Atom Transfer Radical Polymerization (ATRP) of Ethyl Acrylate: Its Mechanistic Studies

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Summary: Atom transfer radical polymerization (ATRP) of ethyl acrylate was carried out in bulk using ethyl 2-bromoisobutyrate as initiator, CuBr as well as CuCl as catalyst in combination with different ligands e.g., 2,2′ bipyridine (bpy)andN,N, N′,N″,N″-pentamethyldiethylenetriamine (PMDETA). In most of the cases very high conversion (72–98%) was achieved. The polymerization was well controlled with a linear increase of molecular weight (M_n^{SEC}) with conversion and relatively narrow molecular weight distributions (polydispersity index 1.2–1.3). Use of PMDETA as the ligand resulted in faster polymerization rate (98% conversion in 1 h) than those using bipyridine (72% conversion in 5 h). The MALDI-TOF-MS analysis of poly (ethyl acrylate) (PEA) prepared by using bpy as ligand showed the presence of halogen as the end group. On the contrary, when PMDETA was used as the ligand, the mass analysis showed no trace of this end group.

Keywords: atom transfer radical polymerization (ATRP); end group; ethyl acrylate; MALDI-TOF-MS; polydispersity index

Introduction

Since its discovery in 1995[1–4], atom transfer radical polymerization (ATRP) has rapidly attracted growing interest because of its versatility in the synthesis of polymers with predictable molecular weights, low polydispersities and specific functionalities. Because it can be applied to great variety of monomers at wide range of temperatures. ATRP[5–10] has become an important synthetic tool to prepare polymers with well-controlled structures and morphology. A large number of polymers and copolymers have been prepared using acrylic monomers and many have found commercial applications in plastics, fibers, adhesives and surface coatings. Among the acrylate family poly (ethyl acrylate) (PEA) is an industrially important polymer because of its low glass transition temperature, durability and the potential use as the soft segment in thermoplastic elastomer (TPE) based on acrylates. PEA is generally prepared via conventional radical polymerization but with unpredictable molecular weight and broad molecular weight distributions. Wootthikanokkhan et al. [11] made a brief study on ATRP of ethyl acrylate (EA) using CuBr/PMDETA (N,N,N′,N″,N″ pentamethyl diethylene triamine) system with varying content of CuBr at 100 °C temperature and they observed broad polydispersity (1.4–2.3) in most cases. They also did not address the nature of the end group in the final polymer by using different ATRP catalysts. In this article, we report the controlled ATRP of EA using different catalysts like CuBr and CuCl in combination with different ligands viz. 2,2′-bipyridine (bpy), PMDETA. The effect of the reaction temperature on the polymerization has also been studied.

Experimental

Materials

Ethyl acrylate (Aldrich, 99%) was purified by vacuum distillation over calcium

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hydride. The distillates were stored at −18 °C before they were used. CuBr (Aldrich, 98%) was stirred with glacial acetic acid and then dried under vacuum at 75 °C for 3 days. The purified CuBr was stored in a nitrogen atmosphere. Ethyl 2-bromoisobutyrate (EBiB), (Lancaster, 98%), 2,2′-bipyridine (bpy) (Lancaster, 98%), PMDETA (Aldrich, 99%). CuCl (Aldrich, 98%) and all other chemicals were used as received.

General Procedure for the ATRP of EA

All the ATRP reactions were carried out in a test tube (8 cm. × 2.5 cm.) provided with a B-14 standard joint and under nitrogen atmosphere. In a typical ATRP reaction, CuBr was charged into the test tube. It was then purged with nitrogen for 15 min. Bipyridine (0.1558 g, 9.8×10^{-4} mol), ethyl acrylate (5 ml, 4.9×10^{-2} mol), (already degassed by purging with nitrogen for 30 min before use) and finally the initiator, EBiB (0.0973 g, 4.9×10^{-4} mol) were added to the test tube in the sequential order via dry and purified syringe at ambient temperature with continuous stirring. The reaction was carried out by immersing into a thermostated oil bath preheated at a temperature of 90 °C. The sample was withdrawn at specific time intervals under nitrogen atmosphere and the conversion was determined by the gravimetric analysis. A part of the sample was passed through a column of neutral alumina oxide prior to size exclusion chromatography (SEC) analysis.

