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Nickel-mediated living radical polymerization of styrene in conjunction with tetraethylthiuram disulfide

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Abstract

The radical polymerization of styrene initiated with tetraethylthiuram disulfide (TD)/nickel (II) chloride ($NiCl_2$)/triphenylphosphine (PPh_3) was of living nature via a one-electron redox reaction between nickel(II) and (III) species. The mechanism belonged to reverse atom transfer radical polymerization (reverse ATRP). The living essence was affected by the molar concentration of the initiator and catalyst. With the feed ratio of $[MMA]_0/[TD]_0$ equal to 1000/1, the kinetics was of first order on the monomer. The values of number-average molecular weights measured by gel permeation chromatography (GPC) of resulting polymers were in close agreement with those calculated by the assumption that one living radical generated one polymer chain, and molecular weight distributions were as low as 1.34. α-S_2CNEt_2 and ω-Cl were demonstrated to end-cap the polymer chain. PSt-*b*-PMMA could be produced by the polymerization of MMA initiated with the resulting PSt-Cl/CuCl/bpy through a normal ATRP procedure. © 2002 Published by Elsevier Science Ltd.

Keywords: Living radical polymerization; Nickel chloride; Reverse atom transfer radical polymerization

1. Introduction

The control on the molecular weight and molecular weight distribution of resulting polymers is poor in conventional radical polymerization processes. The development of living radical polymerization has been a long-standing goal in polymer chemistry.

So far, atom transfer radical polymerization (ATRP) is one of the most efficient methods to control radical polymerizations [1,2]. This living polymerization based on the reversible formation of radicals from organic halides in conjunction with transition metal complexes is a direct extension of organic Kharasch reaction [3,4]. Sawamoto et al. [5], Matyjaszewski et al. [6] and Percec et al. [7] were the first to report ATRP by the use of ruthenium and copper catalysts. Since then, the catalyst has been expanded to other transition metal halides [8–13].

Especially in recent years the number of reviews on the variety of catalysts employed in this process has mushroomed. Nickel, a late transition metal, differs from ruthenium or copper. Due to its preference to oxidative addition and reductive elimination by a two-electron transfer reaction than to a one-electron redox addition process, there have only been a limited number of examples about nickel-catalyzed Kharasch reactions. Even few documents are reported on nickel-based ATRP. Teyssié et al. [9] first introduced homogeneous $[Ni\{o,o'(CH_2NMe_2)_2C_6H_3\}Br]$ catalyst to the controlled polymerization of methyl and *n*-butyl methacrylate (MMA and *n*-BMA). $NiBr_2(Pn\text{-}Bu_3)_2$ or $NiBr_2(PPh_3)_2$ complexes induced living radical polymerization of MMA in the presence of aluminum additive [14,15]. Jérôme et al. [16–18] reported on the controlled radical polymerization of MMA, *n*-butyl acrylate (*n*-BA) and the synthesis of P(MMA)-*b*-P(*n*-BA)-*b*-P(MMA) triblock copolymer with a difunctional initiator catalyzed by $NiBr_2(PPh_3)_2$. Sawamoto et al. [19] gave examples of zerovalent nickel complex, $Ni(PPh_3)_4$, in controlling MMA polymerization with additives. Complex architectural polymer of ruthenium centered six-arm star-shaped PMMA with narrow molecular weight distribution was achieved in the presence of $NiBr_2(PPh_3)_2$ [20]. Without a radical initiator, $NiBr_2(Pn\text{-}Bu_3)_2$ catalyzed air-induced polymerization of phenethyl methacrylate in a living process through an unknown

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Table 1
Data of radical polymerization of St in bulk initiated by TD under various conditions at 105 °C

Entry	$[St]_0/[TD]_0/[NiCl_2]_0$	Ligand	Time (h)	Conversion (%)	$M_{n(cal.)}$ [a]	$M_{n(GPC)}$ [b]	M_W/M_n [c]	f [d]
1[e]	1000/1/0	–	3.3	33	33,000	44,000	1.61	0.75
2[e]	1000/1/0	–	7.5	56	56,000	61,000	1.70	0.92
3	1000/1/5	–	25	27	28,100	126,000	1.60	0.22
4[f]	200/1/3	bpy	5.5	37	–	–	bimodal	–
5[f]	500/1/10	bpy	5.5	62	–	–	bimodal	–
6[f]	200/1/5	PPh_3	12	28	5800	33000	1.21	0.18
7[f]	200/1/10	PPh_3	16.5	38	7900	22000	1.20	0.36
8[f]	500/1/5	PPh_3	22.5	30	15,600	53300	1.11	0.29
9[f]	500/1/5	PPh_3	35	36	18,750	55800	1.12	0.34
10[f]	1000/1/3	PPh_3	39.5	52	54,000	58450	1.29	0.92
11[f]	1000/1/5	PPh_3	24	40	42,000	45000	1.36	0.93
12[f]	1000/1/5	PPh_3	45.5	62	64,600	61850	1.34	1.04
13[g]	1000/1/5	PPh_3	20	35	36,500	39000	1.51	0.94
14[g]	1000/1/5	PPh_3	33	58	60,400	62760	1.48	0.96
15[f]	1000/1/10	PPh_3	23.5	47	48,950	52,000	1.15	0.94

