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Microwave-assisted controlled copolymerization of styrene and acrylonitrile catalyzed by $FeCl_3$/isophthalic acid

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Abstract The copolymer of styrene-co-acrylonitrile (SAN) was synthesized by the atom transfer radical polymerization (ATRP) using $FeCl_3$-isophthalic acid (IA)/2,2′-azobis(isobutyronitrile) catalyst system under microwave irradiation (MI). Compared with conventional heating (CH), the copolymerization rate was accelerated under MI, and the conversion of monomer rapidly achieved 30% in 38 min for MI relative to 8% for CH under other same conditions. The kinetics results indicated that RATRP of St/AN is a 'living'/controlled polymerization, corresponding to a linear increase of molecular weights with the increasing of monomer conversion and a relatively narrow polydispersities index (PDI < 1.25) when the conversion is beyond 30%. The resultant SAN was characterized by FT–IR, NMR, and GPC.

Keywords Microwave irradiation · Reverse atom transfer radical polymerization · $FeCl_3$/isophthalic acid · Styrene · Acrylonitrile

Introduction

Styrene-co-acrylonitrile (SAN) copolymers are the thermoplastics that have important commercial applications in great demand because of their superior optical transparency, thermoplasticity, and easy processability [1]. SAN is typically synthesized with free radical polymerization, which was carried out in bulk, solution as well as emulsion polymerization [2–7]. However, the major drawback of traditional radical polymerization lies in poorly controlled molecular weight distribution due to the high radical concentration. As we know, the molecular

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weight and the distribution of molecular weight are important for the properties of polymers. The development of controlled/'living' radical polymerizations (CRPs) in the 1990s provided possibility to control the molecular weight (MW) and molecular weight distribution (MWD) of polymers. As a member of CRPs, atom transfer radical polymerization (ATRP) has developed into one of the most robust synthetic tools to synthesize the well-defined polymers, including block [8–10], graft [11–13], star [14–16] copolymers. However, the conventional ATRP is imperfect in the initiation system such as the source of the initiator (R-X) is limited and the catalyst is unstable to the air and moisture [17]. To overcome these shortcomings, a so called reverse ATRP (RATRP) has been developed and successfully applied to obtain the well-defined polymers [18]. The ligands used in RATRP are usually Triphenylphosphine (PPh_3) [17] and 2,2′-bypyridine [18] or its derivatives, which are either expensive or toxic. Therefore, exploring a cheap and nontoxic is important and necessary. Recent studies indicated acids could act as a substitute in the RATRP [19–22].

As an alternative to conventional heating, the microwave irradiation has become a popular in organic chemistry [23–25]. Recently, many polymerizations, such as step-growth polymerizations [26–28], ring-opening polymerizations [29–31], traditional radical polymerizations [32] as well as ATRP [33–36] are also well-performed under microwave irradiation. By comparison with conventional heating (CH), polymerization under microwave irradiation (MI) have the advantages of higher reaction rate and greater yield of polymer within a shorter period of reaction time; namely, it can evidently enhance the reactivity of reaction with the fewer side reactions. To our best knowledge, there have been no reports on RATRP of styrene and acrylonitrile under microwave irradiation.

In this study, SAN copolymer was performed by RATRP in *N*,*N*-dimethylformamide (DMF) at 60 °C using $FeCl_3$/isophthalic acid/AIBN catalyst system under microwave irradiation. In additional, the kinetics of polymerization was also investigated.

Experimental

Materials

Styrene (St, Shanghai Chemical Reagents Co., AR grade), acrylonitrile (AN, Shanghai Chemical Reagents Co., AR grade) were distilled under reduced prior to use. 2,2′-azobis(isobutyronitrile) (AIBN, Shanghai 4th factory of chemicals, 99%) was recrystallized twice from methanol. *N*,*N*-dimethylformamide (DMF) was distilled at reduced pressure prior to use. $FeCl_3$, isophthalic acid, and other regents were used as received.

