

REVERSE ATOM TRANSFER RADICAL POLYMERIZATION OF STYRENE WITH COPPER-BASED CATALYST

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Abstract "Living"/controlled radical polymerization of styrene was carried out with diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS)/CuCl₂/bipyridine (bipy) initiation system at 120 °C. The molecular weights of resultant PSt increased with the monomer conversion and the polydispersities were in the range of 1.37 ~ 1.52. A linear $\ln([M]_0/[M])$ versus time plot was also obtained indicating the constant concentration of growing radicals during the polymerization with this initiation system. End group analysis by ¹H-NMR spectroscopic studies showed that the end groups of the polymer obtained is ω -functionalized by a chlorine group from the catalyst and α -functionalized by a (carboxy-cyano-phenyl)-methyl group from the fragments of the initiator. Having Cl atom at the chain end, the PSt obtained can be used as a macroinitiator to promote a chain-extension reaction with fresh St and block copolymerization reaction with a second monomer, such as methyl methacrylate, in the presence of CuCl/bipy catalyst via a conventional ATRP process.

Keywords "Living"/controlled radical polymerization, Reverse ATRP, Styrene, DCDPS/CuCl₂/bipy initiation system

INTRODUCTION

Research in living radical polymerization has been an active field of polymer synthesis because of the merits of radical polymerization, e.g. the tolerance to a wide variety of monomers with various functional groups and mild polymerization conditions^[1]. But due to the facile coupling and disproportion reactions between the propagating radicals during the polymerization, it is very difficult to attain a true living radical polymerization^[2]. In recent years several methods, such as nitroxide-mediated stable free radical polymerization (SFRP)^[3, 4], reversible addition fragmentation chain transfer polymerization (RAFT)^[5] and atom transfer radical polymerization (ATRP)^[6, 7], have been developed to prepare well-defined polymers by radical means.

The metal-catalyzed process, i.e. ATRP, is an efficient way of synthesizing well-defined polymers. Conventionally, in ATRP system the organic halides are used as the initiators to reversibly generate initiating radicals in the presence of complexes of transition metals in their lower oxidation state. The ATRP method was successfully applied to the "living" polymerization of styrenes, acrylates, methacrylates, and acrylonitrile etc. ATRP has also been successfully used to prepare functional polymers, such as block, graft or star copolymers^[8-10]. A variety of transition metals: such as Cu(I)^[11], Ru(II)^[12], Ni(I)^[13], Fe(II)^[14], Rh(II)^[15], Pd(II)^[16] and Re(V)-based^[17] systems were used as catalysts. Among these metals, copper appears to be the most versatile one because a variety of monomers can be readily polymerized in a well-controlled manner. The most exciting example is that employing more solubilizing 4,4'-di-*n*-heptyl-2,2'-dipyridyl (dHbpy) and 4,4'-di-(5-nonyl)-2,2'-dipyridyl (dNbpy) ligands; PSt with a narrow molecular weight distribution (M_w/M_n) as low as 1.05 was successfully synthesized, comparable to the living anionic polymerization^[18].

Though the above-mentioned conventional ATRP method is an efficient way to maintain "living"/controlled radical polymerization of various vinyl monomers, it has two major problems: the halide species RX are toxic

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and the catalysts M_n/L_X can easily be oxidized by the air^[19]. To overcome these drawbacks, the use of conventional radical initiators such as 2,2'-azoisobutyronitrile (AIBN) in the presence of complexes of transition metals in their higher oxidation state has been reported and referred to as "reverse" or "alternative" ATRP by Matyjaszewski *et al.*^[20, 21] and Teyssié *et al.*^[19], respectively. This type of ATRP approaches the same type of equilibrium as the conventional ATRP starting from conventional radical initiators such as peroxide or diazo compounds. Several monomers including styrene (St), methyl methacrylate (MMA), and methyl acrylate (MA) were successfully polymerized via this process. Two kinds of initiators, such as azo- and peroxide compounds, were employed as the initiator in the reverse ATRP system^[19-24]. Because the decomposition of conventional initiators is irreversible, the concentration of primary radicals is rather high, especially at high temperature and at the early stage of polymerization.

