

Review

NEW INITIATION SYSTEMS FOR ATOM TRANSFER RADICAL POLYMERIZATION

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Abstract This review summarizes our achievements in designing new initiation systems for atom transfer radical polymerization (ATRP). First-order kinetics and extension experiments revealed the living nature of these reactions. Tailor-made vinyl polymers with functional end groups were characterized by $^1\text{H-NMR}$ and UV-vis spectroscopic analyses. Replacing traditional radical initiators AIBN and BPO, carbon-carbon bond compounds, 1,1,2,2-tetraphenyl-1,2-ethanediol, diethyl 2,3-dicyano-2,3-diphenylsuccinate and diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate, were utilized in reverse ATRP to produce the initiating radical. Sulfur-sulfur bond iniferter, tetraethylthiuram disulfide (TD), in conjunction with CuBr/bpy or $\text{NiCl}_2/\text{PPh}_3$ complex could control the styrene polymerization via redox reaction. Pseudo-halogen transfer reaction was demonstrated to maintain the dormant-active species equilibrium in normal and reverse ATRP with $\text{Cu}(\text{S}_2\text{CNET}_2)$, $\text{Cu}(\text{S}_2\text{CNET}_2)\text{Cl}$ and $\text{Fe}(\text{S}_2\text{CNET}_2)_3$ as catalysts. The organic halide initiator and reduced transition metal compound that started the living polymerization were produced *in situ* from the components of $\text{TD/FeCl}_3/\text{PPh}_3$, $\text{TD/CuBr}_2/\text{bpy}$ and $\text{Fe}(\text{S}_2\text{CNET}_2)_3/\text{FeCl}_3/\text{PPh}_3$ systems. Accurate control of UV irradiation time favored the radical generation process in photo ATRP with the 2,2-dimethoxy-2-phenylacetophenone/ $\text{Fe}(\text{S}_2\text{CNET}_2)_3$ initiation system.

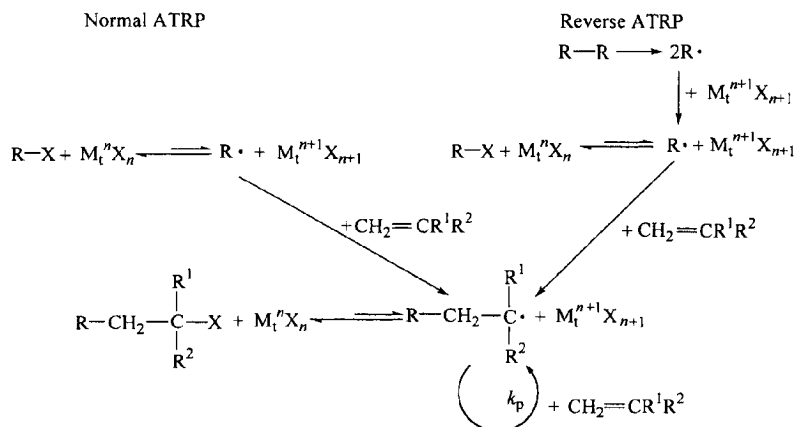
Keywords Atom transfer radical polymerization (ATRP), Initiation system, Pseudo-halogen transfer, *In situ* ATRP, Photo ATRP

INTRODUCTION

Radical polymerization dominates the area of the synthesis of high molecular weight vinyl polymers, but it is difficult to control due to the irreversible termination reactions between radicals by coupling or disproportionation. Since the iniferter-controlled radical polymerization was first introduced by Otsu *et al.*^[1, 2], a number of living radical polymerization systems have been reported successively based on reversible terminations or transfer reactions of propagating radicals. Georges *et al.*^[3] introduced the nitroxide-mediated stable free radical polymerization (SFRP) of styrene (St) using benzoyl peroxide (BPO) and a stable radical, 2,2,6,6-tetramethyl-1-piperidinyloxy. Later, Wang and Matyjaszewski^[4, 5], Sawamoto and coworkers^[6, 7], and Percec *et al.*^[8], reported living radical polymerization mediated by transition metal catalysts. Atom transfer radical polymerization (ATRP) was named on the basis of the atom transfer radical addition (ATRA) essence during the reaction course^[9]. Another addition to this field was reversible addition fragmentation chain transfer (RAFT) via the reversible degenerative exchange reaction of thioesters^[10]. The MADIX (Macromolecular Design via Interchange of Xanthate) technique was used to carry out living radical polymerization of vinyl monomers in an emulsion system^[11].

