Pseudohalogens in Atom Transfer Radical Polymerization of Methyl Methacrylate

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ABSTRACT: In recent advances in controlled radical polymerization, atom transfer radical polymerization (ATRP) has achieved increasing interest. This investigation reports the ATRP of methyl methacrylate (MMA) using pseudohalogens as initiator as well as an anion for copper catalyst. The results were compared with the conventional halide system. Different pseudohalides were used as the initiator for the ATRP of MMA in combination with CuX (X = pseudohalide or halide) as the catalyst. Pseudohalide initiator in combination with Cu(halide) catalyst leads to inefficient ATRP due to slow initiation. Pseudohalide initiator in combination with Cu(pseudohalide) catalyst leads to uncontrolled or no polymerization. The polymers were characterized by using GPC, IR, MALDI-TOF-MS, and TGA analysis. IR and MALDI analysis showed that the resultant polymer had pseudohalide as the end group. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3857–3864, 2007

Key words: ATRP; pseudohalogens; thiocyanate; isothiocyanate; isocyanate; MALDI-TOF
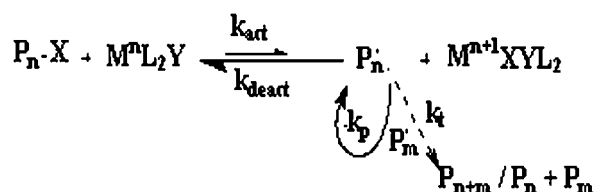
INTRODUCTION

The major disadvantage of radical polymerization is the poor control in molecular weights, molecular composition, and structure because of unavoidable bimolecular termination between the growing radicals. Recent advances in controlled radical polymerization (CRP) have made it viable for the synthesis of polymers with controlled molecular weights, with desirable functionality and with well-defined architecture.[1–6] Among all the CRP methods atom, transfer radical polymerization (ATRP) is very promising as it can be applied to a large number of monomers like (meth)acrylates and styrene derivatives at wide range of temperature (−20 to +200°C) and is tolerant to different functional groups. ATRP works according to the principle of atom transfer radical addition (ATRA), first introduced in 1940s by Kharash.[7] ATRA gained increasing interest because of its stereo-, chemo-, and regio-selectivities and tolerance to many useful functional groups.[8–10] There are reports of ATRP using Cu,[11–21] Fe,[22–24] Ni,[25–27] Ru,[28–30] Rh,[31] and Pd[32] based catalysts. Various ligands have been used to stabilize the metal complex e.g., substituted bipyridines, pyridyl-alkyl imines, aryl-phosphine, and a number of multidentate aliphatic amines. Among all

the catalysts Cu[4] and Ru[5] have been widely studied. Percec coworkers[19–21] used various copper catalysts having different anionic ligands other than conventional halides. They used sulfur based anionic ligands (like butanethiolate, thiophenoxide), selenide, and tellurides. It is reported on the basis of mechanistic model[2,8–10,33] studies that transition metal catalysts stabilized with suitable ligands abstract halogen or pseudohalogens from an activated alkyl (pseudo)halide to form a radical. This radical also known as active species reacts with monomer to undergo propagation. The deactivation takes place by abstracting halogen or pseudohalogen from the XY-Cu(II), reforming the dormant alkyl halide (P$_n$-X) (Scheme 1).

One of the most important characteristics of ATRP is that the polymers prepared by this process contain a halogen atom at one end of the macromolecular chain. These end groups can act as potential sites for macroinitiator as well as undergo various chemical transformations. Thiocyanates, isothiocyanates, and isocyanates are interesting pseudohalides which can undergo different types of chemical transformations under suitable reaction conditions.[34] There are very few reports[19,35,36] of using thiocyanate as a pseudohalide anion for the ATRP catalyst. This investigation reports the use of different pseudohalides as initiators as well as the counter anion for the metal catalyst in ATRP of methyl methacrylate (MMA). In this case, thiocyanate (-SCN), isothiocyanate (-NCS), and isocyanate (-NCO) have been used as the pseudohalogens.

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$$P_n\text{-}X + M^nL_2Y \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^{\cdot} + M^{n+1}XYL_2$$

$$k_p \overset{k_t}{\underset{P_m^{\cdot}}{\nearrow}} P_{n+m}/P_n + P_m$$

M= Metal ion; X, Y = (Pseudo)halide; P_n= Propagating species

Scheme 1 Mechanism of ATRP.

