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A neutral Ni(II) acetylide-mediated radical polymerization of methyl methacrylate using the atom transfer radical polymerization method

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Abstract

A neutral nickel σ-acetylide complex [Ni(C≡CPh)$_2$(PBu$_3$)$_2$] (NBP) is used for possible atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in conjunction with an organic halide as an initiator [R–X: CCl$_4$, CH$_3$Cl, BrCCl$_3$, C$_2$H$_5$Br, and C$_5$H$_9$Br] in toluene at 80 °C. Among these initiating systems, BrCCl$_3$/NBP gave the best controlled radical polymerization of MMA and produced polymer with relatively narrow molecular weight distribution ($M_w/M_n \approx 1.3$). The ATRP of MMA is preliminarily identified by the following facts: (1) the present MMA polymerization initiated by BrCCl$_3$/NBP is completely hindered by the addition of TEMPO; (2) the conversion shows a typical linear variation with time in semilogarithmic coordinates; (3) the measured number-average molecular weights of polymer show a linear increase with conversion and agree closely with the theoretical values; (4) the resulting polymer chain contains a dormant carbon–halogen terminal.
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Keywords: Methyl methacrylate; Nickel acetylide complex; Organic halide; Initiator; Atom transfer radical polymerization

1. Introduction

The past few years have witnessed significant progress in the field of living free radical polymerization [1a]. Among these new developed methods, atom transfer radical polymerization (ATRP) has been extensively studied [1], and a number of transition metal complexes based on Cu [2–5], Fe [6,7], Ni [8–11], Ru [12,13], Pd [14] and so on have been applied to activate the dormant carbon–halogen terminal reversibly into radicals via consecutive single electron redox cycles of the central metals. Transition metal complexes are possible the most important components of ATRP. A key feature of these complexes is that their catalytic activity and selectivity are strongly ligand dependent [1b] as suitable coordination atmosphere is of benefit to their good solubility and low redox potential. So, for further developments of ATRP, it is important to widen and define the effective metal complexes.

Alternatively, a series of Ni(II)-based catalysts, i.e., NiBr$_2$(PPh$_3$)$_2$ [8,10] and NiBr$_2$(PBu$_3$)$_2$ [9], were found to induce ATRP of methyl methacrylate (MMA) in the presence of organic halides as an initiator (such as CCl$_4$, BrCCl$_3$). In the case of NiBr$_2$(PPh$_3$)$_2$ system, since NiBr$_2$(PPh$_3$)$_2$ complex appears not to be soluble or thermally stable enough in organic solvents, a Lewis acid Al(OiPr)$_3$ [8,9] or a high monomer concentration and a large excess of PPh$_3$ are needed to improve the control over the MMA polymerization [10]. On the other hand, the high solubility and thermally stable of NiBr$_2$(PBu$_3$)$_2$ permits living polymerization in the absence of Al(OiPr)$_3$ [9]. In general, homogeneous systems allow for the

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detailed kinetic and mechanistic studies of ATRP as well as for polymers with lower polydispersities. More recently, a zerovalent nickel complex, Ni(PPh$_3$)$_4$, was found to be able to induced ATRP of MMA in conjunction with an organic bromide as an initiator in the presence of Al(OiPr)$_3$ additive [11]. The polymerization behavior is similar to the NiBr$_2$(PPh$_3$)$_2$ system, i.e., in absence of Al(OiPr)$_3$ additive, the polymerization apparently slowed down and the polydispersities became broader. A point of interest in the nickel-based ATRP is that all of these complexes applied are metal halides or zerovalent counterparts. In fact, to the best of our acknowledge, none of late transition metal-based acetylide complex has been examined in ATRP.