ATRP is a most efficient synthetic method for tailor-made polymers. Polymerization of various vinyl monomers, including styrene, methyl methacrylate, butyl acrylate, 2-hydroxyethyl acrylate and acrylonitrile, displays living characteristics: first-order kinetics, predictable number-average molecular weight (M_n) by way of

monomer conversion and low polydispersity index (PDI). Originally, ATRP was divided into two branches, normal ATRP and reverse ATRP, based on the components of the initiation system^[5, 7]. Accordingly the mechanisms are inconsistent as shown in Scheme 1 (ligand, omitted for simplification). In normal ATRP, organic chlorides or bromides ($R-X$, $X = Cl$ or Br) act as initiators, transition metal halides in their lower oxidation state ($M_t^n X_n$), $Cu(I)$, $Fe(II)$, $Ru(II)$, $Ni(II)$, $Rh(I)$ or $Pd(II)$, as catalysts, and electron-donating compounds, bipyridine derivatives, triphenylphosphine (PPh_3) or aliphatic amines, as complex ligands. The initiating radical is produced by the redox reaction of $R-X$ and $M_t^n X_n$ and reversible dynamic equilibrium maintained by the halogen transfer reaction. Conversely, a conventional radical initiator ($R-R$) and transition metal complex in a higher oxidation state ($M_t^{n+1} X_{n+1}$) are used in reverse ATRP. Thermolysis of $R-R$ is responsible for the production of primary radicals. The subsequent abstraction of a halogen atom from $M_t^{n+1} X_{n+1}$ molecules generates the corresponding organic halide $R-X$ and $M_t^n X_n$ species. The propagation is the same as in a normal ATRP procedure.



Scheme 1 Typical ATRP reactions

To deepen the understanding of this living polymerization method, many research groups have carried out studies on many aspects, such as on design of initiating components, on reaction mechanism and on synthesizing precise functional polymers. During the past few years, our lab has focused on the study of initiation systems from various angles, especially on selecting and optimizing the initiators and catalysts, and has had many successes. The achievements will be summarized in the following sections.

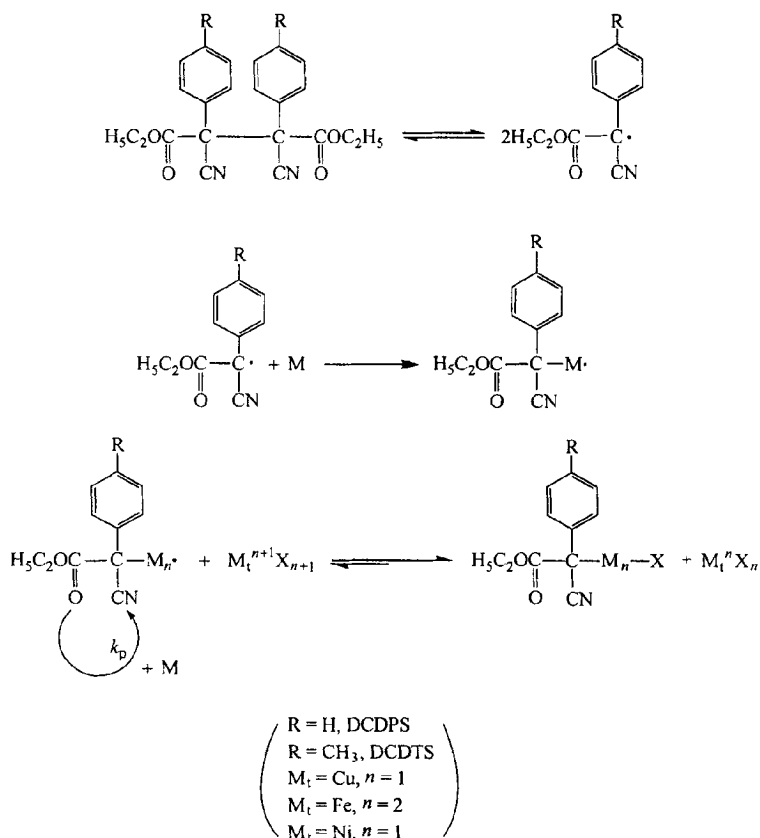
Not only carbon-carbon bond thermal iniferters, 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED), diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS) and diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS), but also sulfur-sulfur bond iniferter, tetraethylthiuram disulfide (TD), were employed to generate the initiating radical in reverse ATRP. New catalysts, $Cu(S_2CNEt_2)$, $Cu(S_2CNEt_2)Cl$ and $Fe(S_2CNEt_2)_3$, were capable of controlling normal or reverse ATRP via the transfer reaction of diethylthiocarbamoylthiyl (S_2CNEt_2) group supporting the dynamic equilibrium between dormant and active species. *In situ* ATRP proceeded with $R-X$ initiator and $M_t^n X_n$ catalyst produced *in situ*. Inducing the production of active radicals, UV irradiation was first employed in living radical polymerization of vinyl monomers in conjunction with non-halide catalyst $Fe(S_2CNEt_2)_3$, *i.e.* photo ATRP. In short, all these reactions demonstrated the characteristic nature of living polymerization: linear plot of $\ln([M]_0/[M])$ versus reaction time, proportional increase of M_n with the monomer conversion and functionalized polymers capable of chain extension.