EXPERIMENTAL

Materials

MMA (Aldrich) was passed through an inhibitor column to get rid of monomethyl ether hydroquinone (an inhibitor for MMA) and then was purified via vacuum distillation. Initiators [like *p*-toluene-sulfonyl chloride (TsCl), ethyl-2-bromoisobutyrate (EBIB), benzyl thiocyanate (BzSCN), benzyl isothiocyanate (BzNCS), and *p*-tosyl isocyanate, etc.] were used as received from Aldrich. The metal catalysts, CuSCN (99%), CuBr (98%), and CuCl (98%) were used as received from Aldrich. 4,4'-di-*n*-heptyl-2,2'-bipyridine (dHbpy) was synthesized according to the literature procedure (see Ref. 12, p 822). *N*-*n*-Pentyl-2-pyridyl-methaneimine (NPPI) was synthesized by the condensation of 2-pyridine carboxaldehyde and *n*-pentyl-amine.[35]

Polymerization

In solution

MMA (10.0 g), *p*-xylene (10.0 g), butylacetate (0.40 g) (as an internal standard for GC), required amount of ligands (like NPPI, dHbpy), and calculated amount of initiator were added to a 100 mL three neck round bottom flask. The flask was equipped with a condenser in one neck and a silicon septum in the other. The mixture was flushed with argon for 15 min. After the addition of a calculated amount of catalyst (CuSCN, CuBr, or CuCl), the flask was kept under vacuum and refilled with argon by three freeze pump/thawing cycles. Polymerization was carried out at 100°C.

In bulk

The same procedure was followed as described for the solution polymerization. In this case, *p*-xylene was used as the internal standard for GC.

Characterization

Monomer conversion was determined from the concentration of residual monomer using a Hewlett–Packard (HP 5890) gas chromatograph. The GC was

equipped with AT-Wax capillary column (30 m × 0.53 mm, ID 10 μm).

Size-exclusion chromatography (SEC)

SEC was performed in THF at the ambient temperature at a flow rate of 1 mL/min. The instrument Waters GPC was equipped with a Waters Model 510 pump, Model 410 refractive index detector, and Model 486 UV detector. A set of two linear columns (mixed-C, Polymer Laboratories) [a PLgel guard (5 μm particles) 50 × 7.5-mm guard column, followed by two PLgel mixed-C (5μm particles) 300 × 7.5 mm columns in series] was used. Low polydispersity linear polystyrene samples (Polymer Laboratories, M = 580 to 7.1×10^6) were used as standards to construct the calibration curve. Molar masses were calculated using the Universal calibration principle and making use of Mark–Houwink parameters (PS: $K = 1.44 \times 10^{-4}$ dL/g, $a = 7.16$; PMMA: $K = 0.944 \times 10^{-4}$ dL/g, $a = 7.19$). Data acquisition and processing were performed using Waters Millennium 32 software (version 3.2).

TGA analysis

TGA analysis was carried out in Perkin–Elmer Pyris TGA 6 instrument at a heating rate of 10°C/min under nitrogen atmosphere.

FTIR analysis

FTIR was recorded in the KBr pellet form of PMMA samples using a Mattson Polaris FTIR instrument with a wave number range of 400–4000 cm^{-1}, and a resolution of 2 cm^{-1}.

Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) analysis

MALDI-TOF-MS analysis was carried out using a Voyager DE-PRO (PerSeptive BioSystem, MA). The MALDI instrument was equipped with a 337-nm pulsed nitrogen laser and a 1.0 m linear time of flight mass spectrometer with a 30 kV source voltage. Solutions of 40 mg dithranol/mL, 5 mg sodium trifluoroacetate/mL, and 1 mg polymer/mL in THF were prepared. The respective solutions were mixed in a ratio 5 : 1 : 5 on a volume basis. Enough of the mixture was applied to the sample position to cover the 2.5 mm diameter sample position (typically 0.3 μL). The spot was allowed to air-dry without any assistance. Mass spectra were acquired by accumulating the spectra from 256 selected laser shots.
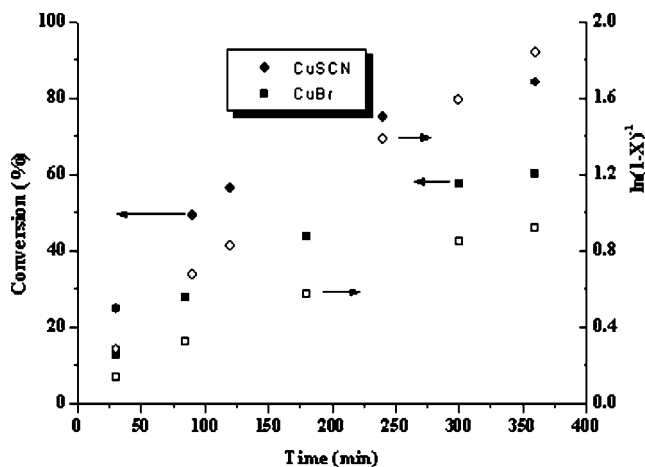
Figure 1 Plots of conversion versus time (filled symbols) and semilogarithmic kinetic plot (open symbols) for the solution ATRP of MMA in p-xylene at $100°C$ using p-toluene-sulfonylchloride (p-TsCl) as initiator and 4,4′-diheptyl-2-2′ bipyridine (dHbpy) as ligand. $[MMA]_o = 5.37M$, $[dHbpy] = 0.107M$, $[p$-TsCl$] = 0.043M$, $[Cu(I)] = 0.043M$.

