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Alternative Atom Transfer Radical Polymerization for MMA Using $FeCl_3$ and AIBN in the Presence of Triphenylphosphine: An Easy Way to Well-Controlled PMMA[†]

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Owing to the paramount importance of radical polymerization, producing many of the presently available polymers, research efforts have been recently devoted to controlling different vinyl monomers polymerizations. A significant part of the corresponding publications were concerned with the use of atom transfer radical polymerization (ATRP), an efficient process catalyzed by transition metal complexes.[1]

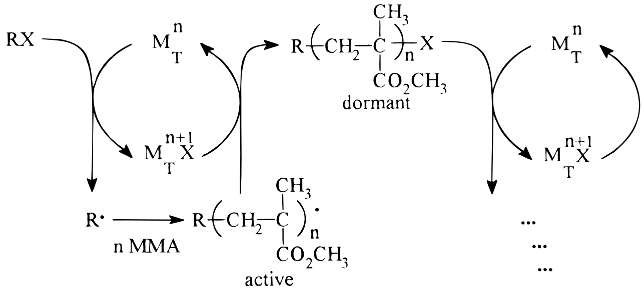
It is, however, important to notice that the generally used initiators are activated halides (i.e., ethyl α-bromoisobutyrate, trichlorobromomethane, α-chloroethylbenzene, α,α′-dichloroacetophenone), often presenting potential drawbacks, particularly for larger scale reactions. That is particularly true in terms of slow or multifunctional initiation, cost, or toxicity. It thus seemed important to circumvent the use of those halogenated compounds, and the so-called alternative ATRP appeared as an easy answer to the problem.

The usual (although oversimplified) representation of a classical ATRP process is depicted in Scheme 1.

In that polymerization, the metal is used in its reduced form $\mathrm{M_T}^n$, which often is air- or moisture-sensitive (e.g., CuCl, $RuCl_2(PPh_3)_3$, $FeCl_2$, Ni(NCN′)Br, etc.). The initiation step consists of a reaction between the catalyst ($\mathrm{M_T}^n$) and the halide species RX. The radical $R^\bullet$ formed can then add one or more monomer units before reacting with the oxidized form of the catalyst, leading to a dormant chain. The repetition of this process produce high polymer chains. This type of ATRP suffers two major drawbacks: first, the use of an halide species RX, which often is toxic or not easily handled or obtained; second, the oxidation of the catalyst by the oxygen included in air. On those premises, Matyjaszewski has already described the use of $CuBr_2$ and AIBN instead of CuBr and an activated halogenated initiator in the presence of 2,2′-bipyridine or 4,4′-dialkyl-substituted 2,2′-bipyridine[2] to control the polymerization of styrene.

Scheme 2 illustrates that "alternative" ATRP. The catalyst is now used in its oxidized state ($\mathrm{M_T}^{n+1}$X) no longer air-sensitive, the initiator being a "classical" radical initiator such as AIBN. The initiation step is obviously the decomposition of that radical initiator. The so-formed radical can then react with the monomer to create a growing chain or directly with the catalyst to form the reduced species $\mathrm{M_T}^n$ and **1**. The situation then becomes exactly the same as in a classical ATRP, **1** being equal to RX.

Scheme 1



Materials. $FeCl_3{\cdot}6H_2O$ and AIBN were used as received from Merck without further purification. MMA (Aldrich) was dried over CaH_2 and distilled to remove the stabilizing agents. Triphenylphosphine (Aldrich) was recrystallized from ethanol to remove triphenylphosphine oxide.

Polymerization. All experiments were performed using a Schlenck device. In a typical run, the different solids are introduced in a glass tube. The tube is then closed with a three-way stopcock and three cycles of vacuum−nitrogen are applied in order to remove oxygen. The liquids are then added via a flamed syringe. Conversion is determined gravimetrically by precipitation in heptane after dissolution of the polymer in THF. The polymers are dried in a oven for 24 h at 80 °C under vacuum. For the kinetics experiment, the conversion is determined gravimetrically after elimination of the solvent and residual monomer.