Characterization

Molecular weights and molecular weight distributions of the polymers were determined by Size Exclusion Chromatography (SEC) at ambient temperature using a Viscotek GPC equipped with a refractive index detector model VE 3580. THF was used as the eluent at a flow rate of 1.0 ml/min and calibration was carried out using low polydispersity polystyrene standards. One ViscoGEL GPC column GMHHR-H #17360 was used. Data acquisition and processing were performed using Viscotek OMNI-01 software. MALDI-TOF-MS analyses were carried out using a Percepctive Biosystems Voyager Elite MALDI-TOF mass spectrometer, equipped with a nitrogen laser (wave length 337 nm). Polymer samples, 2,5-dihydroxybenzoic acid (used as matrix) and sodium trifluoro acetate (used as cationic agent) were dissolved in THF (10 mg/ml solutions of each component) and the resulting solutions were mixed at 100/100/1 volume ratio. All the spectra were averaged over 128 laser shots. The ^{1}H NMR spectra were recorded using a Bruker DPX-300 NMR spectrophotometer using $CDCL_3$ as solvent. DSC measurement was carried out on a DSC 204 instrument at the heating rate 10 °C/min under N_2 atmosphere.

Result and Discussion

The ATRP of EA was carried out in bulk as the function of different reaction parameters viz., catalyst systems, ligand and temperature. Figure 1 shows the kinetic plot of the polymerization carried out at different temperature, 70, 90 and 100 °C using EBiB as the initiator and CuBr as a catalyst in combination with bpy as the ligand.

For all the cases $\ln[1/(1-x)]$ increases linearly with increasing reaction time, demonstrating that the radical species concentration remained constant throughout the reaction. The reaction temperature significantly affected the percentage yield, molecular weight of the final polymer and polydispersity index (Table 1, entry 1–3). Only 52% yield was obtained when the polymerization was carried out at 70 °C for 5 h and also the polydispersity index was relatively broad (1.32). By increasing the temperature to 90 °C, moderate conversion (72%) was achieved after the same time period keeping the low value of polydispersity index (PDI) (1.22). At higher temperature, i.e., 100 °C, the rate of polymerization is high but there is a considerable deviation from linearity indicating the occurrence of some side reactions during the

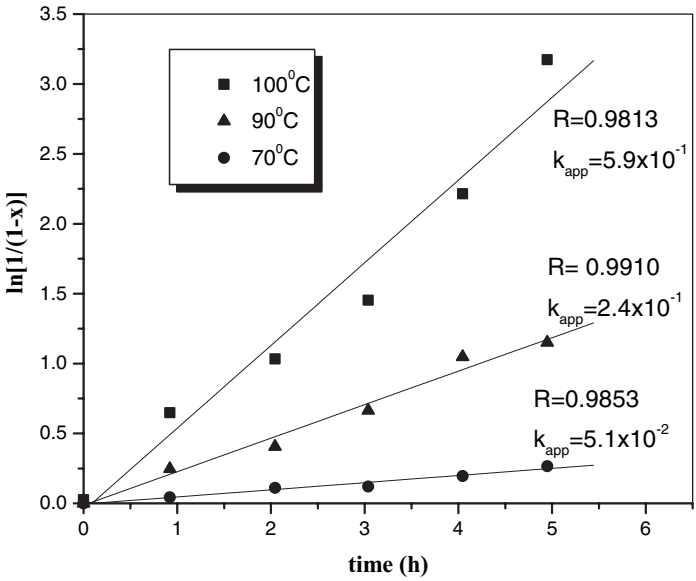


Figure 1.
Kinetic plot of ln [1/(1 − x)] (x = % conversion) versus reaction time for ATRP of EA in bulk at different temperature, 90 °C (triangles), 70 °C (circles), 100 °C (square symbols). [EA]/[EBiB]/[CuBr]/[bpy] : 100/1/1/2. $[EA]_0 = 4.9 \times 10^{-2}$ M, $[EBiB]_0 = 4.9 \times 10^{-4}$ M, $[CuBr] = 4.9 \times 10^{-4}$ M, $[bpy] = 9.8 \times 10^{-4}$ M.

