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# Adventitious Effect of Air in Atom Transfer Radical Polymerization: Air-Induced (Reverse) Atom Transfer Radical Polymerization of Methacrylates in the Absence of an Added Initiator

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ABSTRACT: The effect of air on atom transfer radical polymerization (ATRP) of phenethyl methacrylate (PEMA) was investigated. The results indicated that air alone induced polymerization in the absence of an added initiator with the ATRP catalyst complexes $NiBr_2(Pn\text{-}Bu_3)_2$ and $Cu(n)X_n$/ligand ($n = 1, 2$; X = Cl, Br; ligand = dipyridyl (dpy) or pentamethyldiethylenetriamine (PMDETA)) at high temperatures. Molecular weights of the polymers were not predictable, but the polydispersities were low. Polymers with very low polydispersities (1.08) and high molecular weights (704 000) were obtained with $CuCl_2$/PMDETA catalyst complex. The results indicate that a reverse ATRP mechanism is probably involved in the air-induced polymerization. The extension of the air-induced polymerization to *n*-butyl methacrylate shows that the air-induced polymerization should be generic for methacrylates.

## Introduction

Atom transfer radical polymerization (ATRP) is one of the fastest developing areas of polymer chemistry. When conditions are properly adjusted, it allows well-controlled radical polymerization to give molecular weights that are predictable with polydispersities that are low. A typical ATRP requires an alkyl halide as initiator, a transition metal in a lower oxidation state, and a ligand that complexes with the metal. Various metals and ligands have been used for ATRP chemistry, with the most used metals being nickel[1−3] and copper. $Cu(n)X_n$/ligand (X = Cl or Br, ligand = dipyridyl derivatives or tertiary amines) catalyzed ATRP gives good polymerization with both acrylates[4] and methacrylates[5] under a variety of conditions. Polymerizations at room temperature[6,7] and in aqueous media[8,9] have been reported. It has also been reported that copper catalyzed ATRP can be done in the presence of air when Cu(0) metal is added to the polymerization mixture.[10]

An important variation of ATRP chemistry is reverse ATRP. This method requires a conventional radical initiator such as a peroxide or azobis(isobutyronitrile) (AIBN), a transition metal in a higher oxidation state, and a ligand for metal solubilization.[11,12] This method has been applied successfully to many different systems. For example, styrene was recently polymerized by reverse ATRP using peroxide initiators to give polymers with predictable molecular weights (8400−10 700) and low polydipersities (1.14−1.21).[13]

During the course of our study on atom transfer radical polymerization of phenethyl methacrylate (PEMA), we noticed that the molecular weights obtained were not in good agreement with theoretical values. Variation of experimental conditions led to the observation that air might be interfering with the ATRP polymerization. The effect of air on ATRP polymerization of PEMA was therefore investigated in detail, and the results are described in this paper.

## Experimental Section

Xylene (mixture of isomers) was refluxed over Na metal and vacuum distilled using drying tubes and liquid nitrogen traps. The commercial chemicals, $NiBr_2(Pn\text{-}Bu_3)_2$ (Aldrich, purity 97%), CuCl (Aldrich, purity 99.995%), dpy (dipyridyl, Aldrich, purity 99%), CuBr (Aldrich, purity 99.999%), $CuCl_2$ (Aldrich, purity 99.999%), Cu(0) (Aldrich, for organic synthesis), pentamethyldiethylenetriamine (PMDETA, Aldrich, purity 99%), and phenethyl methacrylate (PEMA, Polysciences, Inc.), were used without purification unless specified. Pure monomers were obtained by removal of inhibitor with column chromatography using basic aluminum oxide as the support (dry filtration method). All glassware, needles and stirring bars were dried overnight in an oven at 150 °C and purged with nitrogen gas before use. Monomers and solvents were also purged with nitrogen.

Molecular weights and molecular weight distributions were estimated relative to polystyrene standards using size-exclusion chromatography (SEC) with THF solvent and four styrene gel mixed-bed columns (7.5 mm i.d. $\times$ 300 nm, 10 $\mu$m particle diameter, American Polymer Standard Corporation, Mentor, OH).

**$NiBr_2(Pn\text{-}Bu_3)_2$ Catalyzed Solution Polymerizations.** To a dry, sealed, and degassed three-necked, round-bottom flask fitted with a stirring bar was added degassed PEMA. The solution was purged with nitrogen for 15 min, and then a 2 mL portion was taken via syringe and used to dissolve $NiBr_2(Pn\text{-}Bu_3)_2$ which was sealed in a vial and then purged with nitrogen. The violet solution was introduced back into the reaction flask by syringe. The flask was again purged with nitrogen for an additional 40 min at ambient temperature. The solution was then immersed in a preheated oil bath at 120 °C with a nitrogen balloon attached via a needle to maintain a positive inert atmosphere. When samples were taken from the polymerization mixture, the pressure was counterbalanced with this nitrogen-containing balloon. Air for initiation was introduced into the system in one of two ways: either by inserting an open needle into the top of the rubber septum and allowing air to diffuse into the system during the time indicated in the tables or via direct injection all at once using a syringe. During and after the introduction of air, the polymerization mixture was not kept under nitrogen positive pressure but only sealed. To ensure that there was no air diffusion through the sealed septa, the septa were further protected by wrapping with electrical tape and Parafilm.