Figure 2 Dependence of molecular weights (filled symbols) and polydispersities (open symbols) of PMMA on monomer conversion for the solution ATRP of MMA in p-xylene at $100°C$ using p-TsCl as initiator and dHbpy as ligand. $[MMA]_o = 5.37M$, $[dHbpy] = 0.107M$, $[p$-TsCl$] = 0.043M$, $[Cu(I)] = 0.043M$.

RESULTS AND DISCUSSION

Pseudohalide as anion for the ATRP catalyst

MMA was polymerized using p-tosylchloride (p-TsCl) as initiator. Polymerization was carried out in p-xylene using CuSCN and CuBr as catalysts in combination with 4,4′-diheptyl 2,2′-bipyridine (dHbpy) as ligand. In the case of CuSCN, the semilogarithmic kinetic plot shows that it is first-order indicating a constant radical concentration during the polymerization (Fig. 1). Figure 2 shows the plot of molecular weights and polydispersities versus conversion. The observed molecular weight shows very little deviation from the theoretical molecular weight indicating that there is a negligible amount of irreversible chain breaking process. Thus the system shows the characteristics of living/controlled polymerization. The same observation was made in CuBr catalyst system. However, in case of CuBr, the rate of polymerization is slow compared to CuSCN. The polymer obtained with CuSCN has broader polydispersity than that obtained in CuBr. In the last communication[35] it was also observed that the polydispersity of PMMA achieved in case of CuSCN catalyst was always higher than in case of CuBr or CuCl as a catalyst irrespective of ligands used, and the CuSCN catalyzed ATRP is usually faster than CuBr and CuCl catalyzed ATRP. Fast polymerization and broad polydispersity indicate that the deactivation process is less efficient in CuSCN catalyst system.

The anion can influence the catalytic activity of the copper catalyst. The thiocyanate (SCN) ligand shows linkage isomerism, as it can either coordinate via S or N atom. Because S atom in -SCN has higher electron density, according to the hard–soft-acid–base[37] (HSAB) principle, Cu will tend to form bond through 'S' atom of -SCN group. In the spectrochemical series,[38] the

ligands are arranged according to their strength of complex formation ability. The 'field factor'[39,40] quantifies the strength of the ligand in the spectrochemical series relative to water as a standard ligand with a field factor (f) of 1.00. The field factors of different ligands are Br (0.72), SCN (0.73), and NCS (1.02). According to the strength of ligands, the deactivating strength of different metal catalysts is in this order: $CuBr_2 > Cu(SCN)(Br) > Cu(SCN)_2$ (it is formed when the benzyl thiocyanate (BzSCN) or benzyl isothiocyanate (BzNCS) is used as initiator). Hence, PMMA prepared with CuBr as a catalyst has lower polydispersity than those prepared by CuSCN as catalyst. Grimaud and Matyjasewski[41] also observed the better efficiency of bromide in the deactivation step. Similar observation

