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Atom transfer radical polymerization (ATRP) of styrene and acrylonitrile with monofunctional and bifunctional initiators

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Abstract

A bifunctional initiator (benzal bromide) was used to initiate the bulk atom transfer radical polymerization of styrene and acrylonitrile at 90 °C with CuBr/2,2-bipyridyl. We compared these results with those of a monofunctional initiator of similar structure (1-bromoethyl benzene) under the same polymerization conditions. The monofunctional initiator worked better than the bifunctional initiator when both comonomers were added simultaneously at the beginning of the copolymerization; the bifunctional initiator was only effective when acrylonitrile was added after 20 min of polymerization with styrene. The styrene–acrylonitrile copolymers were characterized by gel permeation chromatography, ^{13}C nuclear magnetic resonance spectroscopy, Fourier-transform infrared spectroscopy, and refractometry. Copolymer composition was monitored by both ^{13}C NMR and by the change in the specific refractive index increment.

Keywords: ATRP; Block SAN; Bifunctional initiator

1. Introduction

Styrene–acrylonitrile (SAN) copolymers have important commercial applications. These copolymers have a high demand due to their superior optical, chemical, thermal and mechanical properties [1]. SAN is typically synthesized with free-radical polymerization; production can be carried out as bulk, solution, or emulsion free-radical polymerization [2–9]. Conventional free-radical polymerization allows for the efficient production of several polymer types at high yield, but lacks the precise microstructural control attained with living polymerization systems. Living polymerizations can be used to synthesize well-defined polymers with various functionalities, compositions, and chain architectures. Controlled living free-radical polymerization has been successfully used to make SAN copolymers [10–14].

Although several controlled radical polymerization systems have been reported by various groups [14–19], atom transfer radical polymerization (ATRP) remains one of the most powerful, versatile, simple, and inexpensive living polymerization techniques. The use of a range of initiators in ATRP is an effective method for introducing useful functionalities and producing polymers with novel architectures and properties. SAN was one of the copolymers studied by the Matyjaszweski group [14]. They used several types of initiators in their studies.

A systematic study comparing monofunctional and bifunctional initiators of similar structures has not yet been reported for the case of copolymerization with ATRP. Bifunctional initiators have interesting behavior in conventional free-radical polymerization [20]. Compared to monofunctional initiators, they produce polymers with higher conversion for the same polymerization time, higher molecular weight and narrower molecular weight distribution.

In batch copolymerization, if one comonomer is consumed faster than the other, composition drift is observed. During nonliving polymerization, comonomer composition drift produces

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copolymer chains with different intermolecular compositions. In controlled free-radical polymerization (including ATRP), on the other hand, composition drift causes intramolecular comonomer composition changes and produces gradient copolymers. Comonomer reactivity ratios, comonomer feed policies, and initial comonomer compositions are the major factors that can be used to control composition drift.

In a previous investigation, we compared the bifunctional initiator benzal bromide with monofunctional initiators for the synthesis of polystyrene via ATRP [21]. In the present study, we compare the synthesis of SAN copolymers with benzal bromide (bifunctional initiator) and 1-bromoethyl benzene (monofunctional initiator). The chemical structures of both initiators are shown in Fig. 1.

2. Experimental

2.1. Materials

Styrene (>99%) inhibited with 10–15 ppm 4-*tert*-butyl catechol and acrylonitrile (AN) (99%) inhibited with 35–45 ppm monomethyl ether hydroquinone (MEHQ) were purchased from Aldrich. Both styrene and acrylonitrile were first passed thorough an aluminum oxide column to remove the inhibitors and then purged with nitrogen for 30 min. We used benzal bromide (97%) (from Aldrich) as monofunctional initiator and 1-bromoethyl benzene (97%) (from Aldrich) as bifunctional initiator. We used copper(I) bromide (99.999%) complex with 2,2-dipyridyl (99%), purchased from Aldrich, as the catalyst. Both initiators and the catalyst were used as received. Solvents used over the course of the experiments and characterization of the copolymers (ethanol, acetone, chloroform, tetrahydrofuran) were used as received from VWR.

2.2. Simultaneous polymerizations

The catalyst, copper(I) bromide (0.147 g or 0.00102 mol) and ligand 2,2-dipyridyl (0.400 g or 0.00256 mol) were first placed in a round bottom flask and three cycles of nitrogen pressurization followed by vacuum were applied to remove air and moisture from the flask. The deoxygenated monomers, styrene (7.42 mL or 0.064 mol) and acrylonitrile (2.51 mL or 0.038 mol), were added in a ratio of 63 mol% styrene using disposable syringes. The mixture was stirred at room temperature until it becomes homogeneous. The flask was placed in an oil bath at 90 °C and the monofunctional (0.14 mL or 0.00126 mol) or bifunctional initiator (0.167 mL or 0.001026 mol) was added to the flask using disposable syringes.

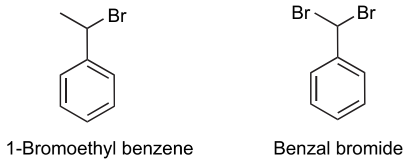

Fig. 1. Chemical structures of the initiators used in this study.

2.3. Sequential polymerizations

The same procedure and amount of chemicals described in Section 2.2 were used, except that the acrylonitrile was added 20 min after introducing the initiators.

2.4. Polymer characterization

Monomer conversion was determined by gravimetry. The content of the flask was first washed with tetrahydrofuran (THF) and the polymer was precipitated using a large excess of ethanol. The precipitated polymer was filtered through filter paper and dried up to constant mass.

