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Articles

Kinetic and Mechanistic Study of Copper Chloride-Mediated Atom Transfer Polymerization of Styrene in the Presence of *N*,*N*-Dimethylformamide

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ABSTRACT: The kinetics and mechanism of the atom transfer polymerization of styrene initiated with 1-phenylethyl chloride/CuCl/2,2′-bipyridine have been investigated in homogeneous media in the presence of dimethylformamide at 130 °C. The results are in agreement with a fisrt-order dependence with respect to CuCl, but an apparent zero-order dependence with respect to the initiator has been observed, contrary to other reports in the literature. This order does not result from side reactions and has been accounted for by assuming a constant value of the [PECl]/[$CuCl_2$] ratio in the range of concentrations investigated. The results do not allow to distinguish between the conventional first-order treatment and that taking into account the persistent radical effect.

Introduction

Copper-based atom transfer radical polymerization provides an easy tool for the control of the radical polymerization of a wide range of monomers,[1,2] and this topic has been widely investigated by various authors.[3−5] Under experimental conditions allowing fast and quantitative initiation, the concentration of active centers during the polymerization essentially depends on the redox equilibrium:

$$P_nX + CuX(L) \overset{K_e}{\rightleftharpoons} P_n^{\circ} + CuX_2(L) \qquad (1)$$

with X being a halogen (Cl or Br) and L a ligand. The polymerization rate is given by the following relationship:

$$R_p = k_p[M]K_e[RX][CuX]/[CuX_2] \qquad (2)$$

with RX being the initiator and assuming that the consumption of the monomer obeys a first-order internal law.

The molar masses can be calculated using the following relationship:

$$M_n = \frac{[M]_0 \cdot \text{yield} \cdot m}{[RX]_0} \qquad (3)$$

with m the molar mass of the monomer.

So far, the accepted criteria for a controlled polymerization are (i) a linear semilogarithmic plot for the consumption of monomer, (ii) molar masses in agreement with the calculated values, and (iii) a polydispersity decreasing with conversion.

However, several side reactions may interfere with this mechanism.

(1) A persistent radical effect[6] causes irreversible termination leading to an accumulation of deactivator ($Cu^{II}X$) and to a decrease of the reaction rate. This effect is particularly important at the very beginning of the polymerization, during which it involves mainly primary radicals and leads to a significant initial buildup of the copper(II) species. Consequently, the concentration of $CuCl_2$ is much higher than that of the propagating radicals, and its determination is one of the difficulties in ATRP. This irreversible termination between growing radicals takes place over the whole polymerization course. At the end of the reaction, reactivation of the chain ends in the absence of monomer leads to either disproportionation or combination reactions between macroradicals and to a loss of functionalization.

(2) Transfer is not suppressed and limits the range of molar masses for which control is effective.[7]

(3) For some monomers, such as styrenics, thermal initiation may become preponderant with respect to catalyzed initiation at low concentrations of initiating species and at high temperatures.[8]

Satisfactory control of the molar masses (with polydispersity decreasing with conversion) and linear semilogarithmic plots for the consumption of monomer have been obtained for a variety of systems, which implies that the incidence of these side reactions is limited if

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experimental conditions are conveniently fine-tuned (temperature, concentrations, range of molar masses) and that the polymerizations are controlled. However, the real mechanism is probably more complex than previously presented, and this may explain the discrepancies observed in the literature data for the orders of reaction with respect to the components of the initiating systems. Although first-order dependences with respect to initiator (RX) and activator (CuX) for both chlorinated and brominated species have been reported in the case of the homogeneous polymerization of styrene,[9] a fractional order (0.8) has been found for CuCl in similar conditions.[4] Similarly, in the case of the polymerization of MMA, either a first-order dependence[10] or fractional orders (0.37 with respect to initiator and 0.80 with respect to activator) have been reported.[4] For methyl acrylate, a 0.8-order dependence was found for the initiator and a nonlinear relationship for the activator.[11]

Several attempts at modeling ATRP have been published.[2,12] In a recent paper,[13] Matyjaszewski showed that a simulation of styrene polymerization yields fractional orders (0.19 for RX and 0.47 for CuX). The proposed explanation was that, for an increase of RX at constant concentration of CuX, the Cu^{II}/Cu^{I} ratio increases, and consequently the reaction order with respect to initiator RX is much lower than unity. The calculation shows a reverse effect when $[Cu^{I}X]$ is increased (decrease of the $[Cu^{II}]/[Cu^{I}]$ ratio at constant RX concentration), but this still leads to an order lower than unity within the considered range of concentrations.

