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"Nascent" Fe(0)-mediated living radical copolymerization of styrene and acrylonitrile

Abstract: In this work, we reported the synthesis of copolymers of poly(styrene-co-acrylonitrile) via single-electron transfer-living radical polymerization using CCl_4 as an initiator and $Zn(0)$/2,2′-bipyridine (Bpy)/$FeCl_2$ as catalyst complexes. The polymerization was carried out at 25°C. The polymerization proceeded in a living fashion based on "nascent" Fe(0) as the source of the transition metal, which was prepared by $Zn(0)$/$FeCl_2$ in situ. The kinetic experimental results showed that the copolymerization is first-order kinetics. The molecular weights increased linearly with respect to monomer conversion, and narrow polydispersity index values were obtained. The effect of the molar ratio of $[Zn(0)]_0$/$[FeCl_2]_0$ on polymerization was investigated. In addition, the polymerization carried out in different solvents was also investigated. The obtained random copolymer was characterized by ^1H NMR and gel permeation chromatography. The living characteristic was demonstrated by chain extension experiment.

Keywords: acrylonitrile; living polymerization; "nascent" Fe(0); SET LRP; styrene.

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1 Introduction

Conventional free-radical polymerization (FRP) is one of the most effective methods to prepare a polymeric material. Nearly 50% of all commercial synthetic polymers are produced via radical chemistry, which provides a spectrum of materials for various markets (1). However, the main disadvantages of FRP are the poor control over the molecular weight and the polydispersity of the synthesized macromolecules. Controlled/living polymerization (CRP) provides an essential technique to synthesize the polymers with predetermined molecular weight and narrow dispersities, such as block and graft copolymers, and star polymers.

In the past decade, a number of CRP methods have been developed, including stable free-radical polymerization (2, 3), atom transfer radical polymerization (ATRP) (4–6), reversible addition-fragmentation chain transfer (7–9) and single-electron transfer-living radical polymerization (SET LRP) (10–12). Although the mechanism of SET LRP is still debated in the literature, this methodology has received great attention since its emergence in 2006 for the first time. A wide variety of vinyl monomers such as methacrylates (13–15), acrylamide (16) and vinyl chloride (10, 17, 18) can be polymerized in a controlled fashion with the use of these or similar systems.

In the SET LRP system, an equilibrium is established between the active species (polymeric radical) and the dormant polymer through a Cu(0)-mediated outer-sphere single-electron transfer process that has a very low activation energy. Compared with normal ATRP, SET LRP has a number of advantages, such as a large number of monomers, higher reaction rate and easy reaction condition, and provides an excellent control over the molecular weight and distribution. Furthermore, Cu(0) power/wire is used as the catalyst source; the merits of using Cu(0) power/wire for the reaction include the easy removal, the reuse of the catalyst and the resulting colorless reaction mixture and colorless polymers due to the parts per million amount of catalyst used during the polymerization process. N-ligands are used in the SET LRP process, such as Me_6-TREN, TREN, PEI and 2,2′-bipyridine (Bpy), which assists in the disproportionation of Cu(I) complexes to generate Cu(0) in situ and Cu(II) complexes. Recent studies indicated that polar solvent could enhance the disproportionation of Cu(I) complexes (19).

Poly(styrene-co-acrylonitrile) (SAN) polymers with narrow polydispersity are used as compatibilizers to improve the interfacial adhesion of different phases (20). Recently, the Cu(0)-catalyzed living radical copolymerization of styrene and acrylonitrile was investigated using ethyl 2-bromoisobutyrate as an initiator and 2,2′-bipyridine as a ligand. The polymerization proceeded smoothly in dimethyl sulfoxide (DMSO) with higher than 90%

conversion in 13 h at 25°C. The polymerization kept the features of controlled radical polymerization (21).

Halogenated alkanes, such as $CHCl_3$ or CCl_4, which is inexpensive and readily available, are typically used in atom transfer radical addition and were among the first studied as ATRP initiators. Fleischmann and Percec (22) first reported the SET LRP of methyl methacrylate (MMA) using CCl_4 as an initiator in the presence of Cu(0) Me6-TREN at 25°C in DMSO. The reaction followed first-order kinetics, and the polymerization could be driven to completion in 10 h.

Iron is the most abundant transition metal element in the earth's crust and is far less toxic than the precious Cu metal catalysts currently used. There are many excellent works on iron catalyst (23–25).

