새로운 루테늄 촉매를 이용한 MMA의 원자 이동 라디칼 중합

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Atom Transfer Radical Polymerization of Methyl Methacrylate by Novel Ru(COD)(L)Cl_2 (L=2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine) Catalyst

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1. INTRODUCTION

Since the pioneering research by Sawamoto and Matyjaszewski,[1,2] transition metal-catalyzed atom transfer radical polymerization (ATRP) has been emerged as a versatile method for radical polymerization of functionalized alkenes.[3-15] Compared to other traditional radical polymerization methods, the transition metal-catalyzed ATRP reactions have been found to be advantageous especially for acrylic compounds in terms of controlling molecular weight distribution and tolerating functional groups.

Ruthenium chemistry has recently progressed to give a great variety of complexes for novel efficient catalytic and stoichiometric reactions.[16] It has also been understood that, particularly for ruthenium complexes, the precise complex design with ligands is especially important for desired reactions to occur. Although $RuCl_2(PPh)_3$-based initiating system is indeed effective in MMA living radical polymerization, it generally requires a long reaction time (sometimes a few days, for completion) and often needs added metal alkoxides such as $Al(O^iPr)_3$ for acceleration of the reaction.[17,18]

In this work, Ru(COD)(L)Cl_2 (L=2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine) have been prepared from the reaction of 2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine with the $[Ru(COD)Cl_2]_2$. Various monomers including methyl methacrylate (MMA) were able to be applied to atom transfer radical polymerization, and the molecular weight and the molecular weight distribution were able to be controlled using novel ruthenium catalyst. Molecular structure of synthesized Ru(COD)(L)Cl_2 was determined by the single crystal X-ray diffraction method. Herein we report the atom transfer radical polymerization of MMA using the novel ruthenium catalyst. The optimum conditions of the ATRP of MMA were found in systematic way.

2. EXPERIMENTAL

Materials. All reactions were carried out in an inert-atmosphere dry box or by using standard high vacuum and Schlenk line techniques unless otherwise noted. $[Ru(COD)Cl_2]_2$ (COD = cyclooctadiene)[19] and methyl pyridine-2-carboximidate[20] were prepared by the cited methods, respectively. Methyl methacrylate (Aldrich, 99%) were distilled before use.

Di-*n*-butylamine (Yakuri, 98%), tri-*n*-butylamine (Yakuri, 99%) and ethyl 2-bromoisobutyrate (EB*i*B, Aldrich, 98%) are dried over CaH_2 and distilled under vacuum and then stored in a dry box under a purified nitrogen atmosphere. Amino alcohol (Aldrich, 99%), aluminum isopropoxide (Aldrich, 99.99+%) were purchased and used without further purification. Unless otherwise noted, all other reagents were received from commercial sources and used without further purification. All solvents were dried by the standard methods.[21] All syntheses and polymerizations were carried out under a purified nitrogen.

Instruments. Both ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian 200 MHz FT-NMR Spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) and were referenced to the residual solvent peaks. The MMA monomer conversion was estimated from both the ^1H-NMR integration ratio of OCH_3 signals from the polymer (3.60 ppm) and monomer (3.75 ppm), and the gas chromatogram (Agilent Technologies 6890N, column : HT5, mobile phase : N_2 gas) integration ratio of the residual monomer and solvents or dodecane as the internal standard. The number-averaged molecular weight (Mn), weight-averaged molecular weight (Mw), and molecular weight distribution (Mw/Mn) were determined from the gel permeation spectroscopy (Waters Breeze GPC System, 1515 Pump, 717 Autosampler, 2414 RI Detector) in tetrahydrofuran (THF) at 40℃. Calibration was performed by using poly(methyl methacrylate) (PMMA) as the standard sample.

Preparation of 2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine. The compound was prepared by following a modified literature procedure.[22] The mixture of methyl pyridine-2-carboximdate (2.72 g) and aminoalcohol (2.54 g) in dichloroethane was refluxed for 2 hr. A brine solution (50 mL) was added to the solution, and the organic layer was separated by a separatory funnel. The combined organic solution was chromatographed on a neutral alumina column (EtOAc : hexanes = 1 : 1) in air. After evaporation of solvent by a rotary evaporator, the product was isolated by vacuum distillation (0.5 torr, 90℃) as a colorless oil in 90% yield.

Preparation of Ru(COD)(L)Cl_2 (L = 2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine). In a 50 mL Schlenk flask, the 2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine (1.26×10^{-2} mmol) was added to $[Ru(COD)Cl_2]_2$ (1×10^{-2} mmol) in toluene solution. The reaction mixture was stirred at 80℃ for 36 hr and 120℃ for 24 hr. After removal of solvent in vacuum, the residue was dissolved in CH_2Cl_2, and the solution was filtered through Celite. Recrystallization from CH_2Cl_2 and hexanes gave ruthenium complex as an air-sensitive orange-red solid.