A theoretical calculation taking into account irreversible termination and persistent radical effect has been proposed by Fischer[14] and applied to ATRP. According to these calculations, the logarithmic plot for monomer consumption should show a $^{2}/_{3}$-order dependence on time and the radical concentration a reverse $^{1}/_{3}$-order dependence. However, rather surprisingly, the concentration of CuX_2 does not appear in the proposed kinetic relationships. Besides, it is stated that thermal initiation and transfer are not taken into account. Similar formulations were proposed by Fukuda et al.[15] in a simpler way.

It has been previously shown that mixtures of styrene, 1-phenylethyl chloride (PECl), copper(I) chloride, and bipyridine in the presence of 10% v/v *N*,*N*-dimethylformamide yield homogeneous media.[8] However, when the initial concentrations of the components of the initiating system (PECl, CuCl, bipy) are varied simultaneously, the apparent rate constant measured (assuming first-order kinetics for the consumption of styrene) is only doubled for a 2-fold increase of the concentrations of both components of the initiating system except in the low concentration range where thermal initiation is significant (Figure 1), while a 4-fold increase would have been expected in the case of first reactions orders with respect to PECl and CuCl. This led us to thoroughly investigate the kinetics of this polymerization, to confirm the reactions orders with respect to the initiating species and to measure the equilibrium constant for the reversible termination. Furthermore, it seemed interesting to check whether the experimental data are in agreement with Fischer's formulation or with the simplified interpretation (first-order plots).

Experimental Section

Styrene (Acros, 99%) was distilled under reduced pressure from calcium hydride powder before use. Copper(I) chloride (CuCl, Aldrich, 99.995+%), phenylethyl chloride (PECl, Acros, 99%), 2,2′-bipyridine (bipy, Aldrich, 99+%), *N*,*N*-dimethylformamide (DMF, Acros, 99+%), and deuterated toluene (C_7D_8, Eurisotop) were used as received. 4,4′-dialkyl-2,2′-bipyridine (dAbipy) (alkyl = 5-nonyl and heptyl) was kindly provided by K. Matyjaszewski. The 1-chloro-1-(4-methylphenyl)ethane, (*p*-methylphenyl)ethyl chloride (MePECl), was prepared by bubbling hydrogen chloride in a dichloromethane solution of *p*-methylstyrene. The solvent was eliminated and the final compound distilled under vacuum and characterized by ^{1}H NMR.

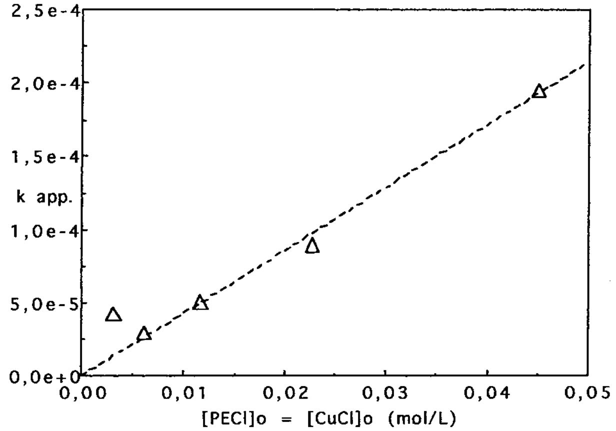

Figure 1. Homogeneous ATRP of styrene at 130 °C in the presence of 10% v/v DMF. Evolution of the first-order apparent rate constant with the concentration of initiator and catalyst. $[Styrene]_0 = 7.86$ mol L^{-1}; $[PECl]_0 = [CuCl]_0 = [bipy]_0/3$.

The reaction mixtures were prepared under nitrogen in a glovebox. The initiator was added last to a mixture of CuCl, styrene, bipy, and DMF. Samples of the homogeneous solution were transferred with a syringe into glass tubes fitted with Teflon stopcocks. The tubes were degassed under vacuum and sealed off after several freeze−thaw cycles. The polymerizations were carried out in a thermoregulated oil bath at 130 °C. The polymers were recovered by precipitation in methanol and pumped overnight in a vacuum oven at 50 °C. The yields were calculated from the weight of recovered polymer.

