

Iron Catalyzed Atom Transfer Radical Polymerization of Methyl Methacrylate Using Diphenyl-2-pyridylphosphine as a Ligand

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Abstract: The living radical polymerization of methyl methacrylate (MMA) by atom transfer radical polymerization, (ATRP) employing a Fe(II)X₂/diphenyl-2-pyridyl phosphine (PyP) catalytic system (X = Cl, Br), was investigated using several initiators and solvents at various temperatures. Most of the polymerizations with the PyP ligand were well controlled, with a linear increase in the number average molecular weights (M_n) vs. conversion, with relatively low molecular weight distributions ($M_w/M_n = 1.2-1.4$) throughout the reactions. The measured weights matched those of the predicted values. The ethyl-2-bromoisobutyrate (EBriB) initiated ATRP of MMA, with the Fe(II)X₂/diphenyl-2-pyridyl phosphine catalytic system (X = Cl, Br), was better controlled in *p*-xylene at 80 °C than the other solvents used in this study.

Keywords: atom transfer radical polymerization, diphenyl-2-pyridyl phosphine ligand, methyl methacrylate, iron halide, iron (Fe).

Introduction

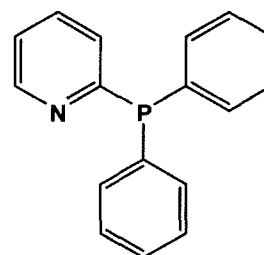
Living radical polymerization (LRP) is a method of synthesizing polymers with controlled molecular weights, which constitutes a promising synthetic tool in polymer chemistry.¹⁻⁵ The living radical polymerization technique includes nitroxide-mediated living radical polymerization (NMRP),^{6,7} atom transfer radical polymerization (ATRP),^{3,5} reversible addition and fragmentation chain transfer (RAFT),⁸ and group transfer polymerization (GTP).^{9,10} In the ATRP system, several transition metals have been investigated in attempt to accomplish the living radical polymerization of a wide range of monomers with alkyl halides¹¹⁻¹⁴ or other initiators¹⁵⁻¹⁹ in different solvents.

The catalyst plays an important role in ATRP and, for this purpose different metal salts have been investigated, including systems based on Cu, Fe, Ni, Rh, Ru, and Pd in conjunction with suitable nitrogen and phosphorus-containing ligands.^{3,20-22} Recently, iron salt based catalysts have attracted a particular attention,^{23,24} owing to their low toxicity, low cost, and biocompatibility.

The important role of the ligand in ATRP is to solubilize the metal salts in the organic media and to adjust the redox potential of the metal center.³ Matyjaszewski and co-work-

ers had made a great deal of effort to determine the relationship between the structure of the ligand and its ability to control the polymerization.²⁵⁻²⁷ Nitrogen ligands have typically been used in the field of ATRP. Bidentate 2,2-bipyridine derivatives and multidentate nitrogen ligands have been shown to be effective in producing polymers with controlled molecular weights. Phosphorus-based ligands have been employed to form a catalyst system with transition metal salts in the field of ATRP. PPh₃ and P(nBu)₃ are the most frequently studied phosphorus ligands in ATRP. However, bidentate catalyst systems with both phosphorus and nitrogen are rarely studied in ATRP systems.

In this study, we found that the ligand, diphenyl-2-pyridyl phosphine (Scheme I) could form a complex with an iron halide. The ATRP of MMA mediated by this system was



Scheme I. The structure of diphenyl-2-pyridyl phosphine.

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able to yield poly(methyl methacrylate) (PMMA) with a well controlled molecular weight and relatively low polydispersity (PDI). The effects of the reaction temperatures, solvents, and initiators on the living radical polymerization are described.