^{13}C NMR spectra were recorded for polymer samples dissolved in deuterated chloroform ($CDCl_3$), using a 300-MHz AC Bruker Fourier-transform spectrometer. The temperature of the probe was 25 °C and the number of scans was 4092. The relative amount of comonomers incorporated into the copolymer was estimated from the integrated area under the appropriate peak intensities, as discussed below.

Molecular weights were obtained using gel permeation chromatography (Waters 590) operating at room temperature with a refractive index (RI) detector on-line with a multiangle laser light-scattering photometer system. THF was filtered and used as the eluent at a flow rate of 1.0 mL/min. Samples for the analysis were prepared as 0.5% solutions in THF and filtered through 0.45 μm filters prior to injection. The dn/dc values used in the calculation of molecular weights were calculated independently using a refractometer (Brice-Phoenix differential refractometer equipped with 632 nm band-pass interference filters, operated at 25 °C).

Fourier-transform infrared (FTIR) spectroscopy was used to measure the composition of the SAN copolymers. The polymer powder was dissolved in THF and a few drops of the solution were added onto a transparent KBr disk. After evaporation of the solvent, a thin polymer film was formed on the KBr disk. The samples were analyzed by FTIR and the spectra were reported after subtracting from a background spectrum for the plain KBr disk. The spectra were recorded from 400 to 4000 cm^{-1}, after 32 scans, with a resolution of 4 cm^{-1}.

Refractive index (RI) measurements were performed on all samples prior to GPC analysis to find the dn/dc ratio. Five different concentrations of the same sample (0.01 g (and less) of SAN in 1 mL of THF) were made by dissolving the copolymer in THF. Each sample was measured on the refractometer and the results from the RI measurements were plotted against the concentration of the sample. A straight line was obtained from the graph and the multiplication of the slope of the curve and the calibration constant of the instrument gave dn/dc.

3. Results and discussion

Initially, polymerizations with the mono- and bifunctional initiators were carried out by adding the two comonomers, styrene and acrylonitrile, simultaneously into the round bottom flask before placing it in the oil bath to start the copolymerization. However, the results from these tests were surprising because monomer conversion with the monofunctional initiator was higher than that with the bifunctional initiator for a given polymerization time. Since the bifunctional initiator has two bromine atoms and, hence, two active radicals, we expected that the polymer chains would grow from both ends with increased monomer conversion and producing polymers with higher molecular weight at a given polymerization time. However, this was not the case: the GPC analysis showed that samples made with the bifunctional initiator had lower molecular weights than those prepared with the monofunctional initiator. Fig. 2 shows that monomer conversion and number average molecular weight of SAN copolymers made with the monofunctional initiator are higher than those using the bifunctional initiator.

In order to help in understanding such unexpected results, pure acrylonitrile was polymerized with the bifunctional (benzal bromide) and monofunctional (1-bromoethyl benzene) initiators. A 5-h polymerization (reproduced several times) with acrylonitrile and the bifunctional initiator (the molar ratio of acrylonitrile to the initiator was 37:1) at 90 °C surprisingly produced no measurable quantities of polymer. This is not the case for the polymerization of acrylonitrile or styrene with the monofunctional initiator. In fact, the polymerization of acrylonitrile using 1-bromoethyl benzene (37:1 molar ratio of monomer to the initiator) reached complete conversion within 10 min.

We may propose two explanations for the lack of polymerization activity of acrylonitrile with benzal bromide: (1) side reactions between acrylonitrile and benzal bromide consume the active species or inhibit the initial activation of benzal bromide; (2) the reaction of the first acrylonitrile molecule with the benzal bromide initiator forms an unsymmetrical substituted structure that is not active to propagate additional acrylonitrile monomers (see Fig. 3). We realize that the mechanism described in Fig. 3 is highly speculative and is just shown here as a conjecture to help explain the results we will discuss in the next paragraphs.

To test this hypothesis, some changes were made in the original batch polymerization process: we started the polymerization with styrene and only added the acrylonitrile into the flask 20 min after injecting the initiator (sequential polymerization). It should be noted that all other experimental conditions were exactly the same as for the simultaneous polymerizations described above. The sequential polymerization process allows styrene to react with the bifunctional initiator first, forming an initial block of polystyrene macroinitiator (PS). The proposed mechanism for the mono- and bifunctional initiators is shown in Fig. 4. The monofunctional initiator forms a copolymer of the type PS-*b*-SAN, and the bifunctional initiator forms a copolymer of the type SAN-*b*-PS-*b*-SAN.

The polymerization time of 20 min with only styrene is required for styrene to initialize the polymerization and overcome the induction time [21]. Figs. 5–7 show that this approach works well: when acrylonitrile was added, the bifunctional initiators had already polymerized some styrene molecules and could continue to grow forming SAN copolymer chains. Three replicate polymerizations were done at different time intervals and the averaged results are shown in Figs. 5–7 (example of error bar calculated as one standard deviation is shown in one of the data).