The molar masses and molar mass distributions were measured by size exclusion chromatography in tetrahydrofuran with a 10^5,10^4,10^3, 500, and 100 Å set of microstyragel columns and a refractometric detector using a polystyrene standard calibration curve. ^{1}H NMR analysis were performed in C_7D_8 at room temperature with a 200 MHz Bruker spectrometer. MALDI-TOF mass spectrometry data were collected using a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer with a nitrogen laser ($\lambda = 337$ nm), a delayed extraction system, and a reflector. Dihydroxybenzoic acid (DHB) or dithranol was used as matrix materials. ESR spectra were recorded on a Bruker ESP 300 spectrometer. The solutions were prepared in a glovebox and transferred into a quartz tube (2 mm i.d.). The tubes were degassed by freeze−thaw cycles under vacuum before sealing off. The system was calibrated in the same conditions with degassed mixtures of styrene, CuCl, bipy, DMF, and variable amounts of $CuCl_2$.

Results and Discussion

(a) Control of the Polymerization. A solution of styrene, PECl, CuCl, and bipy ($[styrene]_0 = 7.85$ mol L^{-1}; ratios styrene/PECl/ CuCl/bipy: 175/1/1/3) has been polymerized at 130 °C. A satisfactory linear semilogarithmic plot is obtained for the consumption of monomer (Figure 2), and the apparent rate constant is derived from this plot ($k_{app} = d(\ln([M]_0/[M]_t)/dt = k_p[P_n°])$ is equal to 1.95×10^{-4} s^{-1}. Taking into account the propagation rate constant for styrene at 130 °C ($k_p = 2600$ L mol^{-1} s^{-1}),[16] the corresponding value of the

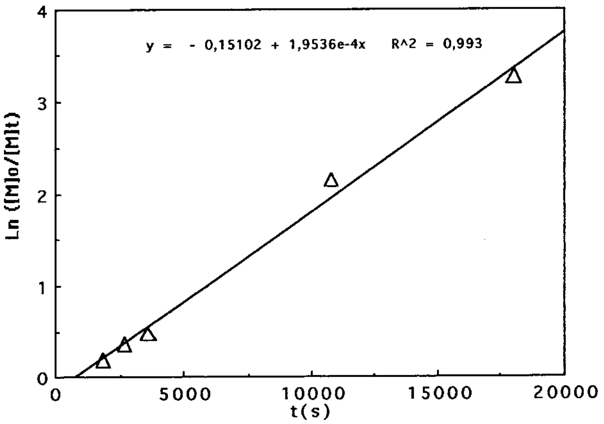

Figure 2. Homogeneous ATRP of styrene at 130 °C in the presence of 10% v/v DMF. Semilogarithmic plot for monomer conversion. $[Styrene]_0 = 7.86$ mol L^{-1}; $[PECl]_0 = [CuCl]_0 = [bipy]_0/3 = 4.5 \times 10^{-2}$ mol L^{-1}.

concentration of propagating radicals is 7.5×10^{-8} mol L^{-1}. As shown in Figure 3, the experimental molar masses correspond to the calculated values for a controlled process (eq 3), and the polydispersity decreases with conversion from 1.49 to 1.29 for 99% conversion. The polymerization is satisfactorily controlled under these conditions.

(b) Measurement of the Equilibrium Constant for Reversible Termination. A key parameter is the redox equilibrium constant. Its determination necessitates the knowledge of the concentration of propagating radicals $[P_n°]$ and that of the copper(II) chloride formed during the initiation period, assuming that $[P_nCl] = [CuCl] = [CuCl]_0 - [CuCl_2]$.

For a polymerization carried out at 130 °C ($[styrene]_0 = 7.85$ mol L^{-1}; ratios styrene/PECl/ CuCl/bipy: 350/1/1/3) and assuming first-order kinetics for the consumption of monomer, the apparent rate constant ($k_{app} = k_p[P_n°]$) is 9.0×10^{-5} s^{-1}. Taking into account the propagation rate constant at this temperature, the concentration of propagating radicals is 3.5×10^{-8} mol L^{-1}. Consequently, measurement of the concentration of $CuCl_2$ in the polymerizing solution allows to calculate the equilibrium concentrations of P_nCl and CuCl, leading to the value of K_e.