In order to attain a the reversible decomposition equilibrium of the initiator in the initiation step in the reverse ATRP system, we first introduced a carbon-carbon bond thermal iniferter such as diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS) instead of AIBN, into the Fe(III)-based catalyst reverse ATRP system^[25-27]. In this article the living radical polymerization of St using a new initiation system, *viz.* DCDPS as the initiator and copper-based metal complex as the catalyst, *i.e.* DCDPS/CuCl₂/bipy, is described. A well-defined polystyrene (PSt) with high molecular weight (up to 47100) and controlled chain end group was obtained through this process. The resultant PSt with a chlorine end capped group can be used as a macroinitiator to promote a chain extension reaction with fresh St and a block polymerization with MMA.

EXPERIMENTAL

Materials

CuCl₂ was purchased from Aldrich Chemical Company and used as received. CuCl was purified by stirring in acetic acid, filtered, washed with ethanol and dried. 2,2'-Bipyridine (bipy) was recrystallized from acetone. Styrene and methyl methacrylate were dried over CaH₂ then distilled under vacuum. DCDPS was prepared according to the method reported previously^[28, 29]. Solvent and other reagents were purified by conventional methods.

Polymerization and Block Copolymerization

The polymerization was carried out in a sealed tube charged with a predetermined amount of a mixture of the reaction components. The mixture was immediately degassed by freeze-thaw cycles and sealed in vacuum. Then it was immersed in an oil bath and heated at the desired temperature. After polymerization for a given time the tube was quenched with ice water to stop the reaction and the resultant polymers were dissolved in tetrahydrofuran (THF), then precipitated with a large amount of methanol and dried. The conversion of polymerization was determined gravimetrically.

Measurements

Molecular weights and molecular weight distributions of the polymer samples were measured at 35°C by gel permeation chromatography (GPC) on a Waters 2410 instrument using THF as the eluent (1.0 mL/min); calibration was with polystyrene standards. ¹H-NMR spectra were taken at 25°C on a Bruker ARX400 (400 MHz) spectrometer in CDCl₃ using tetramethylsilane (TMS) as the internal reference.

RESULTS AND DISCUSSION

As reported by Matyjaszewski and his coworker, control of the polymerization depends to some degree on the concentration of propagating radicals^[7, 11]. In the reported reverse ATRP system using conventional initiator such as AIBN, the decomposition of initiator is irreversible, which makes the concentration of primary radicals rather high, especially at high temperature and at the early stage of polymerization, even using a strong inhibitor, such as CuCl₂, to deactivate the radicals. In fact, the "living"/controlled radical polymerization of St monomer was achieved with the AIBN/CuCl₂/bipy system by using a great excess of deactivator (10 equiv CuCl₂ to AIBN)^[20].

On introducing iniferter DCDPS in place of AIBN in this system, due to the reversibl cleavage of the

iniferter, only a small amount of catalyst (CuCl_2) was needed to inhibit the propagating radicals ($\text{CuCl}_2/\text{DCDPS} = 2$ molar ratio). The lower molar ratio of CuCl_2 to DCDPS used in this work results in a well-controlled radical polymerization of St.

"Living"/Controlled Radical Polymerization of St

Table 1 shows that the measured molecular weight increased with reaction time from 25,500 up to 47,100 as the reaction time extended from 3 h to 36 h for the bulk polymerization of St initiated by the DCDPS/ CuCl_2 /bipy system at 120°C . The molecular weight distributions changed within the range of 1.37–1.52 throughout the polymerization. The GPC elution curves of the resultant PSt are shown in Fig. 1. The curves have a monotonous single peak indicating the controlled manner of polymerization. However, the values of $M_{n(\text{th})}$ are always higher than $M_{n(\text{exp})}$, in which $M_{n(\text{th})}$ is the theoretically calculated number-average molecular weight ($M_{n(\text{th})} = ([\text{St}]_0/2[\text{DCDPS}]_0) \times \text{MW}_{\text{St}} \times \text{conversion}$). The initiating efficiency (f) greater than unity is presumably due to the chain transfer reaction during the polymerization. Similar deviation was observed by Sawamoto *et al.*^[6] and Teyssié *et al.*^[30] with $\text{CCl}_4/\text{RuCl}_2(\text{PPh}_3)_2/\text{MeAl}(\text{ODBP})_2$ and $\text{CCl}_4/\text{Ni}(\text{NCN}')\text{Br}$ initiating systems, respectively. The plot of $\ln([\text{M}]_0/[\text{M}])$ against time t is shown in Fig. 2, which give a straight line passing through the origin, showing that the kinetics is first order in monomer and the concentrations of growing species keep constant during the polymerization. All the above results convincingly reveal that the "living"/controlled radical polymerization of St was well carried out in bulk at 120°C with the DCDPS/ CuCl_2 /bipy initiation system.