polymerization. At low reaction temperature the rate of propagation as well as the rate of deactivation from the active to dormant species during the equilibrium is quite low. Hence the ATRP of EA at 70 °C results in low percent yield and relatively high PDI of the resultant polymer. At 90 °C the polymerization rate is moderate and yield of polymers with good control of the molecular weights and its distributions. Figure 2 shows the linear dependence of molecular weights and a regular decrease in molecular weight distribution with monomer conversion. For CuCl system, the polymerization rate was very low (65% conversion in 10 h) and the experimental molecular weight deviated considerably from the theoretical one (Table 1, entry-5). In this case the observed molecular weight was very high with respect to the theoretical molecular weight. The polydispersity index is also relatively broad (1.33) with respect to CuBr system indicating that there was a poor control in the polymerization process. Lower polydispersities are observed in ATRP using an active organo bromide initiator with CuBr/bpy. The copper (II)-bromine bond strength (~331 kJ/mol) is weaker than the copper (II)-chlorine bond strength(~377 kJ/mol). Hence it leads to the faster deactivation reaction which results in lower value of polydispersity (1.23) in case of CuBr as catalyst compared to the polydispersity value (1.33) when CuCl was used as the catalyst.

Table 1.
ATRP of Ethyl acrylate at different reaction conditions

Entry	Catalytic system	[EA]:[I]:[Cu^I]:[L]	Temp (°C)	Time (h)	Conversion (%)	M_n^{theo}	M_n^{SEC}	MWD
1	CuBr/bpy	100:1:1:2	70	5	52	5200	5700	1.32
2	CuBr/bpy		90	5	72	7200	7810	1.22
3	CuBr/bpy		100	5	95	9500	7370	1.39
4	CuBr/PMDETA	100:1:1:1	90	1	98	9800	10,600	1.23
5	CuCl/bpy	100:1:1:1	90	10	65	6500	10,700	1.33

