Atom Transfer Radical Polymerization of Vinyl Monomers in the Presence of Tetraethylthiuram Disulfide

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Summary: *In situ* ATRPs of MMA, St in the presence of TD catalyzed by $FeCl_3/PPh_3$ and $CuBr_2$/bpy have been studied, respectively. The results showed that the initiator Et_2NCS_2X (X = Cl or Br) and catalyst $FeCl_2$ or CuBr were formed *in situ* from the initiating components and the polymerization exhibited living radical polymerization characteristics. In the case of St polymerization with TD/CuBr/bpy initiating system, an inverse ATRP was observed.

Keywords: atom transfer radical polymerization (ATRP); initiators

Introduction

Radical polymerization is a general process for the synthesis of high molecular weight vinyl polymers, but not a living procedure because of the irreversible termination reactions between two propagating radicals by coupling or disproportionation. Molecular weight and molecular weight distribution are very difficult to be controlled. In 1982 living radical polymerization of vinyl monomers with iniferter was reported by Otsu *et al.* [1, 2], but the obtained polymers were ill controlled with high molecular weight distributions. Successively a number of systems based on reversible termination of propagating radicals were discovered. In 1993, Georges *et al.* [3, 4] introduced a living radical polymerization of styrene (St) using AIBN and a stable radical 2,2,6,6-tetramethyl-1-piperydinyloxy to limit the undesirable coupling and disproportionation reactions. This polymerization is named nitroxide-mediated stable free radical polymerization (SFRP). Later, Wang and Matyjaszewski [5, 6], Sawamoto *et al.* [7, 8], and Percec *et al.* [9, 10], reported a living radical polymerization with transition metal catalysts and Matyjaszewski named the process atom transfer radical polymerization (ATRP). Another process is reversible addition fragmentation chain transfer (RAFT) [11].

ATRP generally can be divided into two types: normal ATRP and reverse ATRP [6]. In normal ATRP, organic chlorides act as initiators, transition metal compounds in their lower

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oxidation state, such as Cu(I), Fe(II), Ru(II), Ni(II), Rh(I), Pd(II), as catalysts, and electron-donating compounds such as 2, 2'-bipyridine (bpy), triphenylphosphine (PPh_3), etc. as metal complex ligands. Various vinyl monomers such as St, methyl methacrylate (MMA), butyl acrylate, 2-hydroxyethyl acrylate, acrylonitrile, etc, have been polymerized successfully by this method, and the polymerization exhibits living polymerization characteristics. Well-defined polymers with ω-halide atom end groups and low polydispersity index (PDI) were obtained. In reverse ATRP, a higher oxidation state transition metal complex and a conventional radical initiator were used instead. In our lab, we have developed some new reverse ATRP initiating systems containing a carbon—carbon bond thermal iniferter, such as 1, 1, 2, 2-tetraphenyl-1, 2-ethanediol (TPED) [12, 13], diethyl 2, 3-dicyano-2, 3-diphenyl-succinate (DCDPS) [14-20] and diethyl 2, 3-dicyano-2, 3-di(p-tolyl)succinate (DCDTS) [21], for instance, TPED/$FeCl_3$/PPh_3, DCDPS/$FeCl_3$/PPh_3, DCDPS/$CuCl_2$/bpy, DCDTS/$CuCl_2$/bpy, DCDPS/$Fe(S_2CNEt_2)_3$ for living radical polymerizations of St and MMA. The results revealed that these polymerizations exhibited some living characteristics and well-defined polymers with functionalized end groups as well as low PDI were obtained.

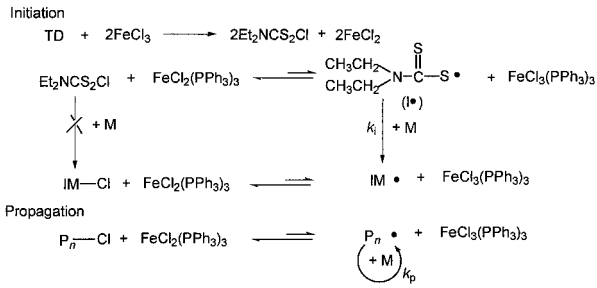
Recently, we have studied ATRP of vinyl monomers in the presence of tetraethylthiuram disulfide (TD) and discovered a new type of ATRP, *in situ* ATRP. In addition, the polymerization of St can proceed via *in situ* ATRP and reverse ATRP with TD in conjunction with different oxidized state metal complex catalyst, Cu (II) and Cu (I), respectively. This article describes the results of *in situ* ATRP of MMA with TD/$FeCl_3$/$PhPh_3$ [22, 23] or St with TD/$CuBr_2$/bpy [24] and reverse ATRP of St initiated with TD/CuBr/bpy [25], respectively.