The concentration of $CuCl_2$ was measured by ESR. The concentration of polystyryl radicals, which is smaller by 5 orders of magnitude than that of $CuCl_2$, cannot be detected under these conditions, and the only measurable signal corresponds to $CuCl_2$. A calibration was made with solutions of known concentrations of $CuCl_2$ in mixtures of styrene and DMF (double integration of the $CuCl_2$ signals vs $CuCl_2$ concentrations). A standard ATRP using the above conditions used for the measurement of k_{app} was carried out at 130 °C over 90 min, and the concentration of $CuCl_2$ in the solution was measured. The integration of the ESR signal corresponds to a concentration of copper(II) chloride equal to 2.7×10^{-3} mol L^{-1}. This means that after 90 min of polymerization about 12% of the initial CuCl is converted into $CuCl_2$ which allows to calculate the value of K_e:

$$K_e = \frac{[P_n°][CuCl_2]}{([PECl]_0 - [CuCl_2])([CuCl]_0 - [CuCl_2])} \quad (4)$$

The corresponding value of K_e is 2.3×10^{-7}. This value is higher than that reported by Matyjaszewski et al.[9] ($K_e = 2.1 \times 10^{-8}$). These authors measured the apparent rate constant of polymerization of styrene in diphenyl ether solution initiated with PECl/CuCl in the presence of 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbipy) at 130 °C and of 10% excess of added $CuCl_2$, considering that the $CuCl_2$ resulting from the persistent radical effect would be negligible compared to the added $CuCl_2$. The discrepancy may result from the different conditions used.

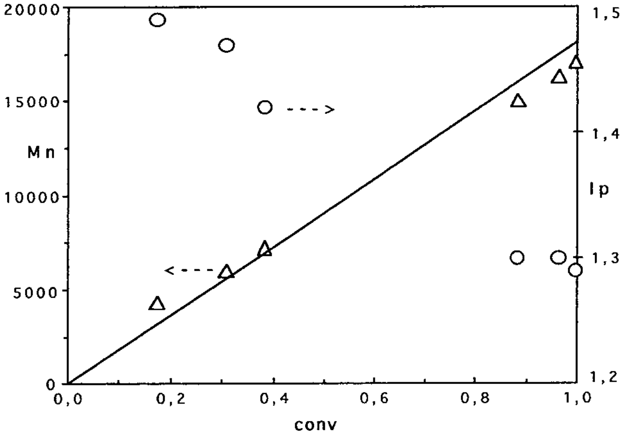

Figure 3. Homogeneous ATRP of styrene at 130 °C in the presence of 10% v/v DMF. Evolution of the molar mass (△) and polydispersity (○) with conversion. $[Styrene]_0 = 7.86$ mol L^{-1}; $[PECl]_0 = [CuCl]_0 = [bipy]_0/3 = 4.5 \times 10^{-2}$ mol L^{-1}.

In a previous paper,[8] we measured the activation rate constant by monitoring the consumption of PECl ($k_{act} = 2 \times 10^{-2}$ L mol $^{-1}$ s^{-1} at 130 °C). This value is in agreement with that reported by Fukuda et al.[17] using NMR measurements at 110 °C. The deactivation rate constant can thus be calculated from the values of K_e and k_{act} ($k_{deact} = k_{act}/K_e = 8.7 \times 10^4$ L mol^{-1} s^{-1}). The reversible deactivation process ($R_{deact} = k_{deact}[P_n°][CuCl_2] = 8 \times 10^{-6}$ mol L^{-1} s^{-1}) is higher by nearly 2 orders of magnitude than the rate of irreversible termination ($R_t = k_t[P_n°]^2 = 10^8 \times (3.5 \times 10^{-8})^2 \simeq 10^{-7}$ mol L^{-1} s^{-1}.

(c) Determination of the Reaction Orders with Respect to CuCl and PECl. The determination of reaction orders is restricted to a rather narrow range of concentrations as thermal initiation interferes for low initiator or activator concentrations, and the reaction medium is no longer homogeneous for CuCl concentrations higher than 5×10^{-2} mol L^{-1}. Polymerizations were carried out at variable CuCl concentration and constant PECl concentration ($[PECl] = [bipy]/3 = 2.27 \times 10^{-2}$ mol L^{-1}). The plot of $\ln(k_{app})$ vs ln[CuCl] (Figure 4) shows that the reaction order with respect to CuCl is approximately 0.85, which is in agreement with the results from the literature which range from 1 with PECl as initiator[9] to 0.8[4] with *p*-methoxysulfonyl chloride, both at 130 °C in the presence of 4,4′-di(5-nonyl)bipyridine. In all cases, the molar masses of the polystyrenes were in good agreement with the calculated values, and the polydispersity decreases with conversion down to 1.3 at high yield.