Figure 3 Plots of conversion versus time (filled symbols) and semilogarithmic kinetic plot (open symbols) for ATRP of MMA in bulk at $100°C$ using benzylthiocyanate (BTC) as initiator and NPPI as ligand. $[MMA]_o = 5.37M$, $[NPPI] = 0.107M$, $[BTC] = 0.043M$, $[Cu(I)]$ [i, e CuBr or CuCl]$ = 0.043M$.
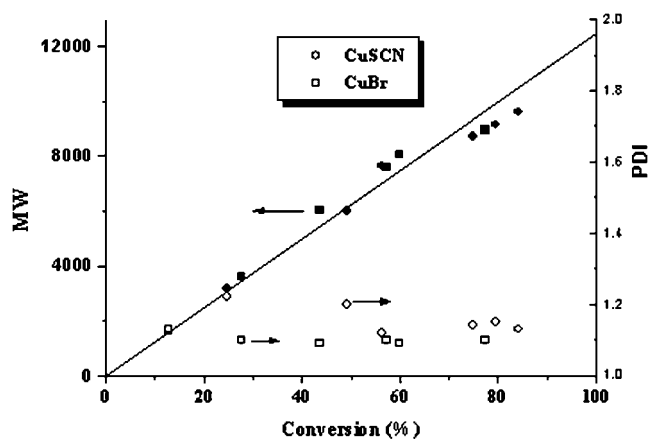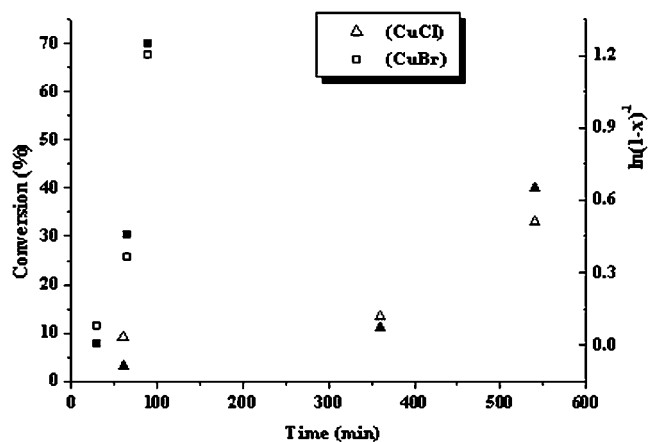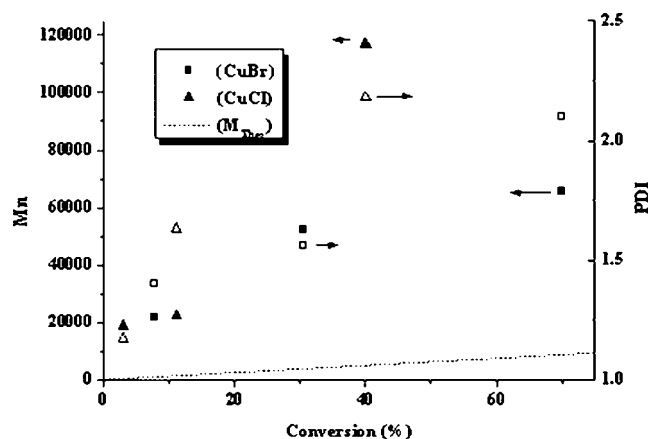
Figure 4 Dependence of molecular weights (filled symbols) and polydispersities (open symbols) of PMMA on monomer conversion for the ATRP of MMA in bulk at 100°C using benzylthiocyanate (BzSCN) as initiator and NPPI as ligand. $[MMA]_o = 5.37M$, $[NPPI] = 0.107M$, $[BzSCN] = 0.043M$, $[Cu(I)]$ [i.e., CuBr or CuCl)] $= 0.043M$.

was made by Bengouh and Fairservice[42,43] in a series of studies of the inhibition of MMA polymerization.

Pseudohalide as initiator in ATRP

Thiocyanate (-SCN), isothiocyanate (-NCS), and isocyanate (-NCO) were used as the pseudohalide initiator for the ATRP of MMA. MMA was polymerized at 100°C using benzyl thiocyanate (BzSCN) as initiator and CuSCN, CuBr, and CuCl as catalysts. The correlation line of the kinetic plot of both BzSCN/CuBr and BzSCN/CuCl systems in Figure 3 shows acceleration which indicates that they have very slow initiation.[2] Figure 4 shows that there is very high molecular weight at the onset and the observed molecular weight is much higher than the theoretical molecular weight. The molecular weight distribution is very high. It is because of the slow initiation as well as slow
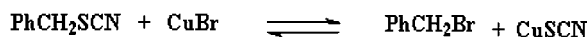
deactivation of the catalysts; Cu(SCN)(Br) or Cu(SCN)(Cl) (generated due to pseudohalogen abstraction as shown in Scheme 1). Faster polymerization in BzSCN/CuBr compared to BzSCN/CuCl is due to the ease of initiation of the C-Br bond when compared with the C-Cl bond. In BzSCN/CuSCN system, the rate of polymerization is very slow, in 70 h only 55% conversion is achieved (sr. no. 3 in Table 1). The kinetic study showed that there was very slow initiation and there was very high molecular weight at the start of reaction. The increase in molecular weight was leveled off after 30 h. The polydispersity was very broad indicating that the polymerization is not controlled. The rate of polymerization is much slower than BzSCN/CuBr and BzSCN/CuCl. Interestingly, there was no polymerization at 80°C using BzSCN/CuSCN system (Table 1; sr. no. 4) which is due to the inefficient breaking of C-S bond in BzSCN at this temperature. But MMA undergoes polymerization at 80°C with BzSCN/CuBr system, which implies BzSCN may not be the only initiating species. This observation can be explained if there is an exchange reaction between the initiator and the catalyst as shown in Scheme 2. It has been reported earlier[44] that in the mixed halogen systems there is an exchange equilibrium between the initiator or the propagating species and the catalyst.

