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Controlled Radical Polymerization of Methyl Methacrylate Initiated by an Alkyl Halide in the Presence of the Wilkinson Catalyst

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Sawamoto et al.[1] and Matyjaszewski et al.[2] were the first to report on the controlled radical polymerization of vinyl monomers on the basis of the Kharasch addition reaction. The mechanism for this polymerization, coined "atom-transfer radical polymerization" (ATRP) by Matyjaszewski, can be schematized as shown in Scheme 1.

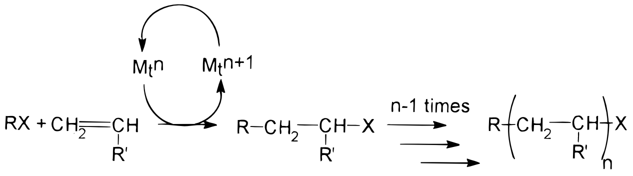
The first catalyst system proposed by Sawamoto (i.e., $RuCl_2(PPh_3)_3$) is efficient only when it is added with a Lewis acid (i.e., $Al(O^iPr)_3$). The combination of Cu salts and bipyridine derivatives used by Matyjaszewski et al. for the polymerization of styrene[2] and MMA[3] requires temperatures of 90 °C and higher, so that the extrapolation of these systems to emulsion (or suspension) polymerization is quite questionable. In order to improve this situation, a new catalytic system has been searched for that would keep the MMA polymerization controlled at a moderate temperature in the absence of a Lewis acid.

Materials. Methyl methacrylate (MMA) and *n*-butylacrylate (*n*-BuA) from Aldrich were distilled over CaH_2 and stored under nitrogen at −20 °C. 2-Hydroxyethyl methacrylate (HEMA) was dried over molecular sieve and distilled under high vacuum just before use. Water was distilled twice and THF was refluxed over Na/benzophenone before being distilled. These two solvents were bubbled with nitrogen for 15 min just before use. $RhCl(PPh_3)_3$, $RhCl_3{\cdot}xH_2O$ and 2,2′-dichloroacetophenone (97%) were used as received from Aldrich. Triphenylphosphine (Aldrich) was recrystallized from ethanol. CCl_4 (Acros) was distilled in order to remove the stabilizers and stored in a THF solution under nitrogen.

Polymerization. The required amount of the Wilkinson catalyst, $RhCl(PPh_3)_3$ or $RhCl_3$ (plus triphenylphosphine, if necessary), was added into a glass tube containing a bar magnet and capped by a three-way stopcock. The tube was purged of air, by a vacuum−nitrogen cycle repeated three times, before being added with the solvent, the monomer, and the initiator, respectively. All these liquids were handled with carefully flamed syringes under nitrogen. The tubes were heated in a thermostated oil bath. When the reaction was complete, the tube was opened, and the reaction mixture was dissolved in THF and then precipitated in cold methanol or heptane. The polymer was filtered off and dried for 24 h at 80 °C under vacuum.

Molecular weight was measured by size exclusion chromatography in THF (at 40 °C), using a Hewlett-Packard model 1090 liquid chromatograph equipped with a Hewlett-Packard model 1037A refractive index detector and calibrated with PMMA standards. ^1H NMR spectra were recorded in $CDCl_3$ with a Bruker AM 400 apparatus at room temperature.

Scheme 1



[a] Where X = Cl, Br, ... and M_t^n is a transition metal at its oxidation state n.

Results and Discussion. In the 1970s, Kameda et al.[4] reported on the polymerization of MMA in the presence of some rhodium complexes. However, the monomer conversion never exceeded 25%, and the recovered polymer was poorly analyzed. Since the Wilkinson catalyst ($RhCl(PPh_3)_3$) is known to be active in the Kharasch addition reaction, we decided to test it in the polymerization of MMA. Percec et al. previously reported the styrene polymerization by ATRP using the Wilkinson catalyst.[5]

The polymerization of MMA was initiated by 2,2′-dichloroacetophenone in the presence of the Wilkinson catalyst (plus 7 equiv of PPh_3) in THF at 60 °C. The experimental data fulfill the criteria for a living polymerization. Indeed, the plots of $\ln[M]_0/[M]$ vs time (Figure 1) and M_n vs conversion (Figure 2) are linear. The linear time dependence of $\ln[M]_0/[M]$ indicates that the concentration of the active species remains constant during polymerization. The lack of transfer reactions is supported by the linearity of the plot of M_n vs conversion. The apparent polymerization rate constant (k_p(app)) ($2.5 \times 10^{-5}\ s^{-1}$) can be approximated from the slope of the $\ln([M]_0/[M])$ vs time dependence, assuming that $\ln([M])_0/[M]) = k_p(\mathrm{app})t$ and $k_p(\mathrm{app}) = k_p[P_n^{\bullet}]$. The use of the Hutchinson equation[6] allows k_p to be known at 60 °C and thus $[P_n^{\bullet}]$ to be estimated as 3.16×10^{-8} $mol{\cdot}L^{-1}$. The efficiency of the initiator (f) has been calculated from the ratio of the experimental and theoretical values of M_n ($M_{n\ SEC}/M_{n\ calc}$), so that the total concentration of the potentially active centers is equal to [2,2′-dichloroacetophenone]f. It is found that only 0.0002% of the chains is active at the same time. This low concentration in active species is consistent with the absence of termination reactions.