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**Table 1. Air-Induced Polymerization of PEMA with $NiBr_2(Pn\text{-}Bu_3)_2$ with Introduction of Air by Diffusion through a Syringe Needle[a]**

| | before air introduction | | | | | after air introduction | | | |
|---|---|---|---|---|---|---|---|---|---|
| entry | time (h) | conv[b] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ | air (min) | time (h) | conv[b] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ |
| 1[c] | 24 | 0 | | | 10 | 26 | 79 | 239 | 1.54 |
| 2 | 19 | 4 | 158 | 1.22 | 10 | 5 | 69 | 261 | 1.24 |
| 3 | 22 | 1 | 28 | 3.01 | 10 | 26 | 51 | 266 | 1.42 |
| 4 | 22 | 11 | 477 | 1.17 | | | | | |
| 5 | 15 | 70 | 266 | 1.32 | | | | | |
| 6[d] | 18 | 4 | 31 | 1.75 | 10 | 72 | 6 | 28 | 1.53 |

[a] Conditions: 120 °C; [PEMA] = 2.13 M (in 6 mL of xylene); $[NiBr_2(Pn\text{-}Bu_3)_2]$ = 69 mM. [b] Calculated by gravimetric methods. [c] Pure monomer (inhibitor removed). [d] No catalyst, only PEMA in xylene [PEMA] = 2.13 M.

**Table 2. Air-Induced Polymerization of PEMA with $NiBr_2(Pn\text{-}Bu_3)_2$ with Introduction of Air by Rapid Syringe Injection[a]**

| | before air introduction | | | after air introduction | | | |
|---|---|---|---|---|---|---|---|
| entry | time (h) | conv[b] (%) | air (mL) | time (h) | conv[b] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ |
| 1 | 24 | 0 | 2 | 24 | 36 | 258 | 1.57 |
| 2 | 24 | 0 | 3 | 24 | 81 | 178 | 1.57 |
| 3 | 24 | 0 | 5 | 24 | 30 | 212 | 1.44 |
| 4 | 1.5 | | 5 | 24 | 43 | 159 | 1.39 |

[a] Conditions: 120 °C; [PEMA] = 2.13 M (in 6 mL of xylene); $[NiBr_2(Pn\text{-}Bu_3)_2]$ = 69 mM. [b] Calculated by gravimetric methods.

Polymerizations were stopped by cooling the mixtures to −78 °C. Polymers were dissolved in xylene and precipitated into methanol. Analyses were carried out after overnight vacuum-drying without further purification.

**CuCl Catalyzed Solution Polymerization**. CuCl and dpy (dipyridyl) were put in a dried three-necked, round-bottom flask which was sealed with rubber septa and purged with nitrogen. Degassed monomer and solvent were added to the flask, and the final solution was stirred and purged with nitrogen for 40 min. Reaction mixtures were kept under positive nitrogen flow during the control period, and septa were reinforced as described above after air introduction. Sampling and introduction of air were performed as mentioned above. Polymerizations were quenched by adding THF and precipitating into methanol.

**Bulk Polymerizations with $CuCl_2$/PMDETA Catalyst Complex (Table 5, Entries 2 and 3)**. $CuCl_2$ (0.28 mmol) was put into a vial fitted with a stirring bar, sealed with septum, and purged with nitrogen gas for 30 min. A three-necked, round-bottom flask containing PEMA (15 mL) was purged with nitrogen gas for 40 min, and a 2 mL portion of this solution was taken and added to the vial containing $CuCl_2$, followed by the addition of PMDETA (0.28 mmol). The vial containing the $CuCl_2$/PMDETA and the monomer was put into a preheated oil bath at 65 °C and stirred for 10 min to solubilize the catalyst. After decantation of the insoluble catalyst and cooling the vial to ambient temperature, the blue solution was transferred back into the reaction flask, so that the total volume of the solution was again 15 mL. A 5 mL portion of this solution was injected into a separate round-bottom flask containing only deoxygenated PEMA (5 mL) to give entry 2 (Table 5). The remaining part (10 mL) of this catalyst solution gave entry 3 (Table 5). Air was introduced via direct syringe injection after the reaction mixtures were brought to 120 °C (30 min). Polymerizations were quenched with THF and precipitated into methanol.

