Copper Catalyzed ATRP of Methyl Methacrylate Using Aliphatic α-Bromo Ketone Initiator

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Summary: The atom transfer radical polymerization (ATRP) of MMA was examined using 3-bromo-3-methyl-butanone-2 (MBB) as an initiator in the presence of CuBr as catalyst and 2,6-*bis*[1-(2,6-diisopropylphenylimino)ethyl]pyridine (BPIEP) as a tridentate N-donor ligand. The effect of various other N-donor ligands including a bisoxazoline ligand, namely, 2,6-*bis*(4,4-dimethyl-2-oxazolin-2-yl) pyridine (d*m*PYBOX) was studied in ATRP and reverse ATRP of MMA. The ATRP of MMA in toluene at 90 °C using MBB as initiator was relatively slow in the case of bidentate and faster in the case of tridentate N-donor ligands. The apparent rate constant, k_{app}, with MBB as initiator and BPIEP as ligand in toluene (50%, v/v) at 90 °C was found to be 7.15×10^{-5} s^{-1}. In addition, reverse ATRP of MMA in diphenylether at 70 °C using BPIEP/$CuBr_2$ as catalyst system was very effective in reducing the reaction time from several hours to 24 h for polymerization of MMA.

Keywords: apparent rate constant; atom transfer radical polymerization (ATRP); bisoxazoline; CuBr; initiator; ligand; methylmethacrylate; polydispersity

Introduction

In recent years, synthesis of well-defined polymers using radical polymerization has become a reality.[1] Atom transfer radical polymerization (ATRP), independently discovered by Matyjaszewski and Sawamoto in 1995, [2,3] is one of the most efficient and versatile methods for the synthesis of polymers with controlled structures. One of the most important characteristics of ATRP is the fact that initiation occurs through an alkyl halide initiator in presence of a catalyst (ligand/CuX) via a redox process and the polymers prepared by this process consists of a halogen atom at the macromolecular chain-end. The terminal halogen of the polymer-chains can be used for reinitiation as well as for various chemical transformations. In order to obtain good control on the polymerization, it is necessary that the rate of initiation should be equal or faster than the rate of propagation. [4,5] Hence, the selection of initiator is very important. Since the bond strength of C–X bond in the initiator varies as R–Cl > R–Br > R–I, [6] frequently used initiators in ATRP contain halogens that are chlorine or bromine. Alkyl (methacrylates), especially, MMA are generally polymerized using α-haloesters as initiators. [4]

Aliphatic α-halo ketones are a potentially new class of initiators exhibiting different electronic property as compared to the well-known α-halo esters in ATRP. Moreover, it is expected that α-bromo ketones could be more reactive initiators on account of nature of inductive effects. The focus of the present work is to examine the efficacy of 3-bromo-3-methyl-butanone-2 (MBB) as an initiator for ATRP of MMA at 90 °C in presence of 2,6-*bis*[1-(2,6-diisopropylphenylimino)ethyl]pyridine (BPIEP) as a tridentate ligand system. Various other bidentate and tridentate N-donors as ligands were also employed using MBB as initiator. 2,6-*bis*[1-(2,6-diisopropylphenyl imino)ethyl] pyridine (BPIEP) and 2,6-*bis*(4,4-dimethyl-2-oxazolin-2-yl) pyridine (d*m*PYBOX) were also used as N-donor ligands for reverse ATRP of MMA

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using diphenylether at 70 °C. Batch and kinetic studies using the aforementioned initiator is also discussed.

Experimental

Reagents

Methylmethacrylate (Aldrich, 99%) was distilled over calcium hydride. Copper(I) bromide (Aldrich, 98%), was purified according to the method of Keller and Wycoff. [7] $CuBr_2$, and $CuCl_2$, were purchased from Aldrich and used directly. 3-bromo-3-methyl-butanone-2 (MBB) was synthesized as reported.[8] Ethyl-2-bromo isobutyrate (EB*i*B, Aldrich) was vacuum distilled before use. 2,2′-azobisisobutyronitrile (AIBN), was purchased from E. Merck (India) and used after purification. The ligands, 4,4′-di(*n*-nonyl)-2,2′-bipyridine (**d*n*Nbpy**); N,N,N′,N′,N″-pentamethyldiethylenetriamine (**PMDETA**); and N,N, N,N,N, N-hexa methyltriethyl enetetramine (**HMTETA**) were purchased from Aldrich whereas 2,6-*bis*(4,4-dimethyl-2-oxazolin-2-yl)pyridine (**d*m*PYBOX**)[9] and 2,6-*bis*[1-(2,6-diisopropyl phenylimino)ethyl]pyridine (**BPIEP**)[8] was synthesized as reported. Unless mentioned otherwise all other reagents were distilled/recrystallized before use.