Polymerization of MMA using the BzBr/CuSCN (sr. no. 6 in Table 1) system is much faster than BzSCN/CuSCN system (sr. no. 3 in Table 1). The BzSCN/CuSCN needs 70 h for 55% conversion (sr. no. 3 in Table 1), whereas the BzBr/CuSCN system needs 60 min for the same conversion. The polydispersity obtained by BzBr/CuSCN system is lower than that obtained by BzSCN/CuSCN system. Davis and Matyjasewski[36] used BzSCN as initiator for the polymerization of styrene and methylacrylate in presence of CuCl, CuBr, and $CuPF_6$, a noncoordinating catalyst. They observed slow initiation and very high molecular weight at the onset of styrene polymerization. The poly-
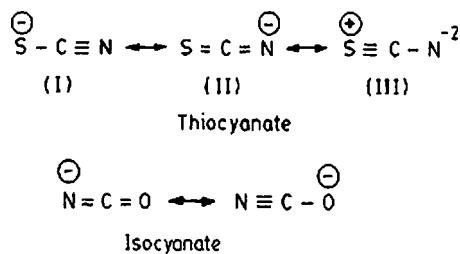
TABLE I
ATRP of MMA with Different Pseudohalide Initiators and Using Different Catalysts

Sr no.	Catalyst	Ligand	Initiator	Temperature (°C)	Time (h)	Conversion (%)	M_{SEC}	PDI	M_{theo}
1	CuCl	NPPI	BzSCN	100	9	40	116793	2.18	5000
2	CuBr	NPPI	BzSCN	100	1.5	70	65637	2.10	8750
3	CuSCN	NPPI	BzSCN	100	70	55	33390	2.08	6875
4	CuSCN	NPPI	BzSCN	80	70	–	–	–	–
5	CuBr	NPPI	BzSCN	80	24	67	45047	4.22	8375
6	CuSCN	NPPI	BzSCN	100	1.5	60	40000	1.60	6000
7	CuBr	dHbpy	BzSCN	100	1	85	60477	1.71	10625
8	CuSCN	dHbpy	BzSCN	100	5	59	98392	1.80	7375
9	CuSCN	NPPI	BzNCS	100	30	–	–	–	–
10	CuBr	NPPI	BzNCS	100	30	40	54337	2.43	5000
11	CuBr	dHbpy	TsNCO	100	22	96	26105	2.38	12000

$[MMA]_o = 8.98M$, $[NPPI] = 0.178M$, $[dHbpy] = 0.15M$, $[EBIB] = [TsCl] = 0.074M$, $[CuSCN] = 0.072M$, $[CuBr] = 0.072M$, $[CuCl] = 0.072M$.

PhCH₂SCN + CuBr ⇌ PhCH₂Br + CuSCN

Scheme 2 Exchange-equlibrium between the initiator and the catalyst.

$$\overset{\ominus}{S} - C \equiv N \leftrightarrow S = C = \overset{\ominus}{N} \leftrightarrow \overset{\oplus}{S} \equiv C - N^{-2}$$

(I)   (II)   (III)

Thiocyanate

$$N = C = \overset{\ominus}{O} \leftrightarrow N \equiv C - \overset{\ominus}{O}$$

Isocyanate

Scheme 3 Different resonating structures of pseudohalides.