Polymerization

All reactions were carried out in an XH-100 laboratory microwave oven (Beijing, China). The MW power was set at 200/400 W and the temperature was measured by an immersed platinum resistance thermometer and controlled automatically by intermittent irradiation. In a typical experiments, 4.08 g of AN (0.077 mol), 12.79 g of St (0.123 mol), 0.164 g of AIBN 0.001 mol), and 100 mL of DMF were first placed in a three-necked bottle. The flask was then degassed with nitrogen for 30 min, and then 0.162 g of $FeCl_3$ (0.001 mol) and 0.324 g of isophthalic acid (0.002 mol) was added. The flask was sealed after degassed with nitrogen, the flask was placed in a thermostated oil bath, and the temperature was controlled by a refluxing solvent of CCl_4. After the desired polymerization time, the round flask was cooled by immersing it into ice water. The reactant was pored into a large amount of methanol for precipitation, the obtained SAN copolymer was dried at 60 °C in vacuo for 24 h. Monomer conversion was determined by gravimetry. The $M_{n(\mathrm{th})}$ of SAN can be calculated by the following equation: $M_{n(\mathrm{th})} = ([\mathrm{St/AN}]_0/2[I]) \times W_{\mathrm{St/AN}} \times x$. Where, $[\mathrm{St/AN}]_0$ is the initial concentration of St/AN, $[I]$ is the concentration of AIBN and $W_{\mathrm{St/AN}}$ is the molecular weight of St and AN, x is the monomer conversion.

Characterization

The molecular weight and molecular weight distribution of the polymer were determined with a Waters 1515 gel permeation chromatography (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 column with molecular weight range 100–500,000 calibrated with polystyrene standard sample. Polystyrene standards are used to calibrate the columns. THF was used as a mobile phase at a flow rate of 1.0 mL/min and with column temperature of 30 °C.

FT–IR spectrum was recorded on a NICOLET 370 FT–IR spectrometer from powder-pressed KBr pellets.

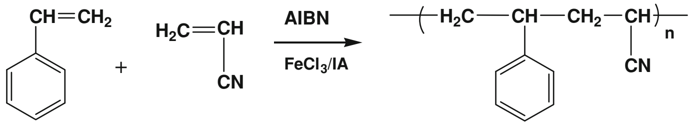
NMR spectrum was recorded on a Bruker 400 MHz Spectrometer instrument using d_6-DMSO as the solvent.

Results and discussion

Preparation of SAN by RATRP

SAN copolymer was prepared by RATRP process using $FeCl_3$-isophthalic acid (IA)/2,2′-azobis(isobutyronitrile) catalyst system under microwave irradiation (MI) as described in Scheme 1.

During the RATRP process, the initiator is first decomposed into two primary radicals, and then the produced radical can react with the monomer and



Scheme 1 Preparation of SAN copolymerization by RATRP

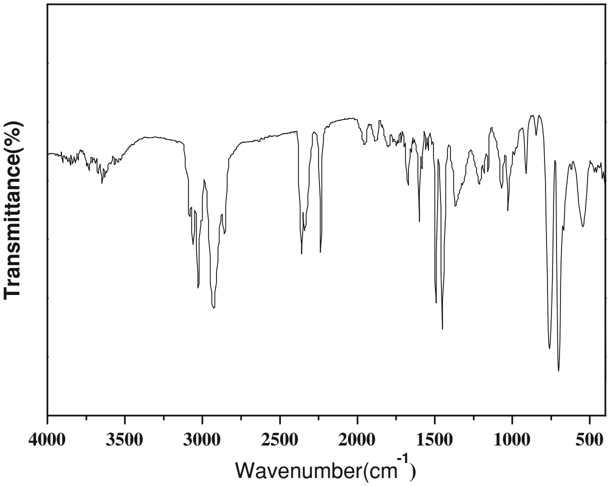


Fig. 1 FTIR spectrum of SAN

$FeCl_3$/isothphalic acid, which is reduced to form $FeCl_2$/isothphalic acid. The polymers propagate via a conventional ATRP process. The obtained SAN copolymer was characterized by FTIR, and the FTIR spectrum was shown in Fig. 1. As indicated, the absorption peak at 2239 cm^{-1} was assigned the nitrile group stretching vibration, the stretching vibration of benzene ring of the PS portion appeared at 1604 cm^{-1}.