A series of polymerizations have been carried out at variable PECl concentrations, keeping constant the concentrations of the other components of the initiating system ($[CuCl]_0 = [bipy]_0/3 = 4.5 \times 10^{-2}$ mol L^{-1}). The semilogarithmic plots for the consumption of monomer are reported in Figure 5, and the values are derived for the apparent rate constants in Table 1. Despite some

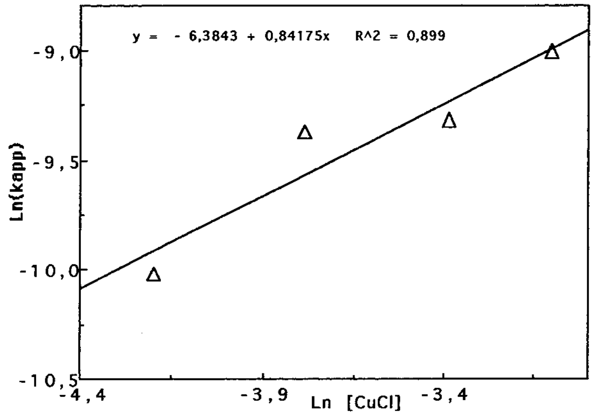

Figure 4. Homogeneous ATRP of styrene at 130 °C in the presence of 10% v/v DMF. Dependence of the first-order apparent rate constant on the catalyst concentration. $[\text{Styrene}]_0 = 7.86$ mol L^{-1}; $[\text{PECl}]_0 = 2.27 \times 10^{-2}$ mol L^{-1}; $[\text{bipy}]_0 = 3[\text{CuCl}]_0$.

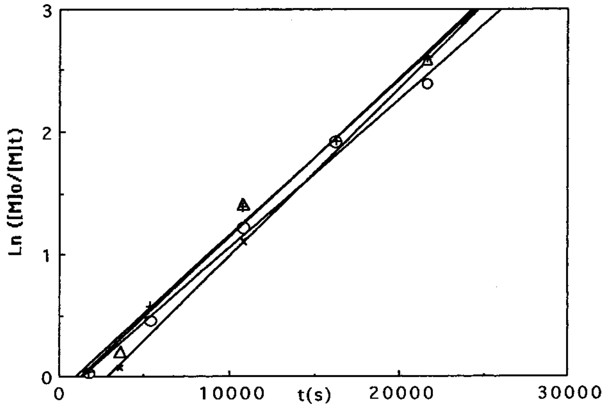

Figure 5. Homogeneous ATRP of styrene at 130 °C in the presence of 10% v/v DMF. Semilogarithmic plots for the consumption of monomer at variable concentration of PECl. $[\text{Styrene}]_0 = 7.86$ mol L^{-1}; $[\text{CuCl}]_0 = [\text{bipy}]_0/3 = 4.5 \times 10^{-2}$ mol L^{-1}. [PECl]: ×, 1.47×10^{-2} mol L^{-1}; ○, 2.27×10^{-2} mol L^{-1}; △, 2.95×10^{-2} mol L^{-1}; +, 3.74×10^{-2} mol L^{-1}.

scatter of the experimental points, the plot of $\ln(k_{\text{app}})$ vs $\ln([\text{PECl}]_0)$ shows that the apparent rate constant is practically independent of [PECl] in the range of concentrations investigated (Figure 6). This has been confirmed using 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbipy) ([dNbipy] = 2[CuCl]) which allows to investigate a larger concentration range in homogeneous conditions and is in agreement with an apparent zero order with respect to PECl which better fits Matyjaszewski's theoretical calculations[13] than the previously reported experimental data.[4,9]

Up to now, ATRP has been routinely treated as being first order for the consumption of monomer and the measurement of $[P_n°]$ reported here relies on this assumption. However, the calculations of Fischer and Fukuda yield a $^2/_3$-power dependence on reaction time for the semilogarithmic plots for the consumption of the monomer:

$$\ln\left[\frac{[\text{M}]_0}{[\text{M}]_t}\right] = \frac{3}{2}k_{\text{p}}\left[\frac{K_{\text{e}}[\text{PECl}]_0[\text{CuCl}]_0}{3k_{\text{t}}}\right]^{1/3} t^{2/3} \qquad (5)$$