## Results and Discussion

The conventional radical polymerization of PEMA in bulk at 65 °C using AIBN initiator gave polymers with high polydispersities (~3.2) and unpredictable molecular weights. Blank reactions carried out with only PEMA with no initiator and no catalyst at 120 °C (in both solution and bulk) for prolonged time periods gave only very small amounts of polymer (Table 1, entry 6; Table 5, entry 10). The removal of the inhibitor from the PEMA had no effect on the latter results.

**Nickel Catalyzed Systems.** The study was carried out in the absence of initiators with solutions containing only the monomer (PEMA), the catalyst $NiBr_2(Pn\text{-}Bu_3)_2$, and the solvent (xylene). The experiments were designed so that air was eliminated completely from the polymerization mixture during the first half of the experiment (control period). Then in the second half, air was introduced into the mixtures. The introduction of air was done in two ways. The first involved inserting a needle into the septum, sealing the reaction flask and allowing air to enter by diffusion during the time indicated in Table 1. The second used a syringe to directly inject a given quantity of air all at once into the flask (Table 2). Conversions and molecular weights before and after air introduction were compared. The results indicate that both conversions and molecular weights increased significantly after introduction of air (Table 1, entries 1−3). Surprisingly the polydispersities of the polymers were all low. The color of the polymerization mixtures mostly remained the same (violet) after the diffusion of air into the monomer solution, but in some cases, a green-blue coloration was also observed at the very end of the polymerization time which probably indicates oxidation of the nickel catalyst. The removal of the inhibitor from the monomer had no significant effect on air-induced polymerizations (entry 1). It is interesting to see that, after the introduction of air, the molecular weight distributions of the final polymers were unimodal, and no peak was observed corresponding to the polymers formed initially during the control period. Entries 4 and 5 indicate that, when the sealed reaction mixtures are not kept under positive nitrogen pressure or the septa seal is not reinforced with tape and Parafilm, polymerization occurs even before deliberate air introduction due to slow air contamination through the septa.

To quantify the effect of air, a series of reactions were carried out in which increasing known amounts of air were injected into the systems all containing the same catalyst concentration. Table 2 (entries 1−3) shows that when air was carefully eliminated during the initial control period, no polymerization occurred. However, when air was injected, polymerization occurred with moderate to high conversions. The results indicate no correlation between the amount of air introduced and conversion. For entry 4, the control period was eliminated, and air was introduced when the reaction mixture was brought to 120 °C under the optimized inert conditions. Results confirm that polymerizations are reproducible but that molecular weights and conversions vary for each individual experiment. This is probably due to the heterogeneous nature of the solutions giving rise to polymerization. Although the mix-

**Table 3. Air-Induced Polymerization of PEMA with CuX/dpy/Cu(0) Catalyst Complexes with Introduction of Air by Diffusion through a Syringe Needle**[a]

| | before air introduction | | | | | | after air introduction | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| entry | [CuX]/[dpy]/[Cu(0)] | time (h) | conv[b] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ | air (min) | time (h) | conv[b] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ |
| 1 | 1CuBr/2/0 | 21 | 0 | | | 10 | 18 | 65 | 53 | 1.72 |
| 2 | 1CuCl/2/0 | 24 | 11 | 19 | 1.94 | 15 | 18 | 69 | 76 | 1.42 |
| 3 | 1CuCl/2/0 | 17 | 7 | 36 | 1.21 | 10 | 24 | 66 | 54 | 1.55 |
| 4 | 1CuCl/2/0 | 4 | | | | 5 | 19 | 52 | 49 | 1.95 |
| 5 | 1CuCl/2/0 | 4 | | | | 10 | 19 | 35 | 50 | 1.63 |
| 6 | 1CuCl/2/5 | 22 | 5 | 80 | 1.25 | 5 | 30 | 27 | 150[c] | 1.62[c] |
| 7 | 1CuCl/2/5 | 17 | 19 | 20[d] | 1.13[d] | 10 | 24 | 50 | 40[e] | 2.23[e] |
| 8 | 1CuCl/2/5 | 18 | | | | 10 | 48 | 30 | 205 | 1.78 |

[a] Conditions: 120 °C; [PEMA] = 2.05 M (in 6 mL of xylene); [CuX] = 10 mM. [b] Calculated by gravimetric methods. [c] A second peak at 2870 was present. [d] A second peak at 3560 was present. [e] Bimodal peak distribution.