Characterizations. The molecular weight distributions were analyzed in THF at 40 °C using a Hewlett-Packard model 1090 liquid chromatograph equipped with columns HP PLgel 5 μm (10^5, 10^4, 10^3, 100 Å) and a Hewlett-Packard model 1037A refractive index detector. Calibration was made with PMMA standard samples (Polymer Laboratories, MW of 625, 1140, 3100, 7800, 20 300, 33 500, 64 000, 107 000, 185 000, 260 500, 400 000, 840 000, 1 420 000). SEC analysis were made on the isolated polymer. ^1H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ with a Brucker AM400 apparatus at 25 °C.

Results and Discussion. Our results convincingly prove that MMA polymerization initiated by AIBN can be closely controlled by the simple addition of $FeCl_3$ and triphenylphosphine. Under those conditions, the kinetics is first order in monomer (see Figure 1). There is an inhibition period resulting from the large excess of $FeCl_3$ at the beginning of the polymerization. During this period, we observe a change of coloration from deep orange to light yellow. This corresponds to the decomposition of AIBN and the establishment of the equilibrium between Fe(II)/Fe(III) as predicted by the "persistent radical effect".[3] The molecular weight of the polymer increases nearly linearly with conversion (see Figure 2); furthermore, very low polydispersities (even <1.3) can be reached by this simple approach. The molecular weight obtained in bulk is higher than in

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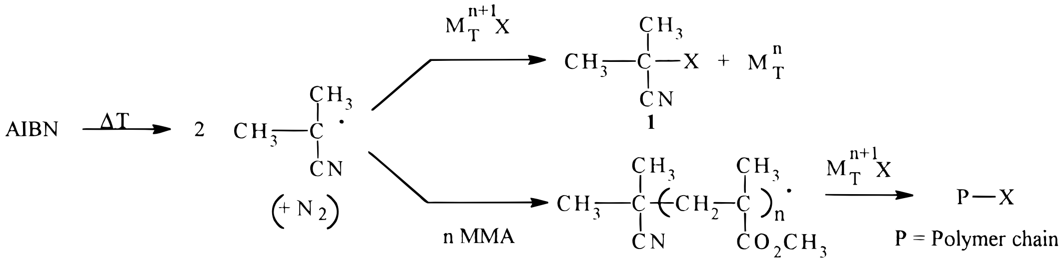
Scheme 2



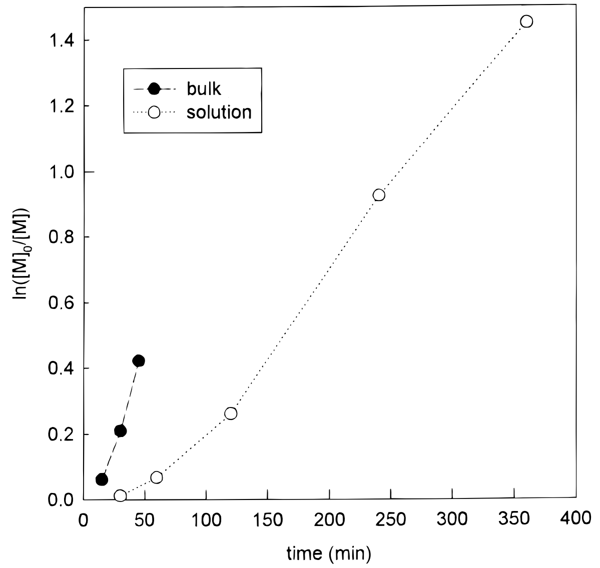


Figure 1. Time dependence of $\ln[M]_0/[M]$ at 85 °C where $[M]_0$ and $[M]$ are the MMA concentration at times 0 and t, respectively. Conditions: (in bulk) $[MMA]_0 = 9.33$ mol·L^{-1}, $[FeCl_3]_0 = 15.5 \times 10^{-3}$ mol·L^{-1}, $[PPh_3]_0 = 46.5 \times 10^{-3}$ mol·L^{-1}, $[AIBN]_0 = 3.8 \times 10^{-3}$ mol·L^{-1}; (in solution) $[MMA]_0 = 6$ mol·L^{-1}, $[FeCl_3]_0 = 9.97 \times 10^{-3}$ mol·L^{-1}, $[PPh_3]_0 = 29.9 \times 10^{-3}$ mol·L^{-1}, $[AIBN]_0 = 2.44 \times 10^{-3}$ mol·L^{-1}.