In the research of alkyne polymerization, some transition metal acetylides were found to be active catalysts for alkynes cyclotrimerization or polymerization [15]. In these reactions, a coordination/insertion mechanism has been suggested. The polymer chain was assumed to begin by insertion of a metal center π-coordinated monomer in the metal-alkynyl bond. Recently, we have shown that neutral Pd(II) or Ni(II) acetylide complexes [M(C≡CR)$_2$(PPh$_3$)$_2$, M=Pd, Ni; R=Ph, CH$_2$OH, CH$_2$OOCCH$_3$, CH$_2$OOCPh, CH$_2$OOCPhOH-o] were efficient initiator for MMA radical polymerization [16]. It is worthy that these Pd(II) or Ni(II) complexes show unique stability in air and good catalytic activity in CHCl$_3$ or CCl$_4$. However, these triphenylphosphine complexes have poor solubility in toluene (which is common used as solvent in ATRP of MMA), and easily appeared to decomposed in prolonged use in polymerization in toluene [16] or in bulk. On the contrary, the tributylphosphine complex, i.e. Ni(C≡CPh)$_2$(PBu$_3$)$_2$ (NBP), has a good solubility and thermally stability in toluene. Given these concepts, this study was to investigate the catalytic activity of a Ni(II) acetylide complex (NBP) for the MMA polymerization using ATRP method for the first time. The preliminary results indicate that the transition metal acetylide complexes may be developed into a new type of catalyst for the ATRP of MMA.

2. Experimental

2.1. Materials

All solvents were analytical grade and dried with activated alumina. MMA was dried over CaH$_2$ and distilled under Ar atmosphere at reduced pressure. CCl$_4$, BrCCl$_3$, C$_2$H$_5$Br, C$_5$H$_9$Br, CHCl$_3$ were distilled under argon atmosphere before use and stood under argon at 0 °C. 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Aldrich) was used as received.

NiCl$_2$(PBu$_3$)$_2$ [17] and Ni(C≡CPh)$_2$(PBu$_3$)$_2$ (NBP) [18] were prepared according to the literatures.

2.2. Polymerization

All procedures for polymerization were carried out under purified Ar atmosphere. A typical polymerization procedure is as follows: into a 30 ml well-dried ampoule, NBP as catalyst, toluene as solvent, and BrCCl$_3$ as initiator in turn, slightly shook to obtained a homogeneous solution, and then MMA was injected. After the mixture stood at 80 °C for a definite reaction time, HCl/ethanol (10%, 0.5 ml) was added to decompose the catalyst, and THF (5 ml) was added to dissolve the resulting polymers, which were precipitated as a white wadding by the addition of large excess of ethanol. Poly(methyl methacrylate) (PMMA) was washed with ethanol and dried in vacuum at room temperature for 24 h. MMA conversion was approximately determined from the amount of PMMA obtained [10]. (The best way to determine the monomer conversion is from the concentration of residual monomer measured by gas chromatography since the low molecular weight PMMA may be soluble in the precipitate.)

2.3. Oligomers for end group characterization

The oligomerization of MMA was carried out with NBP in BrCCl$_3$ (as solvent) at 60 °C when [MMA] and [MMA]/[NBP] are 3.13 M and 30, respectively. The reaction was terminated by adding 1 ml of 10% HCl/methanol after 4 h of oligomerization. The quenched reaction solution was evaporated to dryness to give a solid product, which was subsequently diluted with toluene (≈5 ml). The diluted solution was washed with water, and evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature.

2.4. Measurements

^{1}H-NMR spectra were taken on a Unity Inova-400 (400 MHz) spectrometer in CDCl$_3$ at 25 °C or in CD$_3$COCD$_3$ at 30 °C, using tetramethylsilane as the internal reference. The molecular weight ($M_{n,SEC}$ and $M_{w,SEC}$) and the polydispersity index (M_w/M_n) of PMMA were measured by SEC on a Waters 208 size exclusion chromatography with three μ-styragel linear columns (10^5, 10^4, 10^3) versus polystyrene standard, in THF at 25 °C.

3. Results and discussions

3.1. Effect of organic halides on the MMA polymerization by NBP

The Ni(II)-based acetylide complex Ni(C≡CPh)$_2$-(PBu$_3$)$_2$ (NBP) is easy to prepare and soluble in

common organic solvent. Moreover, it is air and moisture stable and can be handled easily in open air.

