Atom Transfer Radical Polymerization through N-Chlorosulfonamides

B. FILIZ ŞENKAL, GÜRKAN HIZAL, NIYAZİ BIÇAK
Istanbul Technical University, Department of Chemistry, Maslak 80626 Istanbul, Turkey

Received 13 March 2001; accepted 21 May 2001

ABSTRACT: Controlled polymerizations of vinyl monomers such as methyl methacrylate and styrene are achieved using N-chloro,N-propyl-p-toluenesulfonamide (NCPT) together with a cuprous bromide/hexahexyl triethylenetetramine (CuBr/H-TETA) complex. Although N-halosulfonamides are known to decompose radically to give free chlorine, NCPT alone (without a cuprous complex) does not initiate any polymerization even in prolonged reaction times. Instead these add to the double bonds to give 2-chloroethylsulfonamides. In the present polymerization system a good chlorine donor (NCPT) is combined with an organic soluble complex (CuBr/H-TETA) to perform atom transfer radical polymerizations (ATRPs) in homogenous conditions. The linear proportionality of the molecular weights to the conversions and straight lines observed in ln(M0/M) (where M0 and M are the monomer contents at the beginning and at any time, respectively) versus time plots indicate typical controlled polymerization characteristics. The use of freshly prepared NCPT is advisable due to its slow and spontaneous decomposition when standing at room temperatures. Because of their easy preparation, N-chlorosulfonamides can be used and are preferred instead of special halogen compounds commonly used in copper mediated ATRP. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 2691–2695, 2001

Keywords: N-chlorosulfonamide initiator in atom transfer radical polymerization; copper mediated atom transfer radical polymerization; N-chloro,N-propyl-p-toluenesulfonamide

INTRODUCTION

The N-chlorosulfonamides, especially mono- or dichloro-p-toluenesulfonamides (known as chloramine-T and dichloramine-T, respectively), are widely used as chlorine sources for disinfection of aqueous solutions.1 These compounds are also used as chlorinating agents2 or oxidants for alcohols.3 The N-chloro- and N-bromosulfonamides undergo spontaneous slow decomposition to give sulfonamide and hypohalo acids, which in turn yield chlorine or bromine. The decomposition of N-bromosulfonamides is faster and appreciable bromine evolution takes place even at room temperature. Because of this fact, N-bromosulfonamides are not of much interest in chemistry.

Chlorosulfonamides can be prepared by the simple interaction of sulfonamides with a bleaching liquor.4 These add to alkenes to give chloroethylsulfonamide derivatives in high yields. This reaction is speeded up by UV radiation and heat.5

The chemistry of N-chlorosulfonamides induced us to use N-chloro-p-toluenesulfonamides as an initiator in atom transfer radical polymerization (ATRP). Alkyl halogenides, especially α-keto chlorides and bromides, are common initiators in ATRP. Alkyl halogenides with α-hydrogens are not preferred because of HX elimination as a side reaction. Obviously, the carbonyl group connecting with the halomethyl group prevents β
elimination and makes it easier to cleave the carbon–halogen bond.

Since the pioneering study of Wang and Matyjaszewski on copper mediated ATRP,\(^6\,^7\) many halogenides,\(^8\) including sulfonyl chloride,\(^9\,^10\) were studied as initiator components in polymerization. Although R-Br/CuBr-L couples were found to be superior to the R-Cl/CuCl-L system,\(^11\) cross systems of R-Br/CuBr-L were demonstrated to work successfully.\(^12\)

Based on these considerations, in this study we attempted to use N-chloro-N-propyl-p-toluenesulfonamide (NCPT) as a halogen precursor, together with triethylenetetramine having six hexyl groups on the nitrogen atoms (hexylated TETA, H-TETA). The ligand H-TETA forms an organic soluble Cu(I) complex\(^13\) and provides homogenous ATRP conditions.

The aim of the present work was to combine homogeneous ATRP conditions with a good halogen donor, NCPT. The efficiency of the initiation system was investigated in ATRP of methyl methacrylate (MMA) and styrene monomers.

**EXPERIMENTAL**

The styrene (Fluka) and MMA (Fluka) monomers were distilled before use, and the p-toluenesulfonyl chloride (Fluka) was purified by recrystallization from chloroform. All the other chemicals were used without any further purification.

**Measurements**

The \(^1\)H NMR spectra were recorded using a Bruker 250-MHz spectrometer.

Gel permeation chromatography (GPC) traces were taken by using an Agilent 1100 series consisting of a pump, a RI detector, and Waters styrogel (HR 4, HR 3, and HR 2) columns. Tetrahydrofuran was used as the eluent, and the flow rate was 0.3 mL/min.