Table 1. Comparison of Calculated and Experimental Values of the Constant Derived from the $^2/_3$-Order Time Dependence of the Semilogarithmic Plot for Monomer Consumption and Value of the Experimental First-Order Plot for Variable Concentrations of [PECl] and [CuCl][a]

$10^2[\text{PECl}]_0$ (mol L^{-1})[b]	$10^2[\text{CuCl}]_0$ (mol L^{-1})	10^5k_{app} (1st order)	$10^3K(2/3)$ (expt)	$10^3K(2/3)$ (calc)
4.50 a	4.50	19.53	5.89	4.51
2.27 a	2.27	9.00	3.06	2.86
1.16 a	1.16	5.11	2.08	1.83
0.60 a	0.60	3.31	1.41	1.18
0.30 a	0.30	4.29	1.59	0.74
2.27 a	4.50	12.23	3.89	3.59
2.27 a	3.38	8.99	2.89	3.27
2.27 a	2.27	8.48	3.00	2.86
2.27 a	1.50	4.45	1.88	2.49
3.74 a	4.50	12.77	4.06	4.25
2.95 a	4.50	13.07	4.41	3.92
2.27 a	4.50	12.22	3.88	3.59
1.47 a	4.50	13.80	4.61	3.11
9.90 b	4.50	11.23	3.10	5.87
7.50 b	4.50	11.14	2.87	5.35
3.75 b	4.50	12.03	3.28	4.25

[a] Composite termination rate constant: 10^8 L mol^{-1} s^{-1}. Equilibrium constant $K_{\text{e}} = 2.3 \times 10^{-7}$. $k_{\text{p(130°C)}} = 2600$ L mol^{-1} s^{-1}. [b] a = ligand: 2,2′-bipyridine; b = ligand: 4,4′-di(5-nonyl)-2,2′-bipyridine.

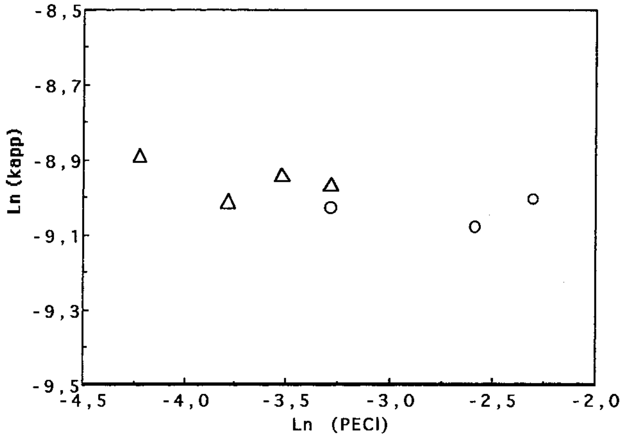

Figure 6. Homogeneous ATRP of styrene at 130 °C in the presence of 10% v/v DMF. Reaction order for PECl. $[\text{Styrene}]_0 = 7.86$ mol L^{-1}; $[\text{CuCl}]_0 = [\text{bipy}]_0/3 = 4.5 \times 10^{-2}$ mol L^{-1}. △: bipy; ○: 4,4′-di(5-nonyl)-2,2′-bipyridine.

The corresponding plots are shown in Figure 7 in the case of the variation of PECl concentration and may be compared with the first-order plots in Figure 5. It appears that the slopes of the plots do not depend on the concentration of PECl. The experimental values of the slopes of these plots are in reasonably good agreement with the calculated values of the constant term in eq 5 (K in Table 1; taking $K_{\text{e}} = 2.3 \times 10^{-7}$ L^2 mol^{-2} s^{-1}, $k_{\text{t}} = 10^8$ L mol^{-1} s^{-1}, and $k_{\text{p}} = 2600$ L mol^{-1} s^{-1}). Thus, the experimental data obtained here do not allow to decide which is the more accurate kinetic treatment, although the conventional first-order plot seems in general agreement with the majority of the systems investigated. It appears from Fischer's treatment (ref 14, p 1889) that the concentration of transient radicals becomes approximately constant, with a slow decrease, after a steep drop at the beginning of the polymerization. This may explain that the usual first-order treatment satisfactorily accounts for the experimental data in many cases and may be taken as a first approximation for the main practical purpose which is to control the molar masses of the polymers. In fact, these systems have never been qualified as living by their first discoverers, but as polymerization systems allowing, under restricted conditions which have been expressly