Experimental

Materials. Methyl methacrylate (MMA) (Aldrich; 99%) was passed through a column filled with neutral alumina, dried over CaH_2 , distilled under reduced pressure, and stored in a freezer under nitrogen. Tetrahydrofuran (THF) (Fisher; HPLC grade) and toluene (Fisher; certified grade) were freshly distilled from Na/K alloy with benzophenone (Aldrich; 99%) and stored under nitrogen. Diphenyl-2-pyridyl phosphine (PyP) (Aldrich; 97%), FeBr_2 (Aldrich; 98%), FeCl_2 (Aldrich; 98%), ethyl 2-bromoisobutyrate (EBriB) (Aldrich; 99%), 2-bromopropionitrile (BPN) (Aldrich; 97%), diethyl 2-bromo-2-methylmalonate (DEBM) (Aldrich; 98%), 2,2-dichloroacetophenone (DCAP) (Aldrich; 97%), 1-phenylethyl bromide (1-PEBr) (Aldrich; 97%), *p*-xylene (Aldrich; 97%), anisole (Aldrich; 99%), diphenyl ether (DPE) (Aldrich; 99%), methyl ethyl ketone (MEK) (Aldrich; 99+%) and other solvents were used without further purification. The monomers and solvents were purged by bubbling with dry nitrogen for 30 min immediately before polymerization.

Polymerization. The ATRP of MMA was carried out in solution. In a typical solution polymerization, a Schlenk flask was charged with FeBr_2 and the ligand. The flask was sealed with a rubber septum and was cycled three times between vacuum and nitrogen to remove the oxygen. The degassed solvent and monomer were then added to the flask through degassed syringes. The solution was stirred for 20 min at room temperature, and then the desired amount of initiator was added. The flask was sealed with a new rubber septum and degassed by three freeze-pump-thaw cycles to remove oxygen. The flask was immersed in an oil bath thermostated at 80 °C. At timed intervals, samples were withdrawn from the flask with a degassed syringe and diluted with THF and then filtered through a column filled with neutral aluminum oxide to remove the iron catalyst. Parts of the polymer solution were used for gas chromatography (GC) measurements in order to determine the monomer conversions. Other parts of the polymer solution were then precipitated using an excess of *n*-hexane and dried under vacuum for 24 h in preparation for gel permeation chromatography (GPC) measurements to determine the molecular weights of the PMMA.

Characterization. The monomer conversion was determined in THF solvent with anisole as an internal standard with a HP 6890 gas chromatography equipped with a FID detector and a J&W Scientific 30 m DB WAX Megabore column. The injector and detector temperatures were kept at 250 °C. The analysis was run isothermally at 40 °C for

1 min, following which the temperature was increased to 120 °C at a heating rate of 20 °C/min and held at this temperature for 1 min, before being increased again to 180 °C at a heating rate of 10 °C/min and being held at this temperature for 1 min. The number-average molecular weight and molecular weight distribution (M_w/M_n) of the PMMA were determined by GPC using Waters columns (Styragel, HR 5E) equipped with a Waters 515 pump and a Waters 2410 differential refractometer using diphenyl ether as an internal standard. THF was used as the eluent at a flow rate of 1 mL/min. Linear PS standards (1.31×10^3 - 3.58×10^6 g/mol) were used for calibration.

Results and Discussion

Effect of Reaction Temperature. Different temperatures were investigated for the ATRP of MMA using the FeBr_2 /diphenyl-2-pyridyl phosphine catalyst system initiated by EBriB in toluene with a monomer concentration of 50% (V/V) for all of the reactions. The molar ratio of MMA to FeBr_2 to the ligand to the initiator was always 200 : 1 : 2 : 1. The kinetic plots of the polymerization are shown in Figure 1. A comparison of the kinetic plots of the polymerization shows that the polymerization was slower at 80 °C than at 90 °C. The linear kinetic plots obtained from all of the reactions indicated that the concentrations of the growing radicals were constant during the polymerization.

The plots of M_n and M_w/M_n at different temperatures are shown in Figure 2. The experimental molecular weight (M_n) values were very close to the theoretical ones calculated from the equation, $M_{n,th} = ([M]_0/[RX]_0)M_M C_M + M_{RX}$, where $[M]_0$ and $[RX]_0$ are the initial concentrations of the monomer and initiator, respectively; M_M and M_{RX} are the molecular weights of monomer and initiator, respectively; and C_M is the monomer conversion. Low polydispersities ($M_w/M_n <$