dispersity of PS was 3.2. BzSCN had very poor initiation in the polymerization of methylacrylate and had resulted very high polydispersity of 3.0. They observed that BzBr/CuSCN was more efficient for ATRP system than BzSCN/CuSCN for styrene and methyl acrylate. Asandei and Percec[19] carried out ATRP of vinyl chloride using thiocyanate and azide initiators. They observed very broad polydispersity (PDI = 2.0–3.0).
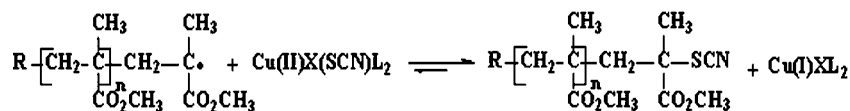
The Table 1 shows the polymerization of MMA using a variety of pseudohalide initiators (other than BzSCN) in presence of different copper catalysts and different ligands. Almost in all cases the polymerization reaction is slow. The molecular weight obtained is much higher than the theoretical molecular weight and also the polymer has very high polydispersity. Use of dHbpy as a ligand leads to faster polymerization compared to NPPI as a ligand for Cu catalyst. For example, in CuSCN/BzSCN system (Table 1, sr. no. 3) 55% conversion is achieved in 70 h using NPPI as the ligand, whereas 59% conversion is achieved in only 5 h using dHbpy as the ligand (Table 1, sr. no. 8) In some cases, there are no polymerization indicating inefficiency in the formation of radical to initiate the polymerization (Table 1). In case of benzyl isothiocyanate (BzNCS) as the initiator there was no polymerization when CuSCN was used as the catalyst (Table 1; sr. no. 9). When CuBr was used as the catalyst polymerization took place (Table 1; sr. no. 10).

MMA was polymerized using *p*-tosylisocyanate (*p*-TsNCO) as initiator in the presence of CuBr/dHbpy system (Table 1; sr. no. 11). The kinetic investigation (not shown here) revealed that the system had

poor initiation and there was very high molecular weight PMMA at the start of the polymerization. The poor initiation is due to stronger S-N bond in TsNCO. When the polymerization starts, the active species are not effectively deactivated by Cu^{II}(NCO)(Br) and hence leads to high polydispersity.

The difference between a pseudohalide and a halide group is that the former is an ambidentate nucleophile due to the resonance effect[34,45,46] as shown in Scheme 3. The thiocyanate (-SCN) group is an ambidentant ligand due to the resonance (Scheme 3) with the charge distribution is more on the S atom [Structure I (71%), II (12%), III (17%) in Scheme 3].[46] Attachment with the macromolecular chain via nitrogen would lead to the inactive species, an isothiocyanate. It was observed that MMA did not undergo polymerization in the presence of CuSCN as catalyst using BzNCS as initiator (Table 1; sr. no. 9). When CuBr was used as catalyst, it led to uncontrolled polymerization (Table 1). It is because of the poor initiation of BzNCS as well as ineffective activation of the polymeric chains having –SCN group which is formed due to the reversible deactivation (as shown in Scheme 4). These dormant species are assumed to have a lower rate of activation, as the bond strength[47,48] of carbon to –SCN, -Br, and -Cl increases in this order; C-Br <C-Cl < C-SCN.

MALDI-TOF-MS was carried out to identify the end group in PMMA obtained by using CuSCN as catalyst. Figure 5 shows the MALDI-TOF-MS of PMMA prepared by ethyl-2-bromoisobutyrate (EBIB)/CuSCN system. MALDI-TOF-MS was carried out in reflectron mode to distinguish different peaks according to the isotopic distribution. These distributions were compared with the distributions of the peaks obtained by using Isopro-3. There are mainly three distributions with a mass difference of the monomer repeat unit of 100 which is a characteristic of the mass spectrum of PMMA. The structures of different macromolecules have been shown in Scheme 5. It indicates that each PMMA macromolecule contains 2-ethyl-isobutyrate as the end group and Na$^+$ as the cation. The peaks at 1597, 1697, etc. ($n = 14$, 15, etc.) are due to PMMA macromolecular chain having –SCN end group. These are shown in Structure I in Scheme 5. The peak at 1597 has been amplified and has been compared with the simulated isotopic distribution (using Isopro 3.0) of Structure I (where $n = 14$) [Fig. 5(b)]. The presence of -SCN group clearly indicates these are the products of

$$R\text{-}[CH_2\text{-}\underset{CO_2CH_3}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\underset{CO_2CH_3}{\overset{CH_3}{\underset{\bullet}{C}}}]_n + Cu(II)X(SCN)L_2 \rightleftharpoons R\text{-}[CH_2\text{-}\underset{CO_2CH_3}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\underset{CO_2CH_3}{\overset{CH_3}{C}}\text{-}SCN]_n + Cu(I)XL_2$$