Polymerization

In a typical solution polymerization for a monomer/initiator concentration ratio of 100:1, the tridentate imine ligand, BPIEP, (0.450 g, 0.935 mmol) degassed monomer, (MMA, 5 mL, 46.8 mmol) and solvent (toluene, 5 mL) were transferred to a flame dried round bottom flask containing CuBr (68 mg, 0.468 mmol). The polymerization mixture was carefully degassed once using freeze-pump-thaw cycle thereafter the initiator (MBB, 0.059 mL, 0.468 mmol) was introduced into the flask through degassed syringe. The solution was degassed three times using freeze-pump-thaw cycles and finally, immersed the reaction flask in an oil bath maintained at 90 °C. After 5.5 h the reaction was quenched by cooling the flask under liquid nitrogen, diluting the final mixture with tetrahydrofuran followed by precipitation of the polymer in excess of hexane. For kinetic experiments aliquots were withdrawn periodically, diluting further by adding 5 mL of tetrahydrofuran followed by quenching and storing it at 0 °C. A part of each sample was used for gas chromatography (GC) measurements to determine monomer conversion relative to *n*-octane as internal standard. The slope of the plot between $\ln\left(\frac{[M_o]}{[M_t]}\right)$ *vs time* gives apparent rate constant, k_{app}, of polymerization.

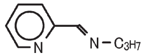
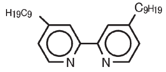
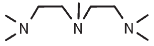
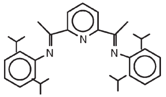
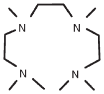
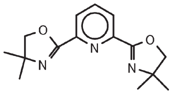
Characterization

The polymer was made free of catalyst using a small alumina column and reprecipitating the eluent in excess of hexane. Molecular weight distributions were measured using GPC-TQ with one linear column (60 cm) and one 100-Å mixed column (60 cm) connected in series using an RI and UV detector and tetrahydrofuran as an eluent (1 mL min^{-1} flow rate). Monodisperse PMMA standards from PSS Germany were used for calibration. For kinetic experiments, monomer conversions were determined using Perkin Elmer XL gas chromatograph equipped with FID detector and a BP1 (non-polar) column using *n*-octane as internal standard.

Results and Discussion

The ATRP of MMA was initiated using 3-bromo-3-methyl-butanone-2 (MBB) in presence of various ligands such as, 4, 4′-di(*n*-nonyl)-2,2′-bipyridine (**d*n*Nbpy**); N,N, N′,N′,N″-pentamethyldiethylenetriamine (**PMDETA)**; N,N,N,N,N, N-hexamethyltriethylene tetramine (**HMTETA**), 2, 6-*bis*(4,4-dimethyl-2-oxazolin-2-yl)pyridine (d*m*PYBOX) and 2,6-*bis*[1-(2,6-diisopropyl phenylimino)ethyl]pyridine (**BPIEP**). The mole ratios of various components used were [MMA]:[MBB]:[CuBr]:[Ligand] = 100:1:1:2. The effect of various N-donors ligands was also examined in reverse ATRP. The N-donors ligands employed in the study possess

Table 1.
ATRP and reverse ATRP of MMA using various N-donors as ligands and MBB/AIBN as initiators.