NBP is employed for polymerization of MMA in conjunction with an organic halide in toluene at 80 °C using ATRP method. In the present conditions, NBP alone shows almost no catalytic activity for the MMA polymerization; however, it shows very high activity for the MMA polymerization in conjunct with an organic halide, effects of organic halides on the MMA polymerization are shown in Table 1. According to the mechanism of nickel-mediated ATRP of MMA [8,9], the organic halide is employed as an initiator in the present polymerization. As shown in Table 1, the polymerization using CCl_4, $BrCCl_3$ or $CHCl_3$ as initiator is very quick as high conversion of 94%, 99%, and 69% (11 h) is obtained, respectively; in contrast, the polymerization with C_2H_5Br or C_5H_9Br is relatively slow. Moreover, the number-average molecular weight ($M_{n,SEC}$, determined by SEC) of the polymers thus obtained with CCl_4 or $CHCl_3$ is much higher than the calculated value ($M_{n,calc}$, assuming that one molecular R–X generates one living polymer chain [11]), indicating there is some radical termination via coupling reaction or side reaction during the polymerization as well as probably due to the initiation slower than the propagation; meanwhile, the $M_{n,SEC}$ of PMMA with C_2H_5Br or C_5H_9Br is much smaller than the calculated value, which may be due to the several new active centers formed during the chain transfer process or redox reaction between Ni(II) and Ni(III) species as well as probably due to the initiation faster than the propagation. Among these organic halide initiators, $BrCCl_3$ gives an initiation efficiency (f) of 0.87 ($f = M_{n,calc}/M_{n,SEC}$), which is most close to 1 and quite similar to the value reported by Sawamoto and co-workers [8] or Jérôme et al. [10]. These results imply that $BrCCl_3$ maybe the most suitable initiator for the ATRP of MMA in the present conditions.

3.2. ATRP of MMA initiated by NBP/BrCCl₃

The MMA polymerization with NBP/$BrCCl_3$ initiating system using ATRP method is carried out in toluene at 80 °C. The NBP/$BrCCl_3$ initiating system induced a smooth polymerization without an induction phase, and conversion reached 95% in 5 h (Fig. 1). The linear time dependence of $\ln([M]_0/[M]$ shown in Fig. 1 is consistent with a controlled polymerization that is first-order with respect to monomer and the concentration of growing radicals remained constant.

Fig. 2 shows the dependence of the number-average molecular weight ($M_{n,SEC}$) and the polydispersity (M_w/M_n) of obtained PMMA versus conversion. The $M_{n,SEC}$ increased in direct proportion to monomer conversion, which is in agreement with a controlled process with an approximately constant number of growing chains. However, although a unimodal distribution is observed, the polydispersity is slightly broad and broaden with conversion. In addition, an initiation efficiency (f) of 0.76 has been calculated at the conversion of 80%.

On the other hand, a series of experiments is carried out, where the mole ratio of monomer to $BrCCl_3$ is varied (100, 250, 500, and 1000), while the concentration of NBP and MMA are kept constant. As shown in Table 2, on the increase in the mole ratio of monomer to $BrCCl_3$ from 100 to 1000 (entries 1–4), the conversion of polymerization is decreased apparently from 99% to 69% while the $M_{n,SEC}$ is varied from 80,000 to 24,700 respectively and accompanied with an increase in the initiation efficiency from 0.36 up to 0.87. These results indicate that the molecular weight can be controlled with use of the bromide initiator $BrCCl_3$ and are similarly to a typical ATRP. However, the polydispersity also slightly broadens from 1.33 to 1.81.

According to the reported results [9], in the ATRP of MMA initiated by $NiBr_2(PBu_3)_2/BrCCl_3$ system, a high

Table 1
Effect of the organic halide on the MMA polymerization with NBP[a]

Entry	[MMA] (M)	[NBP] (mM)	R–X	[R–X] (mM)	Conversion (%)	$M_{n,SEC}$ (×10⁴)	$M_{n,calc}$[b] (×10⁴)	M_w/M_n	f[c]
1	2.8	14	/	/	~0	/	/	/	/
2	2.8	14	CCl_4	4.7	94	11.77	5.64	1.70	0.48
3	2.8	14	$CHCl_3$	4.7	82	17.40	4.92	1.58	0.28
4	2.1	20	C_2H_5Br	3.0	66	1.89	5.28	1.80	2.79
5	2.1	20	C_5H_9Br[d]	3.0	57	1.39	4.56	1.51	3.28
6[e]	2.8	12	$BrCCl_3$	3.0	69	8.00	6.92	1.81	0.87