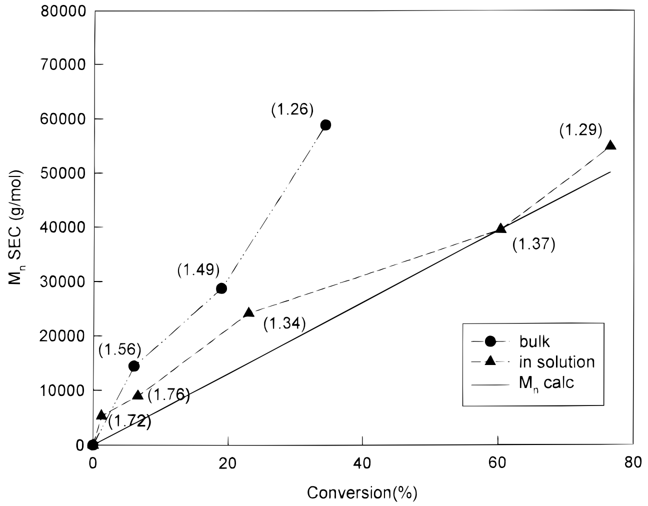


Figure 2. Dependence of the PMMA molecular weight and polydispersity on the monomer conversion. Conditions identical to Figure 1. The polydispersities are indicated between parenthesis. $M_n(\text{calc}) = ([MMA]_0/2[AIBN]_0) \times MW_{MMA} \times$ conversion.

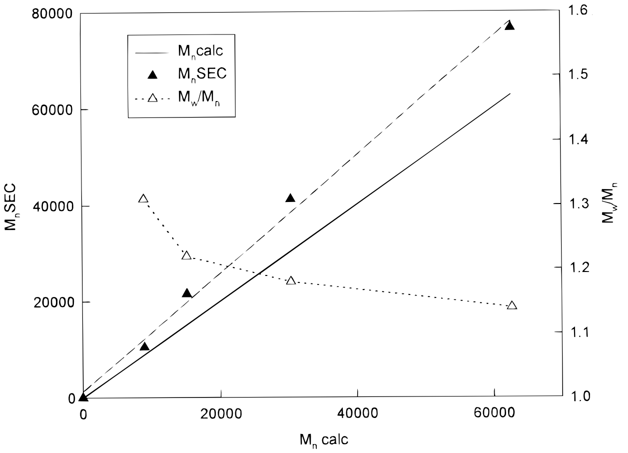


Figure 3. Plot of the M_n(SEC) and M_w/M_n vs calculated M_n from eq 1 (SEC calibration with PMMA standards) for $T = 85$ °C; $[MMA]_0 = 9.33$ mol·L^{-1}; $[AIBN]_0 = 7.23 \times 10^{-3}$, 0.015, 0.029, and 0.048 mol·L^{-1}; $[FeCl_3]_0 = 0.029$, 0.058, 0.116, and 0.193 mol·L^{-1}; $[PPh_3]_0 = 0.087$, 0.174, 0.348, and 0.579 mol·L^{-1}, respectively. All yields are >90%. The dotted line is the mean value for the experimental M_n.

solution, reflecting a loss in initiation efficiency probably due to a larger number of termination reactions (including the AIBN geminate termination in the solvent cage) in the first stage of the polymerization. The resulting rate is remarkably high. A >95% yield is reached after 2 h (in bulk) at 85 °C, even for a 75 000 M_n. As expected, the obtained M_n is determined by the monomer/initiator ratio and can be calculated using eq 1. Figure

$$M_n(\text{calc}) = ([MMA]_0/2[AIBN]_0) \times MW_{MMA} \times \text{conversion} \quad (1)$$

3 shows the dependence of M_n measured by SEC vs M_n calculated using eq 1. The polydispersity decreases when high molecular weight is targeted.

As foreseen, the obtained polymers are not stereoregular and display a microstructure identical to the one noticed in the usual free radical process.