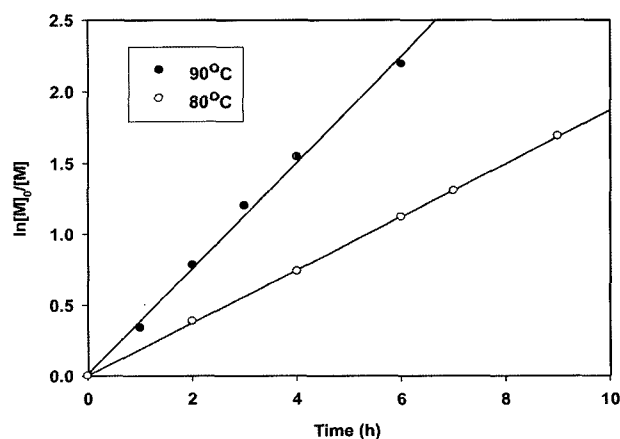


Figure 1. Kinetic plots of $\ln[M]_0/[M]$ vs reaction time, for the ATRP of MMA with $[MMA]_0/[EBriB]_0/[FeBr_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$ in toluene at different temperatures.

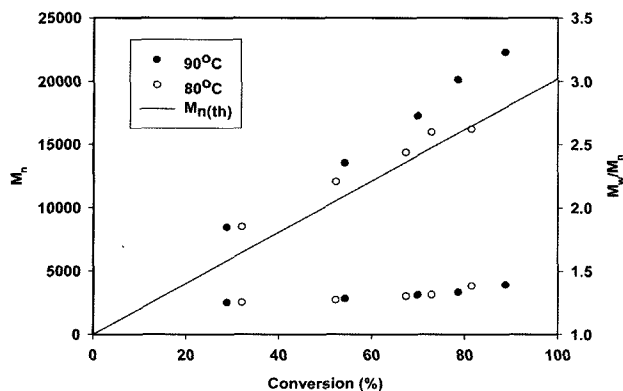


Figure 2. Dependence of molecular weight, M_n , and molecular weight distributions, M_w/M_n , on the monomer conversion for the ATRP of MMA with $[MMA]_0/[EBriB]_0/[FeBr_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$ in toluene at different temperatures.

1.4) were observed at 80 °C, whereas at 90 °C, the polydispersities were slightly higher, probably because the thermal acceleration is greater for propagation than for the interconversion rate between the dormant and activated species with temperature.²⁸ Therefore, the reaction temperature of 80 °C was employed in polymerization studies.

Effect of Catalyst Complex. Figure 3 showed the relationships between $\ln[M]_0/[M]$ and reaction times catalyzed by FeX_2 ($X = Br, Cl$)/PyP. The corresponding plots of $\ln[M]_0/[M]$ vs polymerization time were shown in Figure 3. The mixed halogen system EBriB/ $FeCl_2$ ($k_p^{app} = 0.28 \times 10^{-4} s^{-1}$) showed a slower rate of polymerization than EBriB/ $FeBr_2$ ($k_p^{app} = 0.52 \times 10^{-4} s^{-1}$). The comparison between the two initiation systems, $FeBr_2/EBriB$ and $FeCl_2/EBriB$, showed that $FeBr_2/EBriB$ gave a better control of the polymerization of MMA with the diphenyl-2-pyridyl phosphine ligand. $\ln[M]_0/[M]$ increased linearly with the reaction time,

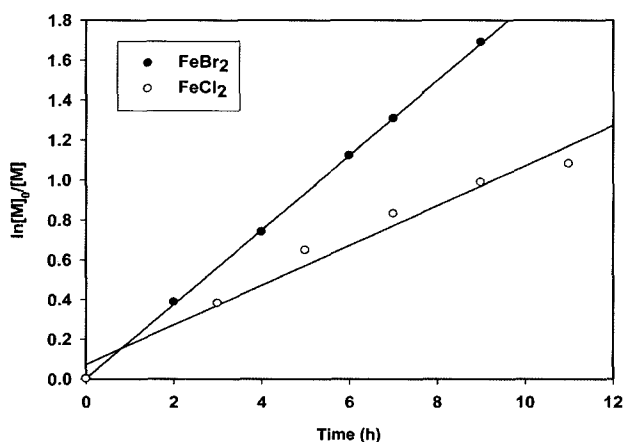


Figure 3. Kinetic plots of $\ln[M]_0/[M]$ vs reaction time, for the ATRP of MMA with $[MMA]_0/[EBriB]_0/[FeX_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$ in toluene at 80 °C ($X = Br$ or Cl).