Table 1. Results of styrene polymerization in bulk at 120°C ^a

Entry	t (h)	Conv. (%)	$M_{n(\text{GPC})}^b$	$M_{n(\text{th})}^c$	M_w/M_n
1	3	19.3	25,500	20,100	1.52
2	6	28.2	27,200	29,300	1.51
3	12	59.3	35,200	61,600	1.37
4	24	75.2	39,600	78,200	1.48
5	36	86.0	47,100	89,400	1.50

^a Conditions: $[\text{St}]_0 = 8.75 \text{ mol L}^{-1}$, $[\text{CuCl}_2]_0 = 8.75 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{bipy}]_0 = 17.5 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{DCDPS}]_0 = 4.38 \times 10^{-3} \text{ mol L}^{-1}$

^b GPC calibrated with PSt standards

^c $M_{n(\text{th})} = ([\text{St}]_0/2[\text{DCDPS}]_0) \times \text{MW}_{\text{St}} \times \text{conversion}$

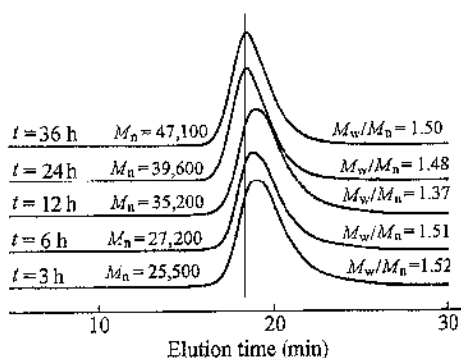


Fig. 1 GPC elution curves of PSt polymerized with DCDPS/ CuCl_2 /bipy initiation system at 120°C
Same conditions as Table 1

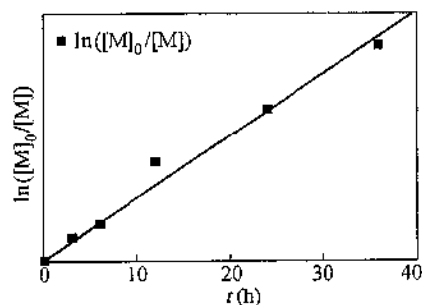


Fig. 2 Time dependence of $\ln([\text{M}]_0/[\text{M}])$ and conversion at 120°C in the bulk polymerization of St, respectively
Same conditions as Table 1

The polymerization of St with this copper-based catalyst proceeded under heterogeneous conditions. By adding a small amount of polar solvent, such as 10% *V/V* dimethylformamide (DMF) or methoxybenzene (anisole), to the reaction mixture, the polymerization system immediately became a homogeneous one and controlling the reaction was easier, as shown in Table 2. This may be attributed to the polarity of the solvent, that

will improve the solubility of the transition metal complex in the reaction system.

Table 2. Results of styrene polymerization in solution at 120°C

Entry	Conditions	<i>t</i> (h)	Conv. (%)	<i>M_n</i> (GPC)	<i>M_n</i> (th) ^d	<i>M_w</i> / <i>M_n</i>
1	In bulk ^a	36	86.0	47,100	89,400	1.50
2	In DMF ^b	68	85.1	82,900	88,500	1.36
3	In anisole ^c	67	80.4	77,700	83,600	1.42

^a Conditions: [St]₀ = 8.75 mol L⁻¹, [CuCl₂]₀ = 8.75 × 10⁻³ mol L⁻¹, [bipy]₀ = 17.5 × 10⁻³ mol L⁻¹, [DCDPS]₀ = 4.38 × 10⁻³ mol L⁻¹