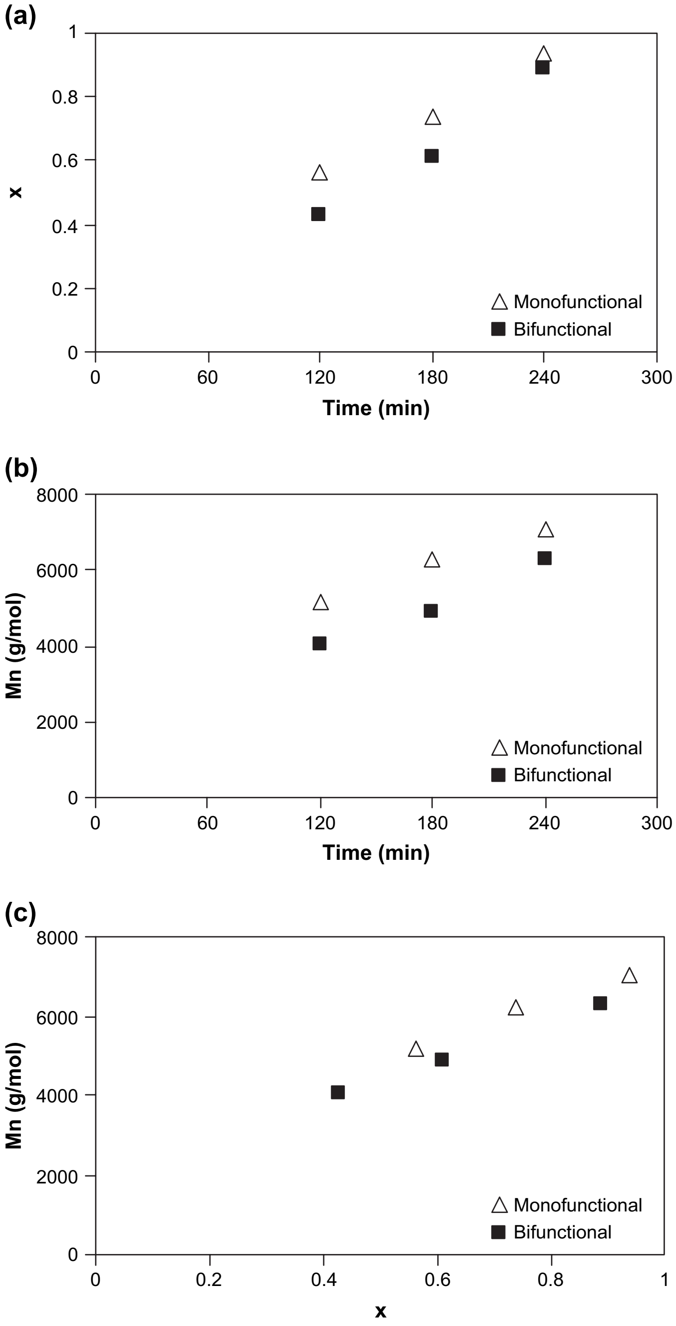

Fig. 2. Comparison of batch ATRP of styrene and acrylonitrile using a monofunctional and a bifunctional initiator when both comonomers are added simultaneously: (a) monomer conversion, *x*; (b) number average molecular weight, Mn vs. time; (c) number average molecular weight vs. conversion (polymerization conditions: $[M]_0/[I]_0/[C]_0 = 100/1/1$. Temperature = 90 °C).

Figs. 5–7 show that the sequential polymerizations worked well and that the bifunctional initiator behaves more closely to what we had originally expected. Fig. 5a shows that monomer conversion with the bifunctional initiator is higher than that with the monofunctional initiator for the same polymerization time. The linear dependence of $\ln([M]_0/[M])$ on time for both

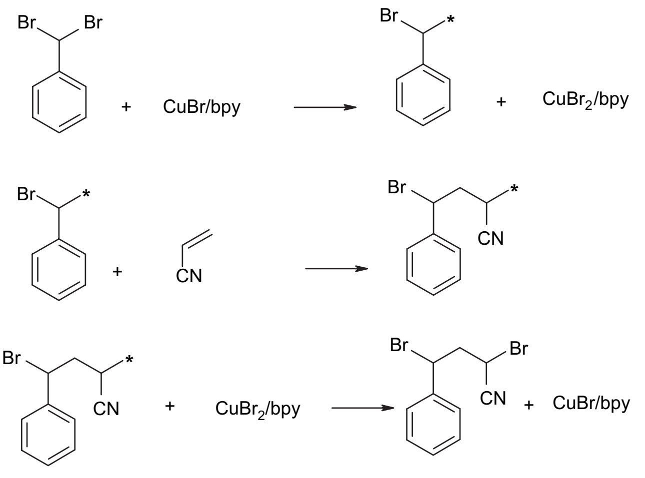

Fig. 3. Mechanism for the formation of an unsymmetrical initiator inactive for acrylonitrile propagation.

initiators, shown in Fig. 5b, is an evidence of living polymerization. The deviation from linearity for polymerizations with the bifunctional initiator after 3 h is likely due to the high monomer conversion (95%).

Theoretically bifunctional initiators should double the number of initiating sites, hence leading to approximately double the polymerization rate. A close inspection of Fig. 5 shows that this is not the case here. This behavior may be due to ratio of the catalyst to the initiator which influences the kinetics. The ratio of the catalyst to the initiator is one to one for both initiators. Due to this competition between the number of sites and the catalyst concentration the rate increased significantly but did not double.

Fig. 6a shows that all polymer samples made with the bifunctional initiator have higher molecular weights than the ones produced with the monofunctional initiator at a given polymerization time. However, if the molecular weight is plotted against conversion (as shown in Fig. 6b) the molecular weight of the polymer made with either initiator is practically the same, as expected. Another indication that both sequential and simultaneous polymerizations were controlled is the increase of polymer molecular weight with monomer conversion, as seen in Fig. 6b.

The molecular weight plots showed a non-zero intercept (Fig. 6). There are probably two reasons for this unexpected result: (a) poor control during the early stages of polymerization, prior to establishing a sufficiently high concentration of Cu(II) and (b) undesired fractionation of very low molecular weight chains at low monomer conversions during the precipitation and polymer recovery steps, leading to measured molecular weights that are higher than actual values (which is more plausible).