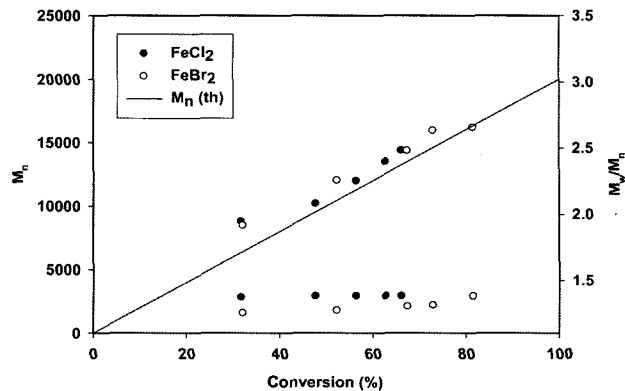


Figure 4. Dependence of molecular weight, M_n , and molecular weight distributions, M_w/M_n , on monomer conversion for the ATRP of MMA with $[MMA]_0/[EBriB]_0/[FeX_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$ in toluene at 80 °C ($X = Br$ or Cl).

which indicated that the radical concentration remained constant during the reaction, whereas the $FeCl_2/EBriB$ system showed curvature in the first-order kinetic plot, which suggested the existence of radical termination during the reaction.

The dependence of the molecular weights on the monomer conversion is shown in Figure 4. The molecular weight of the PMMA prepared with the two different iron salts increased linearly with increasing monomer conversion, and the experimental molecular weights followed the theoretical line. They were slightly higher than the theoretical values in the early stages of the reaction, but approached the calculated values at high conversion in the $FeBr_2/EBriB$ system, thus indicating that the activation/deactivation process was efficient. Moreover, in the case of the $FeBr_2/EBriB$ system relatively low PDIs were observed. However, the PDIs catalyzed by $FeCl_2$ were higher. Further investigation

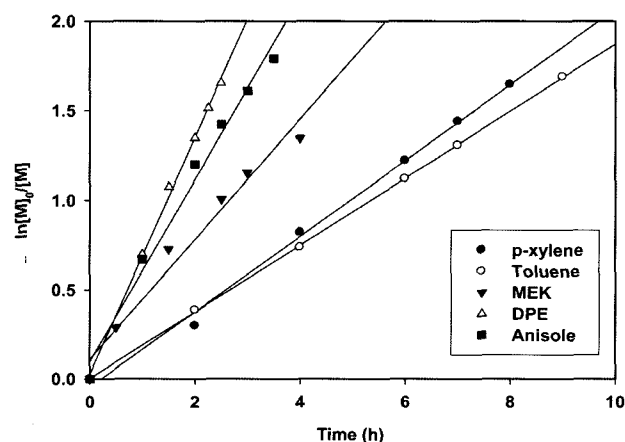


Figure 5. Kinetic plots of $\ln[M]_0/[M]$ vs reaction time, for the ATRP of MMA with $[MMA]_0/[EBriB]_0/[FeBr_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$ in different solvents at 80 °C.

is ongoing to provide a reasonable explanation. These results demonstrated that the polymerization of MMA mediated by FeBr₂/EBriB proceeded via a living process.

Effect of Solvent. The kinetic plots of $\ln[M]_0/[M]$ vs time for the polymerization in different solvents are shown in Figure 5. These ATRPs of MMA using the FeBr₂/diphenyl-2-pyridyl phosphine catalyst system initiated by EBriB were carried out at 80 °C in toluene, *p*-xylene, anisole, DPE, and 2-butanone, with a monomer concentration of 50% (V/V) for all of the reactions. The linear kinetic plots obtained from all of the reactions indicated that the concentration of growing radicals was constant during the polymerization.