R= Initiator fragment, X= Halogen, L= Ligand

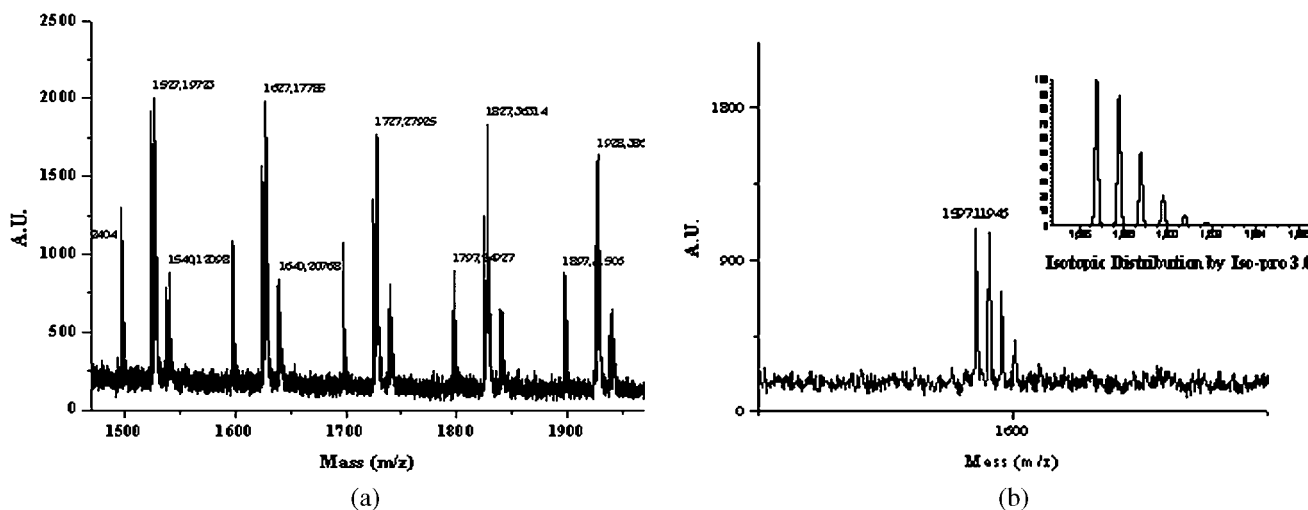**Scheme 4** Reversible deactivation in ATRP catalyzed by CuSCN.

Figure 5 (a) MALDI-MS of PMMA prepared by using EBIB/CuSCN as an ATRP catalyst. (b) Comparison of the amplified MALDI Peak at 1597 with the isotopic distribution simulated by Isopro 3.0.

halogen exchange occurred during the reversible deactivation as enunciated in Scheme 4. The peaks at 1540, 1640, etc. ($n = 14$, 15, etc.) are due to dehalogenated product Structure II in Scheme 5. The peaks at 1527, 1627, etc. may be attributed due to the macromolecular chain having a lactone as the end group (where $n = 13$, 14, etc.) that lost methyl bromide or methyl thiocyanate. They are shown in Structure III. This lactone formation was reported during MALDI-TOF analysis of PMMA prepared by ATRP[49,50]. No bromine groups were detected in the polymer. It may have two possible reasons. Firstly the halide exchange (thiocyanate for bromine) may be more efficient in the case of bromide. Secondly the loss of bromide end groups during MALDI-TOF-MS analysis of C-Br could be complete. It is expected from their bond strength as explained earlier. FTIR spectra of this PMMA showed a small peak at 2155 cm^{-1} indicating

the presence of –SCN group in the macromolecular chain[51] (Fig. 6). However, the presence of –SCN as end group confirms the reversible deactivation step described in Scheme 4.

It was very difficult to analyze the nature of the end groups of the PMMA samples prepared by using pseudohalides as initiator in combination with pseudohalide anion of copper catalyst via MALDI–TOF–MS, because of their uncontrolled molecular weights and very broad polydispersity index.

Thermal analysis

The thermal stability of PMMA has a direct relationship with the structure of polymer.[52] Thermal degradation of PMMA prepared by radical polymerization occurs in several stages due to scission of the head to head linkages, end chain initiation of the vinylic ends,
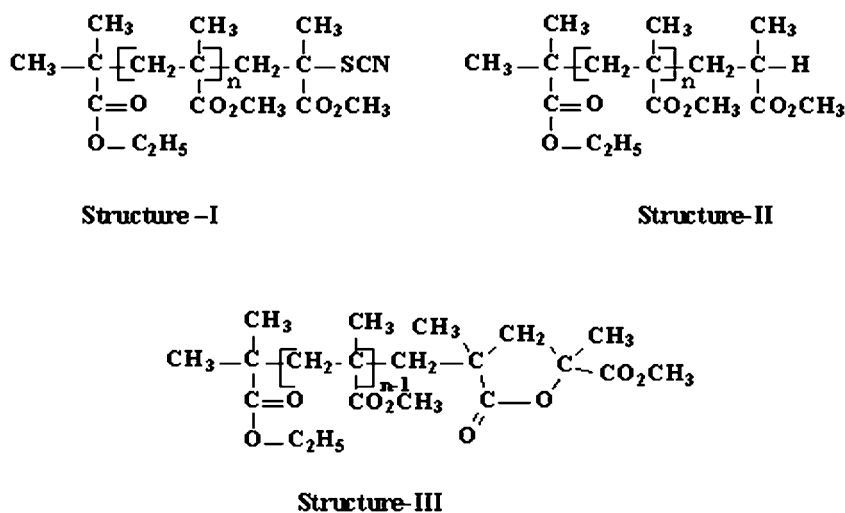
Scheme 5 Different structures of PMMA evidenced by MALDI-TOF analysis.