The molecular weight determined by GPC was compared to the theoretical (calculated) value (Fig. 6b). For both initiators

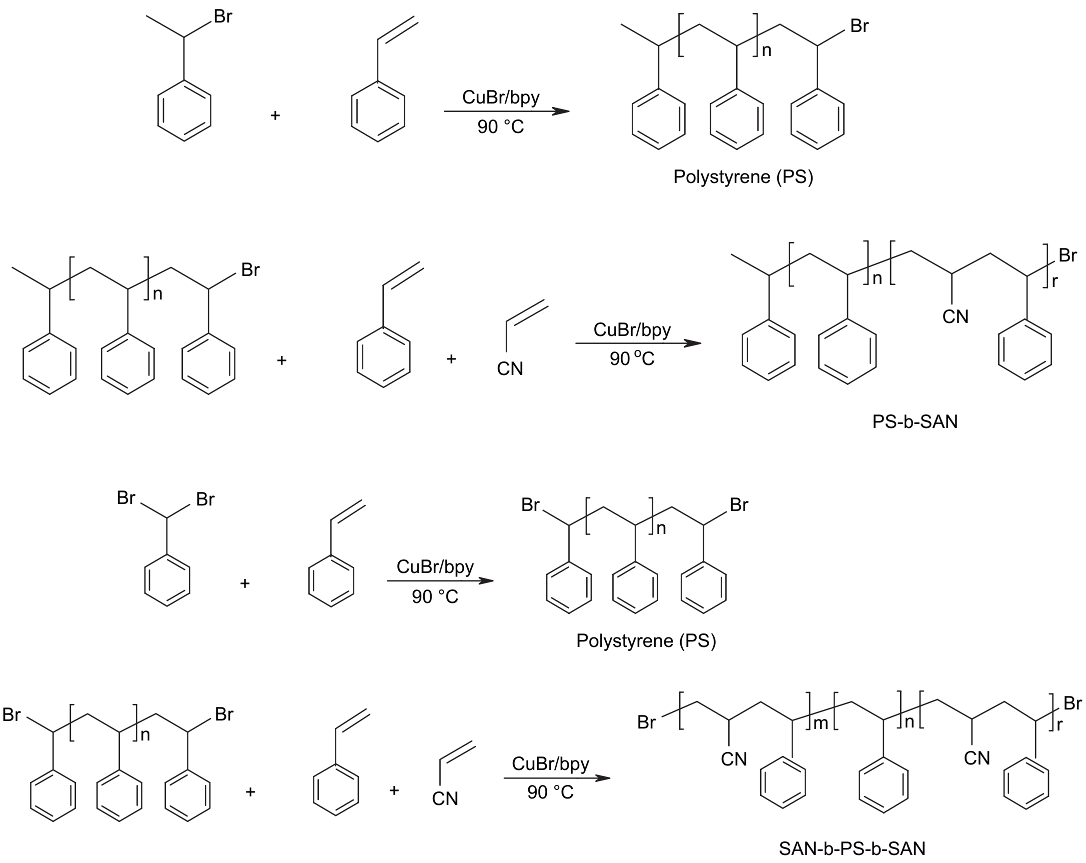

Fig. 4. Proposed mechanism for the formation of PS-*b*-SAN and SAN-*b*-PS-*b*-SAN copolymer using monofunctional (top) and bifunctional (bottom) initiators in the sequential polymerization approach.

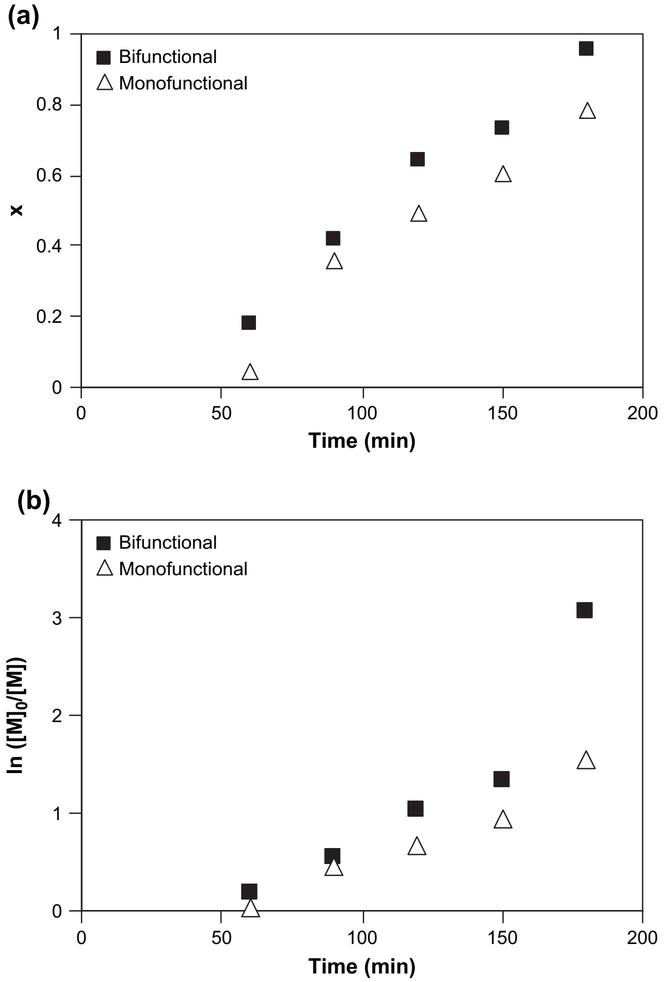

Fig. 5. Comparison of ATRP of styrene and acrylonitrile using a monofunctional and a bifunctional initiator when acrylonitrile is added 20 min after the initiation of the polymerization with styrene: (a) monomer conversion, x; (b) $\ln([M]_0/[M])$ vs. time (polymerization conditions: $[M]_0/[I]_0/[C]_0 = 100/1/1$).