Even at a catalyst/initiator molar ratio equal to 0.1, the polymerization efficiency remains high, whereas the polydispersity increases and the polymerization rate decreases (Table 1). It is remarkable that PMMA synthesized by this method can be used as a macroinitiator for the polymerization of a second MMA feed or of *n*-BuA, even though it has been previously precipitated in methanol or heptane. Data in Table 2 support this conclusion.

It is also worth noting that the polymerization remains controlled when MMA is polymerized in the presence of water (e.g., up to 40% H_2O in THF). So, in a water/THF (2/3, v/v) mixture, a phase separation occurs at high monomer conversion, so that a rich-in-water phase floats on a red-orange gel that contains the polymer, THF, and water. Even under these complex conditions, the polymerization is faster than in a concentrated solution in THF and the "livingness" is preserved as assessed by Figures 1 and 2. Figure 1 indeed shows that the time dependence of $\ln[M]_0/[M]$ is

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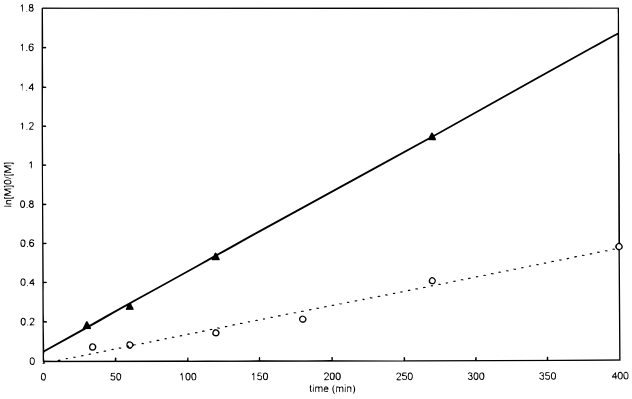

Figure 1. Time dependence of $\ln[M]_0/[M]$ at 60 °C, where $[M]_0$ and [M] are the MMA concentration at times 0 and *t*, respectively. Conditions: (○) solvent, THF; $[MMA]_0 = 8.13$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 13.6 \times 10^{-3}$ mol·L^{-1}; [2,2′-dichloroacetophenone]$_0 = 25.7 \times 10^{-3}$ mol·L^{-1}; $[PPh_3]_0 = 95.2 \times 10^{-3}$ mol·L^{-1}. (▲) solvent, water/THF = 2/3 (volume ratio); $[MMA]_0 = 3.5$ mol·L^{-1}; [2,2′-dichloroacetophenone]$_0 = 11 \times 10^{-3}$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 5.5 \times 10^{-3}$ mol·L^{-1}; $[PPh_3]_0 = 38.5 \times 10^{-3}$ mol·L^{-1}.

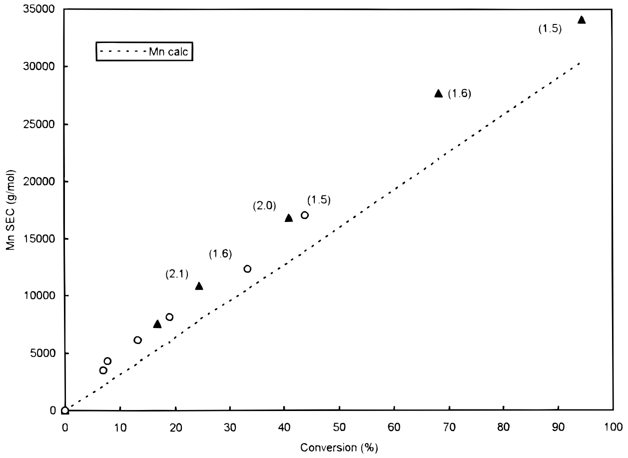

Figure 2. Dependence of the PMMA molecular weight on the monomer conversion at 60 °C. Conditions: (○) solvent, THF; $[MMA]_0 = 8.13$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 13.6 \times 10^{-3}$ mol·L^{-1}; [2,2′-dichloroacetophenone]$_0 = 25.7 \times 10^{-3}$ mol·L^{-1}; $[PPh_3]_0 = 95.2 \times 10^{-3}$ mol·L^{-1}. (▲) solvent, water/THF = 2/3 (volume ratio); $[MMA]_0 = 3.5$ mol·L^{-1}; [2,2′-dichloroacetophenone]$_0 = 11 \times 10^{-3}$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 5.5 \times 10^{-3}$ mol·L^{-1}; $[PPh_3]_0 = 38.5 \times 10^{-3}$ mol·L^{-1}. The polydispersity (M_w/M_n) values are in parentheses. The dotted line is the theoretical M_n: ([MMA]$_0$/[2,2′-dichloroacetophenone]$_0$) × MW$_{\text{MMA}}$ × conversion, in case of a 100% initiation efficiency.