[a] Conditions: toluene, 24 h, 80 °C, under argon.
[b] $M_{n,calc} = ([monomer]_0/[initiator]_0) \times MW \times conversion$, and MW is the molecular weight of MMA.
[c] $f = M_{n,calc}/M_{n,SEC}$.
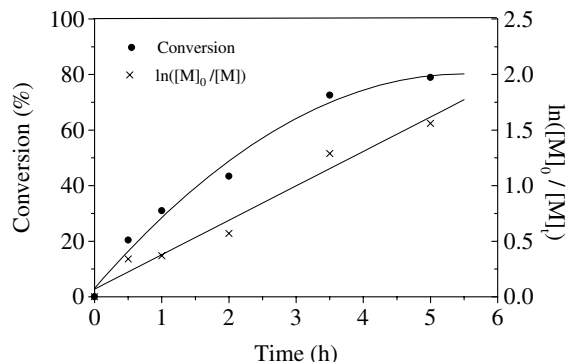[d] C_5H_9Br = cyclopentyl bromide.
[e] 11 h.

Fig. 1. Plots of the conversion and $\ln([M]_0/[M])$ vs time (h) for MMA polymerization in toluene at 80 °C, under argon. Conditions: $[MMA]_0 = 5.6$ M, $[NBP]_0 = 20$ mM, $[CCl_3Br]_0 = 4.7$ mM.
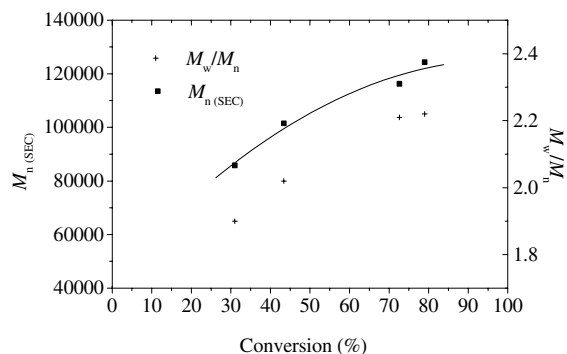

Fig. 2. Conversion dependence on $M_{n,SEC}$ and M_w/M_n for MMA polymerization. Conditions: at 80 °C, $[MMA]_0 = 5.6$ M, $[NBP]_0 = 20$ mM, $[BrCCl_3]_0 = 4.7$ mM, toluene, under argon.

concentration of $NiBr_2(PBu_3)_2$ is of benefit to a faster polymerization and narrower polydispersity, which is most probably because large amount of $NiBr_2(PBu_3)_2$ effectively fastens the interconversion between the dormant and activated species via redox reaction between Ni(II) and Ni(III) species. In the present study, a series of polymerizations at different concentrations of NBP (6–50 mM) have been carried out, and the results are illustrated in Table 2. It is observed that the polymerization proceeded faster as the conversion rapidly changing from 66% up to 96% with the nickel concentration increased from 6 to 12 mM (entries 5–6), while almost no significant increase is observed beyond this level (entry 7, a conversion of 99% is obtained with 50 mM of NBP). The effect of the NBP concentration on the polydispersity is also observed, where they become narrower with higher concentration of NBP. For example, when the NBP concentration is increased from 6 to 50 mM, the polydispersity is obviously decreased from 1.68 to 1.33. As a conclusion, high concentration

of NBP in conjunction with $BrCCl_3$ maybe the most suitable initiating system for the present polymerization because of its high activity (conversion = 99%), high initiation efficiency ($f = 0.75$) and low polydispersity ($M_w/M_n = 1.33$) (entry 7).

### 3.3. Polymerization mechanism and end-group analysis

To clarify the nature of the polymerization, potential terminating agents (methanol used as anion scavenger and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) used as radical scavenger) are added to the reaction system with $NBP/BrCCl_3$ at 80 °C in toluene. Although the present MMA polymerization system cannot be completely hindered by the incorporation of a weak radical inhibitor, e.g., hydroquinone, however, it is completely hindered by the addition of TEMPO, a strong and efficient radical scavenger. Careful experiments showed that no matter when (in the beginning or 2 h of polymerization) TEMPO (2 equiv to NBP) was added into the polymerization system, the polymerization was completely stopped. In addition, methanol, an anion scavenger, did not affect the polymerization, which proceeded without significant changes in rate, molecular weight and its distribution. In addition, the microstructure of PMMA prepared in this work was determined by the ^{1}H-NMR spectrum of PMMA [19]. The syndiotactic contents (rr triad) range from 62% to 65%, which are in line with the tacticity usually reported for PMMA initiated by a free radical initiator, i.e., ∼60–65% syndiotactic triads [19]. These results indicate that the present polymerization proceeded via a radical mechanism.