In this work, random copolymers of p(styrene-co-acrylonitrile) were prepared via SET LRP using CCl_4 as an initiator and "nascent" Fe(0)/2,2′-bipyridine (Bpy) as catalysts. The polymerization was carried out at 25°C in *N,N*-dimethylformamide (DMF). The kinetics on the iron-mediated SET LRP was studied. Also, ^{1}H NMR and gel permeation chromatography (GPC) were utilized to characterize the obtained random copolymer.

2 Experimental

2.1 Materials

Styrene and acrylonitrile were purchased from Tianjin Fuchen Chemical Reagents Factory (Tanjin, China). They were distilled under reduced pressure prior to use. Carbon tetrachloride (CCl_4, 99%), obtained from Hunan HuiHong Reagent Co. Ltd. (Hunan, China), was used without further purification. Anhydrous $FeCl_2$ was obtained from Sinopharm Chemical Reagent Co Ltd. (Shanghai, China). Zinc powder [Zn(0), 98%] was purchased from Shanghai Chemical Reagent. Co. Ltd. (Shanghai, China) and was used as received. DMF, purchased from Tianjin Tianda Chemical Reagents Factory (Tianjin, China), was distilled under reduced pressure prior to use. 2,2′-Bipyridine (Bpy), purchased from Shanghai Yongzeng Chemical Company Ltd. (Tianjin, China), was recrystallized twice from acetone prior to use. Other reagents were used without further purification.

2.2 Polymerization

In a typical experiment, 1.04 g of styrene (0.01 mol), 0.33 g of acrylonitrile (0.006 mol) and a certain amount of Zn(0),

Bpy, DMF, $FeCl_2$ and CCl_4 were in turn placed into a 100-ml, three-neck, round-bottom flask equipped with a magnetic stirring bar, at a ratio of $[styrene]_0/[acrylonitrile]_0/[CCl_4]_0/[Zn(0)]_0/[Bpy]_0/[FeCl_2]_0$ of 200:126:1:0.2:0.4:0.02. The bottle was degassed and charged with N_2. Then the bottle was placed in an oil bath at 25°C.

The SET LRP of acrylonitrile and styrene was carried out. A typical example of the general procedure was as follows: The flask with the reaction mixture was placed in an oil bath at 25°C. After a desired time, the polymer was precipitated in a large excess of methanol. The resultant polymer was filtered and dried at 60°C in vacuo. The monomer conversions were determined gravimetrically.

2.3 Characterization

^{1}H NMR spectrum was recorded on a Bruker 400-MHz spectrometer (Bruker Instruments Inc., Germany) in a $CDCl_3$ solvent and tetramethyl silane as standard.

The number-average molecular weight ($M_{n,GPC}$) and polydispersity index (PDI) values of the copolymers of styrene and MMA were measured on a Waters 1515 GPC system (Wyatt Technology Co., USA), which was equipped with a refractive index detector, using HR1, HR3 and HR4 columns with a molecular weight range of 100–500,000. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 ml/min. The molecular weight analysis was performed at 30°C based on the universal calibration procedure with polystyrene narrow standards.

The theoretical molecular weight ($M_{n,theo}$) of the resulting SAN was calculated by the following equation:

$$M_{n,theo} = ([St]_0 \times F_{St} \times MW_{St} + [AN]_0 \times F_{AN} \times MW_{AN}) / [I]_0 \times Conversion \tag{1}$$

where $[St]_0$ and $[AN]_0$ are the initial concentrations of the monomers in the feed; F_{St} and F_{AN} are the molar fraction of St and AN in the copolymer, respectively, and were determined by ^{1}H NMR; MW_{St} and MW_{AN} are the molecular mass of St and AN, respectively; and $[I]_0$ is the initial concentration of the initiator.

3 Results and discussion

3.1 Preparation of SAN by SET LRP

SAN copolymer was prepared by the SET LRP process using the Fe(0)/Bpy/CCl_4 catalyst system as described in Scheme 1.
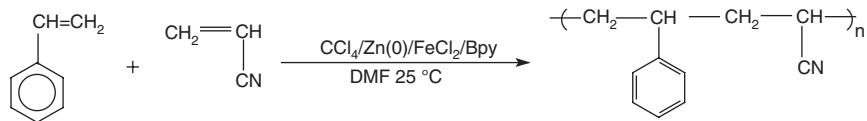
Scheme 1 Mechanism of the SET LRP of St and AN.