**Preparation of H-TETA and NCPT**

The H-TETA was prepared by the Acar and Bicak procedure.\(^13\)

The NCPT was prepared by the reaction of a bleaching liquor with N-propyl-p-toluenesulfonamide that was obtained by condensation of p-toluenesulfonylchloride with two equivalents of propylamine as described in the literature.\(^14\)

Thus, 6.4 g (3 \(\times\) \(10^{-2}\) mol) of N-propyl-p-toluene-sulfonamide was dissolved in 25 mL of ethanol, and 1 mL of acetic acid was added to it. This solution was added dropwise to a stirring solution of 40 mL of commercial bleaching liquor with 15% (w/w) active chlorine at 0 °C. The stirring was continued until the oily product solidified at 0 °C. Stirring was continued for another 2 h at 0 °C and the reaction content was left in a refrigerator for 24 h. The product was isolated and used fresh whenever necessary to avoid its spontaneous decomposition (38–40 °C mp, 6.2-g yield, 83.0%).

**Chlorine Analysis of NCPT**

The chlorine analysis was performed by the iodo-metric method analogue to the procedure described in the literature.\(^15\) Briefly, 0.27 g of NCPT, 0.4 g of KI, 5 mL of acetic acid, and 10 mL of water were mixed and stirred for 10 min in a closed bottle. The iodine that was released was directly titrated with 0.1 M Na\(_2\)S\(_2\)O\(_3\) solution; 21.05 mL of the titer corresponds to 13.85% chlorine content, which accounts for 96.4% of the theoretical value.

**Preparation of Cuprous Bromide**

Because copper(I) halides are highly susceptible to air oxidation, it is difficult to store them. Thus, the CuBr was freshly prepared by modification of the procedure described in the literature.\(^16\) A mixture of 12.5 g (5 \(\times\) \(10^{-2}\) mol) of CuSO\(_4\) \(\cdot\) 5H\(_2\)O and 17.9 g (0.15 mol) of KBr was dissolved in 50 mL of water. While stirring, 10 g (0.8 mol) of Na\(_2\)SO\(_3\) in 50 mL of water was added to the above solution. White CuBr flakes slowly separated from the faintly green solution. Then 1 mL of 0.5 M H\(_2\)SO\(_4\) was added to the mixture and stirred for 15 min. The precipitate was filtered as quickly as possible and successively washed with 50 mL of 0.1 M Na\(_2\)SO\(_4\) solution, 10 mL of distilled water, and 30 mL of glacial acetic acid. The white solid was also washed with alcohol and ether (30 mL of each). The product was transferred to a glass plate and dried under a vacuum at 50 °C for 24 h. The yield was 5.2 g (72.4%). The product was stored in a tightly stoppered dark bottle.

**Polymerization Procedure**

The polymerizations were carried out in bulk polymerization conditions using styrene and MMA monomers at 100 °C. A typical procedure was to use a 100-mL three-necked, round-bottom flask.
equipped with a reflux condenser, a dropping funnel, and a nitrogen inlet into which were placed 25.4 mL (0.25 mol) of MMA, 1 mL ($1.5 \times 10^{-3}$ mol) of H-TETA, and 0.215 g ($1.5 \times 10^{-3}$ mol) of CuBr under a nitrogen flow. The flask was mounted in a silicon oil bath and the mixture was stirred until all the CuBr dissolved (10 min).

The reaction content was heated and kept at a constant 100 °C with stirring. Then 0.371 g ($1.5 \times 10^{-3}$ mol) of NCPT in 5.1 mL (0.05 mol) of MMA was added through the dropping funnel. The solution became brownish-green within 20 min.

The kinetics of the reaction was followed by aliquots taken at appropriate time intervals. The percentage-conversion data and GPC traces are presented in Figures 1–4.

Poly(MMA) prepared by this procedure using a 1/20 NCPT/MMA ratio (in 20 min) gave an ordinary $^1$H NMR pattern with additional weak aromatic proton signals in the 7.6–7.8 ppm range.

RESULTS AND DISCUSSION

Because N-chlorosulfonamides are mild oxidizing and chlorinating agents, they are expected to initiate copper mediated ATRP of vinyl monomers by creating sulfamidyl radicals according to the redox reaction in Scheme 1. The reversible halogen transfer steps in controlling the chain growth must proceed in a normal fashion as for the alkyl bromides in the ATRP.

It is important to note that, unlike alkyl halides, $N$-chlorosulfonamides add to double bonds (Scheme 2). This side reaction is speeded up by UV radiation and heat. The reaction can be considered as competitive with the initiation step outlined in Scheme 1. Nevertheless, these species are expected to take part in the halogen transfer steps, although transfer of chlorine is somewhat slower than bromine. However, a rapid color change after the addition of NCPT revealed that the primary initiation reaction was favored and initiation took place in normal fashion by oxidation of Cu(I).

This initiation mechanism suggested a $p$-toluenesulfonamidyl group in the polymer ends. This was evidenced by $^1$H NMR spectra of a MMA sample.

Figure 1. A kinetics plot for the ATRP of MMA in bulk conditions with a 1/200 ratio of [NCPT]$_0$/[M$_0$] at 100 °C and a 1:1:1 ratio of [H-TETA]/CuBr/NCPT.

