# $FeCp(CO)_2I$: A Phosphine-Free Half-Metallocene-Type Iron(II) Catalyst for Living Radical Polymerization of Styrene[1]

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**Introduction.** The synthesis of polymers with precisely controlled molecular weights has been an important goal in polymer chemistry, which has been achieved via ionic and coordination polymerizations. In this and other aspects radical polymerization has been behind them despite its versatility. However, in these several years living radical polymerization has come true by varying methods. Among them, transition-metal catalysis is one of the most powerful approaches to control radical polymerization, because the activity of the catalyst can be designed by the combination of transition metals and appropriate ligands in response to the structure of monomers.[2]

Thus far, the effective metal catalysts include halides of Ru,[3−6] Cu,[7−12] Fe,[13,14] Ni,[15−17] Rh,[18,19] Pd,[20] and Re[21] with phosphine- or nitrogen-based ligands. These metal complexes play an indispensable role in the polymerization system; a growing radical is reversibly generated from a "dormant species" with carbon−halogen covalent bond, which is derived from an initiator R−X, via a single electron redox cycle like ∼∼C−X + Ru(II) ⇄ ∼∼C• X−Ru(III). Recently we have just reported half-metallocene-type ruthenium(II) complexes with novel class of ligands as catalysts for living radical polymerization, $RuCl(Ind)(PPh_3)_2$ (Ind = $\eta^5$-$C_9H_7$) and $RuClCp(PPh_3)_2$ (Cp = $\eta^5$-$C_5H_5$).[22] In particular, the former with the indenyl ligand proved effective in living polymerization of both MMA and styrene. Such a highly conjugated and electron-donating ligand obviously affects the redox potential of the metal complex to exhibit superior results to the dichloride counterpart, $RuCl_2(PPh_3)_3$.

Besides the ruthenium derivatives, iron complexes catalyze additions of organic polyhalides to olefins. The examples include $Fe_2(CO)_9$,[23] $Me_3NFe(CO)_4$,[23] and $Fe_2(CO)_4Cp_2$.[24] Iron(II)-mediated living radical polymerizations have also been reported, and iron is recognized as one of the most useful metals from the viewpoints of catalytic activity and cost. However, the effective iron(II)-based complexes have been limited to phosphine complexes [$FeX_2(PPh_3)_2$; X = Cl, Br][13] or a mixture of $FeX_2$ (X = Cl, Br) and phosphine- or nitrogen-based ligands.[14] Thus, dicarbonylcyclopentadienyliodoiron(II) [$FeCp(CO)_2I$] is significantly attractive as a catalyst for living radical polymerization because of not only the Cp ligand but also the carbonyl and iodo groups. Some metal carbonyl complexes have thus far been employed by us, and $Ni(CO)_2(PPh_3)_2$[25] proved more active for living radical polymerization of methyl methacrylate (MMA) than $Ni(PPh_3)_4$.[26] We have also reported that an iodide complex such as $ReO_2I(PPh_3)_2$ led to living radical polymerization of styrene in conjunction with an alkyl iodide initiator.[21] In addition, this Fe-based complex is stable against air and moisture in solid state and

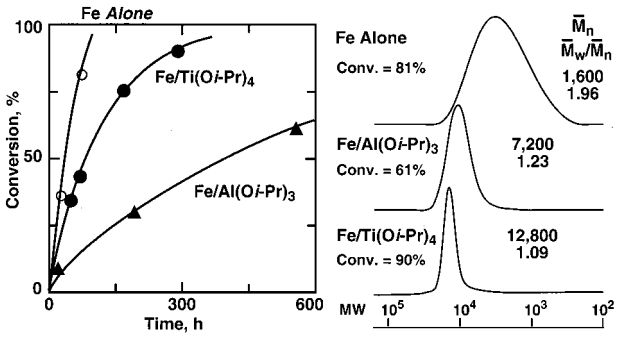
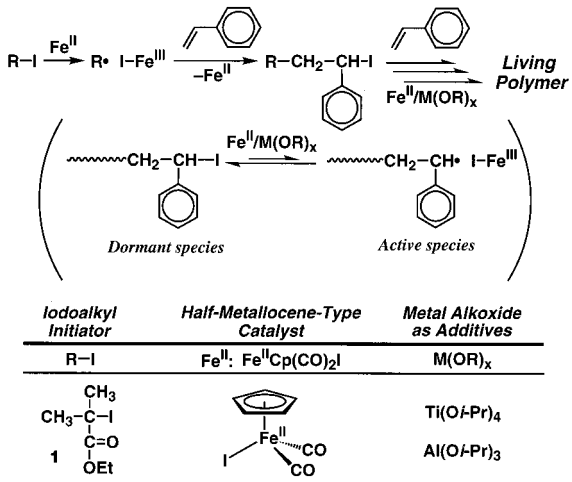