CARBON-CARBON BOND COMPOUND-INITIATED REVERSE ATRP

St polymerization with the traditional radical initiator 2,2'-azobisisobutyronitrile (AIBN)/ $CuCl_2$ /2,2'-bipyridine (bpy) initiation system and MMA polymerization with AIBN/ $FeCl_3$ / PPh_3 were the first reports in the field of reverse (or alternative) ATRP^[12, 13]. The homolytic decomposition of the initiator was responsible for the radical

bpy was needed for reverse ATRP of St producing PSt with PDI = 1.30. In the above mentioned system, $[\text{TPED}]_0/[\text{FeCl}_3]_0 = 1/4$ was required to generate PMMA samples with PDI = 1.13. The irreversible decomposition of AIBN or TPED is responsible for the high concentration of primary radicals, especially at high temperature or at the early stage of polymerization. Therefore, it is difficult to avoid the bimolecular termination of radicals in the system and precludes good control over those vinyl polymerizations. If a radical generator is able to release radicals quantitatively, matching the reversible dynamic equilibrium, then the polymerization will be controlled from the beginning. In experiments, we realized this quantitative radical release by employing reversibly dissociative compounds, DCDPS and DCDTS^[18–26, 29].

With the use of DCDPS and DCDTS, the generation of primary radicals was moderate, in accordance with the dynamic equilibrium of the ATRA process. Various transition metal compounds, like CuCl_2 , FeCl_3 and NiCl_2 , were proved to successfully catalyze vinyl polymerizations initiated with either of them (Scheme 3). For instance, living polymerization of MMA was performed with the DCDTS/ CuCl_2 /bpy initiation system at a low feed ratio of the catalyst ($[\text{DCDTS}]_0/[\text{CuCl}_2]_0 = 1/2$)^[26]. First-order kinetics, resulting linear increase of M_n with monomer conversion and quite narrow PDI (< 1.30) were obtained. $^1\text{H-NMR}$ analysis revealed the presence of α -(carbethoxycyanotolyl)methyl end group from DCDTS molecule and ω -Cl atom from the catalyst in the resulting polymer chain.



Scheme 3 Reverse ATRP initiated with reversible dissociation of carbon-carbon bond compounds

SULFUR-SULFUR BOND COMPOUND-INITIATED REVERSE ATRP

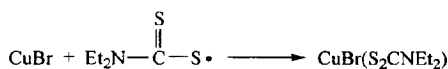
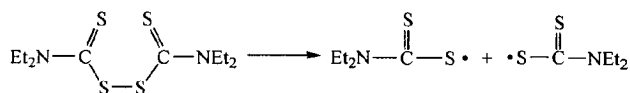
Thiuram disulfides are favorable photo and thermal iniferters for vinyl monomers, but the polymerization can not be well controlled for synthesizing polymers with wide PDI^[2]. In conjunction with transition metal species, the

poor controllability of these vinyl polymerizations is supposed to be improved, which was demonstrated in TD-initiated St polymerization.