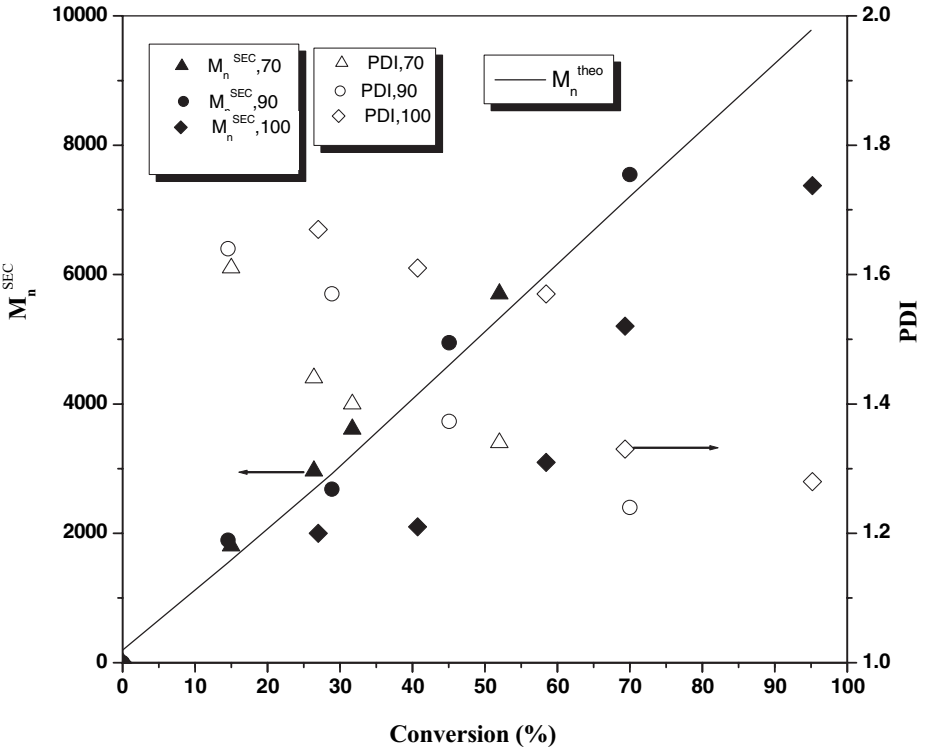


Figure 2.
Plot of M_n^{SEC} (filled symbols) and PDI (blanc symbols) versus monomer conversion for bulk ATRP of EA. [EA]/[EBiB]/[CuBr]/[bpy] : 100/1/1/2.

The effect of PMDETA, a tridentate ligand was also observed. When PMDETA was used as the ligand, the polymerization medium soon became very viscous (within ~15 min of the reaction) and ~98% conversion was achieved within 1 h (Table 1, entry-4). The increased product yield and such a faster polymerization rate using PMDETA as the ligand may be attributed to the greater solubility (and so a higher concentration of the active species) of CuBr in the reaction mixture. Another factor which play a significant role in this respect is the lower redox potential of the copper (I)-PMDETA complex than the copper (I)-bpy complex [13,14]. At the lower redox potential the apparent equilibrium constant for the oxidation reaction of Cu (I) to Cu (II) becomes greater and thus it enhances the rate of the polymerization [14]. The polydispersity index is also quite narrow (1.23) suggesting a well-controlled nature of the polymerization.

End groups on a polymer play an important role in determining the different properties of polymers as well as to further modify it to make polymers with well defined architectures and morphology [15]. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) provides an efficient tool for the determination of the design of repeat units and end groups in chemically heterogeneous polymers like polystyrene,[16] poly (n-butyl methacrylate),[17] poly(methyl methacrylate), [18] poly(p-phenylene) and polypeptides [19].

A selected part of the MALDI-TOF mass spectrum of ethyl acrylate prepared by using CuBr/bipyridine system is shown in Figure 3. In this MALDI spectrum each intense peak is separated by approximately 100 mass units, the molar mass of the repeat unit of EA. On the basis of molecular weight values and the isotope distribution,

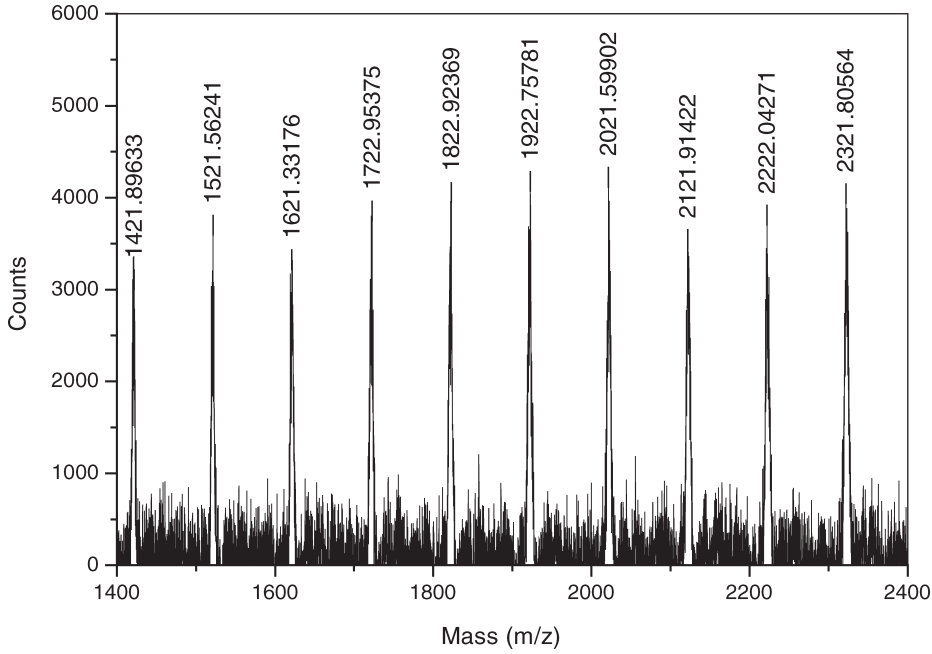


Figure 3.
MALDI-TOF mass spectrum of PEA using CuBr/bpy catalytic system.