Results and Discussion

In situ ATRP with TD/$FeCl_3$/PPh_3 Initiating System

The investigation on polymerization of MMA with TD/$FeCl_3$/PPh_3 initiating system showed the process is a living polymerization[22, 23]. The plot of $\ln[M]_0/[M]$ *versus* time gave a straight line, demonstrating that the kinetics was first-order on monomer, M_n increased with the rising monomer conversion, and PDI was quite low (M_w/M_n =1.1). Since the initiator, diethylthiocarbamoyl chloride, $Et_2NC(S)SCl$ and catalyst $FeCl_2$ were produced from the components in the initiating system, the polymerization was named *in situ* ATRP. Although

the initiation mechanism is rather complicated, the polymerization can be simply indicated as in Scheme 1.



Scheme 1.

In situ ATRP with TD/$CuBr_2$/bpy Initiating System

Li and Qiu [24] reported another *in situ* ATRP process, St polymerization with TD/$CuBr_2$/bpy initiating system. The plot of $\ln([M]_0/[M])$ *versus* time gave a straight line (Fig. 1), indicating that the kinetics was first-order in monomer. M_n increased linearly with the conversion (Fig. 2). The polymerization was inhibited by 2,2-diphenylpicrylhydrazyl (DPPH), a radical scavenger, but not affected by the addition of a protonic solvent, such as methanol. These results reveal the living radical polymerization nature. PDI of the resulting PSt was as low as 1.3, but the initiator efficiency ($f = M_{n\,(cal)}/M_{n\,(GPC)}$) was not high, 0.5.

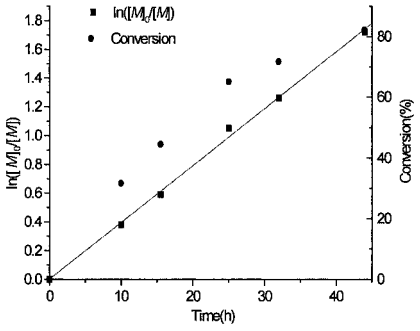


Figure 1. Time dependence of $\ln([M]_0/[M])$ and conversion for ATRP of St at 100 °C. Conditions: $[St]_0$ = 8.7 mol L^{-1}, $[St]_0/[TD]_0/[CuBr_2]_0/[bpy]_0$ = 1000:1:2:4

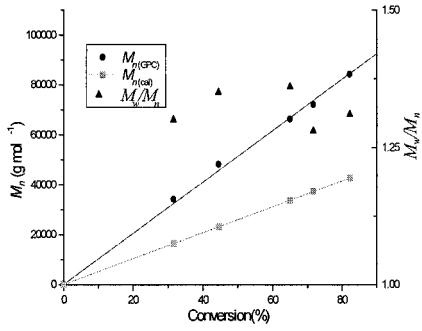


Figure 2. Dependence of M_n and M_w/M_n on monomer conversion for ATRP of St with TD/$CuBr_2$/bpy initiating system at 100 °C. See Figure 1 for the conditions.