**Figure 1.** Polymerization of styrene with **1**/$FeCp(CO)_2I$ in the presence and absence of metal alkoxide [$M(OR)_x$] in toluene at 60 °C: $[styrene]_0$ = 6.0 M; $[\mathbf{1}]_0$ = 60 mM; $[FeCp(CO)_2I]_0$ = 30 mM; $[M(OR)_x]_0$ = 0 (○) or 100 mM. $M(OR)_x$ = Al(O*i*-Pr)$_3$ (▲) or Ti(O*i*-Pr)$_4$ (●).

**Scheme 1**




synthesized very easily without handling under inert gas but has not been employed for radical polymerization.

In this communication, we will report living radical polymerization of styrene with a novel initiating system based on the half-metallocene-type iron(II) complex, $FeCp(CO)_2I$, and an alkyl iodide initiator to give polystyrene with very narrow molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n$ = 1.06−1.09) (Scheme 1). There have been no reports about Cp−carbonyl complexes for living radical polymerization.

**Results and Discussion. (a) Living Polymerization of Styrene.** Styrene was polymerized with Cp−Fe(II) [$FeCp(CO)_2I$] and ethyl 2-iodoisobutylate [**1**: $(CH_3)_2C(CO_2Et)I$] as an initiator in the absence and presence of a metal alkoxide such as Al(O*i*-Pr)$_3$ and Ti(O*i*-Pr)$_4$ in toluene at 60 °C (Figure 1).[27] With Cp−Fe(II) alone, styrene was consumed to 81% conversion in 74 h, where only oligomers were obtained and number-average molecular weights ($\bar{M}_n$) were uncontrollable.[28] $^1$H NMR analysis of the oligomer samples showed that the $\omega$-terminal is not C−I but olefins. On the other hand, in the presence of a metal alkoxide like Al(O*i*-Pr)$_3$ or Ti(O*i*-Pr)$_4$, Cp−Fe(II) gave polystyrene of higher molecular weights. The polymerization rate was slowed on addition of the metal alkoxides; with Ti(O*i*-Pr)$_4$, the monomer conversion reached 90% in 12 days, and with

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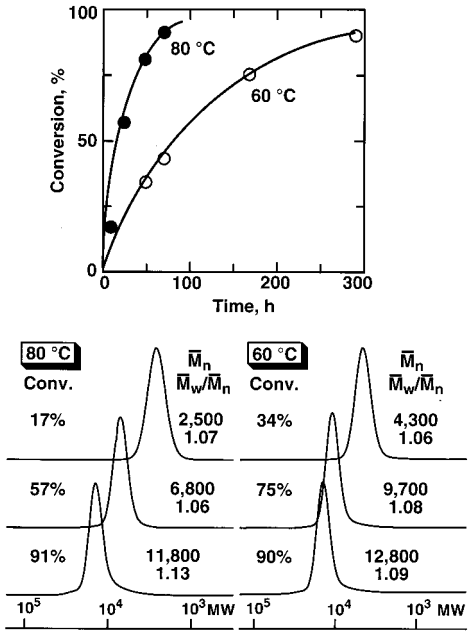


**Figure 2.** Polymerization of styrene with **1**/$FeCp(CO)_2I$ in the presence of $Ti(Oi\text{-}Pr)_4$ in toluene at 60 (●) or 80 °C (○): $[styrene]_0 = 6.0$ M; $[\mathbf{1}]_0 = 60$ mM; $[FeCp(CO)_2I]_0 = 30$ mM; $[Ti(Oi\text{-}Pr)_4]_0 = 100$ mM.