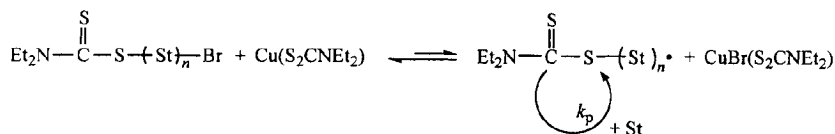
CuBr/bpy-Catalyzed Reverse ATRP

The S—S bond in TD is similar to the O—O bond in benzoyl peroxide (BPO) and is capable of homolytic decomposition on heating. So it was expected that vinyl polymerization with TD initiator could also be a living one in the presence of copper(I) complexes^[30]. When St polymerization was initiated with TD/CuBr/bpy, controlled polymerization was attainable and the mechanism was considered to be consistent with reverse ATRP^[31, 32]. Radical scavenger diphenylpicrylhydrazyl (DPPH) immediately terminated the reaction, which supported its radical essence. The induced decomposition of TD by CuBr can produce the initiating radical $\text{Et}_2\text{NCS}_2\cdot$ and the deactivator $\text{CuBr}(\text{S}_2\text{CNEt}_2)$ (Scheme 4).

Initiation



Propagation



Scheme 4 Reverse ATRP of St with TD/CuBr/bpy initiation system

The position of ω -Br atom in the polymer chain was characterized by ^1H -NMR analysis, demonstrating that the growing radical abstracted bromine atom from the stable $\text{Cu}(\text{S}_2\text{CNEt}_2)\text{Br}$ molecule. The fact that Cu—Br (0.240 nm) bond is longer than that of Cu—S (0.230 nm) accounts for this preferential reaction.

NiCl₂/PPh₃-Catalyzed Reverse ATRP

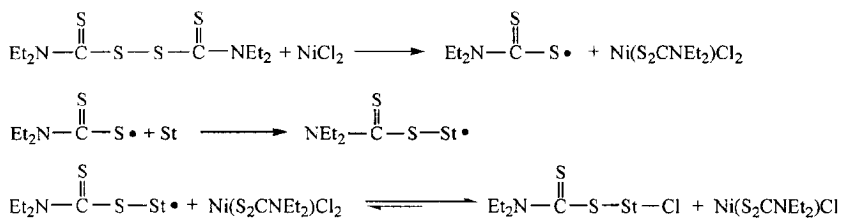
In addition to Cu/Br/bpy complex, a Ni species, $\text{NiCl}_2/\text{PPh}_3$, was also discovered to catalyze the living polymerization of St with TD initiator via a one-electron redox reaction between nickel(II) and (III) species, and the proposed mechanism is shown in Scheme 5^[33]. End group analysis confirmed the presence of α - S_2CNEt_2 and ω -Cl end groups on the resulting polymer chain. It revealed that the growing radical reacted with Cl atom in the generated $\text{Ni}(\text{S}_2\text{CNEt}_2)\text{Cl}_2$ molecule, and is ascribed to the weaker bond energy of Ni—Cl compared to that of Ni—S. The resulting polymer containing ω -Cl atom could be used as a macroinitiator via a normal ATRP process.

PSEUDO-HALOGEN TRANSFER ATRP

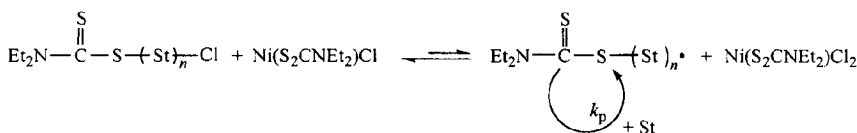
Halides of various transition metals have been utilized in ATRP. Among them, copper species are most widely used because of their low cost and easy availability. In attempts to test the transferability of other atoms or groups, non-halide catalysts have been investigated in the initiation step. Especially, copper catalysts other than chlorides and bromides have been studied extensively and most of them accelerated the reaction rate. However

the resulting chain were always end-capped with halogen atoms. Thiocyanate group (SCN) was found to be transferable in normal ATRP of MMA and eventually terminates the obtained polymer^[34]. In our work, the photo-labile S₂CNEt₂ group was discovered to transfer, maintaining normal ATRP or reverse ATRP even in the presence of chlorine atom^[22, 23, 35–41]. The low bond dissociation energy of Cu—S matches its longer bond length. So the generated radical prefers to capture the S₂CNEt₂ group in the original or generated Cu(S₂CNEt₂)Cl molecule. In the light of the preliminary work of Nishimura *et al.*^[42], it was also found that Fe(S₂CNEt₂)₃ can catalyze vinyl polymerization with DCDPS initiator in a living way^[23]. Consequently the resulting polymers functionalized with this UV sensitive group were able to initiate photo-polymerization via an iniferter mechanism.