the experimental molecular weight deviated from the theoretical one. This deviation was more pronounced at low conversion. Two reasons are proposed: (a) the fractionation of low molecular weight (as discussed above) and (b) the initiation efficiency. The latter can be calculated from the ratio of the theoretical molecular weight to the experimental one. The efficiency values started with low values at low conversion (0.09 for monofunctional and 0.28 for bifunctional) and increased to about 0.77 and 0.72 for bifunctional and monofunctional initiators, respectively. The efficiency at low conversion is probably affected by fractionation of low molecular weight chains.

The polydispersity index (PDI) as a function of polymerization time and monomer conversion of all SAN copolymers is typical for ATRP (Fig. 7). It starts slightly higher than the one at low conversions and then it decreases until most of the monomer is consumed at high conversions. Generally, the bifunctional initiator produced copolymers with lower PDIs than monofunctional initiators.

We used the azeotropic ratio for styrene and acrylonitrile for the sequential polymerizations: 63 mol% styrene and

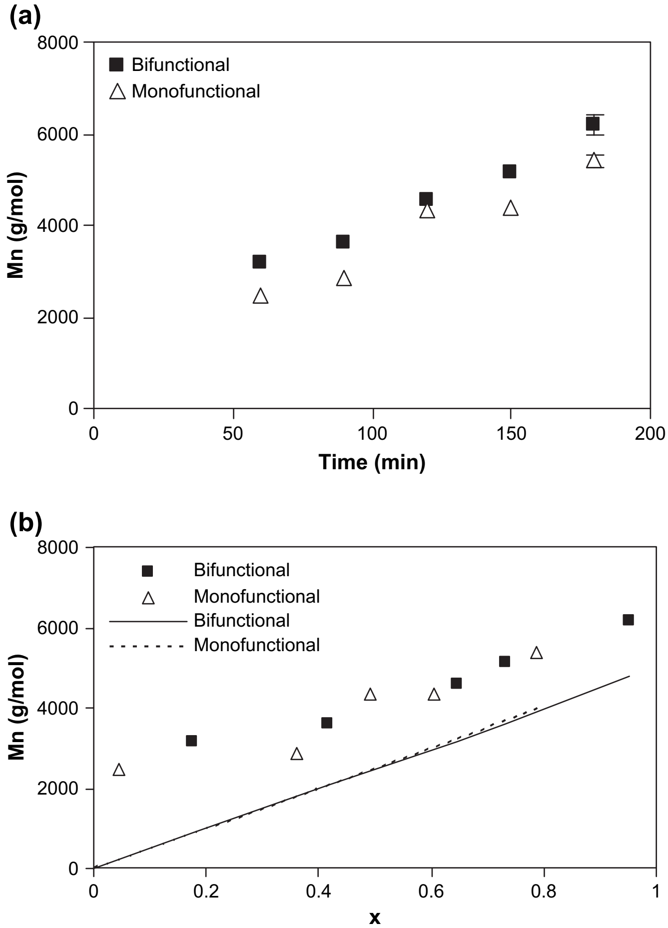

Fig. 6. Comparison of ATRP of styrene and acrylonitrile using a monofunctional and a bifunctional initiator when acrylonitrile is added 20 min after the initiation of the polymerization with styrene: (a) Mn vs. time; (b) experimental Mn (markers) and theoretical Mn (lines) vs. conversion, x (polymerization conditions: $[M]_0/[I]_0/[C]_0 = 100/1/1$).

37 mol% acrylonitrile. The azeotropic ratio will not lead to composition drift when both comonomers are introduced simultaneously at the beginning of the batch polymerization. However, since the acrylonitrile was introduced 20 min after the injection of the styrene, the initial monomer fraction deviated from the azeotropic composition and a drift was expected.

It is common to determine the average comonomer composition of copolymers with ^{1}H NMR. Unfortunately, for SAN copolymers the proton spectra are so poorly resolved that a detailed interpretation was impossible. The methylene and methine protons of the copolymer overlapped in the region 1.2–3.1 ppm. For this reason, we used ^{13}C NMR instead of ^{1}H NMR to determine copolymer's average chemical composition. The ^{13}C NMR spectrum of one representative copolymer sample is shown in Fig. 8. Whereas the nitrile carbon resonance shows multiplet splitting around 120.1–121.4 ppm, the aromatic ring carbons appear in the spectra around 125–126 ppm. The relative intensities of the resonances in this region can be used to calculate the average copolymer composition. Fractions of each comonomer in the copolymer as a function of polymerization time, determined from the ^{13}C NMR spectra by comparing