**Table 4. Air-Induced Polymerization of PEMA at 120 °C with $CuCl_n$/dpy/Cu(0) Catalyst Complexes with Introduction of Air by Rapid Syringe Injection**

| | before air introduction | | | | | | after air introduction | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| entry | [$CuCl_n$]/[dpy]/[Cu(0)] | time (h) | conv[a] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ | air (mL) | time (h) | conv[a] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ |
| 1[b] | 1CuCl/2/0 | 24 | 75 | 19 | 1.49 | 1 | 24 | 76 | 19 | 1.50 |
| 2[b] | 1CuCl/2/0 | 24 | 45 | 23 | 1.54 | 3 | 24 | 70 | 45 | 1.20 |
| 3[b] | 1CuCl/2/0 | 24 | 70 | 27 | 1.34 | | | | | |
| 4[b] | 1CuCl/2/0 | 24 | 0 | | | 3 | 24 | 61 | 99 | 1.50 |
| 5[b] | 1$CuCl_2$/2/0 | 24 | 7 | 9 | 1.46 | 3 | 24 | 86 | 28 | 1.19 |
| 6[b] | 1$CuCl_2$/2/0 | 21 | 0 | | | 1 | 24 | 40 | 59 | 1.14 |
| 7[b] | 1$CuCl_2$/2/0 | 21 | 0 | | | 3 | 24 | 36 | 53 | 1.12 |
| 8[b] | 1$CuCl_2$/2/0 | 24 | 0 | | | 5 | 24 | 51 | 78 | 1.07 |
| 9[c] | 5$CuCl_2$/10/0 | 24 | 0 | | | 5 | 24 | 77 | 123 | 1.38 |
| 10[c] | 5$CuCl_2$/10/0 | 24 | 0 | | | 5 | 24 | 68 | 85 | 1.48 |
| 11[b] | 1CuCl/2/5 | 0.5 | | | | 3 | 24 | 25 | 131 | 1.40 |
| 12[d] | 0/2/0 | 24 | 3 | 81 | 1.46 | 3 | 8 | 82 | 171 | 1.55 |
| 13[d] | 0/2/0 | 24 | 75 | 110 | 1.47 | | | | | |

[a] Calculated by gravimetric methods. [b] [PEMA] = 2.05 M (in 6 mL of xylene); [$CuCl_n$] = 10 mM. [c] [PEMA] = 2.05 M (in xylene); [$CuCl_2$] = 50 mM. [d] [PEMA] = 2.05 M (in xylene); [dpy] = 20 mM.

tures containing the nickel catalyst were homogeneous, the reactions generating the unknown initiating species occurred at the interphase between air (oxygen) and the nickel catalyst complex in solution. Considering this, and the fact that both the amount and the relative concentrations of the nickel catalyst in the lower (II) and higher oxidation state play a crucial role in ATRP, it is difficult to control reaction conditions of the polymerization mixtures. Overall, the results confirm that air in conjunction with $NiBr_2(Pn\text{-}Bu_3)_2$ catalyst complex induces polymerization with PEMA at 120 °C.

**Copper Catalyzed Systems.** A similar study was carried out with copper catalyzed ATRP systems. First, experiments were done with $CuX_n$/dpy complexes (Table 3). It was found that air induced polymerization with both CuBr/dpy (entry 1) and CuCl/dpy (entries 2−8) catalyst complexes. In all cases conversions increased dramatically after the introduction of air. Polydispersities of the polymers obtained ranged from 1.40 to 1.95. The color of the polymerization mixtures was initially brown and changed to green after the introduction of air due to the oxidation of Cu(I) to Cu(II). The solutions then became brown again after a short induction period (5−30 min), indicating regeneration of active Cu(I) species. However, in entry 2, the solution remained green until the polymerization was quenched. Addition of Cu(0) metal to the system did not prevent polymerization but resulted in a bimodal molecular weight distribution when air was introduced by diffusion (entries 6−8). However, when air was injected all at once to copper metal containing solutions, polymer with a unimodal molecular weight distribution was obtained (Table 4, entry 11). Analogous to the nickel catalyzed systems, the molecular weights and the conversions did not correlate with the duration of air exposure. It is important to note that polymerization mixtures with Cu(I)Cl/dpy were heterogeneous. In addition, when the air was introduced, Cu(I) was oxidized to Cu(II), and a part of the deactivated catalyst precipitated onto the walls of the polymerization flask. Thus, the amounts of Cu(I) and Cu(II) species and their relative concentrations in each polymerization mixture were certainly different and perhaps very different.

In an attempt to quantify the effect of air, a set of experiments was carried out in which known amounts of air were injected into solutions all containing the same nominal catalyst concentration after a control period of 24 h at 120 °C (Table 4). Surprisingly, the first set of experiments gave polymers with relatively high conversions and low polydispersities even before the deliberate introduction of air (entries 1−3). The solutions became green after 1 h due to oxidation of Cu(I) to Cu(II), thus indicating the accidental presence of air. These observations show that degassing the solutions with nitrogen must be done very thoroughly (40 min) with the copper catalyst complexes to prevent “spontaneous” polymerization during the control period. More importantly, a simple septum seal is not sufficient to prevent air diffusion during long reaction times at 120 °C, and a positive nitrogen pressure is therefore necessary. When these conditions were satisfied, no polymerization occurred during the control period, and polymerization was achieved only after air introduction (entry 4). Since the color of the copper catalyzed polymerizations changed first to green, indicating the oxidation of Cu(I) to Cu(II) by oxygen, use of $CuCl_2$/dpy