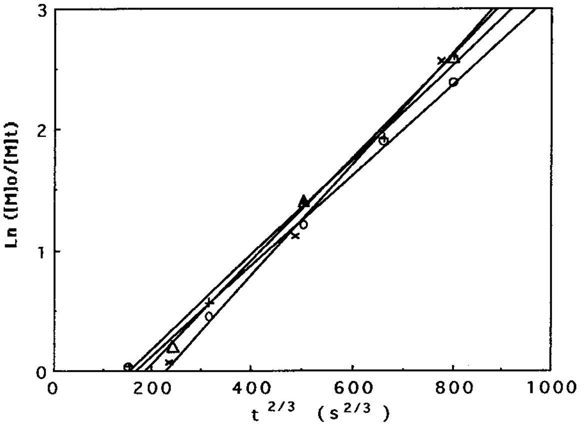

Figure 7. Homogeneous ATRP of styrene at 130 °C in the presence of 10% v/v DMF. Plot of $\ln([M]_0/[M]_t)$ vs $t^{2/3}$. $[\text{Styrene}]_0 = 7.86$ mol L^{-1}; $[\text{CuCl}]_0 = [\text{bipy}]_0/3 = 4.5 \times 10^{-2}$ mol L^{-1}. [PECl]: ×, 1.47×10^{-2} mol L^{-1}; ○, 2.27×10^{-2} mol L^{-1}; △, 2.95×10^{-2} mol L^{-1}; +, 3.74×10^{-2} mol L^{-1}.

stated, a satisfactory control in a limited range of molar masses.

It might be assumed that the zero order with respect to initiator results either from preponderant thermal initiation or from an eventual effect of DMF in rather high concentration which might play a part in initiation.

Thermal initiation continuously creates new chains,[18] and the corresponding active ends react with $CuCl_2$ and enter the reversible termination process. The thermal initiation rate exhibits a third-order dependence on the monomer concentration and rapidly decreases as the monomer is consumed, more so in the case of faster catalyzed initiation, especially at high PECl concentrations. We performed thermally initiated bulk polymerizations of styrene which yielded polymers with molar masses of about 200 000 g mol^{-1}, corresponding to a concentration of chains of 4.5×10^{-3} mol L^{-1} at complete conversion. Assuming a transfer constant to the monomer equal to 3×10^{-4} at 130 °C,[7] the concentration of chains resulting from transfer ($[N]_{tr} = C_M[M]_0$) is about 2.5×10^{-3} mol L^{-1}. This means that the concentration of thermally initiated chains formed during the thermal polymerization is 2×10^{-3} mol L^{-1}.

A simple calculation taking into account the third-order dependence with respect to monomer for initiation, and the 2.5-order for propagation leads to the following relationship for the concentration $[N]_{th}$ of chains formed by thermal initiation at time t:

$$[N]_{th} = k_i\left[\frac{1}{[(^3/_2 k_p(k_i/2k_t)^{0.5})[M]_0^{-1.5}]} - \frac{1}{(^3/_2 k_p(k_i/2k_t)^{0.5})^2 t + [(^3/_2 k_p(k_i/2k_t)^{0.5})[M]_0^{-1.5}]}\right] \quad (6)$$

k_i, k_t, and k_p being respectively the initiation, termination, and propagation rate coefficients ($k_i = 3 \times 10^{-10}$ L^2 mol^{-2} s^{-1}: $k_t = 10^8$ L mol^{-1} s^{-1}; $k_p = 2600$ L mol^{-1} s^{-1}). This relationship yields a value of 1.6×10^{-3} mol L^{-1} of chains thermally initiated at complete conversion, in reasonably good agreement with the previous data, which represents less than 10% of the concentration of PECl in the concentration range used in ATRP. Even if the corresponding active chains enter the reversible process through reaction with $CuCl_2$, the resulting increment of radical concentration is too low to account for a zero order with respect to PECl.