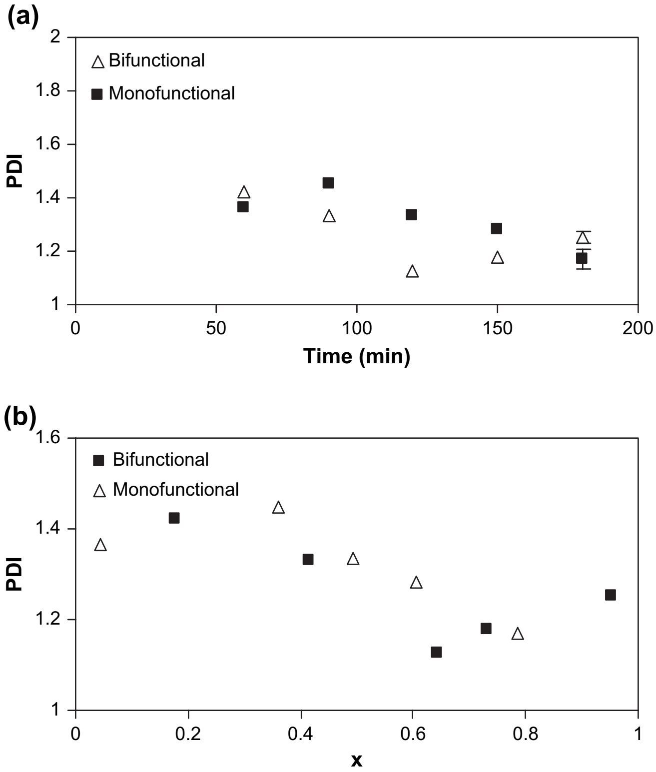

Fig. 7. Comparison of ATRP of styrene and acrylonitrile using a monofunctional and a bifunctional initiator when styrene is added 20 min before acrylonitrile: (a) PDI vs. time; (b) PDI vs. conversion, *x* (polymerization conditions: $[M]_0/[I]_0/[C]_0 = 100/1/1$).

the styrene (aromatic ring) peak with the nitrile group, are shown in Fig. 9.

Note that the comonomer fractions in Fig. 9 correspond to the cumulative average composition for the total polymerization time. For the case with bifunctional initiator when acrylonitrile was injected 20 min after styrene injection, there is a block of polystyrene at the middle of the chain SAN-*b*-PS-*b*-SAN. Similarly, for the monofunctional initiator there is a block of polystyrene PS-*b*-SAN at one of the chain ends. The composition of the SAN copolymer segments, discounting the initial polystyrene block, can be obtained by subtracting the contribution of the polystyrene block. This is possible because the length of the polystyrene block can be obtained from the styrene conversion after the initial 20 min of polymerization using the following equation:

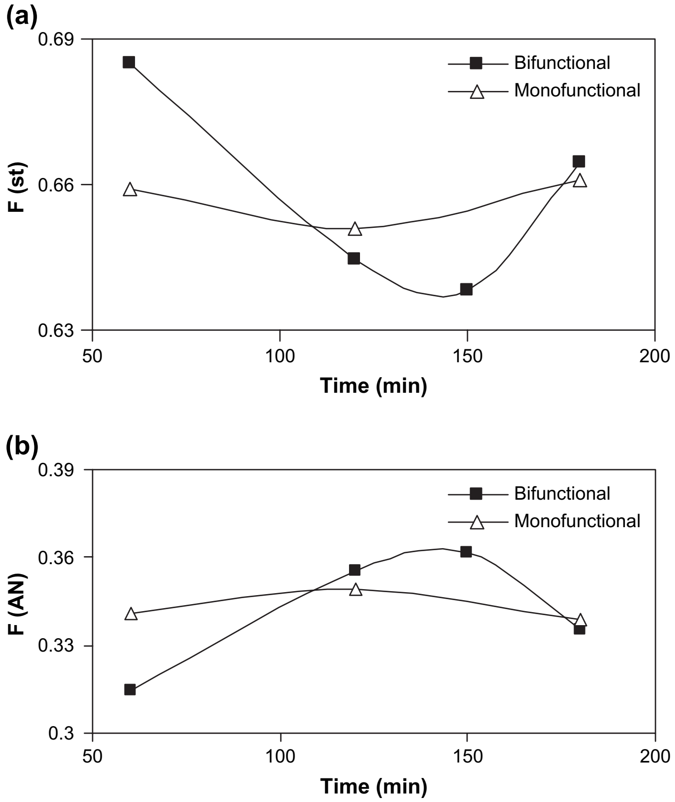

Fig. 9. SAN copolymer composition measured with ^{13}C NMR: (a) styrene fraction vs. polymerization time for both initiators; (b) acrylonitrile fraction vs. polymerization time for both initiators (polymerization conditions: $[M]_0/[I]_0/[C]_0 = 100/1/1$. Temperature = 90 °C).

$$\mathrm{CF}_{\mathrm{a}}^{t} = \frac{n_{\mathrm{a}}^{t}}{n_{\mathrm{s}}^{t} - n_{\mathrm{s}}^{20} + n_{\mathrm{a}}^{t}} \tag{1}$$

where CF is the corrected molar fraction in the copolymer and *n* is the number of moles. The subscripts a and s indicate the type of the copolymer (acrylonitrile and styrene). The superscripts (*t* and 20) indicate the time. The corrected copolymer composition is summarized in Table 1. The values in Table 1 cannot be compared with the values obtained from the NMR test since NMR shows the cumulative composition. This was mainly done to get a sense of the range where the values would fall into.

Before determining their molecular weight by GPC, it was necessary to measure the refractive index of the copolymers

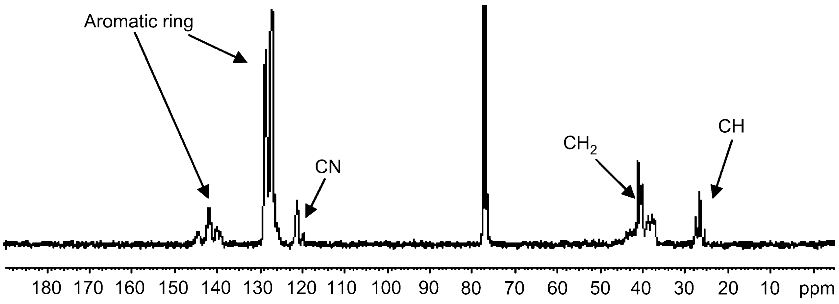

Fig. 8. ^{13}C NMR spectrum of a representative SAN copolymer made by sequential copolymerization.