Polar solvents can increase the activity of the ATRP of MMA, because of their ability to form a homogeneous solution.^{27,29} However, relatively higher M_w/M_n values were observed when anisole and DPE were used as solvents. Apparently, the solubility of system was not strongly affected since the PDIs were lower when non-polar solvents were used. Schubert *et al.*¹⁴ also studied the effect of sol-

vents on the ATRP of MMA catalyzed by FeBr₂/N-Alkyl-2-pyridylmethanimine and found that 2-butanone gave faster polymerization than *p*-xylene, but a higher reaction temperature was used in 2-butanone. The kinetic parameters determined from Figure 5 are shown in Table I. k_p^{app} values were obtained from the slope of the linear part of the kinetic curve. Some variation can be observed in the values of k_p^{app} with different solvents. The polymerization proceeded faster in polar solvents than in non-polar solvents. A similar trend has been reported by Madruga *et al.*³⁰ and Matyjaszewski *et al.*³¹

Figure 6 shows the dependence of M_n and M_w/M_n on the monomer conversion in different solvents. The molecular weights of the PMMA prepared in all of the solvents increased linearly with increasing monomer conversion. In the case of the polymerization using *p*-xylene as a solvent, the experimental molecular weights followed the theoretical line and low PDIs were obtained. However, the molecular weights were higher than the theoretical values in the case of the other polar solvents in which medium and slightly higher PDIs were observed. This observation could be a result of a slow initiation process compared with propagation. All of these results indicated that *p*-xylene was the best solvent for the ATRP of MMA using the FeBr₂/diphenyl-2-pyridyl phosphine catalyst system among all the solvents used. Therefore, *p*-xylene was used as the solvent in the subsequent experiments.

Effect of Initiator. Four different initiators were investigated for the ATRP of MMA using the FeBr₂/diphenyl-2-pyridyl phosphine catalyst system in *p*-xylene at 80 °C. Figure 7 shows the kinetic plots of the ATRP of MMA with different initiators. In the EBriB and 1-PEBr systems, the $\ln[M]_0/[M]$ data increased linearly with the reaction time, which indicated that the radical concentration remained

Table I. Kinetic Parameters of ATRP of MMA at 80 °C in a 50 vol% Solution^a

| Solvent | FeX ₂ /initiator | $k_p^{app} \times 10^4$ (s ⁻¹) |
|------------------|-----------------------------|--|
| Toluene | FeBr ₂ /EBriB | 0.52 |
| | FeCl ₂ /EBriB | 0.28 |
| <i>p</i> -Xylene | FeBr ₂ /EBriB | 0.59 |
| | FeBr ₂ /1-PEBr | 0.44 |
| | FeBr ₂ /BPN | 0.60 |
| | FeBr ₂ /DEBM | 0.56 |
| | FeBr ₂ /DCAP | 0.12 |
| MEK | FeBr ₂ /EBriB | 0.93 |
| Anisole | FeBr ₂ /EBriB | 1.42 |
| DPE | FeBr ₂ /EBriB | 1.84 |

^aIn all cases, the concentration ratio was $[MMA]_0/[EBriB]_0/[FeX_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$.

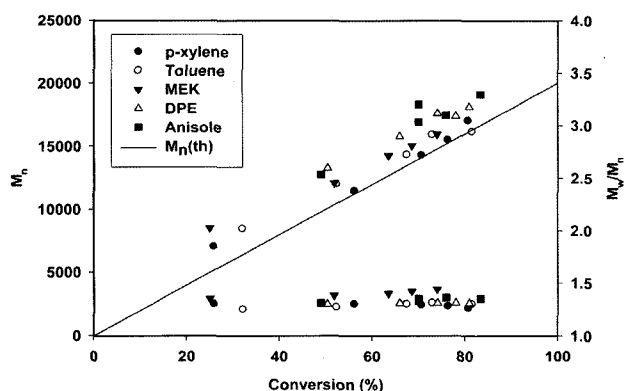


Figure 6. Dependence of molecular weight, M_n , and molecular weight distributions, M_w/M_n , on monomer conversion for the ATRP of MMA with $[MMA]_0/[EBriB]_0/[FeBr_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$ in different solvents at 80 °C.