**Table 5. Air-Induced Bulk Polymerization of PEMA at 120 °C with $CuCl_n$/PMDETA Catalyst Complexes with Introduction of Air by Rapid Syringe Injection**[a]

| | before air introduction | | | | | | after air introduction | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| entry | $CuCl_n$ | time (h) | conv[b] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ | air (mL) | time (h) | conv[b] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ |
| 1[c] | $CuCl_2$ | 0.5 | | | | 3 | 3 | 29 | 460 | 1.07 |
| 2[d] | $CuCl_2$ | 0.5 | | | | 3 | 0.8 | 43 | 378 | 1.19 |
| 3[d] | $CuCl_2$ | 0.5 | | | | 3 | 0.8 | 49 | 512 | 1.11 |
| 4[e] | $CuCl_2$ | 24 | 6 | 177 | 1.42 | 3 | 7 | 81 | 704 | 1.08 |
| 5[f] | CuCl | 24 | 8 | 144 | 1.58 | 3 | 7 | 25 | 388 | 1.49 |
| 6[g] | | 0.5 | | | | 3 | 24 | 6 | 163 | 1.95 |
| 7[g] | | 24 | 28 | 296 | 1.88 | | | | | |
| 8[g] | | 24 | 29 | 144 | 1.56 | | | | | |
| 9[h] | | 48 | 59 | 429 | 1.54 | | | | | |
| 10[i] | | 24 | 0.2 | | | 3 | 24 | 2 | 73 | 1.62 |

[a] Number of moles used to prepare the catalyst solution are given (see Experimental Section). [b] Calculated by gravimetric methods. [c] [PEMA] = 5.16 M (8 mL, purified); $CuCl_2$ = 0.11 mmol; PMDETA = 0.14 mmol. [d] See Experimental Section. [e] [PEMA] = 5.16 M (10 mL); $CuCl_2$ = 0.13 mmol; PMDETA = 0.17 mmol. [f] [PEMA] = 5.16 M (10 mL); CuCl = PMDETA = 0.10 mmol. [g] [PEMA] = 5.16 M (10 mL); PMDETA = 0.13 mmol. [h] [PEMA] = 5.16 M (10 mL); PMDETA = 0.13 mmol (purified). [i] PEMA only; [PEMA] = 5.16 M.

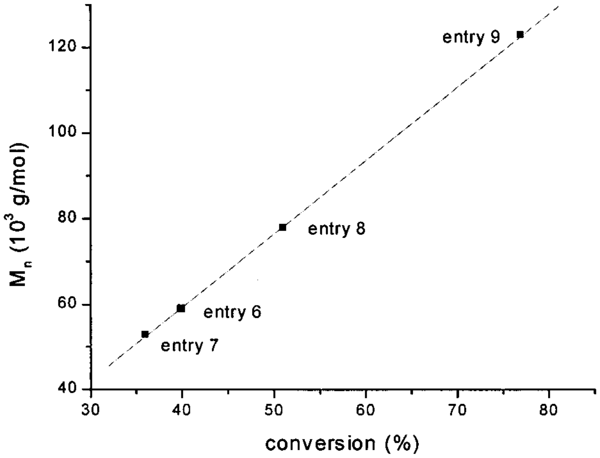

**Figure 1.** Plot of $M_n$ vs conversion obtained from entries 6 to 9 (Table 4).

complex as a catalyst was evaluated instead of CuCl/dpy (entries 5−10). No polymerization occurred during the control period, but after air injection, polymers with unexpectedly low polydispersities were obtained. The color of the polymerization mixtures remained green due to excess, insoluble $CuCl_2$ particles, but when these particles were allowed to settle, the clear part of the solution was yellow-brown, indicating regeneration of the Cu(I) species during polymerization.

Parallel reactions were carried out with the $CuCl_2$/dpy catalyst complex where the amount of air injected was increased (1, 3, and 5 mL) while catalyst concentration was kept constant (Table 4, entries 6−8). No correlation was found between the amount of air introduced and the conversions or molecular weights. Interestingly, conversion versus molecular weight plots of these individual experiments gave a linear plot (Figure 1). Increases in both the catalyst−ligand complex and air concentration simultaneously (entries 9 and 10 compared to entry 6) resulted in higher polydispersity, higher conversion, and higher molecular weight which again fit the linear plot (entry 9, Figure 1). The comparison of entries 8 and 9 (or 10) shows that, when 5 times more catalyst complex was used and the amount of injected air was kept constant, both molecular weight and conversion increased. This can be attributed to higher polymerization rate due to higher active catalyst-complex concentration. The very heterogeneous nature of these polymerization conditions makes attempts at quantifying the effects of the variables very difficult. Entries 9 and 10 show the difficulty in reproducing conversions and molecular weights for a given set of experimental conditions.