General Procedure for Polymerization of MMA. In a glove box, Ru-catalyst, MMA, additive, and solvent were added to a 50 mL Schlenk flask equipped with a stirring bar. The reaction flask was immersed in an oil bath which was preset at desired temperature. After stirring for 10 min, the appropriate amount of initiator (EB*i*B) was added *via* a degassed micro-syringe. Samples were withdrawn periodically *via* a degassed syringe (2 mL), and were diluted by adding 5 mL of CH_2Cl_2. Each sample solution was analyzed by GPC. The monomer conversion of each sample was also estimated from the ^1H-NMR integration ratio of OCH_3 signals. Each sample for GPC measurement was isolated by pouring the CH_2Cl_2 solution of the polymer into large excess amount of MeOH and dried under vacuum to constant weight.

3. RESULTS AND DISCUSSION

Characterization of 2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine. Synthesized ligand was characterized from its ^1H-NMR, ^{13}C-NMR spectra and GC/MS. ^1H-NMR (200 MHz, $CDCl_3$) δ 9.19 (NH), 8.64, 7.80, 7.35 (pyridine ring), 5.37 (OCH), 1.41 (CH_3); ^{13}C-NMR (50 MHz,

$CDCl_3$) δ 165.2 (C=NH), 148.9, 147.9, 137.0, 125.0, 120.7 (pyridine ring), 68.7 (OCH), 21.6 (CH_3). MS-FAB *m/z* = 176(M^+).

Characterization of Ru(COD)(L)Cl_2 (L=2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine). Synthesized Ruthenium catalyst was characterized from its ^{1}H-NMR, ^{13}C-NMR spectra and a single crystal X-ray diffraction. ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 8.56 (NH), 8.0, 7.6 (pyridine ring), 5.12 (OCH), 2.2 ~ 1.7 (CH_2); ^{13}C-NMR (50 MHz, CD_2Cl_2) 165.8 (C=NH), 150.0, 148.2, 138.5, 127.5, 122.2 (pyridine ring), 82.0 (OCH), 33.3, 24.7 (CH_2). MS-FAB *m/z* = 443.1508(M^+).

Solvent Effect. Molecular weight was in the range of 28,000 and 64,000 depending upon used [monomer] : [solvent] ratio. Molecular weight distribution was in the range of 1.21 and 1.49, which was comparable to the polymerization of MMA. In view of these results, [solvent] : [monomer] = 4 : 1 might be optimum ratio.

Table 1. Solvent Effect on Homopolymerization of MMA by ATRP[a]

Entry	S/M[b]	Conversion(%)[c]	$M_{n,th}$[d]	$M_{n,GPC}$	M_w/M_n
1	1:1	99	10095	63840	1.49
2	2:1	95	9695	43770	1.38
3	4:1	90	9195	29280	1.23
4	8:1	74	7595	28930	1.21

[a] $[Ru\text{-catalyst}]_0$: $[Al(O^iPr)_3]_0$: $[EBiB]_0$: $[MMA]_0$ = 1 : 4 : 2 : 200 ; reaction time : 12 h ; temp : 80℃; in a toluene solution. [b] Determined by ^{1}H-NMR. [c] Determined by ^{1}H-NMR. [d] $M_{n,th}$ = $Mw_{EBiB}+Mw_{MMA}\times\{[MMA]_0/[EBiB]_0\}$(conversion).

Temperature Effect. Molecular weight distribution was in the range of 1.3 and 1.8. Molecular weight distribution was as low as 1.24 when the applied temperature was 80℃. From these results, it is thought that the optimum polymerization temperature of MMA is about 80℃ in toluene solution.

Table 2. Temperature Effect on Homopolymerization of MMA by ATRP[a]

Entry	Temp(℃)	Conversion(%)[b]	$M_{n,th}$[c]	$M_{n,GPC}$	M_w/M_n
1	70	60	6195	53800	1.43
2	80	64	9595	19244	1.24
3	90	57	5895	93100	1.78

[a] $[Ru\text{-catalyst}]_0$: $[Al(O^iPr)_3]_0$: $[EBiB]_0$: $[MMA]_0$ = 1 : 4 : 2 : 200 ; reaction time : 12 h; in a toluene solution (sol/mon = 4 : 1). [b] Determined by ^{1}H-NMR. [c] $M_{n,th}$ = $Mw_{EBiB}+Mw_{MMA}\times\{[MMA]_0/[EBiB]_0\}$(conversion).

4. CONCLUSIONS

In summary, 2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine was found to be novel ligand for the ruthenium catalyzed polymerization of MMA. $Ru(COD)(L)Cl_2$ (L = 2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine) have been prepared from the reaction of 2-(4,5-dihydro-5,5-dimethyloxazol-2-yl)pyridine with the $[Ru(COD)Cl_2]_2$ at 120℃ in toluene solution. Various monomers including methyl methacrylate (MMA) were able to be applied to atom transfer radical polymerization, and the molecular weight and the molecular-weight-distribution were able to be controlled using novel ruthenium catalyst. Molecular structure of synthesized $Ru(COD)(L)Cl_2$ was found out using the single crystal X-ray diffraction method. The optimum reaction condition of the ATRP of MMA was found to be $[catalyst]_o/[Al(O^iPr)_3]_o/[EBiB]_o/[MMA]_o$=1 : 4 : 2 : 200 at 80℃ in toluene solution, which yielded well-defined PMMA with a narrow molecular weight distribution of 1.23.

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