The SAN copolymer was further verified by ^1H NMR spectrum. In the ^1H NMR spectrum (Fig. 2), the chemical shift $\delta = 6.5$–7.5 ppm corresponded to the phenyl protons of styrene. The chemical shift at $\delta = 3.3$ and 1.76 were attributed to the protons of CH of acrylonitrile and St, respectively. Moreover, the mole ratio of St to AN was estimated about 1 according to the integral area ratio of protons at $\delta = 3.3$ and 1.76. The weak chemical signals situated at $\delta = 4.5$–5.3 ppm was proton of end group of –CHCl.

However, the methylene and methyne protons of the copolymer is overlapped in the region 1.2–3.1 ppm, and the poor resolution makes a detailed interpretation was impossible. For this reason, ^{13}C NMR spectrum of one representative copolymer sample is shown in Fig. 3. Whereas the aromatic ring carbons appear around 125–126 ppm, the nitrile carbon resonance shows multiplet splitting around 120.1–121.4 ppm, the methylene carbons appear in the spectrum around 36–42 ppm, the methine protons of the copolymer show multiplet splitting around 25–28 ppm [37].

Kinetics of RATRP under conventional heating (CH) and MI process

In this study, the kinetics of RATRP of copolymerization of St and AN was investigated. The polymerization was performed at 60 °C in DMF, and the mole