[a] $M_{n(cal.)}$, calculated by $([St]_0/[TD]_0) \times MW_{St} \times$ (Conversion/100), where MW_{St} is the molecular weight of styrene.
[b] $M_{n(GPC)}$ measured by GPC with PSt standards.
[c] M_w/M_n, molecular weight distribution.
[d] f, initiator efficiency, calculated by $M_{n(cal.)}/M_{n(GPC)}$.
[e] At 100 °C.
[f] $[NiCl_2]_0/[Ligand]_0 = 1/3$.
[g] $[NiCl_2]_0/[Ligand]_0 = 1/2$.

mechanism [21]. ATRP of side-group siloxane containing monomer mediated by $NiBr_2(PPh_3)_2$ was reported recently [22].

However, so far, there are few reports concerning nickel complexes used for controlled radical polymerization of styrene (St). In the presence of a hexa-substituted ethane thermal iniferter, nickel(II) chloride ($NiCl_2$) complexed by PPh_3 was first reported to successfully catalyze the radical polymerization of St at 120 °C, resulting in first-order kinetics and linear increase of molecular weight with the monomer conversion by the redox cycle between nickel(I) and (II) catalysts [23].

The success of controlled radical polymerization of St initiated by tetraethylthiuram disulfide (TD) in conjunction with Cu(II) [24] and Cu(I) [25] catalysts promoted us to examine other transition metal catalysts. Here we give an example of evaluating the catalytic activity of $NiCl_2$ in St radical polymerization at a relatively lower temperature, 105 °C. The mechanism, supposed to be based on the halide atom transfer reaction between Ni(II) and Ni(III) species, is quite different from other reports.

2. Experimental

2.1. Materials

TD was synthesized by the documented procedure [24, 25], m.p. 73–74 °C. After passing through a column of silica to remove the inhibitor, St and MMA (98%) were distilled under vacuum. $NiCl_2 \cdot 6H_2O$ (Analytic Reagent, AR) was treated with thionyl oxychloride to obtain anhydrous $NiCl_2$. Cuprous chloride (CuCl) was synthesized from $CuCl_2 \cdot 2H_2O$ (AR) and purified by the literature method [26]. PPh_3 (Aldrich) and 2,2′-bipyridine (bpy, AR) were recrystallized from absolute ethanol to remove triphenylphosphine oxide and impurities, respectively.

2.2. Polymerization

Monomer, initiator, catalyst and ligand were transferred into a baked glass tube. Three freeze–pump–thaw cycles were performed to remove oxygen molecules, and the tube was sealed under high vacuum and placed in an oil bath held by a thermostat at 105 °C. Polymerization was stopped by cooling the tube into liquid nitrogen at a certain time. Afterward, the tube was opened and the contents dissolved in tetrahydrofuran (THF). Polymers were recovered by precipitation into absolute methanol, filtered and dried under vacuum until constant weight.

2.3. Characterization

The monomer conversion was calculated gravimetrically. ^1H NMR spectra were recorded in $CDCl_3$ with a Bruker ARX400 (400 MHz) apparatus at 25 °C with tetramethylsilane (TMS) as the internal reference. Ultraviolet absorption of the polymers was measured in cyclohexane solutions [27] with an Ultraviolet Cary-1E instrument. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymers were measured by a Waters 515 gel permeation chromatography (GPC) instrument equipped with Styragel Columns (10^2-, 10^3-, and 10^4- Å pore sizes) in