Obviously, the Fe/AIBN ratio is a key parameter here. Indeed, if there is not enough Fe(III), the radicals formed will not be “stabilized” and so termination can occur. If there is too much $FeCl_3$, the rate will probably be very slow because of its inhibiting effect (more dormant sites). That is the reason why a ratio of 2 equiv of Fe(III) relative to the AIBN-based radicals was chosen.

End Group Characterization. If the chain end is a chlorine atom, a recovered PMMA should be able to initiate the polymerization of a fresh feed of MMA in the presence of a classical ATRP catalyst, $NiBr_2(PPh_3)_2$, for example.[4] The experience confirms this hypothesis, as shown by chromatograms of an isolated PMMA (synthesized with $AIBN/FeCl_3/PPh_3$) and of the final polymer obtained after 85% conversion of an additional crop of monomer, using that $NiBr_2(PPh_3)_2$ catalyst (Figure 4). The polydispersity of the final polymer is actually lower than the one of the macroinitiator, and reinitiation proceeds with 89% efficiency.[5] This experi-

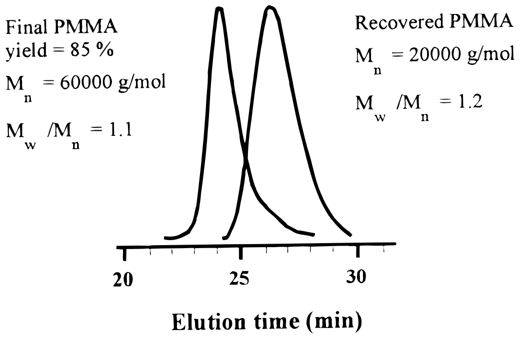


Figure 4. SEC chromatograms of the isolated PMMA used as initiator and of the final polymer (after precipitation in heptane). Conditions: $T = 85$ °C; $t = 16$ (h); solvent, toluene; $[\text{macroinitiator}]_0 = 13.2 \times 10^{-3}$ mol·L^{-1}; $[\text{MMA}]_0 = 5.34$ mol·L^{-1}; $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 13.2 \times 10^{-3}$ mol·L^{-1}.

ment thus demonstrates the quantitative presence of a chlorine atom at the chain end of the macroinitiator (within the precision of the GPC detection). Furthermore, the ^{1}H NMR spectrum shows a signal at 3.79 ppm corresponding to the methyl ester group at the chain end as mentioned by Sawamoto.[1g] A signal at 125 ppm is also detected in ^{13}C, proving the presence of the CN group of the AIBN moiety in the α of the chain.

Conclusion. The simple addition of FeCl_3 and triphenylphosphine to a bulk (or solution) polymerization of MMA initiated by AIBN allows the synthesis of polymers displaying precisely controlled high MW and very narrow MWD. This procedure avoids the problems potentially associated with the use of an halide initiator. The polymers obtained are α-functionalized by a nitrile group and *ω*-functionalized by an halide atom, which can then be used to obtain block copolymers by addition of a second monomer in a classical ATRP process. The use of a functional diazocompound as initiator (such as 4,4′-azobis-4-cyanopentanoic acid) lead to a carboxylic acid functionalized polymer.[6]

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(5) Initiation efficiency = $M_n(\text{calc})/M_n(\text{SEC})$ with $M_n(\text{calc}) = ([\text{MMA}]_0/[\text{macroinitiator}]_0) \times \text{MW}_{\text{MMA}} \times$ conversion.

(6) Conditions: $T = 85$ °C; solvent, toluene; $[\text{MMA}]_0 = 5.34$ mol·L^{-1}, $[4,4'\text{-azobis-4-cyanopentanoic acid}]_0 = 4.09 \times 10^{-3}$ mol·L^{-1}, $[\text{FeCl}_3]_0 = 16.6 \times 10^{-3}$ mol·L^{-1}, $[\text{PPh}_3]_0 = 49.8 \times 10^{-3}$ mol·L^{-1}; reaction time, 18 h; yield, 50%; $M_n(\text{SEC}) = 77\,000$, $M_w/M_n = 1.14$. See also: Baumert, M.; Mülhaupt, R. *Macromol. Rapid Commun.* **18**, 787 (1997).

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