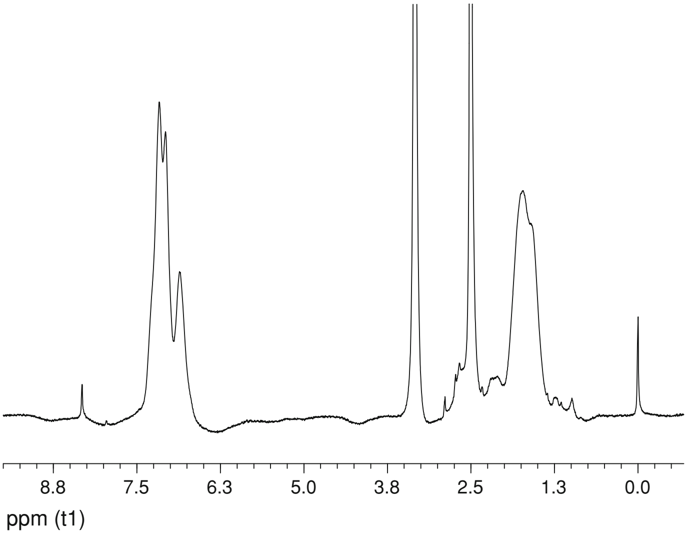


Fig. 2 ^{1}H NMR spectrum of SAN

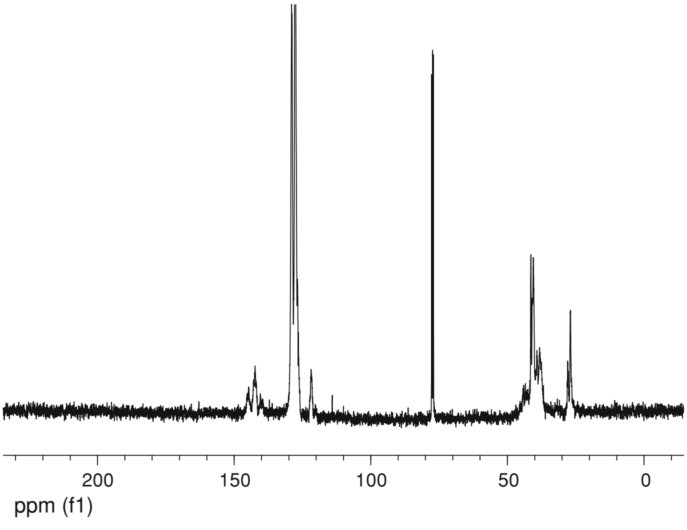


Fig. 3 ^{13}C NMR spectrum of SAN

ratio of $[M]_0$/[AIBN]/[$FeCl_3$]/[IA]was fixed to 200:1:1:2. The semilogarithmic plot of $\ln([M]_0/[M])$ versus the polymerization time was shown in Fig. 4.

According to Fig. 4, it was found that the semilogarithmic plot of $\ln([M]_0/[M])$ verse reaction time is nearly linear, which suggested that the chain growth from the macroinitiator was almost consistent with a ''controlled'' or ''living'' process. In order to compare the results affected by CH, we conducted the ATRP of two monomers under the same condition in CH process, which shown in Fig. 4b.

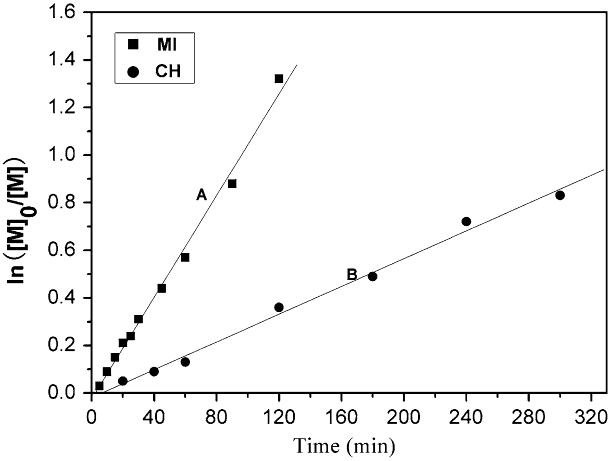


Fig. 4 Dependence of ln($[M]_0$/$[M]$) and reaction time during RATRP [St + AN]$_0$/[AIBN]$_0$/[FeCl$_3$]/[IA] = 200:1:1:2

In additional, an induction period of about 2.5 min for MI and about 7.5 min under for CH were observed, respectively. The induction periods correspond to the decomposition of AIBN and to the establishment of the equilibrium between Fe(III) and Fe(II), as described by Xu et al [32]. The radical polymerization rate can be expressed in the following equation:

$$-\mathrm{d}[M]/\mathrm{d}t = k_p[P\cdot][M] \tag{1}$$

By integration of Eq. 1, the kinetic equation was obtained as:

$$\ln([M]_0/[M]) = k_p^{\mathrm{app}}t \tag{2}$$

The value of slope is equal to the value of the apparent rate constant (k_p^{app}). Therefore, we could obtain the rate of polymerization was 1.8×10^{-4} s^{-1} for MI and 4.85×10^{-5} s^{-1} for CH, respectively. Therefore, the copolymerization of St/AN under MI were faster than that under CH. Conversion 30% was achieved in 38 min as compared to only 8% conversion under CH.

Figure 5 shows that the dependence of the number-average molecular weights on monomer conversion for St/AN copolymerization in DMF at 60 °C. From the Fig. 5, it can be seen that the values of M_n increase linearly with conversion under MI and under CH, and the molecular weight increased from 930 to 6520 g/mol under MI and from 860 to 5130 g/mol under CH when the conversion of monomer from 3 to 74% under MI and from 5 to 60% under CH, respectively. From the Fig. 5, the M_ns were almost matched with their corresponding theoretical molecular weights, especially in higher monomer conversions.