$Al(Oi\text{-}Pr)_3$, it reached only 61% in 23 days. This is in sharp contrast to the previous observation that such additives accelerates most of the metal-mediated radical polymerizations.

The polystyrene obtained with both metal alkoxides showed narrow MWDs. The $\bar{M}_n$ agreed with the calculated values assuming that one molecule of **1** generates one living polymer chain. Especially with $Ti(Oi\text{-}Pr)_4$, polystyrene of very narrow MWD was obtained throughout the polymerization ($\bar{M}_w/\bar{M}_n = 1.06-1.09$). A control experiment, with **1** and $Al(Oi\text{-}Pr)_3$ in the absence of Cp−Fe(II), resulted in a very slow styrene consumption to give oligomers (16% conversion in 148 h; $\bar{M}_n = 2400$; $\bar{M}_w/\bar{M}_n = 1.77$). We are currently examining what exactly happened between Cp−Fe(II) and the metal alkoxide; however, these control experiments showed that each of three components, alkyl iodide, Cp−Fe(II) complex, and metal alkoxide, is essential for the living radical polymerization of styrene.

It is interesting to note that $FeCp(CO)_2Cl$, the chloride derivative of $FeCp(CO)_2I$ [Cp−Fe(II) in this paper], shows no catalytic activity in radical additions of polyhalides to olefins.[24] In fact, as we have shown in Figure 1, the styrene polymerization with the iodide [Cp−Fe(II)] alone is uncontrollable, while living polymerization is induced by the combination of $Ti(Oi\text{-}Pr)_4$ and Cp−Fe(II). Thus, the catalytic activity of Cp−Fe(II) in radical addition or polymerization is modified by $Ti(Oi\text{-}Pr)_4$ via certain interaction between the two components.

The Cp−Fe(II)-based initiating system was then employed at a higher temperature; styrene was polymerized with **1** and Cp−Fe(II) in the presence of $Ti(Oi\text{-}Pr)_4$ in toluene at 80 °C (Figure 2). The polymerization proceeded relatively fast and reached around 90% in 70 h, and the obtained polystyrenes showed very narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.1$). These polydispersity indexes are one of the narrowest among thus far reported for the controlled radical polymerizations of styrene.[9,11] The $\bar{M}_n$ increased in direct proportion to monomer conversion and almost agreed with the calculated values. To

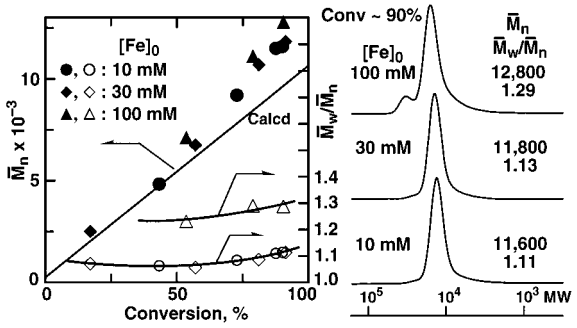


**Figure 3.** $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of polystyrene obtained with **1**/$FeCp(CO)_2I$/$Ti(Oi\text{-}Pr)_4$ in toluene at 80 °C: $[styrene]_0 = 6.0$ M; $[\mathbf{1}]_0 = 60$ mM; $[FeCp(CO)_2I]_0 = 10$ (●, ○), 30 (◆, ◇), or 100 mM (▲, △); $[Ti(Oi\text{-}Pr)_4]_0 = 100$ mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per initiator **1**.

examine the activity of the Cp−Fe(II) complex, we have performed polymerization of styrene with the other transition metal complexes, $ReO_2I(PPh_3)_2$ and $RuCl_2(PPh_3)_3$, in the presence of $Ti(Oi\text{-}Pr)_4$ in toluene at 60 °C. The polymerization with $FeCp(CO)_2I$ was clearly slower than those with $ReO_2I(PPh_3)_2$ and $RuCl_2(PPh_3)_3$; however, MWDs with $FeCp(CO)_2I$ were much narrower [$\bar{M}_w/\bar{M}_n = 1.22$ (93% conversion in 97 h) with $ReO_2I(PPh_3)_2$; $\bar{M}_w/\bar{M}_n = 1.26$ (92% conversion in 112 h) with $RuCl_2(PPh_3)_3$]. These results indicate that the activity of the catalysts increases in the following order: $FeCp(CO)_2I < RuCl_2(PPh_3)_3 \leq ReO_2I(PPh_3)_2$. The slow polymerization with Cp−Fe(II) is probably due to a lower concentration of propagating radical species, which diminishes side reactions such as recombination between them, to yield well-defined polystyrene.