Entry No.	Ligand[c]		ATRP[a]					Reverse ATRP[b]				
	Structure	Notation	Conv[d] (%)	$\overline{M_{n,SEC}}$[e] ($\times10^{-3}$)	$\overline{M_{n,Cal}}$[f] ($\times10^{-3}$)	$\frac{\overline{M_w}}{\overline{M_n}}$[g]	I_{eff}[h]	Conv (%)	$\overline{M_{n,SEC}}$ ($\times10^{-3}$)	$\overline{M_{n,Cal}}$ ($\times10^{-3}$)	$\frac{\overline{M_w}}{\overline{M_n}}$	I_{eff}
1		**NPPI**	3	2.20	0.30	1.06	0.14	5	2.40	0.50	1.07	0.21
2		**d*n*Nbpy**	1	2.50	0.10	1.07	0.04	85	20.0	8.50	1.11	0.42
3		**PMDETA**	98	14.7	9.80	1.34	0.67	90	60.4	9.00	1.63	0.15
4		**BPIEP**	73	8.80	7.30	1.26	0.83	84[j]	23.1	8.40	1.21	0.40
5		**HMTETA**	98	18.7	9.80	1.41[i]	0.52	90	45.0	9.00	1.54	0.20
6		**d*m*PYBOX**	20	5.40	2.00	1.36	0.40	50[k]	7.30	5.00	1.61	0.68

[a] $[M]_o = 4.68$ M, ATRP of MMA in 50% v/v of toluene wrt monomer at 90 °C for 5.5 h using MBB as initiator; [MMA]: [MBB]: [CuBr]: [Ligand] = 100: 1: 1: 2.

[b] $[M]_o = 5.08$ M, reverse ATRP of MMA in 50% v/v of anisole wrt monomer at 70 °C for 24 h using AIBN as initiator; [MMA]: [AIBN]: [$CuBr_2$]: [Ligand] = 100: 0.5: 1: 2.

[c] NPPI: N-(*n*-propyl)-2-pyridylmethanimine; d*n*Nbpy: 4,4′-di (*n*-nonyl) 2,2′-bipyridine; PMDETA: N,N,N′,N′,N″-pentamethyldiethylenetriamine; BPIEP: 2,6-*bis*[1-(2,6-diisopropylphenylimino)ethyl]pyridine; HMTETA: (N,N, N,N,N,N-hexa methyltriethylenetetramine); d*m*PYBOX: 2,6-*bis*(4,4-dimethyl-2-oxazolin-2-yl)pyridine.

[d] gravimetric.

[e] obtained from SEC.

[f] $M_{n\ cal}$ = % conversion (grams of monomer / moles of initiator).

[g] calibrated with PMMA standards.

[h] $I_{eff} = M_{n,Cal}/M_{n,SEC}$.

[i] bimodal distribution.

[j] 20 h.

[k] bulk reaction for 27 h.

different electronic as well as steric properties.

Table 1 shows the results of polymerization of MMA. The ATRP of MMA using MBB as initiator produces PMMA in the presence of all the N-donor ligands used in this study. However, the initiation efficiency of MBB in the presence of bidentate ligands is relatively poor (Table 1: entry 1, 2). It has been previously reported that the initiator efficiency of ethyl-2-bromoisobutyrate in the presence of a tridentate ligand, namely BPIEP, is high for MMA polymerization. [8] The difference in the reactivity of α-bromoketone (MBB) and α-bromoester (EB*i*B) initiators in ATRP could be attributed to the relative coordinating ability of the initiators with CuX in ATRP. Few α-haloketone initiators are known for ruthenium [10,11] and nickel catalyzed [12] living radical polymerization of MMA with aluminum triisopropoxide [$Al(OiPr)_3$] as additive. However, control over polymerization is lost when they are used with copper catalyzed homogeneous systems, probably, because of the stronger electron-withdrawing power of the ketone's carbonyl that results in the reduction of electrophilic radicals into anions by highly active Cu(I) catalysts.[13]

Polymerization of MMA using bidentate ligands (NPPI and d*n*Nbpy) is very slow resulting in low molecular weight PMMA with narrow molecular weight distribution. The reason for this behavior is attributed to an association between the copper complex and the initiator. However, the reaction is very fast and uncontrolled with multidentate linear amines (PMDETA and HMTETA) as shown in Table 1. Nevertheless, initiator efficiencies are better as compared to the bidentate ligands. It is also evident from the Table 1 that MBB works efficiently with a sterically hindered tridentate N-donor ligand (BPIEP). This indicates that the bromoketone is not effectively coordinating with Cu^I in the presence of tridentate ligands with large steric hindrance around the coordination site.