The polydispersity index (PDI) as a function of monomer conversion of all copolymer of SAN is also depicted in Fig. 5. The value of PDI of SAN decreased from 1.46 to 1.22 under MI and from 1.42 to 1.21 under CH. The values of PDI are less than 1.25 when the conversion is beyond 30%. It implied a well-controlled polymerization process.

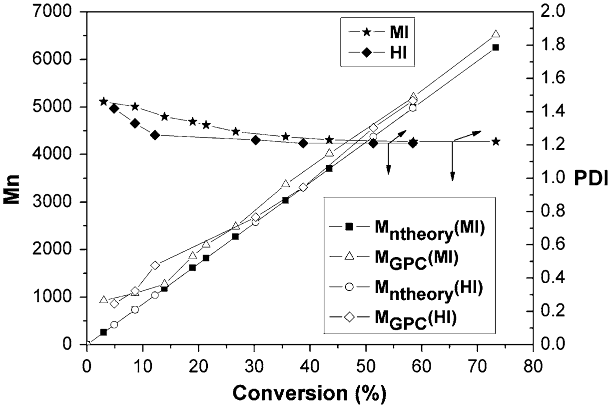


Fig. 5 Dependence of the molecular weights and molecular weight distributions on monomer conversion for St/AN copolymerization in DMF at 60 °C under MI and under CH. $[St + AN]_0/[AIBN]_0/[FeCl_3]/[IA] = 200:1:1:2$; MI power 300 W

The effect of initiator concentration on RATRP copolymerization of St and AN

Figure 6 showed the $\ln([M]_0/[M])$ verse time for the RATRP copolymerization of St/AN with different initiator concentrations 0.01, 0.02, 0.03 mol L^{-1}, respectively. The copolymerization rate increased with an increasing the amount of initiator since more radicals can be generated. From the Fig. 6, the value of slope is equal to the value of the apparent rate constant (k_p^{app}), which is 2.7, 2.2, 1.8 × 10^{-4} s^{-1}, respectively. It indicates that the rate of copolymerization increases with increasing the initiator concentration.

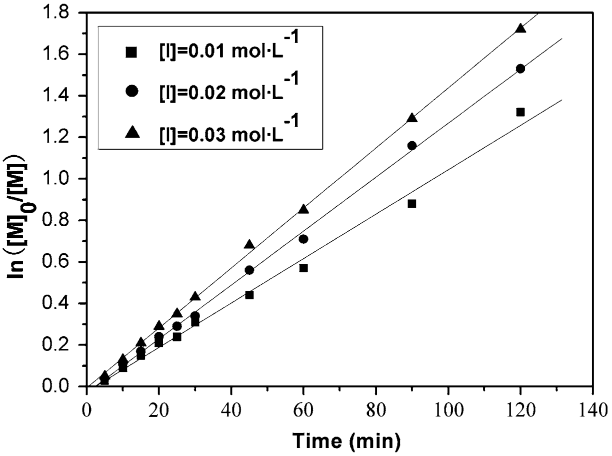


Fig. 6 Kinetics of the solution copolymerization of St/AN under MI and CH in DMF at 60 °C. $[AIBN]_0$ is 0.01, 0.02, 0.03 mol L^{-1}, respectively. $[St + AN]_0/[AIBN]_0/[FeCl_3]/[IA] = 200:1:1:2$; MI power 300 W

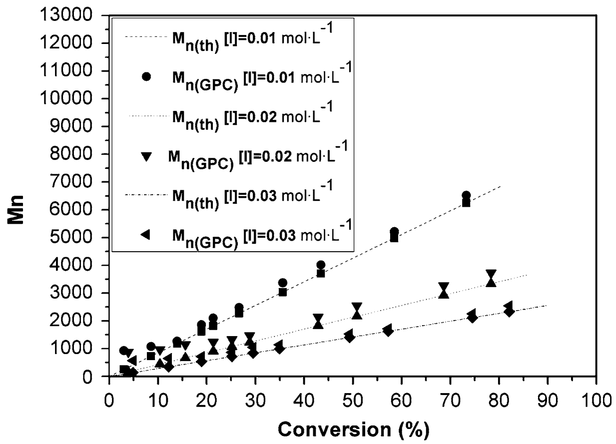


Fig. 7 Dependence of the molecular weights on monomer conversion for St/AN copolymerization in DMF at 60 °C under MI. $[AIBN]_0$ is 0.01, 0.02, 0.03 mol L^{-1}, respectively. $[St + AN]_0/[FeCl_3]/[IA] = 200:1:2$; MI power 300 W