Figure 3 shows the effects of Cp−Fe(II) concentration on the living polymerization of styrene with **1** in the presence of $Ti(Oi\text{-}Pr)_4$ in toluene at 80 °C, where the complex concentration was varied in the range 10−100 mM. Irrespective of the Cp−Fe(II) amount, the polymerization proceeded at nearly the same rate to reach around 90% in 70−76 h. At lower concentrations (10 and 30 mM), the obtained polystyrene showed narrow MWDs, whereas bimodal peaks of narrow MWDs at 100 mM. As indicated by their peak tops' molecular weights (one doubled from the other), this bimodal distribution is due to radical recombination; i.e., the excess amount of Cp−Fe(II) increases the concentration of propagating radicals. However, the two-peaked MWD also supports that this polymerization proceeds via radical intermediates because nothing else but radical polymerization could induce such recombination reactions.

**(b) End-Group Analysis.** The terminal structure of the polystyrene obtained with **1** and Fe(II)−Cp was analyzed by $^1H$ NMR spectroscopy (Figure 4). In addition to the large absorptions of the main chain repeat units (*c*, *d*, and *f*), the characteristic signals of the initiator moiety (α-end) and the *ω*-end iodide were observed; peaks *a* and *b* around 0.9 ppm for the protons of the ester group and the geminal methyl groups, respectively. The small absorption around 4.6 ppm (peak *e*, split due to a steric difference) is attributed to the methine proton adjacent to the *ω*-end iodine. The $\bar{M}_n$ obtained from the α-end signals [$9f/5(a + b)$] was 2400, in good agreement with that by SEC [$M_n = 2400$] calibrated against polystyrene standard samples. The number-average end functionality ($\bar{F}_n$) was close to unity for both α- and *ω*-terminals: $\bar{F}_n(\alpha) = 1.00$; $\bar{F}_n(\omega) = 1.12$;

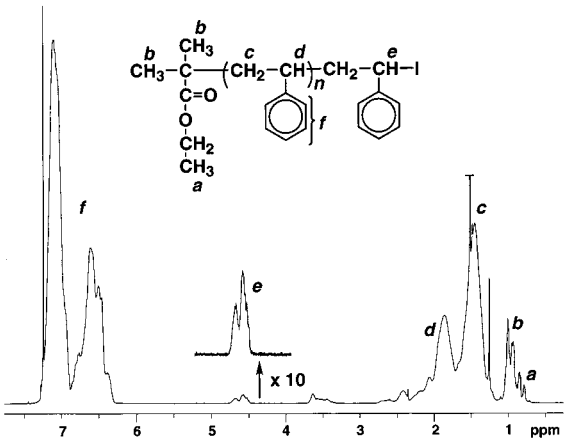


**Figure 4.** $^1$H NMR spectrum (500 MHz) of the polystyrene obtained with $(CH_3)_2C(CO_2Et)I/FeCp(CO)_2I/Ti(O\textit{i}\text{-}Pr)_4$ at 80 °C: $\bar{M}_n$(NMR) = 2400; $M_n$(SEC) = 2400; $M_w/M_n$ = 1.07. $\bar{F}_n(\alpha)$ = 1.00; $\bar{F}_n(\omega)$ = 1.12 (see text).

$\bar{F}_n = \bar{M}_n(\text{SEC})/\bar{M}_n(\text{NMR})$. These data indicate that **1** served as the initiator that forms one living polystyrene chain per molecule and that the polymerization proceeded via activation of the terminal C−I bond derived from the initiator. The steric structure of the obtained polystyrene (*mm*:*mr*:*rr* = 12:21:67; by $^{13}$C NMR) is similar to a typical atactic polystyrene initiated by AIBN in toluene at 60 °C (*mm*:*mr*:*rr* = 13:21:66) also supporting the radical mechanism.

