Polymerization

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Phosphorus-Containing Ligands for Iron(III)-Catalyzed Atom Transfer Radical Polymerization**

Zhigang Xue, Nguyen Thuy Ba Linh, Seok Kyun Noh, and Won Seok Lyoo*

Atom transfer radical polymerization (ATRP), a representative example of a living radical polymerization, has developed rapidly since it was proposed in 1995.[1] Reported herein is the iron(III)-catalyzed ATRP with phosphorus ligands in the absence of any radical initiator or reducing agent.

In recent years, ATRP has become a ubiquitous tool for the synthesis of a wide range of materials with predetermined molecular weights and narrow molecular weight distributions.[2] ATRP employs a redox process with transition-metal complexes in which a halogen atom is transferred reversibly between the transition metal and the end of the polymer chain. The mechanism relies on creating a dynamic equilibrium between a low concentration of growing radicals and a large amount of dormant species which are unable to propagate and self-terminate. Therefore, some side reactions can be limited, and the living process of polymerization is efficient.

The complex plays an important role in ATRP, and for this purpose researchers put a great deal of effort into researching the effect of various complexes on polymerization; for example, copper,[2] iron,[3] ruthenium,[2a,4] and other metals.[5] Our interest in ATRP is to develop new iron complexes with phosphorus ligands. Iron-salt-based catalysts have attracted particular attention owing to their low toxicity, low cost, and biocompatibility. According to published reports, some iron complexes were active catalysts for normal and reverse ATRP of methyl methacrylate (MMA) and styrene (St) with various ligands.[3] Notwithstanding phosphorus-based ligands have been employed to form catalyst systems with transition-metal salts in the field of ATRP,[2a] but bidentate phosphorus-containing ligands are rarely studied in ATRP systems.[3c,d]

The use of air stable catalysts in their higher oxidation state was successfully developed and used as a tool in synthesizing polymer materials. The reverse ATRP requires a conventional radical initiator such as a peroxide or 2,2′-azobisisobutryonitrile (AIBN) to generate a lower oxidation state of the transition-metal complex.[6] The reducing agent[7] can reduce the higher oxidation state transition metal through a single electron process in activator generated by electron-transfer (AGET) ATRP. Compared to the reported reverse ATRP or AGET ATRP methods, our catalyst systems were developed by only using iron(III) in the absence of additives. As a result, the reaction systems are less toxic and less expensive, which makes them attractive for potential practical applications. Very recently, Schubert and co-workers [8] reported that the ATRP of MMA with only copper(II) resulted in well-defined polymers. However, low initiation efficiencies were obtained.

We have recently reported that the normal ATRP of MMA with the $FeBr_2$/2-(diphenylphosphino)pyridine (dppp) catalyst was well-controlled and gave polymers with low polydispersities (PDI; $M_w/M_n < 1.3$) and molecular weights, which agreed with the theoretical values.[3c] Control of the molecular weight was also good with the $FeBr_2$/2-((diphenylphosphino)methyl)pyridine (dppmp) catalyst, but the polydispersities were higher ($M_w/M_n > 1.5$). The addition of $FeBr_3$ to the ATRP system at the beginning of the reaction improved the ability to control the polymerization.[3d]

Herein we report, for the first time, the iron(III)-catalyzed ATRP with phosphorus ligands (Figure 1) in the absence of a radical initiator or reducing agent. The use of oxidatively stable catalysts overcomes the air-sensitivity problem which is associated with lower oxidation state metals, and makes the preparation and storage of the ATRP catalyst systems more facile. Notably, there is no need to premix the transition metal with the ligand and then isolate the catalyst complex. The ligand and $FeBr_3$ can simply be mixed and directly reacted with the monomer. Therefore, isolating and purifying the catalyst is not necessary, thus saving on cost.

Polymerizations of MMA catalyzed by iron(III)/phosphorus ligands by using ethyl 2-bromoisobutyrate (EBriB) as an initiator were performed in toluene at 80 °C. The linear

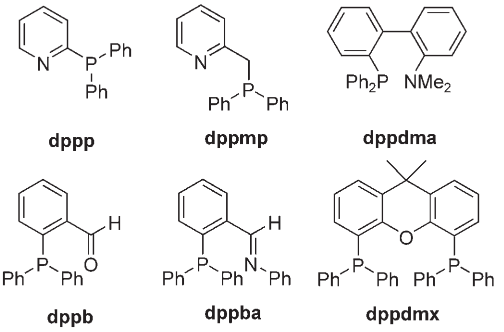

Figure 1. The structures of phosphorus-containing ligands.