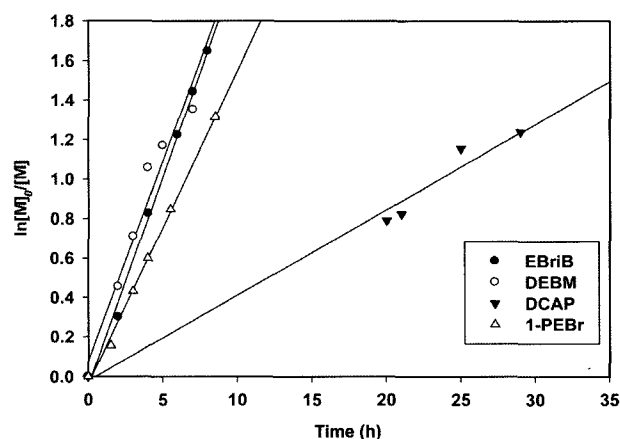


Figure 7. Kinetic plots of $\ln[M]_0/[M]$ vs reaction time, for the ATRP of MMA with $[MMA]_0/[Initiator]_0/[FeBr_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$ in *p*-xylene at 80 °C using four different initiation systems.

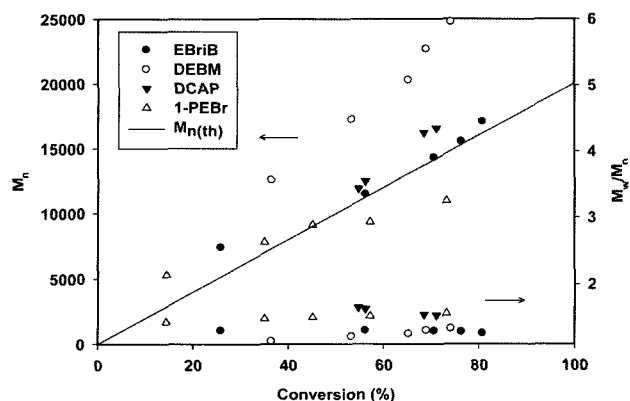


Figure 8. Dependence of molecular weight, M_n , and molecular weight distributions, M_w/M_n , on monomer conversion for the ATRP of MMA with $[MMA]_0/[Initiator]_0/[FeBr_2]_0/[PyP]_0 = 200 : 1 : 1 : 2$ in *p*-xylene at 80 °C using four different initiation systems.

constant during the reactions, whereas DEBM and DCAP showed significant curvature in the first-order kinetic plots, which indicated that the termination was detectable. Especially, in the DCAP/ $FeBr_2$ initiation system, the rate of initiation was much slower than that of propagation. The values of k_p^{app} for the ATRP of MMA with different initiators are collected in Table I. Practically no variation can be observed in the values of k_p^{app} in the EBriB and DEBM systems.

Figure 8 shows the dependence of M_n and M_w/M_n on the monomer conversion with the introduction of different initiators. The number-average molecular weight (M_n) increased linearly with increasing monomer conversion. In the case of EBriB initiator, the molecular weight values were very close to the theoretical values, whereas in the case of the other initiation systems, such as DEBM and DCAP, the molecular weight of the resulting polystyrene was higher than the theoretical value, indicating lower efficiency of the initiator system. A possible explanation for this behavior is that the occurrence of slow initiation with respect to the fast propagation of monomer.¹⁷ It is worth noting that the PDIs of the PMMA prepared from the DEBM and 1-PEBr initiated ATRP increased with increasing monomer conversion, indicating the presence of radical termination during the polymerization. In the case of DEBM initiated polymerization of MMA, relatively low PDIs were obtained in the initial stage, which indicated that the PMMA were linear chains and the ATRP process was well controlled. However, the secondary reactions gradually increased as the polymerization reaction progressed, and this was reflected in an increment of PDIs with the conversion.

Conclusions

In summary, this article describes the use of ligand, diphenyl-2-pyridyl phosphine, in the ATRP process of MMA. A

range of different temperatures, solvents, and initiators in conjunction with $Fe(II)X_2$ have been shown to be effective for the ATRP of MMA with this ligand. With EBriB as an initiator, the MMA solution polymerization in *p*-xylene at 80 °C followed first order kinetics with respect to the monomer. Deviation from the theoretical molecular weight, and slightly higher polydispersities were observed in some polar solvents. EBriB afforded better control of the polymerization, whereas the other initiators used in this study gave rise to uncontrolled molecular weights, indicating the presence of radical termination during the polymerization.

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