Table 1
Molar fraction of acrylonitrile in the SAN copolymer. Cumulative copolymer composition (from ^{13}C NMR) and corrected fraction excluding block of polystyrene made during the first 20 min of polymerization

Initiator	Polymerization time (h)	Cumulative ^{13}C NMR fraction of AN	Corrected fraction of AN
Monofunctional	1	0.341	0.414
Monofunctional	2	0.349	0.355
Monofunctional	3	0.339	0.342
Bifunctional	1	0.315	0.458
Bifunctional	2	0.355	0.387
Bifunctional	2.5	0.362	0.390
Bifunctional	3	0.336	0.356

and to find the specific refractive increment (dn/dc). The dn/dc ratio for a copolymer varies according to the weight fraction of each comonomer incorporated into the polymeric chains:

$$\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\text{copolymer}} = \sum \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{i}} w_{\mathrm{i}} \tag{2}$$

where n is the refractive index, c is the weight concentration (in $g_{\text{polymer}}/g_{\text{solution}}$) and the index i corresponds to the homopolymer type.

The dn/dc ratio for pure polystyrene in THF is 0.185 mL/g. Acrylonitrile is not soluble in THF; therefore, there is no experimental value for its dn/dc ratio in this solvent. When the incorporation of styrene in the SAN copolymer increases, the dn/dc ratio gets closer to 0.185 mL/g. Similarly, higher acrylonitrile incorporations will cause the dn/dc ratio to deviate from 0.185 mL/g. Based on that, the copolymer composition was correlated to the measurements of the dn/dc ratio. Fig. 10a shows how the values of dn/dc vary as a function of polymerization time; where the bifunctional initiator incorporated acrylonitrile faster than the monofunctional initiator and, therefore, shows a sharper decrease in the dn/dc ratio. This result supports the measures with ^{13}C NMR. The highest content of the acrylonitrile in SAN (from both ^{13}C NMR and refractometry analyses) is achieved after 2.5 h of polymerization with the bifunctional initiator.

Interestingly, the drift that appears with respect to time (Fig. 10a) in bifunctional initiators is also present with respect to conversion (Fig. 10b). The same results were observed by plotting the copolymer composition against conversion (Fig. 11). This behavior was due to the initial monomer ratios. After 20 min of reaction, the bifunctional initiator consumed more styrene than the monofunctional initiator and therefore the ratio of the acrylonitrile was higher.

Generally, the comonomer composition in the copolymer can be calculated from dn/dc values using the following equation:

$$\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\text{copolymer}} = \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\text{monomer 1}} w_1 + \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\text{monomer 2}} w_2 \tag{3}$$

where w_1 and $w_2 = (1 - w_1)$ are the weight fractions of the two comonomers in the copolymer. Unfortunately, the dn/dc of acrylonitrile in THF is unavailable because acrylonitrile is insoluble in THF. Therefore we could not use Eq. (3) in this study to measure copolymer composition, but this would be a useful approach for copolymers where both dn/dc ratios are known for the respective homopolymers when an on-line refractometer is installed with the GPC.

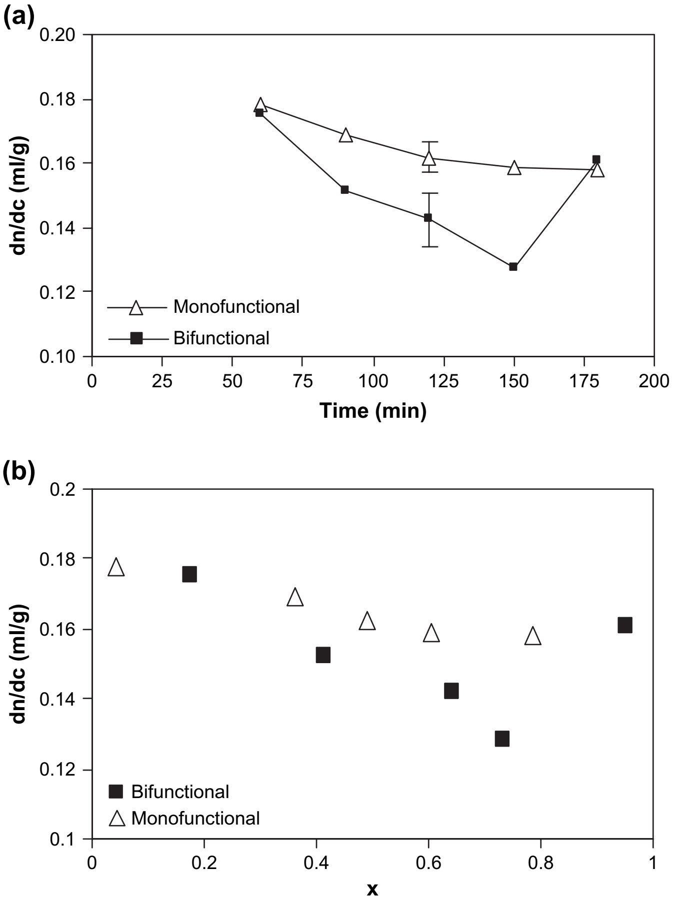

Fig. 10. dn/dc ratios of SAN polymerized with ATRP at 90 °C using monofunctional and bifunctional initiators as a function of: (a) polymerization time; (b) conversion (polymerization conditions: $[\mathrm{M}]_0/[\mathrm{I}]_0/[\mathrm{C}]_0 = 100/1/1$). The error bars represent one standard deviation from two replicates done for each sample.