Initiation



Propagation



Scheme 5 Reverse ATRP of St with TD/NiCl₂/PPh₃ initiation system

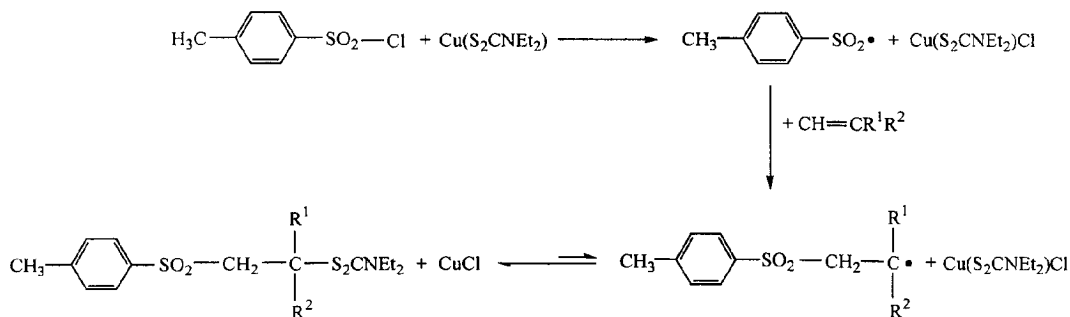
Normal ATRP with Cu(S₂CNEt₂) Catalyst

Non-halide Cu(S₂CNEt₂) was synthesized in our lab and its utilization in ATRP proved to be successful. Good control over MMA polymerization was achieved using the *p*-toluenesulfonyl chloride (*p*-TsCl)/Cu(S₂CNEt₂)/bpy initiation system^[35, 36]. The redox reaction of *p*-TsCl and Cu(I) species results in a *p*-toluenesulfonyl radical which will activate MMA, forming a monomer radical and the related Cu(II) catalyst, Cu(S₂CNEt₂)Cl, by analogy with transition metal catalyzed ATRA (Scheme 6). The propagation is then supported by repeating the cycle of the radical addition reaction to monomer molecules. This living radical polymerization could also be performed at low temperatures, such as 80 °C, with linear kinetic plots through the origin. The reaction system can be diluted with organic solvents and therefore the polymerization rate was decreased, though solvent polarity exerted no effect on the living nature. With decreasing polarity from acetonitrile to toluene, the polymerization rate decreased. For example, the apparent propagation rate constant was $9.5 \times 10^{-5} \text{ s}^{-1}$ in acetonitrile solvent but $4.7 \times 10^{-5} \text{ s}^{-1}$ in toluene, compared with the value of $15.3 \times 10^{-5} \text{ s}^{-1}$ in bulk at 100 °C. The resulting *M_n* was in good agreement with the predetermined value and PDI was quite low (< 1.10). End group analysis and other experiments demonstrated the presence of α -(*p*-SO₂C₆H₄CH₃) and ω -S₂CNEt₂ end groups in the polymer chain.

Reverse ATRP with Cu(S₂CNEt₂) or Cu(S₂CNEt₂)Cl Catalyst

Initially, reverse ATRP of vinyl monomers with BPO only proceeded in conjunction with copper(I) species on the basis of induced BPO decomposition. In our research, living radical polymerization of MMA initiated by BPO could be realized with either Cu(S₂CNEt₂)/bpy or Cu(S₂CNEt₂)Cl/bpy catalyst^[35, 37, 38]. The comparable results are compiled in Table 1. The rate was slower with Cu(S₂CNEt₂)Cl/bpy complex, reaching 19% monomer conversion in 14 h and 61% in 62 h, than that with Cu(S₂CNEt₂)/bpy, which would become solid after 10 h and reached 54% conversion. This fact can be ascribed to the different mechanism of these polymerizations. The primary radical is generated from the essentially rapid Cu(S₂CNEt₂)-induced BPO decomposition (Scheme 7)^[35, 36]. However, the radical is produced by BPO thermolysis in the case of BPO/Cu(S₂CNEt₂)Cl/bpy

system (Scheme 9)^[38]. The subsequent reaction is mediated by the cycle of monomer addition and reversible S_2CNEt_2 transfer reactions. Similarly, abstraction of MMA molecules and active copper(I) compound by the generated radical accounts for the deviation of M_n (GPC) from the calculated value (Scheme 8). It is the redox ability of BPO that makes the initiation step complex.