The obtained SAN copolymer was characterized by the ^{1}HNMR spectrum, as shown in Figure 1. The chemical shift (δ=6.5–7.5 ppm) corresponded to the phenyl protons of styrene. The chemical shift at δ=2.0–2.3 and 2.9–3.3 ppm was attributed to the protons of CH_2 of acrylonitrile and to the protons of CH_2 and CH of St, respectively. The molar compositions were determined by comparing the relative intensities of the resonance signals at 6.7–7.4 and 2.9–3.3 ppm.

3.2 Kinetics of the copolymerization of acrylonitrile and styrene by SET LRP

In the present work, Fe(0)-mediated living radical copolymerizations of St and AN were carried out at 25°C in DMF with a molar ratio of $[St]_0/[AN]_0/[CCl_4]_0/[Zn(0)]_0/[Bpy]_0/$ $[FeCl_2]_0$ at 200:126:1:0.2:0.4:0.02. The plot of monomer conversion and $\ln([M]_0/[M])$ vs. the polymerization time is shown in Figure 2.

As seen in Figure 2, $\ln([M]_0/[M])$ increases linearly with increasing polymerization time, demonstrating that the radical concentration remains constant through the polymerization process. However, an induction period (about 12 min) was observed under this polymerization condition, which indicates that some time was needed to establish a dynamic equilibrium between the concentrations of the Fe(II) and Fe(III) species as the reaction proceeded during the polymerization process. The apparent rate constant k_p^{app}, derived from $\ln([M_0/M])=k_p^{app}t$, which was 6.94×10^{-6} s^{-1} according to Figure 2.

Figure 3 shows the dependence of the molecular weights ($M_{n,GPC}$) and molecular weight distribution (PDI) vs. the conversion for SET LRP of St and AN in DMF at 25°C with CCl$_4$ as an initiator and Bpy as a ligand. As observed in Figure 3, the M_n values increased linearly with monomer conversion
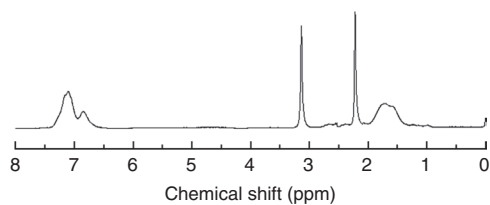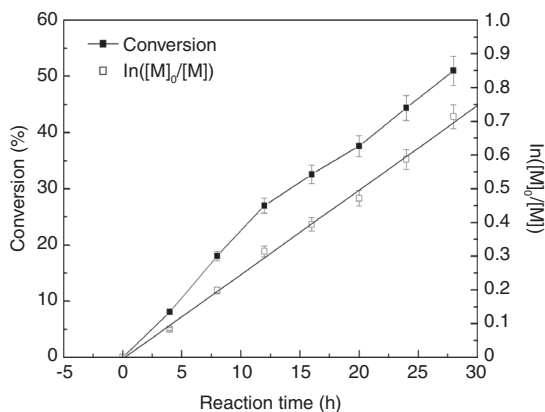

Figure 2 Plots of monomer conversion and $\ln([M]_0/[M])$ vs. time for SET LRP of styrene and AN in DMF at 25°C with CCl$_4$ as an initiator and Bpy as a ligand.
$[St]_0/[AN]_0/[CCl_4]_0/[Zn(0)]_0/[Bpy]_0/[FeCl_2]_0$=200:126:1:0.2:0.4:0.02.
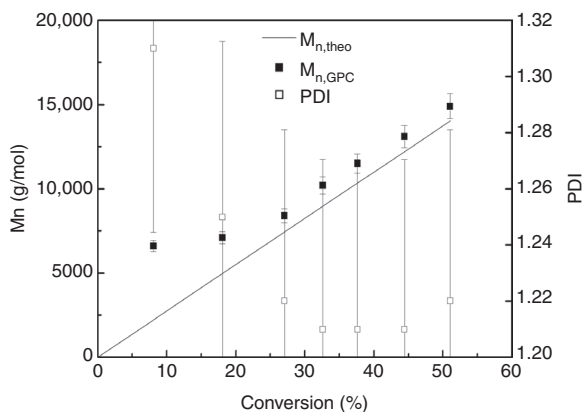

Figure 3 Dependence of the molecular weights (M_n) and molecular weight distribution (PDI) vs. the conversion for SET LRP of St and AN in DMF at 25°C with CCl$_4$ as an initiator and Bpy as a ligand. Reaction conditions were the same as those in Figure 2.