FTIR was also used to identify the incorporation of both comonomers into the polymeric chains. Results from FTIR confirmed, as expected, that these copolymers were composed of styrene and acrylonitrile units. The absorption band at 1601 cm^{-1} is representative of the aromatic ring of the styrene comonomer, while the one at 2235 cm^{-1} identifies the nitrile group of the acrylonitrile comonomer. Fig. 12 compares FTIR spectra for pure polystyrene and two SAN copolymers containing different fractions of acrylonitrile. The stronger absorbance at 2235 cm^{-1} for the copolymer made with the bifunctional initiator confirms the ^{13}C NMR results that the bifunctional initiator incorporates more acrylonitrile (after 2.5 h of polymerization) than the monofunctional initiator after 1 h of polymerization (see Fig. 9). The ratio between the nitrile peak (2235 cm^{-1}) and the phenyl peak (1601 cm^{-1}) is 0.83 after 1 h of reaction and it increases to 0.915 after 2.5 h of polymerization.

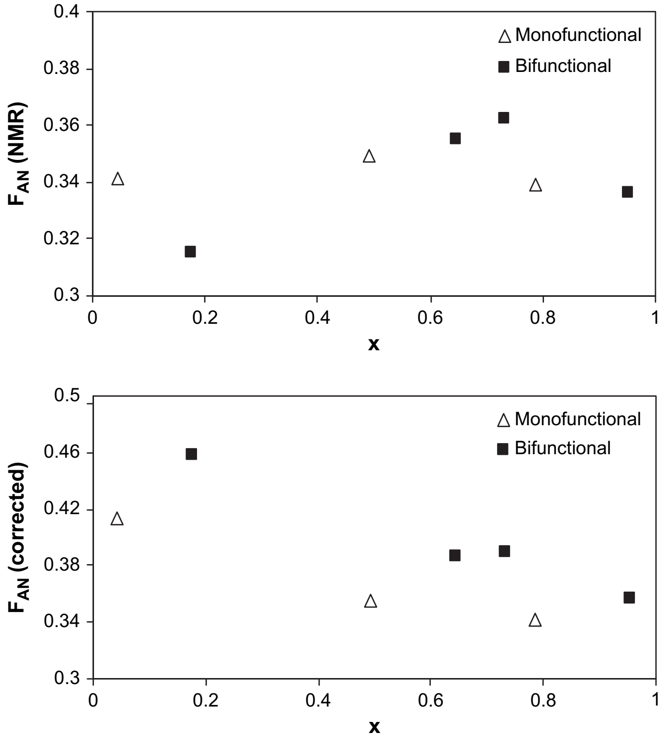

Fig. 11. Copolymer composition of acrylonitrile in SAN polymer vs. total conversion: (a) measured with ^{13}C NMR; (b) corrected composition (polymerization conditions: $[M]_0/[I]_0/[C]_0 = 100/1/1$. Temperature = 90 °C).

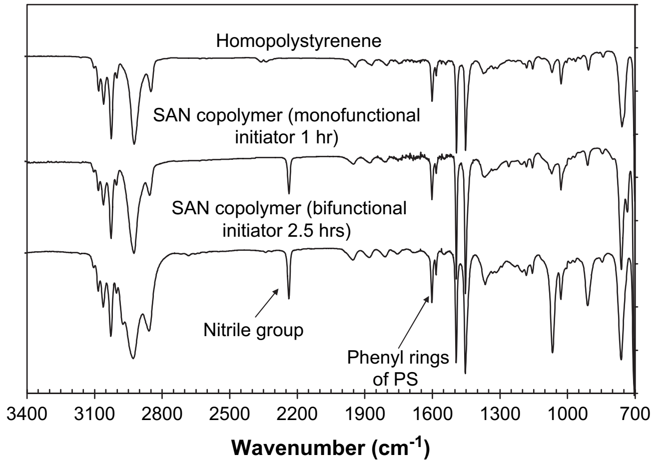

Fig. 12. FTIR spectra for pure polystyrene and two SAN copolymer samples with different fractions of acrylonitrile (spectra presented in transmittance units, curves shifted horizontally for clarity).

4. Conclusion

Bulk atom transfer radical polymerization of styrene and acrylonitrile with a bifunctional (benzal bromide) and monofunctional initiator (1-bromoethyl benzene) was successfully conducted in this investigation. Two polymerization procedures, simultaneous and sequential polymerizations, were compared. During simultaneous addition of styrene and acrylonitrile, the monofunctional initiator makes polymers with higher monomer conversion and molecular weights for the same polymerization time. This unusual result may be due to side reactions between the acrylonitrile and the benzal bromide initiator or due to the formation of species inactive for acrylonitrile polymerization after the first acrylonitrile insertion.

On the other hand, the sequential addition of comonomers (styrene first, followed by acrylonitrile after 20 min of polymerization) gave different results. The bifunctional initiator produced SAN with higher conversion, higher molecular weight, and narrower molecular weight distribution than the monofunctional initiator under these polymerization conditions.

Copolymer composition as a function of time was monitored by ^{13}C NMR, FTIR, and refractometry. All these techniques indicate that composition drift is more pronounced with the bifunctional initiator is used.

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