The air induced polymerizations with $CuCl_n$/dpy ($n$ = 1 or 2) were as fast as the conventional ATRP of PEMA (24 h; 65% conversion; [PEMA] = 2.05 M; in xylene); [PEMA]/[I] = 200; PDI = 1.52). The polydispersities obtained with the $CuCl_2$/dpy/$O_2$ system were lower than for the CuCl case and comparable to values for conventional ATRP.

The second copper catalyst complex tested was $CuCl_2$/PMDETA (Table 5). Unlike the previous experiments where the catalyst and the ligand (dpy) were added into the reaction flask together at the very beginning, in these experiments, the $CuCl_2$/PMDETA solution (in 2 mL PEMA) was prepared separately, and only the homogeneous (soluble) part of the solution was injected into the reaction flask containing additional monomer for polymerizations (see Experimental Section). We observed that a very small amount of the $CuCl_2$ (<10%) was going into the solution when the $CuCl_2$/PMDETA ratio was 1/1. Thus, the actual catalyst concentrations in the mixtures were much lower than the amounts used to prepare the catalyst complex solutions, and excess ligand was present. The attempt to completely solubilize the $CuCl_2$ with even greater excess ligand (1/14) failed, and the nominal ratio was kept at 1/1. Polymerizations with $CuCl_2$/PMDETA catalyst complexes were fast compared to previous catalyst systems, and molecular weight distributions were very low (Table 5). Polymerization mixtures were slightly blue at the beginning due to the Cu(II) species but turned to yellow-brown after the injection of air (3−10 min) and then changed to yellow as the polymerization proceeded. The color of the conventional ATRP polymerization mixture of PEMA with the CuCl/PMDETA catalyst complex is often colorless initially but turns gradually to light green. In general, polymerizations were stopped when the solutions gelled (entries 1−3). However, when they were allowed to react further after gelation (entry 4), polymers with very high molecular weights and low polydispersities were obtained. Entry 4 also shows that no significant polymerization occurred before air introduction. Polymerization was also achieved with the CuCl/PMDETA catalyst complex (entry 5). A test reaction was carried out where the momomer and the reaction mixture were not purged with inert gas and the three-necked reaction flask was closed off with septa. Under these conditions, no polymerization occurred. The blank reaction (entry 10) carried out with only monomer, in the absence of the catalyst complexes, indicated that no polymerization occurred even after the introduction of air. The results confirm that the catalyst complex is needed for polymerization.

To investigate the effect of catalyst concentration, two parallel polymerizations were performed (entries 2 and 3). In these experiments, equal amounts of air were introduced into the polymerization mixtures which differed only in relative concentrations of the $CuCl_2$/PMDETA complexes. Although the absolute concentrations of the catalyst complexes were unknown, the relative concentrations were adjusted by dilution of a stock solution so that the ratio for entry 2 was $^1/_2$ that of entry 3. Both the molecular weight and the conversion were higher for the system containing twice the $CuCl_2$/PMDETA catalyst complex concentration.

The air-induced polymerizations of PEMA with the $CuCl_2$/PMDETA complex required longer times and higher temperatures than for conventional ATRP of PEMA (25 °C, 6 min, [PEMA]/[I] = 170, [CuCl] = [PMDETA] = 30 mM, in bulk, 94% conversion). However, the difference in rate might be due to the very low concentration of the initial Cu(II)$Cl_2$/PMDETA catalyst compared to the Cu(I)Cl/PMDETA catalyst complex used for conventional ATRP, which is completely soluble and homogeneous.

A kinetic study was carried out to further evaluate the nature of the air-induced polymerization. It is important to specify again that, due to the unknown concentration of Cu(II) in solution, the results are only qualitative. As seen in Figure 2, after an induction period, the molecular weight increased with conversion, and the polydispersity decreased as the molecular weight increased similar to a typical ATRP. We believe that during this induction period the Cu(II)Cl/PMDETA catalyst complex generates the initiating radical species by reacting with oxygen.

The results obtained so far suggest that the air induced polymerization in the presence of ATRP catalyst complexes proceeds through a reverse ATRP mechanism since the observed color changes during the polymerizations with $CuCl_2$ reveal that the active Cu(I) species is generated under these conditions. The kinetic evidence shows that molecular weights increase linearly with increasing conversion while the polydispersities decrease, supporting the controlled nature of the polymerization.

**Effect of Temperature on Air-Induced Reverse ATRP.** To test the effect of temperature on air induced polymerization, both nickel and copper catalyzed polymerizations were carried out at lower temperatures. When air-induced polymerization with the $NiBr_2(Pn\text{-}Bu_3)_2$ catalyst complex was performed at 90 °C instead of 120 °C (all other conditions the same), no polymerization occurred in 48 h. However, when the temperature of this same solution was increased to 120 °C, the whole mixture gelled in 24 h (94% conversion).