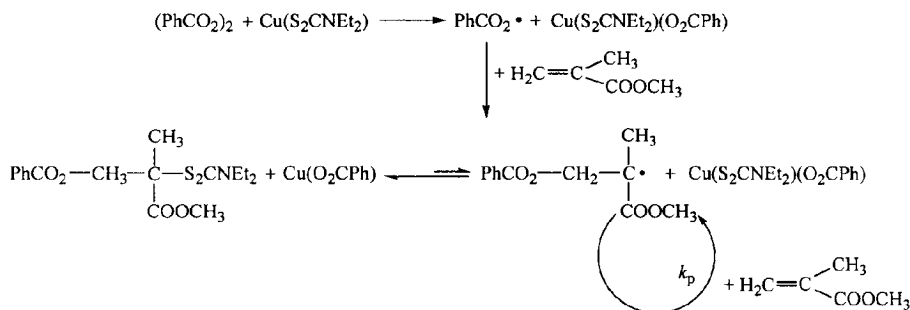
Scheme 6 *p*-TsCl initiated ATRA with pseudo-halogen S_2CNEt_2 transfer

Table 1. Copper species-catalyzed MMA polymerization with BPO initiator^[37, 38]

Entry	Catalyst	[BPO] ₀ /[Catalyst] ₀ ^a	Time (h)	Conversion (%)	M_n (GPC) ^b	PDI
1	$\text{Cu}(\text{S}_2\text{CNEt}_2)$	1/1	5.3	34	94000	1.16
2	$\text{Cu}(\text{S}_2\text{CNEt}_2)$	1/1	10	54	146100	1.32
3	$\text{Cu}(\text{S}_2\text{CNEt}_2)\text{Cl}$	1/2	14	19	26900	1.17
4	$\text{Cu}(\text{S}_2\text{CNEt}_2)\text{Cl}$	1/2	62	61	96500	1.24

^a $[\text{MMA}]_0 = 9.4 \text{ mol/L}$, $[\text{MMA}]_0/[\text{BPO}]_0 = 1000/1$, $[\text{Catalyst}]_0/[\text{bpy}]_0 = 1/3$, in bulk, at 100°C

^b M_n (GPC), calibrated with PSt standards



Scheme 7 Reverse ATRP with BPO/ $\text{Cu}(\text{S}_2\text{CNEt}_2)$ /bpy initiation system

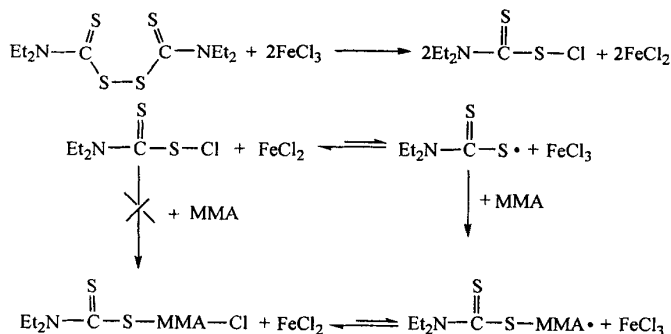
In contrast, $\text{Cu}(\text{S}_2\text{CNEt}_2)\text{Cl}$ -based reverse ATRP with AIBN produced well-defined PMMA and PSt with predictable M_n . The end group analysis using ^1H -NMR and UV-vis spectra illustrated the position of ω - S_2CNEt_2 group in the resulting polymer chain^[39]. Pseudo-halogen S_2CNEt_2 group transfer took place in the reaction as shown in Scheme 9. AIBN thermally decomposes and generates the initiating radical which is responsible for the propagation and capture of S_2CNEt_2 group from the deactivated catalyst. The rate of MMA polymerization with AIBN/ $\text{Cu}(\text{S}_2\text{CNEt}_2)\text{Cl}$ /bpy initiation system in organic solutions increased with rising solvent polarity from toluene to acetonitrile, but both were lower than in bulk. The living radical polymerization could also be performed at a moderate temperature 80°C with a decreased propagation rate. The resulting polymers were tailor-made with predictable M_n and narrow PDI (< 1.20). GPC curves were symmetric and uni-modal, indicating that no side reactions occurred. St polymerization was performed successfully at 120°C , producing PSt with expected targeted M_n value and narrow PDI ($= 1.19$) by using a high feed ratio of the catalytic species ($[\text{AIBN}]_0/$