However, MBB (Table 1, run number 4) initiates the polymerization of MMA more efficiently as compared to EB*i*B (DP = 100, $M_{n,SEC} = 14{,}000$, PDI = 1.27, $I_{eff} = 0.60$) when employed with BPIEP as ligand under similar experimental conditions.

In addition, a new N-donor ligand, namely, 2,6-*bis*(4,4-dimethyl-2-oxazolin-2-yl) pyridine (d*m*PYBOX) was also explored for the ATRP of MMA using MBB as initiator. The coordination site of the ligand (N=C-py-C=N) is similar for BPIEP and d*m*PYBOX, except, for the steric hindrance around the coordination site. The color of the complex is bright brick red and does not undergo any change during the reaction. The rate of polymerization is slower (run number 6) relative to BPIEP and PMDETA but higher than NPPI and d*n*Nbpy as ligands. The molecular weight is lower than targeted. These results indicate very slow initiation followed by deactivation. This is attributed to the fact that the copper (I) complex with d*m*PYBOX might be more stable thereby disturbing the equilibrium dynamics of the reaction. If the number of nitrogen atom increases beyond three in ligands, then an uncontrolled polymerization occurs resulting in bimodal distribution (run number 5).

In view of the structural resemblance between the initiator MBB and the propagating chain end of methylvinylketone (MVK), we attempted the ATRP of MVK using MBB/Cu^IBr, by ATRP and MBB/AIBN as reverse ATRP. Surprisingly, there was no polymerization in both the processes. This has been attributed to a strong association between monomer and catalyst.[14]

Kinetics of ATRP of MMA Using 3-Bromo-3-Methyl-Butanone-2 (MBB) as Initiator

Kinetic study of ATRP of MMA in presence of BPIEP/CuBr as catalyst system was performed in toluene at 90 °C and MBB as initiator. The following mole ratios were used: [MMA]:[MBB]:[CuBr]:[BPIEP] = 100:1:1:2. The semi-logarithmic time conversion plot shows a straight line indicating absence of termination reaction in the polymerization (Fig. 1). An apparent rate constant of polymeriza-

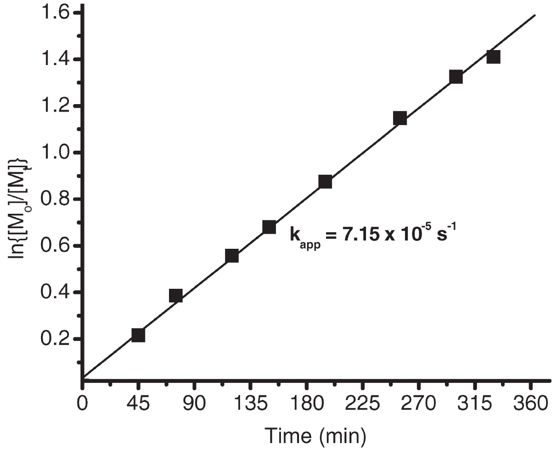


Figure 1.
Semi logarithmic kinetic plots for the ATRP of MMA at 90 °C using different initiators. [MMA] = 4.68 M. [MMA]: [MBB]: [CuBr]: [BPIEP] = 100: 1: 1: 2.

tion, k$_{app}$, was found to be 7.15×10^{-5} s^{-1}. The rate of polymerization using MBB is fast as compared to a α-bromoester initiator (EB*i*B: k$_{app}$ 3.4×10^{-5} s^{-1}).[8] The polymer conversion is high, i.e., 85% in contrast to the aromatic α-haloketones as initiators which gave 90% conversion in 60–80 h.[10] Fig. 2 shows the dependence of M$_{n,SEC}$ with conversion as well as molecular weight distribution of the polymer. It is seen that the molecular weight data obtained from SEC had a curvature indicating the presence of transfer reactions during the polymerization.

However, the molecular weight distribution of the polymer was relatively narrow, i.e., ≤1.26 as compared to the conventional (or redox initiated) radical polymerization. Thus, a strong electron withdrawing effect of keto carbonyl in MBB resulted in higher rate of initiation as compared to EB*i*B in ATRP.