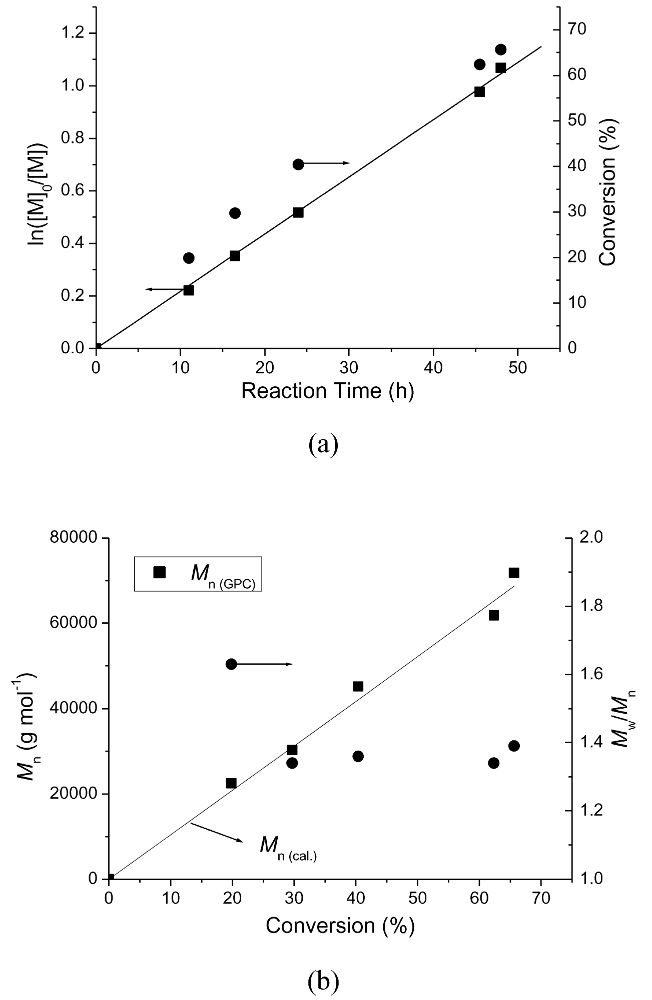


Fig. 1. St polymerization in bulk with TD/$NiCl_2$/PPh_3 initiation system at 105 °C. Conditions: $[St]_0 = 8.7$ mol l^{-1}, $[St]_0/[TD]_0/[NiCl_2]_0/[PPh_3]_0 = 1000/1/5/15$, (a) kinetic plot, (b) dependence of M_n and M_w/M_n on the monomer conversion.

THF at 35 °C with a flow rate, 1.0 ml min^{-1}. Columns were calibrated with PSt standard samples (M_n in the range of 600,000–1000). Waters Millennium 32 was used as data processing software.

3. Results and discussion

3.1. Living polymerization of St with TD/$NiCl_2$/PPh_3 initiation system

Comparison experiments were carried out to estimate the catalytic activity of $NiCl_2$ with TD as the initiator in the radical polymerization of St, and the results are summarized in Table 1.

The polymerization of St with TD initiator alone is of radical nature with rapid reaction rate, resulting in ill-controlled polymers of high M_n and wide M_w/M_n (entries 1 and 2). Adding $NiCl_2$ alone with the ratio of $[TD]_0/[NiCl_2]_0 = 1/5$ to the system, slowed down the rate and produced polymers with high M_n and wide M_w/M_n (entry 3). In the presence of TD and $NiCl_2$, bpy addition could not lower down the reaction rate, and the obtained polymer was ill-controlled with bimodal peaks in GPC traces (entries 4 and 5). Otherwise, in conjunction with PPh_3, the propagating step slowed down, and the obtained PSt had rather narrow M_w/M_n (<1.50) (entries 6–15). With the feed ratio of $[St]_0/[TD]_0$ equal to 200/1 or 500/1 (entries 6–9), $M_{n(cal.)}$, calculated by Eq. (1) on the assumption that one initiating radical generated one polymer chain, was much less than $M_{n(GPC)}$, a value equivalent to PSt standards measured by GPC, resulting in quite low initiator efficiency, *f*, estimated by $M_{n(cal.)}/M_{n(GPC)}$. However, at the ratio of $[St]_0/[TD]_0 = 1000/1$, the addition of $NiCl_2$/PPh_3 controlled the radical polymerization, resulting in polymers with predetermined M_n and narrow M_w/M_n (entries 10–15). Comparing the effect of different ratios of $[NiCl_2]_0/[PPh_3]_0$, it is obvious that excess of PPh_3 ligand lowered down the value of M_w/M_n.