reaction.

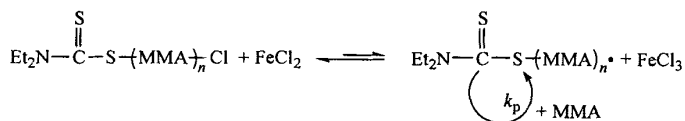
In Situ ATRP with TD/FeCl₃/PPh₃ Initiation System

The investigation of MMA polymerization with TD/FeCl₃/PPh₃ initiation system was carried out with the original intention that TD, structurally similar to BPO and capable of homolytic decomposition, could control vinyl polymerization in a similar way to BPO. Unfortunately the reaction was controlled with difficulty when TD was added to the mixture of MMA, FeCl₃ and PPh₃, and the polymerization started immediately at 100 °C. By chance, we found that PMMA with narrow PDI could be achieved in a very short time when the reaction mixture was stirred vigorously at ambient temperature overnight. The kinetics was first-order in monomer, M_n increased with rising monomer conversion, and PDI was quite low (= 1.10). So it is obvious that the mechanism for MMA/TD/FeCl₃/PPh₃ system does not belong to the area of reverse ATRP. Based on end group analysis, the proposed polymerization mechanism is simplified as shown in Scheme 10. Reaction of TD and FeCl₃ at room temperature produces the initiating organic halide and corresponding Fe(II) species. The subsequent reactions are identical to those in ATRP. As the initiating components, Et₂NCS₂—Cl and FeCl₂, are produced *in situ* in the system and polymerization follows ATRP mechanism, it was first named *in situ* ATRP^[43, 44].

Initiation



Propagation



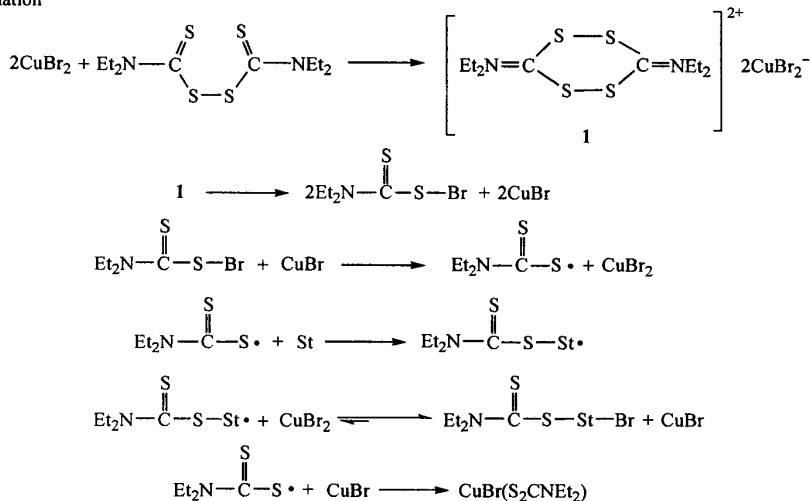
Scheme 10 Simplified mechanism for *in situ* ATRP of MMA with TD/FeCl₃/PPh₃ initiation system

In Situ ATRP with TD/CuBr₂/bpy Initiation System

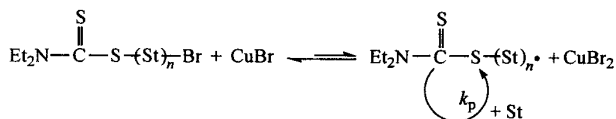
Subsequently, our research demonstrated that St polymerization with TD/CuBr₂/bpy initiation system belonged to *in situ* ATRP too^[45]. First-order kinetic plots through the origin and proportional increase of M_n with the conversion were obtained. The polymerization was inhibited by radical scavenger, DPPH, but not disturbed by the addition of protonic solvent, methanol. These results revealed its radical polymerization nature. PDI of the resulting PSt was as low as 1.30, but the measured M_n was half of the targeted value, in accordance with the supposition that side reactions of the active radical occurred in the system.