Figure 2. A kinetics plot for the ATRP of styrene in bulk conditions with a 1/100 ratio of [NCPT]$_0$/[M$_0$] at 100 °C and a 1:1:1 ratio of [H-TETA]/CuBr/NCPT.

Figure 3. (■) The variation of the molecular weight with conversion and (×) the corresponding polydispersity for the MMA polymerizations with the same conditions as Figure 1.
polymer obtained in a separate experiment using a 1/20 initiator/monomer ratio and the same reaction conditions. The $^1$H NMR spectra of the purified polymer sample clearly showed weak aromatic proton signals in the 7.6–7.8 ppm range. This evidence established the proposed initiation mechanism.

The MMA and styrene polymerizations both gave linear $\ln(M_0/M)$ (where $M_0$ and $M$ are the monomer contents at the beginning and at any time, respectively) versus time plots (Figs. 1, 2). The polymerization of MMA was also about 3 times faster than that of styrene. The low conversion for 20 min of the reaction period fell below the linear plot in Figure 1 for the MMA polymerization. However, in such a low conversion, a low molecular weight (28,400 Da) product might not be precipitated quantitatively. Therefore, it is difficult to assign an induction period for the polymerization.

The rate constants obtained from the slopes were $k = 1.47 \times 10^{-4} \text{ s}^{-1}$ and $4.09 \times 10^{-5} \text{ s}^{-1}$ for MMA and styrene polymerizations, respectively. The corresponding molecular weight conversion data gave linear relationships (Figs. 3, 4) as expected. In both graphs the extrapolated lines do not pass through the origin of the axes. In other words, rapid chain growth took place at the earlier stage of the polymerizations.

This revealed a fast initiation that could not be balanced by a relatively slow halogen transfer process. In a 1/200 [NCPT]/[M$_0$] ratio, except for 79% of the conversion yield, the polydispersity was in the 1.10–1.16 range for the MMA polymerizations. For the styrene polymerization the polydispersity index deviated considerably from unity and rose to 1.16–1.40 for 1/100 [NCPT]/[M$_0$] (Fig. 4).

To indicate high conversions the polymerizations were performed by separate experiments using sealed tubes at longer times. The reaction mixtures became too viscous and handling of aliquots was almost impossible. Because of this fact, corresponding high conversions (more than 70%) represented high polydisperisities in both MMA and styrene polymerizations (Figs. 3, 4). In these cases the mixtures could not be stirred and controlling of polymerizations was greatly suppressed because of slow diffusion of the copper complex in the gelled matrix. As a consequence, the polydisperisities derived at high conversions are not reliable in the bulk conditions studied.

The apparent initiator efficiency of NCPT was somewhat low in both polymerizations. The apparent initiation efficiency ($f$) was defined as the molar ratio of polymer chains obtained to the one expected. It was simply deduced by the formula $f = pMr/M_n$, where $p$ denotes the conversion ratio, $M$ is the molecular weight of the monomer, $M_n$ is the number-average molecular weight from GPC traces, and $r$ is the molar ratio of th monomer to the initiator. The value of $f$ was in the 0.12–0.15 range in earlier stages of the styrene poly-

Scheme 1. The redox initiation of vinyl polymerization through $N$-chlorosulfonamides.

Scheme 2. Addition of $N$-chlorosulfonamides to ethylenic double bond.

Figure 4. (■) The variation of the molecular weight with conversion and (×) the corresponding polydispersity for the styrene polymerizations with the same conditions as Figure 2.
merization. After 5 h it rose to the 0.25 level, presumably due to reduced combination rates of the chain growing. Similar behavior was observed in the MMA polymerization. In that case the \( f \) gradually increased almost linearly with the conversion and was between 0.17 and 0.27.

Because the ligand used in the study led to a soluble copper complex, the kinetic parameters that were derived must be more reliable. Additionally, polymerizability in the presence of radically cleavable NCPT was evidence for confirmation of the radical nature of the ATRP, which settled some contradictory mechanisms\(^{12} \) that were proposed. Because halosulfonamides are known to decompose by splitting of the \( N \)-halogen bond and yield sulfamidyl radicals, initiation by NCPT implied that ATRP proceeded via radicals, at least in the initiation step. The only disadvantage of NCPT was its spontaneous decomposition when standing, which meant that freshly prepared NCPT must be used. However, the chlorine content of an NCPT sample that was left to stand for 5 days at room temperature was found to be only 3.6% less than the theoretical amount of the chlorine.

In conclusion, ATRP can be initiated using \( N \)-halosulfonamides, which reveals the possibility of grafting through \( N \)-halosulfonamide groups. Because halosulfonamides are readily prepared, these can be used as initiators in ATRP instead of special halogenides. Presumably this methodology can be extended to grafting on polyamides through \( N \)-haloamide groups.

REFERENCES AND NOTES