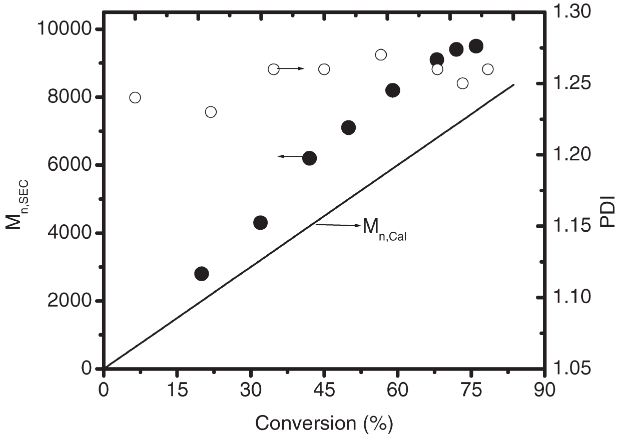


Figure 2.
Dependence of molecular weight and polydispersity on conversion in the solution ATRP of MMA at 90 °C with [I] = 0.0468 M. Open symbols represent polydispersities and filled symbol represents M_n-(GPC).

Influence of Different N-Donors as Ligands in Reverse ATRP of MMA

The conventional radical initiators (AIBN: 2,2′-azobisisobutyronitrile; BPO: benzoyl peroxide) when employed with a copper halide (CuX_2, X = Cl, Br) in higher oxidation state during the polymerization of a vinyl monomer is termed as reverse ATRP. Matyjaszewski and coworkers [15] reported that BPO/ CuBr/ dNbpy could be used as a reverse ATRP initiating system for bulk polymerization of styrene at higher temperature (110 °C). Using substituted 2,2-bipyridine (bpy), Xia and Matyjaszewski carried out the RATRP of MMA under homogeneous conditions.[16] Polymerizations were generally carried out at lower temperature, where initiator decomposes more slowly and better control could be realized. However, the low temperature usually causes long induction time and results in slower polymerization rate. Typical time scale in reported literature for RATRP of MMA is in the range of 50–100 h. [17–20]

We examined the efficacy of different N-donors for RATRP of MMA in anisole (Table 1) at 70 °C. For DP of 100, the mole ratios of different components taken are $[MMA]:[AIBN]:[CuBr_2]:[L] = 100:0.5:1:2$. In all cases except PMDETA and HMTETA, the color of reaction mixture turned from pale yellow to brown or brick red on heating, thereby, indicating the change of Cu^{2+} to Cu^{+} in solution. The color change supports the occurrence of reverse ATRP. However, in toluene the cupric complex is insoluble, which is detrimental to the occurrence of redox reaction and formation of dormant and active species in equilibrium. Therefore, no controlled polymerization was observed. Table 1 shows that when the reaction was performed in polar solvent using a tridentate ligand, BPIEP, a fairly good control was observed within 24 h giving conversions upto 95% with PDI < 1.20. Among the other N-donor ligands the reaction is slow in the case of NPPI yielding polymers with PDI < 1.18 whereas all other ligands except d*m*PYBOX resulted in uncontrolled polymerization as seen from the Table 1. d*m*PYBOX, exhibited reasonable initiator efficiency with little broadening of MWD with MBB as initiator as compared to other N-donors. Thus, reverse ATRP of MMA was successful using BPIEP as ligand in solution as well as in bulk.

Conclusions

An aliphatic α-bromoketone, namely, 3-bromo-3-methyl-butanone-2 (MBB) was effectively employed as an initiator in ATRP of MMA at 90 °C in toluene using BPIEP/ CuBr as catalyst system. Other N-donors were also examined as ligands. The results indicate that a tridentate ligand, BPIEP, is more fficient than bidentate ligands in ATRP. The rate of polymerization follows first order kinetics indicating the presence of a low radical concentration throughout the reaction. The apparent rate constant of polymerization was found to be 0.715×10^{-4} s^{-1}. As revealed from observed monomer conversions, the rate of the polymerization was relatively slower with bidentate ligands. Initiator efficiencies were also better with bulky tridentate N-donor (BPIEP) as ligand and poorer with bidentate ligands. This could be due to the association of the carbonyl group of the initiator with that of imine N-atom of bidentate ligands. MBB failed to polymerize methyl vinyl ketone (MVK) inspite of the structural resemblance of the initiating radical to the propagating radical. Reverse ATRP of MMA using Cu^{II}/AIBN system showed good control over polymerization in solution as well as in bulk.

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