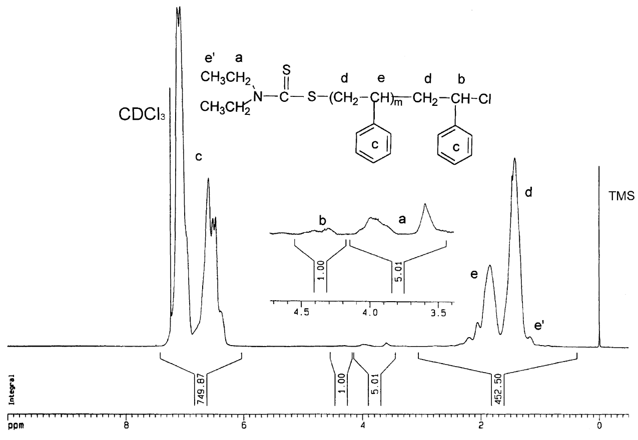


Fig. 2. Representative 400 MHz ^1H NMR spectrum of PSt obtained with TD/$NiCl_2$/PPh_3 initiation system at 105 °C. (in $CDCl_3$). Sample: $M_{n(GPC)} = 15{,}900$ g mol^{-1}, $M_w/M_n = 1.73$.

$$M_{n(cal.)} = ([St]_0/[TD]_0) \times MW_{St} \times \text{Conversion} \qquad (1)$$

Living nature of this polymerization is shown in Fig. 1. The linear plot of $\ln([M]_0/[M])$ versus reaction time through the origin indicated that the polymerization was of first-order on the monomer without induction time and that the concentration of active centers remained constant throughout the course. $M_{n(GPC)}$ increased gradually with the monomer conversion up to 66%, and was close to $M_{n(cal.)}$. M_w/M_n was shown to be as low as 1.34.

Both α- and ω-end groups of a PSt sample prepared were characterized by ^1H NMR spectroscopy as demonstrated in Fig. 2. Besides signals at δ 6.5–7.0 ppm (c) and δ 1.0–2.3 ppm (d, e) ascribed to the repeated monomer unit, characteristic resonance originating from the initiator and catalyst moieties are visible at δ 3.5–4.0 ppm (a) and δ 4.3–4.5 ppm (b), respectively. The former signal derives from the methylene protons of S_2CNEt_2 group while the later is assigned to the terminal methyne adjacent to the Cl

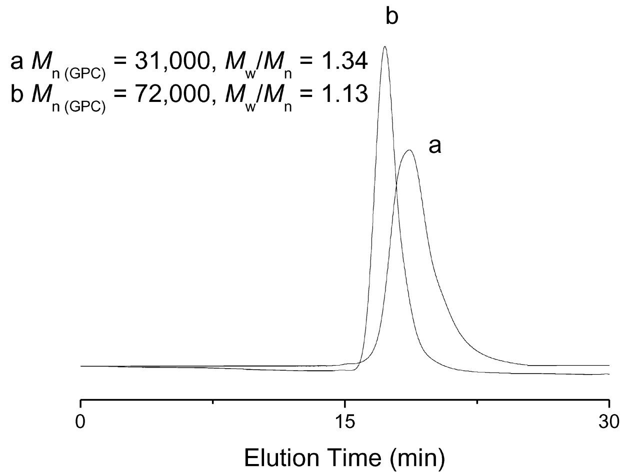


Fig. 3. GPC traces of polymers before and after a normal ATRP procedure initiated with the obtained PSt. Conditions: (a) the obtained PSt–Cl, (b) PSt-*b*-PMMA, 105 °C, bulk, $[MMA]_0 = 9.4$ mol l^{-1}, $[PSt{-}Cl]_0 = 6.4 \times 10^{-3}$ mol l^{-1}, $[PSt{-}Cl]_0/[CuCl]_0/[bpy]_0 = 1/1/3$.

atom. Additionally, the integral ratio of the two signals is 5/1, demonstrating that the chain transfer reaction of TD is negligible because the ratio will be 8/1 when the polymer is ended with S_2CNEt_2 group at both sides.

Diethylthiocarbamoylthiyl group, S_2CNEt_2, is an UV light sensitive group, displaying absorption at 282 nm [28] in the spectrum. By calculation from the absorption in cyclohexane solution, it was demonstrated that 0.9 S_2CNEt_2 group was present in every polymer chain.

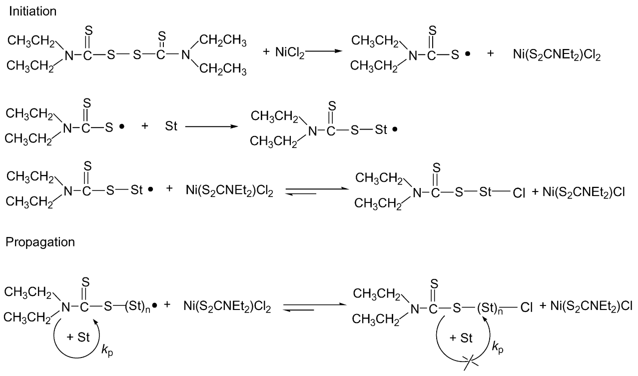
So it can be concluded that S_2CNEt_2 group and Cl atom reside at α- and ω-end of the polymer, respectively.