^b Conditions: [St]₀ = 7.88 mol L⁻¹, [CuCl₂]₀ = 7.88 × 10⁻³ mol L⁻¹, [bipy]₀ = 23.6 × 10⁻³ mol L⁻¹, [DCDPS]₀ = 3.94 × 10⁻³ mol L⁻¹

^c Same conditions as entry 2

^d *M_n*(th) = ([St]₀/2[DCDPS]₀) × MW_{St} × conversion

End Group Analysis and Block Copolymerization

It was confirmed by ¹H-NMR spectroscopy that the PSt produced by this initiation system is end-functionalized with an α-(carboxy-cyano-phenyl)-methyl and an ω-chlorine group, as shown in Fig. 3. The broad signal at ca. δ = 4.33 is assigned to the ω-end group, that is, —CH₂C(Ph)H—Cl, which was similarly observed in the paper of Matyjaszewski *et al.*^[20]. The signals at δ = 1.14, 4.08 and 7.41 are attributed to the protons of methyl (f), methylene (e) and the phenyl groups (d), respectively, at the α-chain end which comes from the fragments of DCDPS. Accordingly, the PSt, which was end-functionalized with an α-(carboxy-cyano-phenyl)-methyl group from DCDPS fragments and an ω-chlorine atom group from catalyst, was obtained by this initiation system.

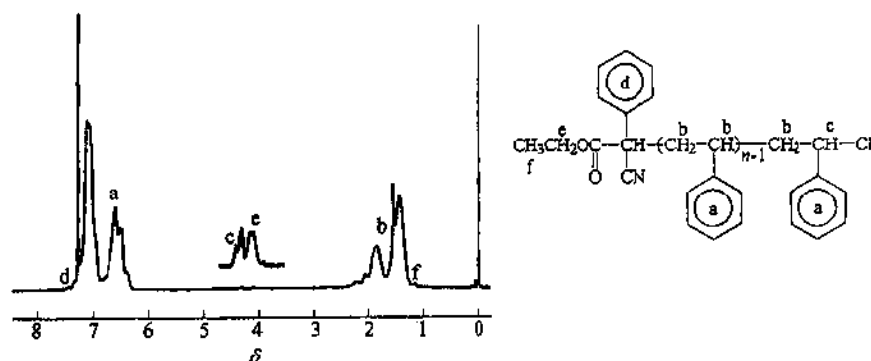


Fig. 3 ¹H-NMR spectrum of resultant PSt (*M_n* = 13300, *M_w*/*M_n* = 1.56) initiated with DCDPS/CuCl₂/bipy (1/2/6) in bulk

To investigate the “living” nature of the polymerization, the chain extension reaction of St was carried out in bulk at 110°C with a macroinitiator, PSt obtained with ω-Cl end group (*M_n* = 25,500 and *M_w*/*M_n* = 1.52), in the presence of CuCl/bipy as catalyst via a conventional ATRP. The *M_n* of the final PSt increased to 143,700 (*M_w*/*M_n* = 1.25), which was demonstrated by the GPC curves shown in Fig. 4. By using the chlorine-terminated PSt as the macroinitiator for the atom transfer radical copolymerization of MMA and PSt-*b*-PMMA block copolymer was obtained. Fig. 5 displays the GPC elution curves of the polymers. There is no additional peak in the final product, confirming that block copolymer has been formed. These results indicate that the DCDPS/CuCl₂/bipy initiation system induced “living” polymerization via a reverse ATRP process.

Polymerization Mechanism

A polymerization mechanism is proposed as depicted in Scheme 1. In the initiation step, the DCDPS iniferter first reversibly cleaves to the primary radicals (R•), which is different from the irreversible process of the conventional initiators in the reverse ATRP system reported before. Then the primary radicals add to the monomer to form the activated monomer radicals. The monomer radicals can react with monomers to create the

propagating chains or directly react with $\text{CuCl}_2/\text{bipy}$ complex by abstracting the chlorine atom to generate an organic chloride and a lower oxidation state metal complex CuCl/bipy . Then the polymer propagates exactly via a conventional ATRP process.