and a good correlation was achieved between the experimental and the theoretical values, indicating good controllability over the polymerizations in this case. The PDIs of the obtained copolymer remained narrow (<1.25) when the conversion was in the range of 18.05–51.04%. However, PDI values were relatively high at the beginning of the polymerization reactions but decreased to lower values with the progress of SET LRP, indicating that radical terminations occurred. The corresponding GPC traces are depicted in
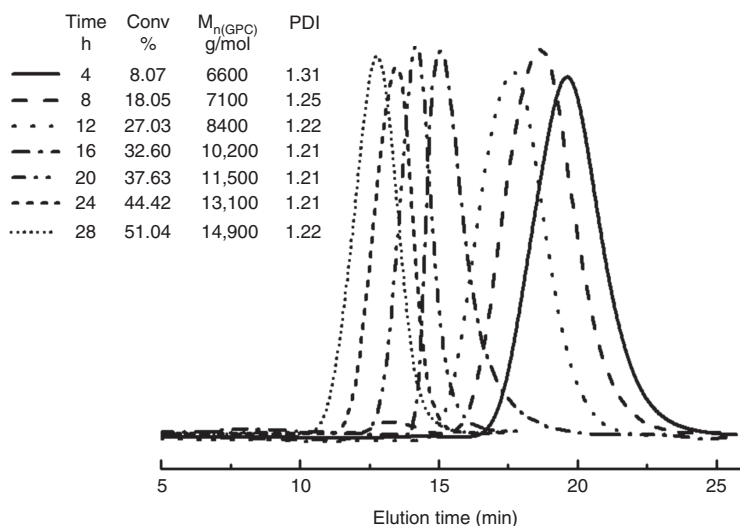

Figure 1 ^{1}H NMR spectrum of SAN.

	Time h	Conv %	$M_{n(GPC)}$ g/mol	PDI
——	4	8.07	6600	1.31
– –	8	18.05	7100	1.25
· · ·	12	27.03	8400	1.22
– · –	16	32.60	10,200	1.21
– · ·	20	37.63	11,500	1.21
– – –	24	44.42	13,100	1.21
·······	28	51.04	14,900	1.22

Figure 4 Evolution of GPC traces for SET LRP of St and AN in DMF at 25°C with CCl_4 as an initiator and Bpy as a ligand. $[St]_0/[AN]_0/[CCl_4]_0/[Zn(0)]_0/[Bpy]_0/[FeCl_2]_0 = 200:126:1:0.2:0.4:0.02$.

Figure 4. The traces shifted cleanly and completely, confirming the increase in the molecular weights of polymers with monomer conversions. These observations suggest that the Fe(0)-mediated copolymerization of St and AN proceeds in a controlled manner.

3.3 Effect of $[Zn(0)]_0/[FeCl_2]_0$ ratio on the Fe(0)-mediated living radical copolymerizations of St and AN

The ratio of $[Zn(0)]_0/[FeCl_2]_0$ is an important parameter when preparing a catalyst complex for living radical polymerization because it has a strong effect on the polymerization rate and on the level of control attained in the polymerization. In this work, the effect of $[Zn(0)]_0/[FeCl_2]_0$ ratio on polymerization was investigated; the molar ratio of $[St]_0/[AN]_0/[CCl_4]_0/[Zn(0)]_0/[Bpy]_0$ was 200:126:1:0.2:0.4. The results are shown in Table 1.

From Table 1, it can be seen that the conversion increased from 13.73% to 44.52% when the ratio varied

from 0.2:0.03 to 0.2:0.002 within the same reaction time. The molecular weights are close to theoretical values, and the PDI values are low. However, the PDI values became broader when the molar ratio of $[Zn(0)]_0/[FeCl_2]_0$ was 0.2:0.001. It indicated that there was not enough Fe^{2+} to initiate the polymerization and maintain the equilibrium. Furthermore, when the molar ratio of $[Zn(0)]_0/[FeCl_2]_0$ was 0.2:0, the PDI value was 1.65, indicating that the polymerization was uncontrolled without $FeCl_2$.

3.4 Effect of solvent on the Fe(0)-mediated living radical copolymerization of St and AN

The choice of solvent is also important for the ATRP. To determine the effect of solvent on the polymerization of St and AN initiated by CCl_4 and catalyzed by Fe(0)/Bpy, several solvents at 25°C were investigated, including DMF, N-methyl-2-pyrrolidone, water and methanol. The molar ratio of $[St]_0/[AN]_0/[CCl_4]_0/[Zn(0)]_0/[Bpy]_0/$

Table 1 Effect of $[Zn(0)]_0/[FeCl_2]_0$ ratio on Fe(0)-mediated living radical copolymerizations of St and AN in DMF at 25°C.