Table 1. Effect of the Catalyst-to-Initiator Molar Ratio on the MMA Polymerization in THF at 60 °C

entry	time (h)	[catal]$_0$/[init]$_0$	conv (%)	$M_{n\,\text{SEC}}$[a]	M_w/M_n	f[b]
1	24	0.5	100	28 500	1.6	0.7
2	21	0.1	75	18 500	1.9	0.8

[a] By SEC with a PMMA calibration. [b] $f = M_{n\,\text{calc}}/M_{n\,\text{SEC}}$ with $M_{n\,\text{calc}}$ = ([MMA]$_0$/[initiator]$_0$) × MW$_{\text{MMA}}$ × conversion. Conditions: $[MMA]_0 = 7.5$ mol·L^{-1}; [2,2′-dichloroacetophenone]$_0 = 39 \times 10^{-3}$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 19.5 \times 10^{-3}$ mol·L^{-1} and 3.9×10^{-3} mol·L^{-1} for entries 1 and 2, respectively; $[PPh_3]_0 = 0.14$ mol·L^{-1} and 27.3×10^{-3} mol·L^{-1} for entry 1 and 2, respectively.

linear not only in THF but also in a water/THF (2/3, v/v) mixture. Clearly, the polymerization kinetics is faster in this water/THF mixture even at a smaller MMA concentration (3.5 M) than in THF (8.1 M). Figure 2 shows that the PMMA molecular weight is also linearly dependent on the monomer conversion. The control of the molecular weight in the water/THF mixture is effective up to at least a molecular weight of 200 000 as shown in Table 3. The livingness of the MMA polymerization has been confirmed by adding a second MMA feed to a completely polymerized system. This second polymerization is quantitative after 23 h, and only a slight increase in polydispersity is observed (Figure 3) which is consistent with the polymerization resumption by most the PMMA chains.

Quite interestingly, the catalyst can be prepared in situ by mixing $RhCl_3$ and 4 equiv of triphenylphosphine[7] in the water/THF mixture for 1 h at 60 °C before the addition of the monomer and the initiator. The polymerization control is actually the same as when the

Table 2. Resumption of MMA and *n*-BuA Polymerization at 60 °C by Preformed PMMA Chains

entry	conversion (%)	$M_{n\,\text{SEC}}$[a]	M_w/M_n	f[b]
PMMA used as macroinitiator		15 500	1.3	
poly(MMA-*b*-MMA)[c]	85	85 000	2.2	0.92
poly(MMA-*b*-*n*-BuA)[d]	44	29 000[e]	2.0	

[a] By SEC with a PMMA calibration. [b] $f = M_{n\,\text{calc}}/M_{n\,\text{SEC}}$ with $M_{n\,\text{calc}}$ = ([monomer]$_0$/[initiator]$_0$) × MW$_{\text{monomer}}$ × conversion. [c] $[MMA]_0 = 9.35$ mol·L^{-1}; [PMMA macroinitiator]$_0 = 12.9 \times 10^{-3}$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 11.5 \times 10^{-3}$ mol·L^{-1}; $[PPh_3]_0 = 89.3 \times 10^{-3}$ mol·L^{-1} . Reaction time, 5 h. [d] [*n*-BuA]$_0 = 6.97$ mol·L^{-1}; [PMMA macroinitiator]$_0 = 13 \times 10^{-3}$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 11.7 \times 10^{-3}$ mol·L^{-1}. Reaction time, 5 h. [e] Apparent M_n measured by SEC with a PMMA calibration, which explains why the calculation of *f* is meaningless.

Table 3. Effect of the Monomer-to-Initiator Molar Ratio on the MMA Polymerization in a Water/THF (2/3, v/v) Mixture at 60 °C

entry	[MMA]$_0$/ [CCl$_4$]$_0$	conversion (%)	$M_{n\,\text{calc}}$[a]	$M_{n\,\text{SEC}}$[b]	M_w/M_n
1	270	100	27 000	28 500	1.48
2	542	100	54 300	56 300	1.51
3	992	93	92 400	98 200	1.67
4	2157	86	158 300	185 700	1.70
5	3019	82	203 500	248 500	1.70

[a] $M_{n\,\text{calc}}$ = ([monomer]$_0$/[initiator]) × MW$_{\text{MMA}}$ × conversion. [b] By SEC with a PMMA calibration. Conditions: reaction time, 24 h; $[MMA]_0 = 3.5$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 2[CCl_4]_0$.