The reaction mechanism is illustrated in Scheme 11. The initiator, Et₂NCS₂—Br, and active species CuBr are produced *in situ* from the reaction of TD and CuBr₂ in two steps. When heated, the product (1) of the reaction at room temperature dissociates at the weak S—S bond and produces the organic halide and copper(I) catalyst that initiates the polymerization. The generated primary radical Et₂NCS₂• initiates monomer, with the production of active monomer species. On the other hand, Et₂NCS₂• radical may also consume CuBr catalyst and form the corresponding copper(II) counterpart, CuBr(S₂CNEt₂), thus decreasing the initiator efficiency.

Initiation



Propagation

Scheme 11 *In situ* ATRP of St with TD/CuBr₂/bpy initiation system***In Situ ATRP with Fe(S₂CNEt₂)₃/FeCl₃/PPh₃ Initiation System***

Transition metal dithiocarbamates like Fe(S₂CNEt₂)₃ are capable of releasing radicals under UV irradiation, but at a moderate temperature of 80 °C, the thermal dissociation is incomplete and disfavors the generation of initiating S₂CNEt₂ group in a living process. So we proposed *in situ* ATRP mechanism for the living radical polymerization of the MMA/Fe(S₂CNEt₂)₃/FeCl₃/PPh₃ system^[46]. The initiator Et₂NCS₂—Cl and reduced catalyst FeCl₂ are created from the reaction of Fe(S₂CNEt₂)₃ and FeCl₃. UV-vis and ¹H-NMR analyses confirmed that the resulting PMMA is terminated with α-S₂CNEt₂ and ω-Cl end groups.

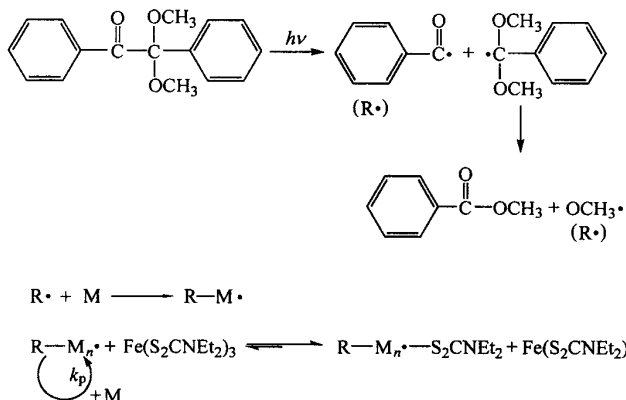
Scheme 12 Photo ATRP with DMPA/Fe(S₂CNEt₂)₃ initiation system

PHOTO ATRP

Photo-induced radical polymerization has always been a useful technique in polymer synthesis. Although a remarkable visible light effect on ATRP has been reported in the literature^[47], no paper concerning photo-induced ATRP appeared until the first report of vinyl ATRP in toluene at ambient temperature with 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photo initiator and $\text{Fe}(\text{S}_2\text{CNET}_2)_3$ as the catalyst under UV irradiation without external ligand^[48, 49].

From kinetic analysis and extension experiments, photo-induced solution polymerization with $\text{DMPA}/\text{Fe}(\text{S}_2\text{CNET}_2)_3$ proceeded in a living manner. The mechanism is depicted in Scheme 12. Under UV irradiation, DMPA dissociates and produces active benzoyl and also methyl radical (both represented as $\text{R}\cdot$). As in a typical reverse ATRP, the generated radical is trapped by $\text{Fe}(\text{S}_2\text{CNET}_2)_3$, forming the dormant species and active counterpart $\text{Fe}(\text{S}_2\text{CNET}_2)_2$. The dynamic equilibrium is then built up by the S_2CNET_2 transfer reaction under UV light. We suppose that the different activities of the initiating radicals and the heterogeneous reaction system accounted for the relatively large PDI value of the resulting polymers ($= 1.50$).

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