stirred for 1 h at that temperature. After polymerization was started by injecting MMA by a syringe to the solution of **1** or **2** at 0°C, the mixture was kept for 1 h at 0°C and for the period mentioned in Tables 1 and 2 for each run at room temperature with stirring. After acidic methanol (ca. 1 N HCl/MeOH) was added to quench the polymerization, PMMA was isolated by reprecipitation from CHCl₃ to MeOH and dried under reduced pressure.

Measurements

¹H-NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-*d* (CDCl₃) at 25°C. Tacticity of PMMA was determined from the integral ratio of C-CH₃ signals, which separated into three peaks with respect to the *mm* (1.21 ppm), *mr* (1.02 ppm), and *rr* (0.83 ppm) triads. Number-average-molecular weight (*M_n*) and molecular weight distribution (MWD, *M_w*/*M_n*) were measured by GPC on a Shimadzu C-R4A system equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standards.

Results and discussion

The reaction of chromium carbonyl Cr(CO)₆ with organolithium reagents has been generally utilized as a first step reaction for preparation of various chromium carbene complexes, and the generation of acyl carbonyl ate complex [nBuC(=O)Cr(CO)₅]⁻Li⁺ (**1**) by the reaction has been established [15,16]. We expected that as well as the same type of iron complex in Eq. (3), **1** could effectively perform Michael addition to MMA resulting in the formation of chromium carbonyl ate complex **3**, which had an enolate as a ligand on the metal center. If the enolate group on **3** has enough nucleophilicity to perform Michael addition to another MMA molecule, we can realize the polymerization, in which the propagating species has transition metal enolate structure as illustrated in Scheme 1. Furthermore, we expect that the reactivity of the propagating end group incorporating Cr(CO)₅ may be different from that of lithium enolates, resulting in the unique polymerization behavior of MMA.



Scheme 1. Polymerization of MMA initiated with **1**

To a light brown solution of **1** prepared by the reaction of Cr(CO)_6 with 0.9 equiv. of $n\text{BuLi}$ in toluene, 29 equiv. of MMA was added at 0°C . The polymerization was carried out for 1 h at 0°C and for 12 h at room temperature resulting in the formation of PMMA in a high yield (Table 1, run 1). For comparison, the polymerization was also carried out under the similar conditions without Cr(CO)_6 (Table 1, run 2). GPC analyses of the PMMAs in Table 1 revealed that both polymers had very broad MWDs.

Table 1. Polymerization of MMA initiated with $n\text{BuLi}$ in the presence and absence of Cr(CO)_6 ^{a)}

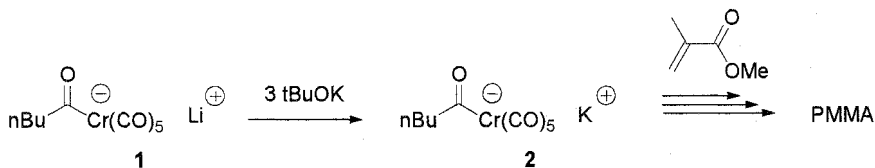
run	initiator (I)	[MMA]/[I]	time ^{b)} (h)	yield (%)	$M_n^c)$ ($\times 10^{-4}$)	$M_w/M_n^c)$	tacticity (%) ^{d)}		
							<i>mm</i>	<i>mr</i>	<i>rr</i>
1	$n\text{BuLi}/\text{Cr(CO)}_6$ (1) ^{e)}	29	12	90	6.03	4.93	86	10	4
2	$n\text{BuLi}$	25	14	100	2.60	8.47	78	13	9

^{a)} in toluene; ^{b)} reaction time at room temperature; ^{c)} determined by GPC based on polystyrene standards; ^{d)} determined by $^1\text{H-NMR}$; ^{e)} $[\text{nBuLi}]/[\text{Cr(CO)}_6] = 0.9$

As for the tacticity of the PMMAs in Table 1, the *mm* triad of the PMMA obtained by **1** is 8% higher than that of the polymer produced without Cr(CO)_6 . The apparent difference of the tacticity between these PMMAs demonstrates that the steric environment around the metal center, which should be most responsible for the stereoselection in the transition state of the propagation, is different between the two propagating species. We assume that the steric effect observed in the polymerization (run 1) can be ascribed to the presence of Cr(CO)_5 moiety in the propagating chain end, although we have no direct evidence to prove the mechanism of the initiation and propagation. Unfortunately, the attempt to characterize the chain end structure of PMMAs obtained with **1** or **2** by MALDI-TOF-MS analyses was unsuccessful since no signal derived from PMMAs was observed in the measurements. In any case, we believe that the addition of Cr(CO)_6 can be a very convenient method to improve the isospecificity of this anionic polymerization.