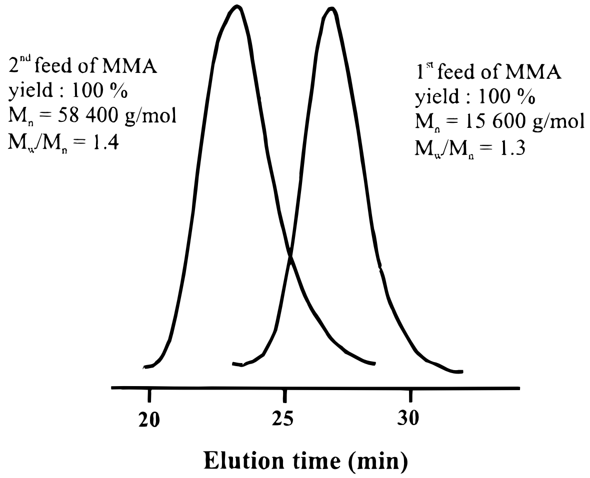

Figure 3. Comparison of the size exclusion chromatograms of the polymer before (first feed) and after (second feed) the resumption of polymerization. Conditions: solvent, water/THF (2/3, v/v constant); $[MMA]_0 = 3.5$ mol·L^{-1}, constant; $[CCl_4]_0 = 26 \times 10^{-3}$ mol·L^{-1}; $[RhCl(PPh_3)_3]_0 = 26 \times 10^{-3}$ mol·L^{-1}. Reaction time, 21 h for the first feed and 23 h for the second feed. SEC was calibrated with PMMA standards.

preformed Wilkinson catalyst (from Aldrich) is used.[8] This is a worthwhile observation, since it indicates that $RhCl_3$ can be easily combined with different phosphines in various ratios. The effect of these experimental variables is currently being investigated and will be the topic of a forthcoming publication.

The polymerization mechanism is more likely radical since the PMMA tacticity (typically $rr{:}rm{:}mm = 64{:}32{:}4$) fits the tacticity known for a radical polymerization. Furthermore, Galvinoxyl (5 equiv compared to the initiator), a well-known radical inhibitor, inhibits the MMA polymerization. The ω-chain end group has been identified by ^1H NMR. Indeed, a signal at 3.77 ppm is characteristic of a terminal ester group adjacent to a chlorine atom. Furthermore, the superposition of the SEC chromatograms recorded with both the refractive index and the UV detectors (254 nm) confirms that the chains are α-end-capped by the aromatic ring of the initiator (2,2′-dichloroacetophenone), in agreement with ^1H NMR signals between 7.5 and 8 ppm, to which PPh_3 residues can however contribute.

Finally, a random copolymer of methylmethacrylate and 2-hydroxyethyl methacrylate (MMA/HEMA molar ratio, 9/1) has been successfully synthesized (apparent $M_n = 11\,700$; and polydispersity, 1.4). The incorporation of HEMA is confirmed by ^1H NMR analysis. It is worth recalling that the hydroxyl pendent groups of this copolymer are potential initiators for the ring-opening polymerization of ϵ-caprolactone in the presence of small amounts of aluminum isopropoxide. The synthesis of poly(MMA-*g*-ϵ-caprolactone) will be reported in the near future.

Conclusion. Although the Wilkinson catalyst is less efficient than the Sawamoto and Matyjaszewski systems in terms of polymerization kinetics, it allows MMA to be polymerized in a living manner at a temperature as low as 60 °C and in the absence of any Lewis acid. This control is observed not only in a concentrated THF solution but also in a water/THF mixture. This catalyst, which is thus efficient under mild conditions, can be prepared in situ and used in the presence of protic substances. It allows copolymers such as poly(MMA-*co*-HEMA) to be prepared.

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(9) Conditions: $T = 50$ °C; reaction time, 18 h; solvent, THF, $[MMA]_0 = 5.55$ mol·L^{-1}, $[HEMA]_0 = 0.5$ mol·L^{-1}, $[RhCl(PPh_3)_3]_0 = 18.4 \times 10^{-3}$ mol·L^{-1}, $[PPh_3]_0 = 13 \times 10^{-2}$ mol·L^{-1}, [2,2′-dichloroacetophenone]$_0 = 36.8 \times 10^{-3}$ mol·L^{-1}. Conversion, 85%. The percentage of HEMA determined by ^1H NMR, 9.6%.

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