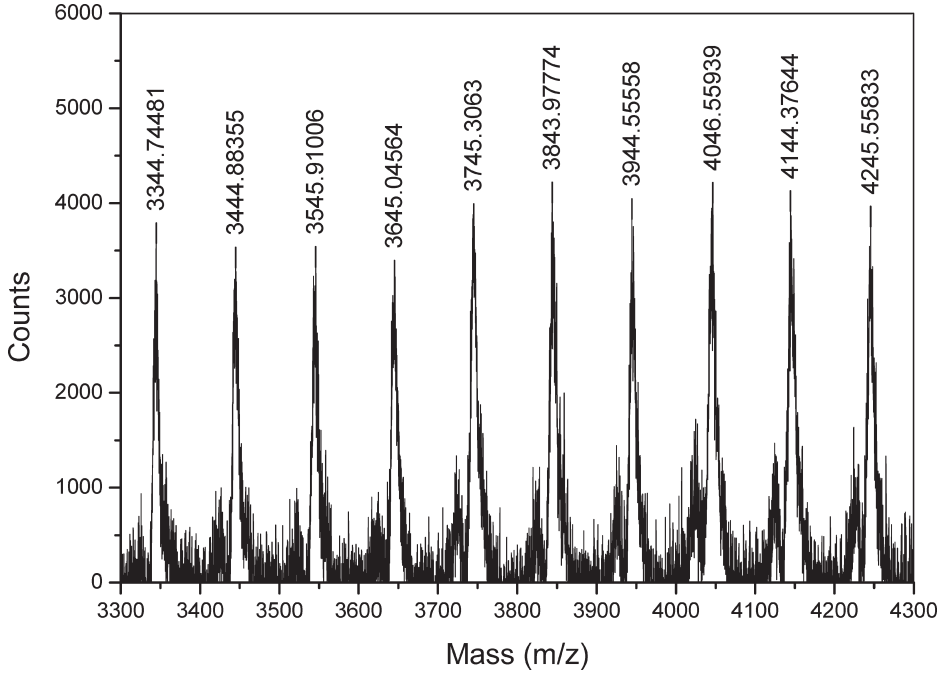


Figure 4.
MALDI-TOF mass spectrum of PEA using CuBr/PMDETA catalytic system.