In a similar way, when a solution of PEMA with $CuCl_2$/PMDETA was stirred at 80 °C for 50 h, the color of the solution became yellow-brown 10 min after the injection of air; polymer was formed in 23% conversion with a bimodal molecular weight distribution ($M_n$ = 131 500; PDI = 1.89). However, when the temperature of the same solution was increased to 100 °C, the polymerization mixture gelled in only 1 h (70% conversion). The resulting polymer had a unimodal molecular weight distribution ($M_n$ = 372 500; PDI = 1.34) with a small tail at the lower molecular weight end.

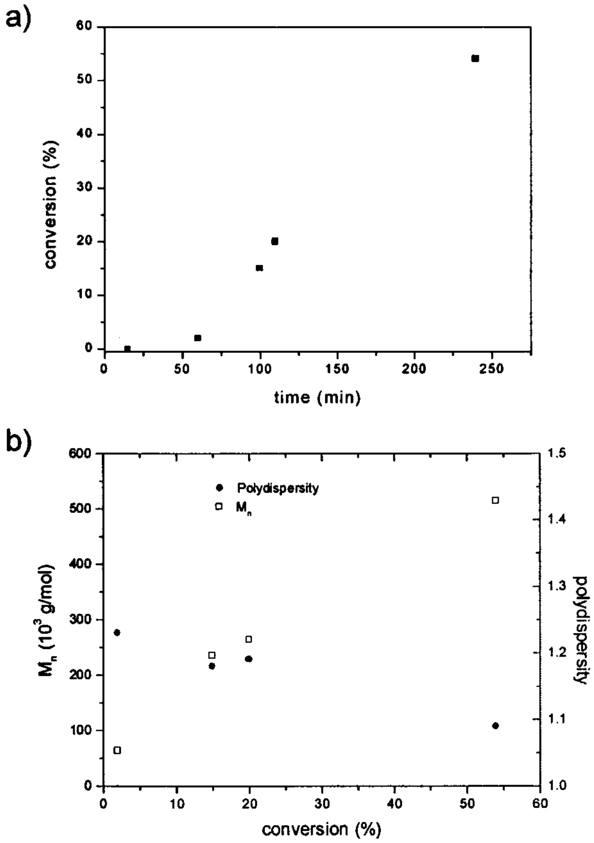

**Figure 2.** (a) Conversion vs time and (b) $M_n$ and polydispersity vs conversion for air-induced bulk polymerization of PEMA with $CuCl_2$/PMDETA catalyst complex; conditions: 120 °C; [PEMA] = 5.16 M (bulk); $CuCl_2$ = 0.13 mmol; PMDETA = 0.17 mmol.

**Table 6. Air-Induced ATRP Polymerization of BMA and PEA with $CuCl_2$/PMDETA Catalyst Complex with Introduction of Air by Rapid Syringe Injection[a]**

| entry | monomer | air (mL) | time (h) | conv[b] (%) | $M_n$ ($10^3$ g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| 1[c] | BMA | 3 | 0.6 | 21 | 282 | 1.27 |
| 2[d] | BMA | 3 | 4 | 60 | 596 | 1.10 |
| 3[e] | PEA | 3 | 24 | 40 | 130 | 1.65 |

[a] The number of moles of $CuCl_2$ and PMDETA used to prepare the catalyst solution is given; purified monomers. [b] Calculated by gravimetric methods. [c] 110 °C; [BMA] = 6.3 M (8.4 mL); $CuCl_2$ = PMDETA = 0.13 mmol. [d] 110 °C; [BMA] = 6.3 M (8.4 mL); $CuCl_2$ = 0.13 mmol; PMDETA = 0.17 mmol. [e] 120 °C; [PEA] = 5.6 M (9.3 mL); $CuCl_2$ = 0.13 mmol; PMDETA = 0.17 mmol.

These results indicate that the air-induced polymerizations require high temperatures (>100 °C). Beside the known effect of temperature on the rate of polymerization, it is most likely that the high temperature is necessary to generate the initiating species. That is, at low temperatures the energy of activation for either the formation of the unknown initiating species or its decomposition to radicals is not achieved.

**Air-Induced Polymerizations with Other Acrylates and Methacrylates.** To test the generality of the air-induced ATRP, *n*-butyl methacrylate (BMA) and phenethyl acrylate (PEA) were polymerized with $CuCl_2$/PMDETA under the same reaction conditions (Table 6). In the case of BMA, polymers with low polydispersities and very high molecular weights were obtained (Table

6, entries 1 and 2). Thus, the air-induced ATRP is not specific to PEMA but should be generic for methacrylates at temperatures above 100 °C.

Phenethyl acrylate (PEA) was also tested, and a polymer with moderate molecular weight and relatively high polydispersity was obtained (Table 6, entry 3). The conditions for this polymerization were not optimized, but this result shows that PEA polymerization was slower than the corresponding methacrylate polymerizations, in agreement with the suggested ATRP mechanism (conventional ATRP of PEA requires 90 min at 50 °C).