and due to random scission of the polymer chain. Figure 7 shows the TGA of PMMA ($M_n = 98,000$, MWD 2.0) prepared by conventional radical polymerization using AIBN as initiator and of PMMA prepared by ATRP using CuSCN as catalyst. It clearly shows that PMMA prepared by conventional radical polymerization (i.e., by AIBN) has at least two stages of degradation. The first derivative of TGA of PMMA ($M_n = 12,000$, MWD = 1.30) prepared by CuSCN as ATRP catalyst and EBIB as initiator shows that it has mainly a major decomposition at 380°C which is due to random scission of the main polymer. It indicates that the PMMA prepared by ATRP using CuSCN as catalyst has very insignificant number of macromolecular chains which might arise due to bimolecular termination reactions. Jerome and coworkers[24,26] reported a single decomposition of PMMA prepared by ATRP using Ni based catalysts.

CONCLUSIONS

ATRP of MMA using CuSCN as catalyst and *p*-tosyl chloride as initiator lead to faster polymerization and the polydispersity index (PDI) is higher when compared with that obtained with CuBr as catalyst. It is because of the slower deactivation of CuSCN catalyzed system and slow activation of the macromolecular chain with pseudohalide as end group formed via pseudo(halogen) exchange. FTIR and MALDI-TOF analysis clearly showed that PMMA macromolecular chain had -SCN as the end group.

Pseudohalide initiators like BzSCN, BzNCS, and TsNCO as initiator lead to inefficient ATRP due to very slow initiation. It leads to very high molecular weight at the onset of ATRP. This is because of the inefficient initiation and very slow deactivation of the catalyst having pseudohalogen anion. For a successful ATRP of MMA using pseudohalide initiators, design
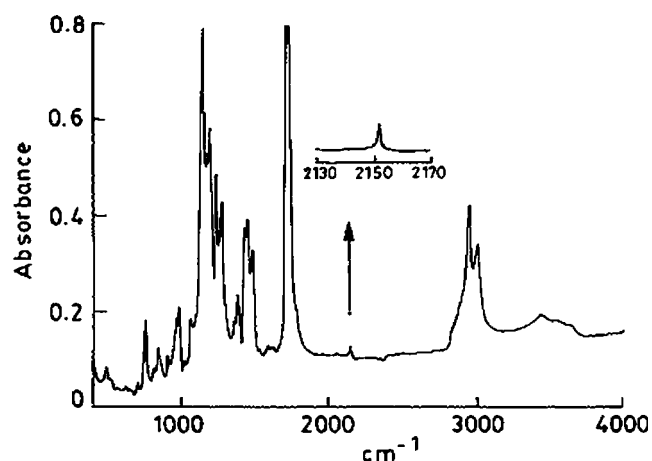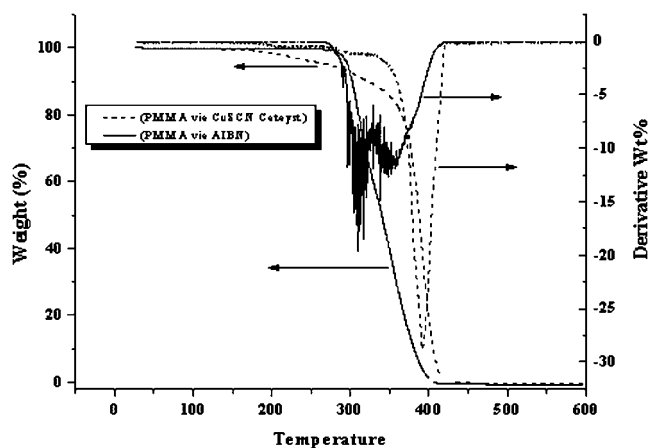

Figure 7 TGA and DTG analysis PMMA prepared by ATRP using EBIB/CuSCN system and by conventional free radical polymerization using AIBN as initiator.

of new initiators having pseudohalogen end group is necessary.

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Figure 6 FTIR of PMMA-SCN prepared by using EBIB/CuSCN as an ATRP catalyst system.

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