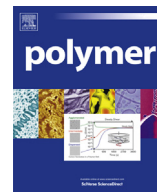




Contents lists available at ScienceDirect

## Polymer

journal homepage: [www.elsevier.com/locate/polymer](http://www.elsevier.com/locate/polymer)

# One pot, two step sequence converting atom transfer radical polymerization directly to radical trap-assisted atom transfer radical coupling

Elizabeth M. Carnicom, William E. Coyne, Kenneth D. Myers, Eric S. Tillman\*

Department of Chemistry, Bucknell University, Lewisburg, PA 17837, USA

## ARTICLE INFO

## Article history:

Received 17 June 2013

Received in revised form

19 August 2013

Accepted 21 August 2013

Available online xxx

## Keywords:

Atom transfer radical polymerization

Atom transfer radical coupling

Polystyrene

## ABSTRACT

Monobrominated polystyrene (PStBr) chains were prepared using standard atom transfer radical polymerization (ATRP) procedures at 80 °C in THF, with monomer conversions allowed to proceed to approximately 40%. At this time, additional copper catalyst, reducing agent, and ligand were added to the unpurified reaction mixture, and the reaction was allowed to proceed at 50 °C in an atom transfer radical coupling (ATRC) phase. During this phase, polymerization continued to occur as well as coupling; expected due to the substantial amount of residual monomer remaining. This was confirmed using gel permeation chromatography (GPC), which showed increases in molecular weight not matching a simple doubling of the PStBr formed during ATRP, and an increase in monomer conversion after the second phase. When the radical trap 2-methyl-2-nitrosopropane (MNP) was added to the ATRC phase, no further monomer conversion occurred and the resulting product showed a doubling of peak molecular weight ( $M_p$ ), consistent with a radical trap-assisted ATRC (RTA-ATRC) reaction.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Atom transfer radical polymerization (ATRP) is a simple method to produce well-defined polymers bearing a halogen terminus [1–4]. Shown in Scheme 1 (top) are the mechanistic steps in a typical ATRP reaction leading to brominated polystyrene (PStBr). An equilibrium between the chain end, benzylic radical and the dormant, bromine-capped chain end is a requirement, with the position of the equilibrium tunable by manipulating the experimental parameters [5–9]. Retention of the chain end halogen is essential for post-polymerization reactions, but is also a hallmark of a well-controlled polymerization that produces a polymer sample with low polydispersity. When ATRP reactions are halted at lower monomer conversions and/or performed with Cu(II)Br in the initial reaction mixture, quantitative chain end functionality is often the result [10–12].

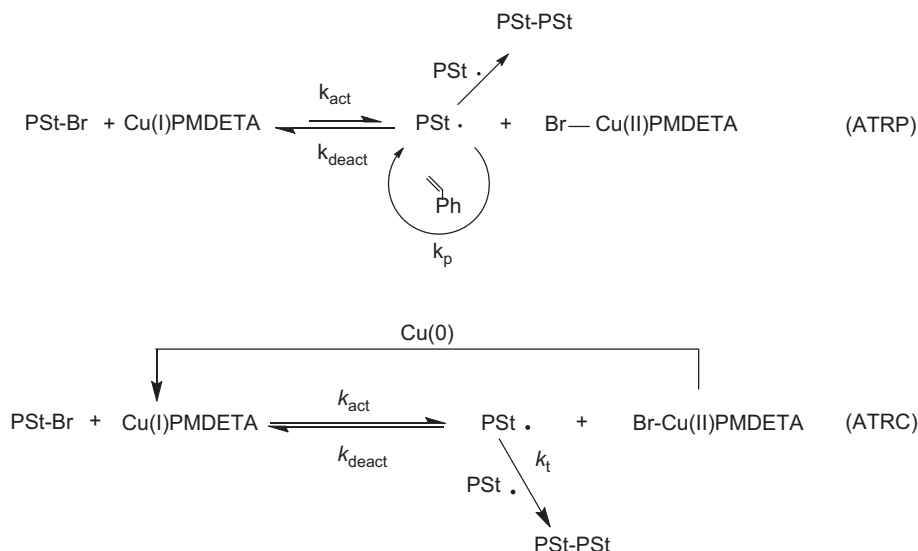
The simplest post-polymerization reaction that involves halogen-capped polymers prepared by ATRP is atom transfer radical coupling (ATRC, Scheme 1 bottom) [13–16], which is simply

the purposeful radical–radical termination reaction of ATRP. The polymer product from ATRP can be used in its native form for ATRC, because the same structural features that allowed for successful propagation in the ATRP reaction often make for a successful ATRC reaction. One criteria is that the favored radical–radical termination pathway is head-to-head coupling, as is the case for PSt as shown in Scheme 2 (top) [17], and not disproportionation, as is the case for poly(methyl methacrylate) [17,18]. ATRC reactions are performed in a very similar manner to ATRP reactions, except with conditions favoring a larger concentration of polymer radicals, meaning simply a higher  $K_{\text{ATRP}}$  value. To accomplish this, higher amounts of ligand-bound catalyst are added along with a reducing agent, often elemental copper metal, to prevent the build-up of Cu(II)Br as the ATRC reaction proceeds [19–21].