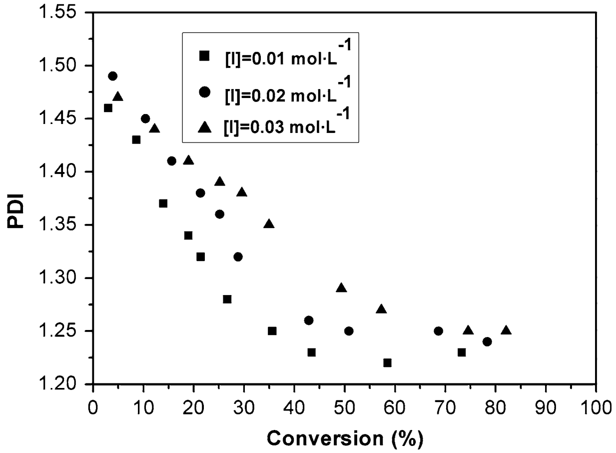


Fig. 8 Dependence of PDI on monomer conversion for St/AN copolymerization in DMF at 60 °C under MI. $[AIBN]_0$ is 0.01, 0.02, 0.03 mol L^{-1}, respectively. $[St + AN]_0/[FeCl_3]/[IA] = 200:1:2$; MI power 300 W

The molecular weight and polydispersity index are given in Figs. 7 and 8. As indicated, the linear increase of molecular weights with the monomer conversion, while the variation of PDI was little. The M_n values are close to their corresponding theoretical ones. Moreover, the low polydispersities of the polymer chains (<1.3) when the conversion is beyond 30% (see Fig. 8).

The effect of the ratio of $FeCl_3$/IA on RATRP copolymerization of St and AN under MI.

The effect of acid on the RATRP copolymerization of St/AN under MI was further investigated, and the results are shown in Fig. 9.

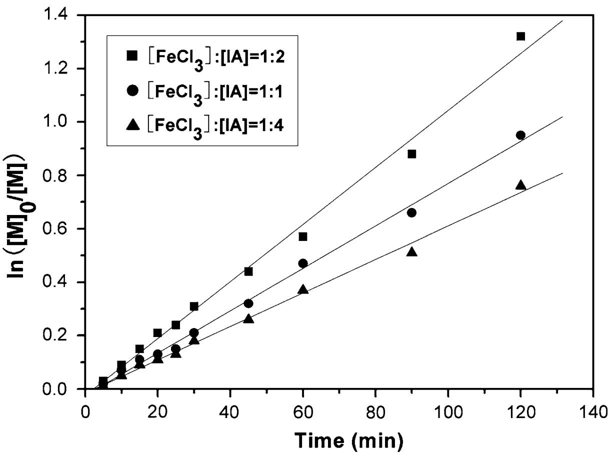


Fig. 9 Kinetics of the solution copolymerization of St/AN under MI in DMF at 60 °C. The molar ratios of $[FeCl_3]$:[IA] = 1:1, 1:2, 1:3, respectively.$[St + AN]_0/[AIBN]_0/[FeCl_3]$ = 200:1:1; MI power 300 W