According to the mechanism provided by Sawamoto [9] for ATRP of MMA with $NiBr_2(PBu_3)_2$-based system, the resulting polymer chain contains a dormant carbon–halogen terminal, which is reversible and could be homolytically cleaved into a carbon radical to induce a new living radical polymerization. Thus, the polymer obtained with $NBP/BrCCl_3$ system should be able to initiate the polymerization of a fresh feed of MMA. It is observed that no PMMA was prepared after 48 h of polymerization using MMA/NBP system without initiators in toluene at 80 °C. However, if a carefully isolated PMMA ($M_{n,SEC} = 24,000$; $M_w/M_n = 1.74$; ∼20 mg) was added with NBP instead of $BrCCl_3$, 97% conversion of monomer is observed after 48 h of polymerization in toluene at 80 °C, with an increase of $M_{n,SEC}$ up to 74000 and of the polydispersity to 2.68. The experimental result demonstrates the presence of a bromine atom at the end of the PMMA, and indicates that the polymerization possibly proceeds via the reversible activation of the C–Br bond originating from $BrCCl_3$ by the Ni(II) acetylide complex. On the other hand, as seen from Fig. 3, ^{1}H-NMR spectrum of the oligomer (OMMA) shows a series of small peaks at the range of 7.47–7.77 ppm,

Table 2
The MMA polymerization with NBP/BrCCl₃ initiating system using ATRP method

Entry	[NBP] (mM)	[BrCCl₃] (mM)	[MMA]/ [BrCCl₃]	Time (h)	Conv (%)	$M_{n,SEC}$ ($\times 10^4$)	$M_{n,calc}$ ($\times 10^4$)	M_w/M_n	f
1	12	3	1000	11	69	8.00	6.92	1.81	0.87
2	12	6	500	11	71	7.82	3.55	1.62	0.45
3	12	12	250	11	85	4.24	2.13	1.57	0.50
4	12	30	100	11	90	2.47	0.90	1.33	0.36
5	6	24	125	24	66	1.82	0.83	1.68	0.45
6	12	24	125	24	96	2.06	1.20	1.52	0.58
7	50	24	125	24	99	1.65	1.24	1.33	0.75

Conditions: [MMA]₀ = 2.8 M, toluene, 80 °C, under argon.
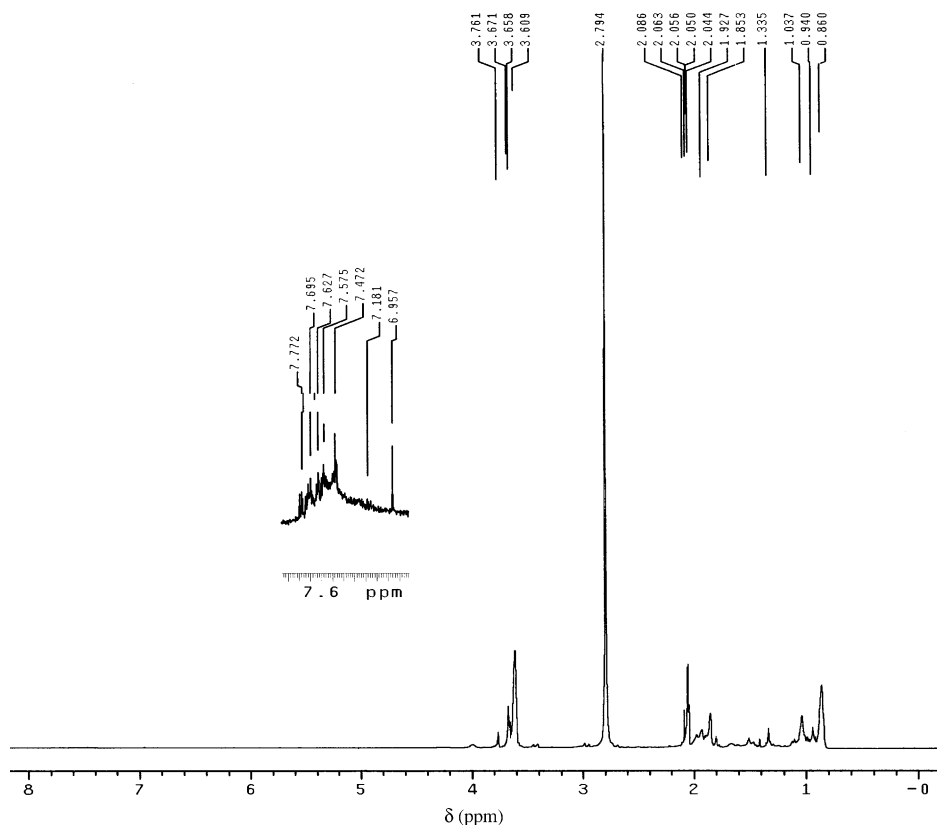
Fig. 3. ¹H-NMR spectrum of OMMA (CD₃COCD₃, 400 HMz, 30 °C).