No.	$[Zn(0)]_0/[FeCl_2]_0$ ratio	Time (h)	Conversion (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PDI
1	0.2:0.03	20	44.52	12,237	13,100	1.22
2	0.2:0.01		30.11	8276	8900	1.21
3	0.2:0.005		21.65	5950	6300	1.21
4	0.2:0.002		13.73	3774	5100	1.24
5	0.2:0.001		7.22	1984	4800	1.32
6	0.2:0		1.35	712	2800	1.65

Table 2 Effect of solvent on Fe(0)-mediated living radical copolymerizations of St and AN at 25°C.

No.	Solvent	Time (h)	Conversion (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PDI
1	DMF	24	44.42	12,209	20,300	1.21
2	*N*-methyl-2-pyrrolidone		12.53	3444	19,300	1.25
3	DMF/H$_2$O (v/v=95:5)		48.22	13,254	24,000	1.23
4	Methanol		11.66	3205	15,900	1.25
5	H$_2$O		14.75	4054	14,300	1.24

M$_{n(GPC)}$=16,100 g/mol
PDI=1.37

M$_{n(GPC)}$=9600 g/mol
PDI=1.21
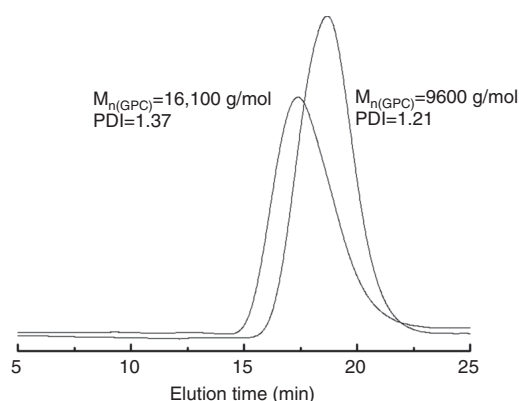
Figure 5 GPC curves of St and AN in DMF at 25°C. [St]$_0$/[AN]$_0$/[maroinitiator]$_0$/[Zn(0)]$_0$/[Bpy]$_0$/[FeCl$_2$]$_0$ was 200:126:1:0.2:0.4:0.02.

[FeCl$_2$]$_0$ was 200:126:1:0.2:0.4:0.02. The results are listed in Table 2.

As shown in Table 2, for the SET LRP in different solvents, the conversion reached 48.22% in 24 h in DMF/H$_2$O and 11.66% in methanol. $M_{n,GPC}$ increased linearly with increasing monomer conversion and was very close to the theoretical values. The polymer was obtained in DMF with lower PDI values than those in other solvents, indicating a better control over the copolymerization of styrene and acrylonitrile.

3.5 Chain extension of SAN using SAN as macroinitiators

The predetermined quantity of SAN (obtained by copolymerization) was dissolved in DMF. Then a predetermined quantity of styrene, acrylonitrile, Zn(0) powder, Bpy and FeCl$_2$ was added; the molar ratio of [St]$_0$/[AN]$_0$/[macroinitiator]$_0$/[Zn(0)]$_0$/[Bpy]$_0$/[FeCl$_2$]$_0$ was 200:126:1:0.2:0.4:0.02. Chain extension polymerization was carried out at 25°C. Figure 5 shows the GPC traces for the macroinitiator as

well as for the resulting random copolymer. The macroinitiator has a M_n of 9600 g/mol and a PDI value of 1.22, with the resulting copolymer having an experimentally determined M_n of 16,100 g/mol and a PDI value of 1.37. The GPC traces indicated an extremely high initiation efficiency, with the resulting copolymer possessing an essentially symmetrical unimodal molecular distribution.

4 Conclusions

The single-electron transfer-living radical copolymerization of St and AN was investigated using CCl$_4$ as an initiator and Fe(0)/Bpy as a catalyst at 25°C. The kinetic experimental results showed that the single-electron transfer-living radical copolymerization of St and AN obeyed the first-order kinetics. The molecular weights increased linearly with the increase in monomer conversion with lower PDI values. The molar ratio of [Zn(0)]$_0$/[FeCl$_2$]$_0$ could affect the copolymerization rate. The copolymerization in DMF appears to give the best results in terms of copolymerization rate and PDI values. As-prepared SAN copolymer possessed a chlorine-terminated atom, which could be reactivated during the chain extension reaction process.

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