When the polymerization was conducted in the presence of 3 equiv. of $t\text{BuOK}$, the

polymerization behavior became quite different (Scheme 2, Table 2). MWDs of the resulting PMMAs were much narrower ($M_w/M_n = 1.8 \sim 2.2$) than the value of the polymer obtained without tBuOK (run 1 in Table 1, $M_w/M_n = 4.93$). The MWDs were also narrower than that of the polymer obtained by the combination of nBuLi and tBuOK under the same conditions (run 5 in Table 2, $M_w/M_n = 2.40$). In addition, the M_n s of the PMMAs increased linearly up to 102,300 with the increase of the feed ratio of MMA to the initiator (Table 2, runs 1 ~ 4). These results indicate that the conversion of the counter cation from Li to K generating **2** resulted in the drastic improvement of the initiation efficiency, although the rate of the initiation would not be fast enough to give narrow MWD PMMAs.



Scheme 2. Polymerization of MMA initiated with **2**

Table 2. Polymerization of MMA initiated with nBuLi/Cr(CO)₆/tBuOK (**2**) and nBuLi/tBuOK^{a)}

run	initiator (I)	[MMA]/[I]	time ^{b)} (h)	yield (%)	M_n^c ($\times 10^{-4}$)	M_w/M_n^c	tacticity (%) ^{d)}		
							<i>mm</i>	<i>mr</i>	<i>rr</i>
1	2 ^{e)}	112	17	94	1.52	1.87	27	53	20
2	2 ^{e)}	333	12	89	2.56	1.83	27	54	19
3	2 ^{e)}	530	12	100	5.42	2.23	26	54	20
4	2 ^{e)}	1083	13	100	10.23	1.91	23	55	22
5	nBuLi/tBuOK ^{f)}	98	17	94	2.35	2.40	32	45	23

a) in toluene; b) reaction time at room temperature; c) determined by GPC based on polystyrene standards; d) determined by GPC based on polystyrene standards; e) determined by ¹H-NMR; f) [nBuLi]/[Cr(CO)₆]/[tBuOK] = 0.9/1.0/3.0; g) [nBuLi]/[tBuOK] = 0.9/3.0

The presence of Cr(CO)₆ also gave significant influence on the tacticity of the resulting PMMAs under this condition. As shown in Table 2 (runs 1 ~ 4), the PMMA obtained by **2** was rich in heterotactic structures (*mr* = ca. 54 %), whereas the polymerization under the similar condition without Cr(CO)₆ afforded a PMMA with 45 % of *mr* triad (Table 2, run 5). Accordingly, the 9 % increase of the *mr* selectivity can be ascribed to the incorporation of Cr(CO)₅ moiety into the propagating species. Since there have been a limited number of reports on the synthesis of heterotactic PMMA [17,18], it is noteworthy that the use of Cr(CO)₆ and tBuOK provides a convenient method to afford high molecular weight heterotactic-rich PMMAs in high yields even at 0°C.

Conclusion

We have demonstrated that the addition of $\text{Cr}(\text{CO})_6$ is effective to enhance the stereoselectivity in $n\text{BuLi}$ initiated anionic polymerization of MMA although the overall tendency (isotactic- and heterotactic-rich PMMAs are obtained by the polymerizations with Li^+ and K^+ , respectively) is apparently determined by the kind of the counter cation. An isotactic PMMA and high molecular weight heterotactic-rich PMMAs were obtained by these initiating systems. The origin of the effect would be ascribed to the incorporation of $\text{Cr}(\text{CO})_5$ moiety in the propagating species.

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