A fresh feed of MMA added to the resulting PSt in the presence of CuCl/bpy was smoothly polymerized at 105 °C, and M_n of the block copolymer increased further by GPC measurement as displayed in Fig. 3. PSt-*b*-PMMA with $M_{n(GPC)} = 72{,}000$, $M_w/M_n = 1.13$ was obtained without the shoulder peak of the pre-polymer, indicating that PSt was involved in the chain extension reaction.

3.2. Polymerization mechanism

The above results illustrate that $NiCl_2$ can catalyze the living radical polymerization of styrene initiated with TD. Ligand PPh_3 complexed and subsequently partially solubilized the nickel species in St. At the beginning of the polymerization, a change of color from orange to red may correspond to the decomposition of TD and the established equilibrium between Ni(II) and Ni(III) as predicted by the persistent radical effect [29]. On the basis of a single-electron transfer mechanism of Kharasch addition reaction in the presence of Ni(II) species [30–32], the polymerization is supposed to be proceeding as outlined in Scheme 1 (PPh_3 ligand omitted for simplification).

Under heating, $NiCl_2$ induced the homolysis of TD [33]. One initiating radical and the corresponding Ni(III) species [34], $Ni(S_2CNEt_2)Cl_2$, are generated. The radical is capable of reacting with a St molecule to form a monomer radical, which either reversibly combines with the Ni(III) species or propagates excessive monomer molecules, repeating the redox reaction. The generating radical abstracts Cl atom because of the weaker bond energy of Ni–Cl than that of Ni–S, which is resulted from the fact that the bond length of Ni–Cl, 2.27 Å [35], is longer than that of Ni–S, 2.20 Å [36]. The propagating radical is maintained by the Cl atom transfer reaction between the dormant chain and the corresponding Ni(II) catalyst. As a result, Cl atom terminates the polymer chain, which is in accordance with ^{1}H NMR and UV analyses that every polymer chain has one photo-labile group, S_2CNEt_2. Because the initially added catalyst $NiCl_2$ consumes one molar concentration of $Et_2NCS_2^{\bullet}$ radical generating $Ni(S_2CNEt_2)Cl_2$, only one molar concentration of TD is employed in the calculation of $M_{n(cal.)}$ in Eq. (1). This calculation is similar to the reference reporting reverse ATRP of St initiated with BPO/CuBr/dNbpy [37] and of MMA with BPO/Cu (S_2CNEt_2)/bpy [38].



Scheme 1. Polymerization mechanism supposed for living radical polymerization of St initiated with $TD/NiCl_2/PPh_3$.

The competition between the reaction of the radical addition to monomer molecules and the side ones of the reacting components may account for the different initiator efficiency at various molar ratio of $[St]_0/[TD]_0$. Excessive $NiCl_2$ addition in the solution containing TD produces tris(*N*,*N*-diethyldithiocarbamato)nickel(IV) chloride complex, $Ni(S_2CNEt_2)_3Cl$ [39]. As the ratio of $[St]_0/[TD]_0$ is equal to 200/1 or 500/1, the quantity of the initiator and catalyst is more than that at 1000/1 ratio, which results in the larger possibility of the side reaction. While in the dilute system, $[St]_0/[TD]_0 = 1000/1$, this effect is not so obvious, so the living behavior of the radical polymerization of St at 105 °C is not significantly affected.

Further efforts are under progress to give experimental support for this research work.

4. Conclusions

The simple addition of $NiCl_2/PPh_3$ to a bulk polymerization of St initiated by TD allowed the first-order kinetics and the synthesis of polymers displaying controlled M_n up to 72,000 and M_w/M_n as low as 1.34. The molar ratio of the monomer to initiator was indispensable in inducing the propagation in a living procedure. The controlled nature of the polymerization was demonstrated at low molar concentrations of the initiator and the catalyst though side reactions affected it at higher feeds. The polymers obtained are functionalized by α-diethylthiocarbamoylthiyl group and ω-chlorine atom, which can then be used to initiate a normal ATRP process by addition of a second monomer.

Thus far, the living radical polymerization of styrene with TD initiator can be successfully carried out catalyzed by three different transition metal compounds, $CuBr_2$, CuBr and $NiCl_2$, through different mechanic process.

Acknowledgements

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