## Comments

A redox type mechanism might be responsible for initiation. The oxidative nature of Cu(I)Cl/$O_2$[14−18] and Cu(II)$Cl_2$/$O_2$[19−22] systems, as well as the Ni(II)/$O_2$[23−26] complexes, are well-known in the literature. The $O_2$/Cu(I)/amine oxidation system has been used for C−C coupling of activated methine compounds, N−N coupling reactions, oxidative cleavage reactions, and oxidation reactions.[27] The same catalyst system can form radicals when reacted with organic substrates which can initiate polymerizations.[27,28] It has been recently reported that in Cu$Cl_2$/PMDETA catalyzed ATRP systems PMDETA might be involved in termination reactions.[29] It has also been shown that *N*,*N*,*N′*,*N′*-tetramethylenediamine, an analogous amine to PMDETA, can initiate polymerization with persulfates by forming a redox initiation system.[30] In a similar manner, Cu$Cl_n$/ligand/$O_2$ might be responsible for the initiation. In fact, control experiments were performed with the monomer (PEMA) and the ligands PMDETA and dpy separately, with no copper catalyst. Surprisingly, for the PEMA/dpy system, introduction of air after the usual control period of 24 h did induce polymerization with high conversion (Table 4, entry 12). The molecular weight distribution obtained (1.55) was lower than for AIBN-initiated polymerizations but higher than for Cu$Cl_2$-containing systems. It is important to mention that, at least in one case, the dpy/PEMA system polymerized even before the deliberate introduction of air, indicating the presence of adventitious air in the reaction mixture (Table 4, entry 13). These results indicate that systems containing Cu$Cl_n$/dpy or only dpy behave in a similar way, and polymerization occurs only after introduction of air.

Control experiments performed with the PMDETA/PEMA system (Table 5, entries 7−9) indicate that polymerization occurred even before the introduction of air, and this could not be prevented despite use of a freeze−evacuate−thaw procedure and maintenance of a positive argon pressure to eliminate air. Purification of PMDETA (99.9% pure by GC) by column filtration on aluminum oxide had no effect on the results (entry 9). However, when air was injected after the mixtures were brought to 120 °C (30 min, Table 5, entry 6), no significant polymerization was observed. This result indicates that systems containing PMDETA require copper catalyst to induce polymerization in the presence of air. It is important to state that, in the previous systems containing both PMDETA and Cu$Cl_2$, no significant polymerization occurred before the introduction of air (Table 5, entry 4). In addition, polymerizations containing only PMDETA required much longer polymerization times, and the molecular weight distributions were higher compared to the Cu$Cl_2$/PMDETA catalyzed systems. These results indicate that in the presence of PMDETA ligand the copper catalyst is needed for air-induced polymerization. The comparison of the blank reactions with dpy and PMDETA suggests that the behaviors of the two ligands in the presence of oxygen are different.

The polymerization conditions do not allow quantification of the effects of individual components (catalyst, ligand, air) on the air-induced ATRP. The polymerization mixtures are heterogeneous, and therefore the rate dependency for each individual experiment is probably different. Because of the low solubility of the Cu$X_n$, an unknown amount of noncomplexed free ligand (dpy or PMDETA) must be present within the reaction media. If the initiation takes place via amine oxidation, the concentration of both free and bound amine should effect the amount of the initiator formed. Also, it is known that the ligand/catalyst concentration ratio affects the rate of polymerization.[4,5] The behavior of oxygen should be very complex, as well. Reactions between oxygen and reagents in solution are heterogeneous in nature. The action of oxygen can come from the combined reactivity of the Cu$Cl_n$/ligand/$O_2$ system as well as from the reactions of oxygen with each individual component of the catalyst complex. For example, the Cu$Cl_2$−$O_2$ combination has been used for chlorination reactions.[31] Oxygen may also be involved in termination reactions of growing radicals at an early stage of the polymerizations which would affect the molecular weights and conversions. It is also likely that more than one initiating species is responsible for the air-induced polymerization, and both the number and the mechanism of these initiation reactions might be dependent on substrate, monomer, ligand, and solvent.

## Conclusions

In conclusion, this qualitative study indicates that polymers with moderate to very high molecular weights and low polydispersities can be obtained by air-induced polymerization under ATRP conditions with both nickel and copper catalyst systems at high temperatures. Air-induced polymerizations probably involve a reverse-ATRP mechanism. It is most likely that oxidation reactions are involved in the generation of the initiating species. The clarification of the initiation mechanism of these air-induced polymerizations requires an extensive research which goes beyond the limits of the present project. Finally, the effect of air on ATRP polymerizations should be kept in mind as a source of deviation under conventional ATRP conditions at high temperatures.

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