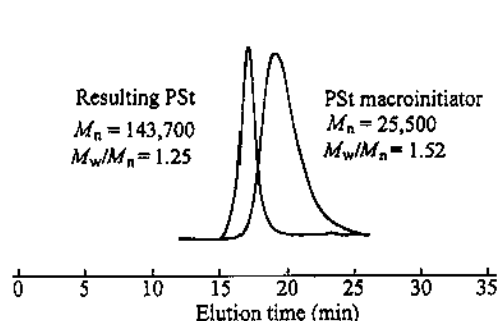


Fig. 4 GPC curves of PSt before and after chain extension reaction in the presence of CuCl/bipy system at 110°C
 Conditions: $t = 36$ h, $[\text{St}]_0 = 8.75 \text{ mol L}^{-1}$, $[\text{PSt}]_0 = 1.43 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{CuCl}]_0 = 2.86 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{bipy}]_0 = 8.58 \times 10^{-3} \text{ mol L}^{-1}$

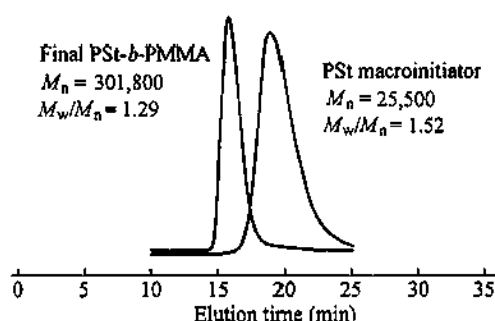
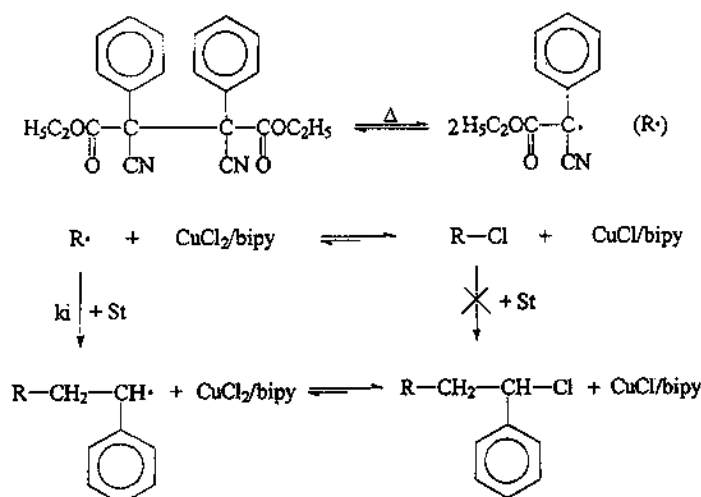
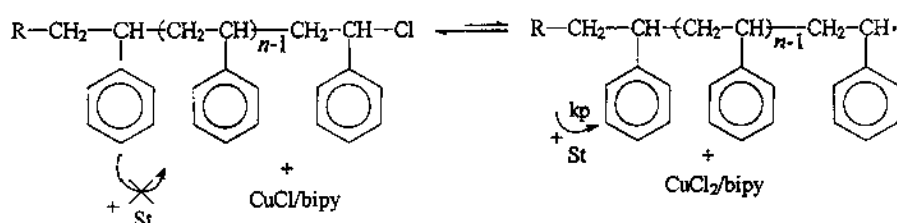


Fig. 5 GPC elution curves of PSt before and after copolymerization with MMA in the presence of CuCl/bipy system at 110°C
 Conditions: $t = 40$ h, $[\text{MMA}]_0 = 9.38 \text{ mol L}^{-1}$, $[\text{PSt}]_0 = 1.51 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{CuCl}]_0 = 3.02 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{bipy}]_0 = 9.06 \times 10^{-3} \text{ mol L}^{-1}$

Initiation:



Propagation:



Scheme 1

CONCLUSION

In conclusion, the "living"/controlled radical polymerization of St was successfully carried out with DCDPS/CuCl₂/bipy initiation system at 120 °C. The polymerization mechanism belongs to a reverse ATRP process. A well-defined PSt with a α -(carbethoxy-cyano-phenyl)-methyl and a ω -chlorine as the end groups and with high molecular weight (up to 47,100) and quite narrow polydispersity index ($M_w/M_n \approx 1.50$) was obtained. The chain extension and block copolymerization reactions also confirm that the PSt obtained could act as a macroinitiator with that ω -chlorine group.

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