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[*] Z. Xue, N. T. B. Linh, Prof. S. K. Noh
School of Display and Chemical Engineering
Yeungnam University, 214-1 Dae-dong Gyeongsan
Gyeongbuk, 712-749 (Republic of Korea)
Fax: (+82) 53-810-4631
E-mail: sknoh@ynu.ac.kr

Prof. W. S. Lyoo
School of Textiles, Yeungnam University
Gyeongbuk (Republic of Korea)

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increase observed for all complexes indicated that the concentration of growing radicals remained constant during the polymerization process (Figure 2a). The polymerization of MMA catalyzed by $FeBr_3$/dppmp had an induction time, which was perhaps caused by the slow formation of the catalytic species at the start of the reaction.

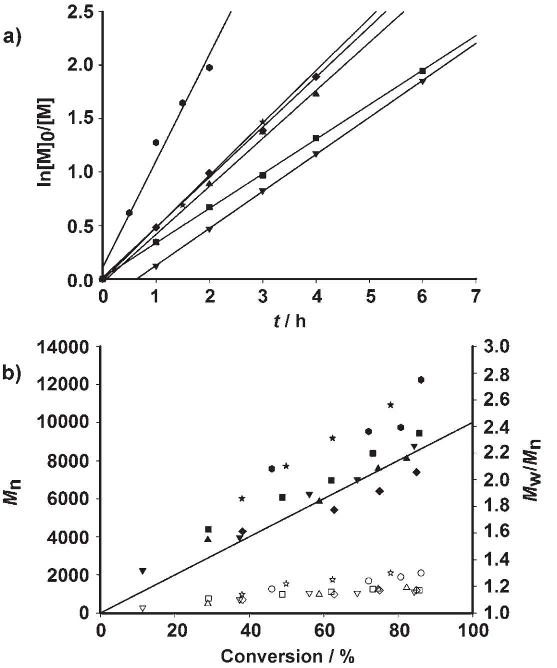

Figure 2. a) Kinetic plots of $\ln[M]_0/[M]$ versus reaction time and b) dependence of molecular weights, M_n (filled symbols, see key below), and molecular weight distributions, M_w/M_n (open symbols), on the monomer conversion for the ATRP of MMA in toluene with different complexes at 80 °C. $[MMA]_0 = 4.67$ M; $[MMA]_0/[EBriB]_0/[FeBr_3]_0/[Ligand]_0 = 100:1:1:2$. ● = tpp; ■ = dppp; ▼ = dppmp; ▲ = dppdma; ◆ = dppb; ★ = dppba; —— = $M_{n,theor.}$. tpp = triphenylphosphine.

The dependence of M_n and M_w/M_n on the monomer conversion within different catalyst systems is shown in Figure 2b. The molecular weights of all the polymers increased linearly with the conversion. In the case of dppba, the measured molecular weights were lower than the theoretical values, presumably because of the formation of additional polymer chains that could be generated by transfer reactions.[3a,9] Additionally, in the cases of tpp and dppba, the molecular weights were much higher than the theoretical values, which indicate a low initiation efficiency. Moreover, relatively high polydispersities ($M_w/M_n = 1.14$–1.33) were obtained. However, when dppp or dppmp was employed as the ligand the molecular weights matched the theoretical values better, and the molecular weight distributions (M_w/M_n=1.04–1.17) were narrower.

To identify the living characteristic of the ATRP of MMA catalyzed by the high oxidation state metal in the absence of any radical initiator or reducing agent and the same experiments with $CuBr_2$/amine complexes were also run (Table 1, entries 7–9).