We have used radical trap-assisted ATRC (RTA-ATRC) reactions to produce PSt dimers [22], block copolymers [23], and even cyclic polymers [24]. RTA-ATRC is schematically shown in Scheme 2 (bottom), with the coupling of the polymer chains occurring in a stepwise sequence. The polymer radical is initially converted into a persistent, nitroxide radical (PSt-NO•), which serves as a protecting group in that it resists many reaction pathways of an active, chain end radical such as propagation with monomer and disproportionation. Also, this nitroxide radical is not in equilibrium with a dormant form, and locks the chain end into a species that is still

\* Corresponding author. Tel.: +1 570 577 3265; fax: +1 570 577 1739.

E-mail address: [etillman@bucknell.edu](mailto:etillman@bucknell.edu) (E.S. Tillman).

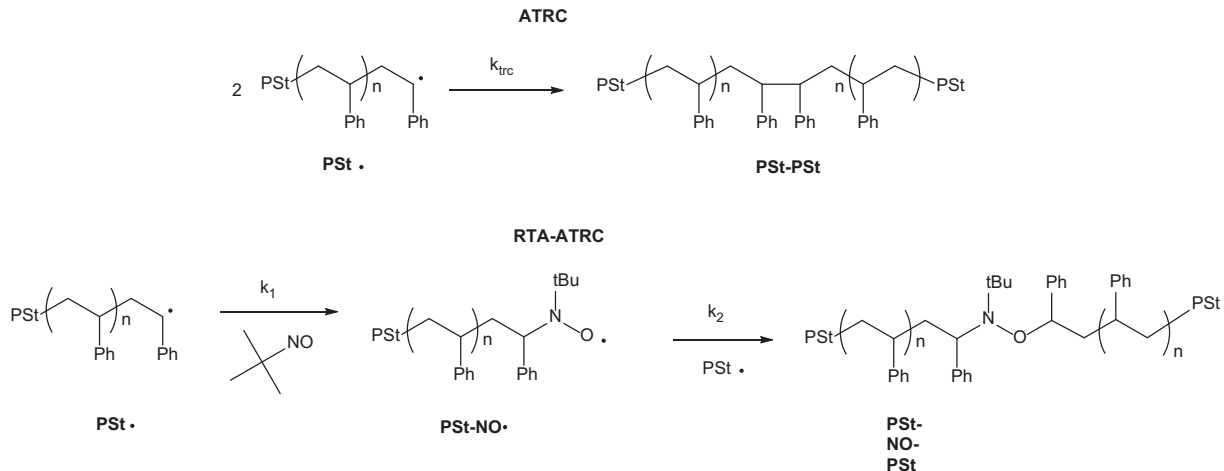


**Scheme 1.** Mechanistic summary of atom transfer radical polymerization (ATRP) of styrene and atom transfer radical coupling (ATRC) of polystyrene.

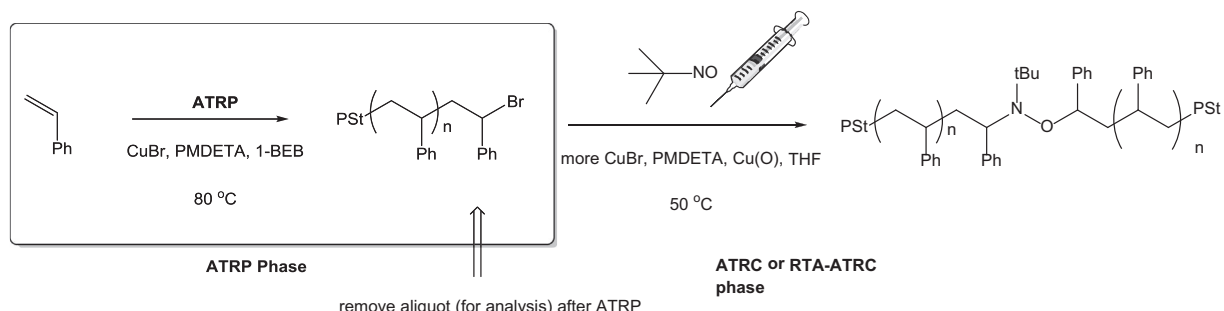
able to undergo radical–radical coupling. The rate constant for trapping of the second PSt radical by the chain nitroxide,  $k_2$ , is much faster than  $k_1$  [25], the rate constant for the initial reaction between the PSt radical and radical trap.

In sequential ATRP–ATRC reactions, the polymer formed during the ATRP phase of the reaction is traditionally isolated and purified. This is done to separate the polymer from unconverted monomer,

and also to remove metal (much of which will be in the oxidized state that would prevent or slow an ATRC reaction) and ligand. As a consequence, two separate reactions must be performed with new reagents being weighed and charged into the reaction flask for both the ATRP and ATRC phase of the reaction. In this contribution, we show that an ATRP reaction of styrene can be directly crossed over to an RTA-ATRC simply by the further addition of metal, ligand and



**Scheme 2.** Coupling of polystyrene radicals ( $\text{PSt}\cdot$ ) by ATRC (top) and by radical trap-assisted ATRC (RTA-ATRC) (bottom).



**Scheme 3.** Summary of ATRP directly to RTA-ATRC sequence. When 2-methyl-2-nitrosopropane is omitted, the reaction sequence would be ATRP directly to ATRC.

Download English Version:

<https://daneshyari.com/en/article/5181882>

Download Persian Version:

<https://daneshyari.com/article/5181882>

[Daneshyari.com](https://daneshyari.com)