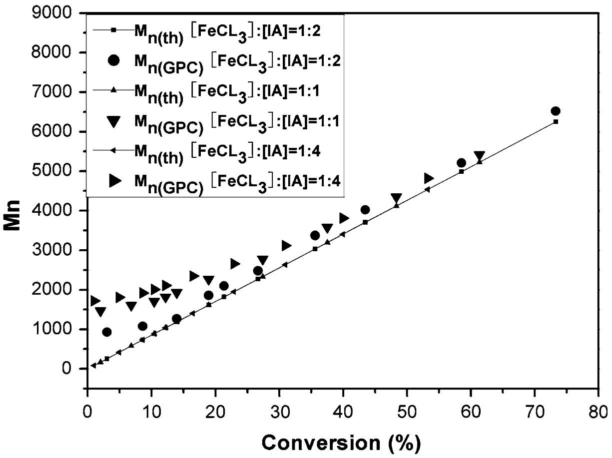


Fig. 10 Dependence of the molecular weights on monomer conversion for St/AN copolymerization in DMF at 60 °C under MI. The molar ratios of $[FeCl_3]$:[IA] = 1:1, 1:2, 1:3, respectively.$[St + AN]_0/[AIBN]_0/[FeCl_3]$ = 200:1:1; MI power 300 W

Based on Fig. 9, the rates of copolymerization of k_p^{app} were 1.33, 1.8, 1.02×10^{-4} s^{-1}, corresponding to the ratio of $[FeCl_3]$:[IA] of 1:1, 1:2, and 1:3, respectively. This suggested that the concentration of acid has an important role in reacting with active species or catalyzing the elimination of the initiator.

The dependence of the molecular weights and molecular weight distributions on monomer conversion for St/AN copolymerization are shown in Figs. 10 and 11. From the Fig. 10, the number molecular weight increases with the increasing of monomer conversion. The experimental molecular weight deviates from the theoretical one, especially at low conversion (<20%). This was attributed to the

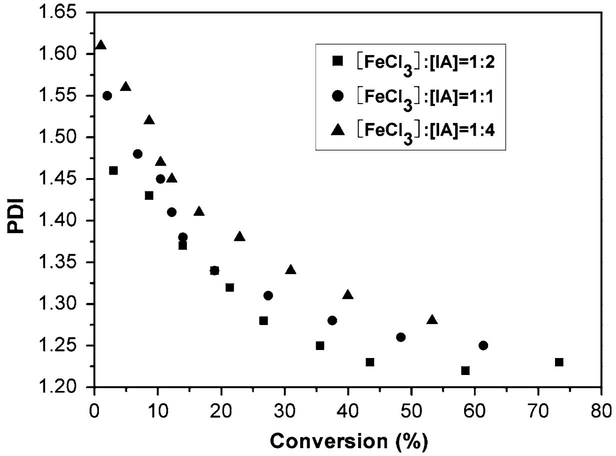


Fig. 11 Dependence of PDI on monomer conversion for St/AN copolymerization in DMF at 60 °C under MI. The molar ratios of $[FeCl_3]$:[IA] = 1:1, 1:2, 1:3, respectively. $[St + AN]_0/[AIBN]_0/[FeCl_3] = 200:1:1$; MI power 300 W

poor control on the copolymerization in the early stages, which also reflected by the values of PDI. The values of PDI were broader at low conversion (<35%), while the value almost kept constant when the conversion is beyond 35% at the ratio of $[FeCl_3]$:[IA] = 1:2.

The effect of monomer concentration on RATRP copolymerization of St and AN

The RATRP copolymerization of St and AN were conducted at the different monomer concentration. The results are shown in Fig. 12.