Table 1: Results of the Fe- and Cu-mediated polymerizations of MMA.[a]

Entry	Catalyst	t [h]	Conv. [%]	$M_{n,theor.}$[c] [g mol^{-1}]	$M_{n,GPC}$ [g mol^{-1}]	PDI
1[b]	$FeBr_2$/dppdmx	20	89	9100	12300	1.59
2[b]	$FeBr_3$/dppdmx	20	83	8500	9200	1.20
3	$FeBr_2$/dppp	5	82	16550	17050	1.37
4	$FeBr_3$/dppp	9	87	17550	17500	1.18
5	$FeCl_3$/dppp	8	76	15350	14500	1.26
6	$FeBr_3$/tmeda	30	55	11200	70600	1.74
7	$CuBr_2$/tmeda	9	85	17200	23700	1.18
8	$CuBr_2$/pmdeta	6	72	13100	14600	1.16
9	$CuBr_2$/hmteta	6	91	18500	18400	1.16

[a] Reactions were performed in toluene at 80 °C; $[MMA]_0 = 4.67$ M, $[MMA]_0/[catalyst]_0/[EBriB]_0 = 200:1:1$; [b] $[MMA]_0/[catalyst]_0/[EBriB]_0 = 100:1:1$; [c] $M_{n,theor.} = ([MMA]_0/[EBriB]_0) M_{MMA} \times$ Conv.(%) $+ M_{EBriB}$; M_{MMA} and M_{EBriB} are the molecular weights of the monomer (MMA) and the initiator (EBriB). hmteta = 1,1,4,7,10,10-hexamethyltriethylenetetramine.

The molecular weight and molecular weight distribution of poly(methylmethacrylate) (PMMA) obtained from $CuBr_2$/hmteta were well behaved ($M_w/M_n = 1.16$). The advantage of polymerizations catalyzed by high oxidation state metal salts is that it overcomes the limitation of using transition-metal complexes, which can be easily oxidized to higher oxidation states an interrupt the process. To compare the normal ATRP with the system in this study, polymerizations of MMA with $FeBr_2$/phosphorus ligands were conducted (see Table 1 and the Supporting Information). In the cases of polymerizations with $FeBr_2$/dppdmx and $FeBr_2$/dppp, the molecular weights were higher than the predicted values, and the PDI values were high, both of which indicated that the lower efficiency of the initiation with the catalyst system was presumably caused by the slow deactivation. However, the ATRP of MMA in the presence of $FeBr_3$/dppdmx or $FeBr_3$/dppp can give PMMA with a molecular weight that matches the theoretical values and quite a low polydispersity (Table 1, entries 2 and 4).

To study the applicability of our systems, the polymerizations of methyl acrylate (MA), *n*-butylmethyl acrylate (BMA), and styrene were also performed by using $FeBr_3$/dppp as the catalyst. As shown in Table 2, the molecular weights of prepared PMA and PS were close to the theoretical values, and the polydispersities were very low. In addition, $FeBr_3$/dppp can still mediate a controlled BMA polymerization ($M_w/M_n = 1.35$) in spite of the low initiator efficiency. Notably, the slow rate of MA polymerization may be related to the gradual precipitation of the complex from the reaction.

Removing the catalyst after polymerization is a very important step because it can affect the properties of the polymer. Therefore, many purification methods have been explored for ATRP.[10] Using a small amount of catalyst is the simplest method for reducing the catalyst residue from ATRP polymers.[11] In the cases where the polymerization was carried out with a ratio of 0.1 or 0.05 of the catalyst to the initiator, the high initiation efficiencies and narrow molecular weight distributions were obtained (Table 2, entries 4 and 5). Even with the ratio of 0.01 of the catalyst to the initiator, the polydispersity ($M_w/M_n = 1.33$) was still low, representing the maintenance of the living character at low catalyst concen-

Table 2: ATRP reactions of different monomers catalyzed by $FeBr_3$/dppp.

Entry	Substrate	[Fe]/[I]	t [h]	Conv. [%]	$M_{n,theor.}$ [g mol^{-1}]	$M_{n,GPC}$ [g mol^{-1}]	PDI
1	MA[a]	1	24	40	3600	4300	1.18
2	MA[b]	1	24	35	3200	4000	1.20
3	BMA[c]	1	9	54	15 400	20 700	1.35
4	MMA[d]	0.1	4	42	4400	5100	1.16
5	MMA[d]	0.05	4	41	4300	6500	1.23
6	MMA[d]	0.01	12	54	5600	11 100	1.33
7	MMA[e]	1	10	55	44 100	70 400	1.16
8	St[e]	1	12	54	5800	6750	1.12
9	St[e]	1	24	82	8700	9050	1.16
10	St[g]	1	24	75	7950	8500	1.12