In conclusion, the novel initiating systems based on Cp−Fe(II) and an alkyl iodide initiator induced living radical polymerization of styrene to give well-defined polystyrene in the presence of a suitable metal alkoxide. Especially with Ti(O*i*-Pr)$_4$ at 60 °C, precisely controlled polystyrene has been obtained ($\bar{M}_w/\bar{M}_n$ < 1.1). This Cp-based Fe(II) complex has also proved effective for living polymerization of methyl acrylate.[29] We will report this shortly along with its application to the synthesis of block copolymers.

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## References and Notes

(1) This work was presented in part at the 48th Annual Meeting of the Society of Polymer Science, Kyoto, Japan, May 1999; paper IPd030: Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1999**, *48* (2), 135.

(2) For recent reviews on living radical polymerizations, see: (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (b) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365. (c) Malmström, E. E.; Hawker, C. J. *Macromol. Chem. Phys.* **1998**, *199*, 823. (d) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371. (e) Colombani, D. *Prog. Polym. Sci.* **1997**, *22*, 1649. (f) *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998. (g) Sawamoto, M.; Kamigaito, M. In *Synthesis of Polymers (Materials Science and Technology Series)*; Schlüter, A.-D., Ed.; Wiley-VCH: Weinheim, Germany, 1999; Chapter 6.

(3) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

(4) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070.

(5) Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron* **1997**, *53*, 15445.

(6) Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2244.

(7) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

(8) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.

(9) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.

(10) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.

(11) Percec, V.; Barboiu, B.; Kim, H.-J. *J. Am. Chem. Soc.* **1998**, *120*, 305.

(12) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190.

(13) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.

(14) Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. *Macromolecules* **1997**, *30*, 8161.

(15) Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576.

(16) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2249.

(17) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6756.

(18) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.

(19) Moineau, G.; Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1998**, *31*, 542.

(20) Lecomte, Ph.; Draiper, I.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R. *Macromolecules* **1997**, *30*, 7631.

(21) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 2420.

(22) Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3820.

(23) Elzinga, J.; Hogeveen, H. *J. Org. Chem.* **1980**, *45*, 3957.

(24) Davis, R.; Durrant, J. L. A.; Khazal, N. M. S.; Bitterwolf, T. E. *J. Organomet. Chem.* **1990**, *386*, 229.

(25) Ida H.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47* (2), 149.

(26) Uegaki, H.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3003.

(27) The polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock or in baked and sealed glass tubes. All reagents were used after ordinary purifications, the metal complexes were handled in a glovebox under dry and oxygen-free argon, and the toluene solvent was bubbled with dry nitrogen for more than 15 min immediately before use. A typical example with $FeCp(CO)_2I$ in conjunction with **1** and Ti(O*i*-Pr)$_4$ is given below. Styrene (2.20 mL), tetralin (0.660 mL), and solutions of **1** (887 mM in toluene; 0.216 mL) and Ti(O*i*-Pr)$_4$ (0.0945 mL) were added into $FeCp(CO)_2I$ (29.2 mg) sequentially in this order at room temperature under dry nitrogen; the total volume of the reaction mixture was thus 3.20 mL. Immediately after mixing, aliquots (0.4 mL each) of the solution were injected into baked glass tubes, which were then sealed and placed in an oil bath kept at 80 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with tetralin as an internal standard. The quenched reaction solutions were diluted with toluene (ca. 10 mL) and vigorously shaken with an absorbent [KYOWAAD-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical Industry Co., Ltd.] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was washed with water and evaporated to dryness to give the products, which were subsequently vacuum-dried overnight.

(28) The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform eluent at room temperature on three polystyrene gel linear columns (Shodex K-805L × 3) that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI

refractive index and 970-UV ultraviolet detectors. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemical; $\bar{M}_n = 580-1\,547\,000$; $\bar{M}_w/\bar{M}_n \leq 1.1$) as well as the monomer. $^1$H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz for proton. Polymers for $^1$H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

(29) Onishi, I.; Baek, K.-Y.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1999**, *48* (2), 136.

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