From the Fig. 12a, it can be seen that the dependences of $\ln([M]_0/[M])$ on reaction time at different monomer concentration are in accordance with the characteristic of ATRP. The conversion of monomers increased with increasing of reaction time and the plots of $\ln([M]_0/[M])$ versus time have well first-order

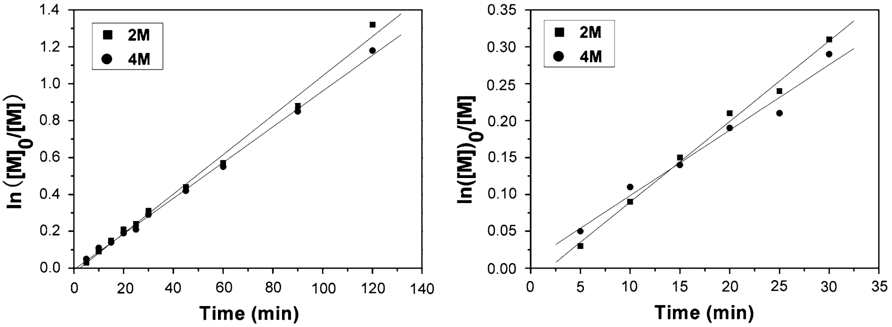


Fig. 12 Kinetics of the solution copolymerization of St and AN under MI in DMF at 60 °C. $[St + AN]_0/[AIBN]_0/[FeCl_3]/[IA] = 200$ or $400 :1:1:2$; MI power 300 W

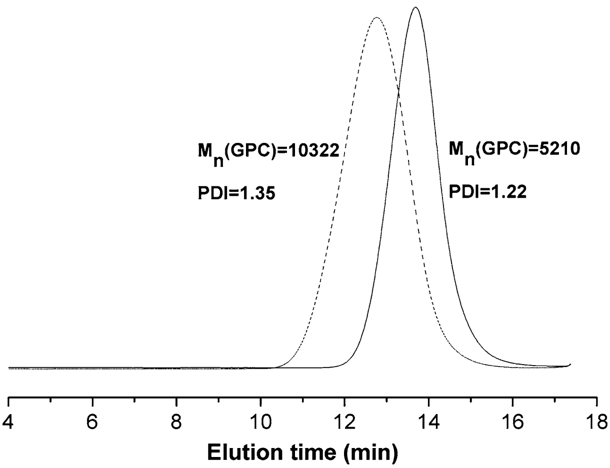


Fig. 13 GPC curves of St and AN under MI in DMF at 60 °C. $[St + AN]_0/[Macroinitiator]_0/[FeCl_3]/[IA] = 200:1:1:2$; MI power 300 W

linearity. But, the copolymerization rate starts slightly higher (for $[St + AN]_0 = 4$ mol L^{-1}) than the one (for $[St + AN]_0 = 2$ mol L^{-1}) at low conversions and it decreases when the reaction time is beyond 15 min (Fig. 12b).

Chain extension of poly(SAN)

To confirm the existence of 'living' chain ends, chain extensions of the obtained chlorine-terminated SAN were performed under MI. The 1.7 g SAN sample (Mn = 5210, PDI = 1.22) was first dissolved in DMF as macroinitiator, and then styrene (4.2 g, 0.04 mol) and acrylonitrile (1.33 g, 0.025 mol), and $FeCl_3$ (3.25×10^{-4} mol), and IA (6.5×10^{-4} mol) were added. After 0.5 h polymerization under MI, the polymerization was terminated. The obtained polymer was further purified by washed with water and methanol. And the dried polymer was analyzed with GPC. And the GPC result was indicated in Fig. 13. According to Fig. 13, the Mn increased from 5210 to 10322 g/mol. Meanwhile, the PDI also increased from 1.22 to 1.35. The increasing of Mn suggested the dormant sites at the SAN chain ends have allowed reactivation during the subsequent polymerization process.

Conclusion

The RATRP of St/AN using AIBN as an initiator and $FeCl_3$/IA as a catalyst combination could be successfully performed at 60 °C under MI. The copolymerization rate is faster under MI than that under CH. The kinetics experimental results showed that copolymerization of St/AN is a 'living'/controlled process under MI, the linear increase of molecular weights with the increasing of monomer conversion. The values of PDI were broader at low conversion and almost kept constant at high conversion. As prepared SAN copolymer possessed a chlorine-terminated atom, which could be reactivated during the chain extension reaction process.

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