[a] 80 °C, toluene; $[MA]_0 = 5.55$ M; $[EBriB]_0 = 55.5$ mM. [b] 80 °C, toluene; $[MA]_0 = 5.55$ M; $[MBrP]_0 = 55.5$ mM. [c] 90 °C, toluene; $[BMA]_0 = 3.15$ M; $[EBriB]_0 = 15.8$ mM. [d] 80 °C, toluene; $[MMA]_0 = 4.67$ M, $[EBriB]_0 = 46.7$ mM. [e] 80 °C, toluene; $[MMA]_0 = 4.67$ M, $[EBriB]_0 = 5.84$ mM. [f] 110 °C, no solvent; $[St]_0 = 8.70$ M; $[PEBr]_0 = 87.0$ mM. [g] 110 °C, no solvent; $[St]_0 = 8.70$ M, $[PECl]_0 = 87.0$ mM, Fe = $FeCl_3$. MBrP = methyl 2-bromopropionate, PEBr = 1-phenylethyl bromide, PECl = 1-phenylethyl chloride.

tration (Table 2, entry 6). The low initiation efficiency may be because of side reactions caused by trace amounts of oxygen or other impurities.[11] In addition, the $FeBr_3$/dppp system provided very good control of obtaining high molecular weight PMMA (Table 2, entry 7). The polydispersity remained narrow ($M_w/M_n = 1.16$).

To understand the mechanism of polymerization of MMA initiated by $FeBr_3$/dppp/EBriB, a radical scavenger (2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) or galvinoxyl) was added to the reaction system after 1 hour. After 9 hours the molecular weights had not changed and the molecular weight distributions remained narrow, which indicated that the polymerization was immediately and completely terminated by the radical scavengers (see the Supporting Information). Therefore, the iron(III)-catalyzed polymerization of MMA proceeded by a radical mechanism. In addition, the controlled nature of the $FeBr_3$/dppp system was confirmed by adding a fresh portion of MMA in a chain extension experiment, in which an increase in the M_n of PMMA was observed and the polydispersities remained narrow (see the Supporting Information).

In summary, the results reported herein strongly indicate that iron(III)-mediated polymerization in the absence of any radical initiator or reducing agent proceeds through a living radical polymerization mechanism. In addition, it is particularly interesting that the iron(III)-catalyzed ATRP of MMA with phosphorus-containing ligands was found to be a better controlled ATRP compared to the conventional system. The ATRP reactions of MA, BMA, and styrene were successfully performed by using $FeBr_3$/dppp as the catalyst. A living polymerization of MMA could also be achieved at low catalyst concentration. The effort to characterize the catalytic species is still ongoing, and studies are now in progress to explore the new catalyst systems for polymerizing different monomers.

Experimental Section

All reagents and solvents were purchased from commercial sources and used without additional purification.

General procedure for iron(III)-catalyzed ATRP of MMA: A Schlenk flask was charged with $FeBr_3$ (69.1 mg, 0.234 mmol) and the dppp ligand (123.1 mg, 0.467 mmol). The flask was sealed with a rubber septum and was cycled three times between vacuum and nitrogen to remove the oxygen. The degassed solvent (4 mL) (in solution polymerization), anisole (1 mL), and MMA (5 mL, 46.7 mmol) were then added to the flask by using degassed syringes. The solution was stirred for 20 min at room temperature and then EBriB (34.7 μL, 0.234 mmol) was added. The flask was sealed with a new rubber septum and degassed by three freeze/pump/thaw cycles to remove the oxygen. The flask was immersed in a thermostated oil bath. At timed intervals, samples were withdrawn from the flask with a degassed syringe, diluted with THF, and then filtered through a column filled with neutral aluminum oxide to remove the iron catalyst. Parts of the polymer solution were used for gas chromatography (GC) measurements to determine the monomer conversions. Other parts of the PMMA solution were then precipitated by using an excess of n-hexane, and these polymers were dried under vacuum for 24 h in preparation for gel permeation chromatography (GPC) measurements to determine the molecular weights of the polymers. More details are given in the Supporting Information.

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