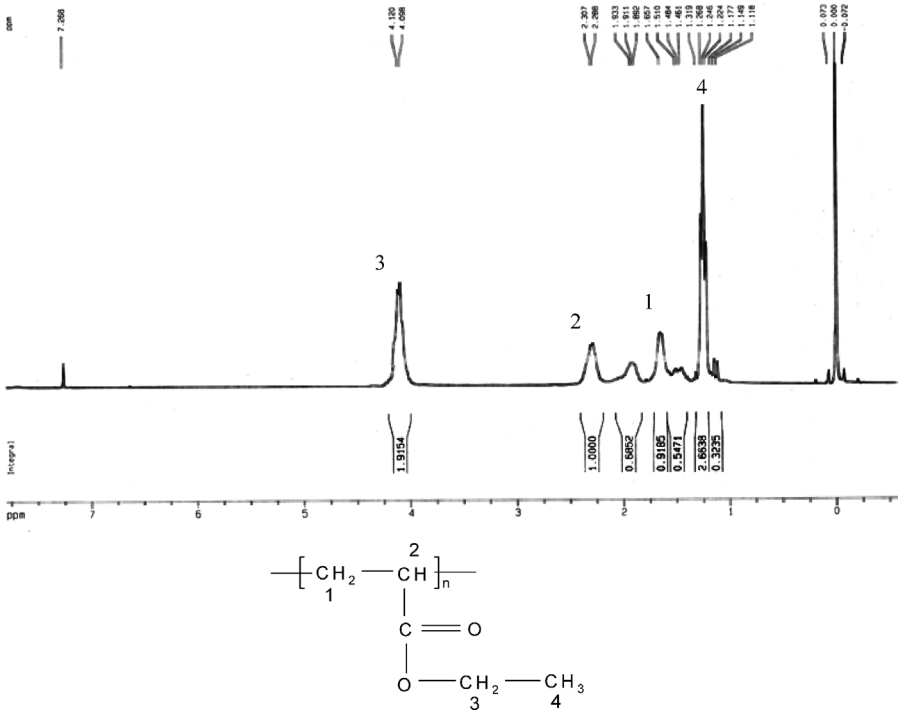
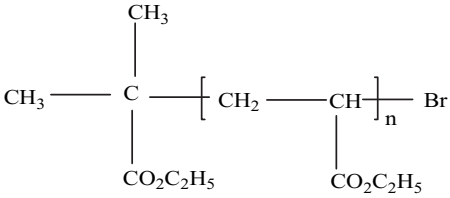


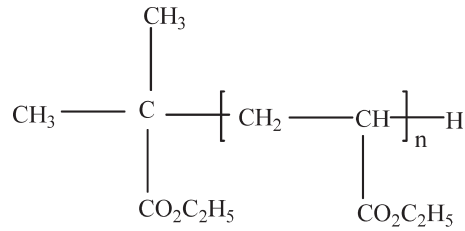
Figure 5.
^{1}H-NMR spectra of poly (ethyl acrylate).

the signals of the each major peak correspond to the structure (I). For example, the peak at 2121 can be assigned due to structure-I where n = 19 and Na-salt as the cationic agent.



structure I

Figure 4 shows the MALDI-TOF-MS of PEA prepared by using CuBr/PMDETA system. Here the most intense peaks can be best explained by the structure (II), the peak at 3843 can be assigned due to the following structure (II) when n = 37. It is interesting to note that loss of this end group was observed and simple H-terminated polymer (structure II) was obtained when PMDETA was used as ligand instead of bpy.



structure II

Muller et al.[20] observed that ATRP of MMA in presence of PMDETA ligand leads to the polymer with no halogen end group. He proposed that PMDETA when used in ATRP in excess to the initiator, it acted as a ligand during polymerization and as a transfer agent at the end of the polymerization.

Figure 5 shows the 1H NMR spectra of PEA prepared by CuBr/bpy system. The peak at δ = 1.3 ppm are due to –CH_3 group, δ = 1.4–1.6 ppm to different –CH_2– protons

in the PEA backbone. The peaks at $\delta =$ 2.3 ppm are attributed to –CH– and $\delta = 4.0$–4.2 ppm are due to–OCH_2– protons. According to the literature report, for the protons of end group [–CH(Br)–] should appear at $\delta = \sim 4.1$ ppm.This peak is emerged inside the resonances of –OCH_2–. However, the MALDI-TOF-mass spectra indicate that there was –Br end group in PEA prepared by CuBr/bpy system. DSC analysis showed that the glass transition temperature (T_g) of the synthesized polymer is $-24\,^{\circ}C$.

4. Conclusion

We have compared the ATRP of EA in terms of different ligands, catalysts and reaction temperatures. In bulk polymerization both the catalytic systems (bpy and PMDETA) produces PEA with predetermined molecular weight and low polydispersity index (1.2). The reaction temperature had a positive effect on the polymerization rate but the optimum reaction temperature was found to be $90\,^{\circ}C$. ATRP of EA using PMDETA ligand was much faster than that using bpy as the ligand MALDI-TOF mass spectrometry showed that when the Cu halide/bpy catalytic system was used halogen was present as the end group. Loss of this end group was observed in case of CuBr/PMDETA system.

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