which could be assigned to the chemical shifts of phenyl protons of C≡CPh group in NBP. Although these peaks are very small, repeated tests always show that there are several peaks at the same range of chemical shifts. These results indicate the present polymerization also might be partly induced by an alkynyl radical, which might be one causes of the relatively broad molecular weight distribution.

To examine the living nature of the MMA polymerization with NBP/BrCCl₃ initiating system using ATRP method, a fresh feed of MMA was added to the reaction

mixture [1] when most of the initial monomer charge was consumed (⩾70% conversion). After the addition, a smooth second-phase polymerization took place, and at least 70% consumption of the added MMA is reached in an additional 18 h, while the molecular weight (M_n) increased from 13,200 to 84,200 with MWDs ($M_w/M_n =$ 1.90 and 2.83, respectively) remaining unimodal and

[1] Conditions: [MMA] = 2.8   M,   [MMA]/[NBP] = 200, [MMA]/[BrCCl₃] = 800, toluene, 80 °C, under argon.

shifted to a higher molecular weight. These results showed that NBP/BrCCl$_3$ system is suitable for ATRP of MMA.

4. Conclusions

This paper presents a novel type of nickel(II)-based MMA polymerization initiator using ATRP method. A highly soluble and air/thermally stable nickel acetylide complex, Ni(C≡CPh)$_2$(PBu$_3$)$_2$ (NBP), induced possibly ATRP of MMA in conjunction with an organic halide such as BrCCl$_3$, similarly to the reported Ni(II) derivatives [8–11]. Compared to the Ni(II) halides such as NiBr$_2$(PBu$_3$)$_2$ and NiBr$_2$(PPh$_3$)$_2$ [8–10] or the Ni(0) complex such as Ni(PPh$_3$)$_4$, the Ni(II) acetylide complex induced a significantly faster living radical polymerization of MMA, i.e., 99% conversion of 24 h polymerization, and give polymers with relatively narrow molecular weight distributions ($\sim$1.33). Molecular weights of obtained PMMA can be controlled by feed ratio of monomer to initiator. Although a higher concentration of the acetylide complex or a suitable organic halide partner is of benefit to improve the control over the MMA polymerization, the ability of the Ni(C≡CPh)$_2$(PBu$_3$)$_2$-mediated initiator system for inducing ATRP of MMA is relatively poor as compared to the reported system [8–11], i.e., a broaden of the polydispersity with the increase of monomer conversion (Fig. 2). The polymerization most probably proceeds via the homolytic cleavage of the terminal C–X bond assisted by the redox reaction of the complex between Ni(II) and Ni(III) species. This study has shown that divalent nickel complex with metal–carbon bond is a potential effective catalysts for the ATRP of MMA and may lead to a new type of catalyst for ATRP.

Further investigation focuses on improving the control ability of NBP-mediated initiator system together with the precise polymerization mechanism are now in progress.

Acknowledgements

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