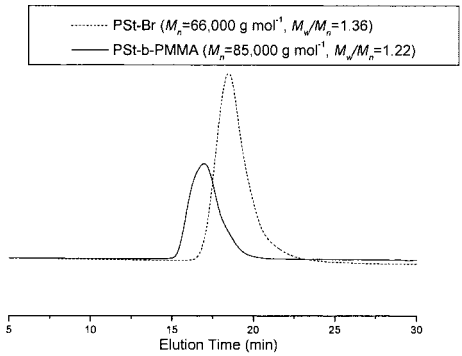
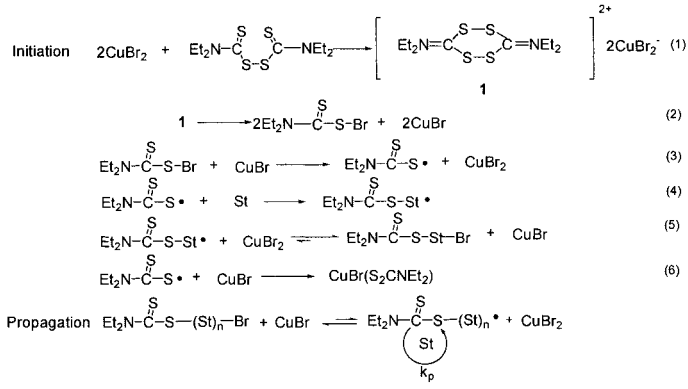


Figure 3. GPC curves of PSt—Br and PSt-b-PMMA initiated with PSt—Br catalyzed by CuCl in bulk at 100 °C. Conditions: $[MMA]_0$ = 9.32 mol L^{-1}, $M_{n\,(PSt—Br)}$ = 66,000 g mol^{-1}, M_w/M_n = 1.36, $[MMA]_0$:$[PSt—Br]_0$:[CuCl]:[bpy] = 2350:1:1:3.

From ^1H NMR spectroscopy, the resulting polymer have α-$S_2CN(CH_2CH_3)_2$ and ω-bromine end groups. It can be used as a macroinitiator to initiate MMA polymerization in the presence of CuCl/bpy complex. M_n rises from 66,000 to 85,000, and PDI become narrower, from 1.36 to 1.22 (Fig. 3). The obtained PS-b-PMMA was characterized by NMR and DSC analyses.

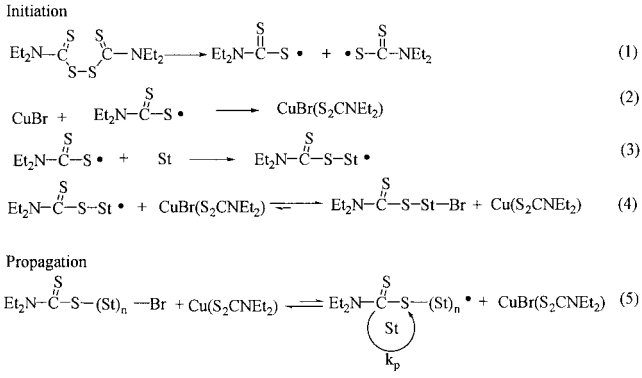
The mechanism of St polymerization with TD/$CuBr_2$/bpy initiating system is proposed in Scheme 2 (bpy are omitted for simplification). The initiator, Et_2NCS_2Br, and catalyst CuBr are produced from the reaction of TD and $CuBr_2$ as shown in equations 1-2. The generated primary radical dtc· (eq. 3) initiates monomer, generating active monomer species. The primary radical dtc· may also oxidize CuBr to the corresponding stable cupric species, CuBr(dtc), resulting in the decreased initiator efficiency.



Scheme 2.

Reverse ATRP with TD/CuBr/bpy Initiating System

When the polymerization of St was initiated with TD/CuBr/bpy, we found that it belonged to a reverse procedure [25]. The kinetic plot was first order in monomer and M_n of resulting polymer was in good agreement with the calculated one. Radical scavenger DPPH immediately terminated the polymerization, which supported the radical essence of the polymerization.



Scheme 3.

The presence of ω-Br end group in the polymer chain was characterized by ^{1}H NMR analysis. The PSt obtained can be used as a macroinitiator catalyzed with CuCl/bpy to initiate MMA polymerization for synthesis of PS-b-PMMA. When polymerization was carried out at 100 °C for 7 h, and $[MMA]_0$:$[PSt\text{-}Br]_0$/$[CuCl]_0$/$[bpy]_0$ = 1340:1:1:3, Mn increased from 50,000 to 105,000 and PDI decreased from 1.40 to 1.23.

The polymerization mechanism of St with TD/CuBr/bpy initiating system is similar to the BPO/CuBr/bpy initiation system [26, 27], as shown in Scheme 3.

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