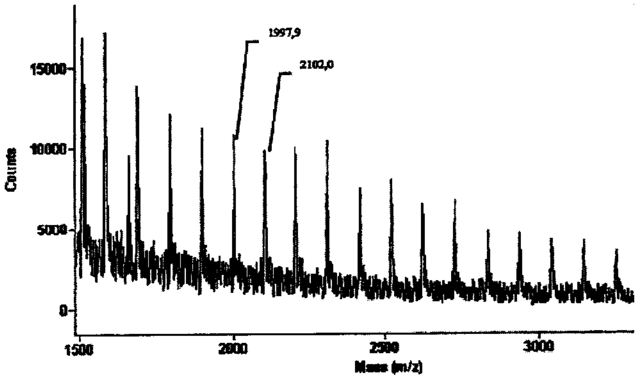

Figure 8. MALDI-TOF spectrum of a polystyrene ($M_n = 2900$ g mol^{-1}; $M_w/M_n = 1.28$) initiated with (p-methyphenyl)ethyl chloride at 130 °C after 30 mn reaction. DMF: 10% v/v; $[\text{Styrene}]_0 = 7.86$ mol L^{-1}; $[\text{MePECl}]_0 = [\text{CuCl}]_0 = 2.27 \times 10^{-2}$ mol L^{-1}.

Furthermore, the mechanism of the initiation process has been investigated using 1-(p-methylphenyl)ethyl chloride as initiator. The resulting polymers were analyzed by MALDI-TOF mass spectrometry in order to distinguish the chains formed by thermal initiation, which have a styryl end group, from those resulting from catalytic initiation which have a (p-methylphenyl)ethyl end group. For an ATRP of styrene at 130 °C ($[\text{Sty}] = 7.85$ mol L^{-1}; $[\text{MePECl}]_0 = [\text{CuCl}]_0 = [\text{bipy}]_0/3 = 2.3 \times 10^{-2}$ mol L^{-1}), the yield after 30 min was limited to 1.5% ($M_n = 2900$ g mol^{-1}; polydispersity = 1.28). The MALDI-TOF mass spectrum of the polystyrene is shown in Figure 8. The peaks at m/z = 1998 and 2102 correspond to the following ionic species: $[CH_3{-}CH(p\text{-}CH_3Ph){-}(CH_2{-}CH(Ph))_n{-}CH{=}CH(Ph),Ag^+]$ with n equal to 16 and 17, respectively. Although the experimental molar mass is about 5 times the calculated one, which shows that initiation is not complete at this stage, no peak corresponding to chains bearing an initial styrene end group could be detected, which implies that catalyzed initiation is the main process and that thermal initiation is negligible under the conditions used for the polymerization.

Another possibility would be a contribution of DMF to the initiating process either directly or through interaction with PECl which would yield a constant concentration of radicals, independent of the PECl concentration. A comparison of thermal polymerizations of styrene in bulk, of styrene in the presence of 10% v/v DMF, and of styrene in the presence of (10% v/v DMF + CuCl + bipy) shows that the polymerization rates are similar (Figure 9). This confirms that the DMF alone does not take part in initiation.

The last possibility might be a reaction between DMF and PECl which would play a part in initiation. To investigate the possible influence of DMF on the homolysis of PECl, the evolution of solutions of PECl ($[\text{PECl}]_0 = 9.9 \times 10^{-1}$ mol L^{-1}) in deuterated toluene in the presence of 10% and 50% v/v DMF at 130 °C has been monitored by ^{1}H NMR. After 10 h heating, the characteristic peaks of styrene appear (CH(Ph) at 6.6 ppm, CH_2 at 5.1 and 5.8 ppm). However, in the presence of 10% v/v DMF, less that 10% of the PECl is decomposed in 10 h (Figure 10, upper graph), while about 50% decomposition is observed in the presence of 50% v/v DMF (Figure 10, lower graph). It can be concluded that

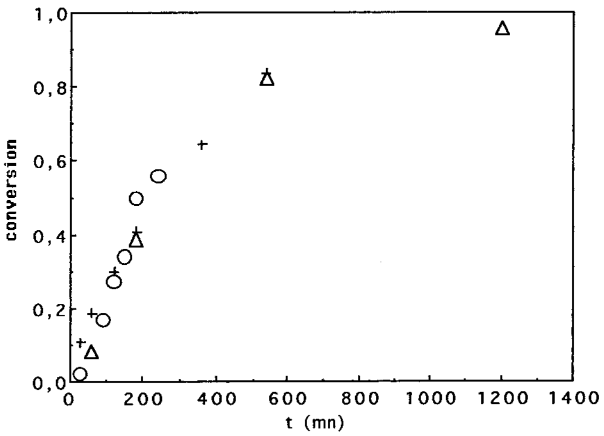

Figure 9. Thermally initiated polymerizations of styrene at 130 °C. ○: bulk polymerization; $[\text{styrene}]_0 = 8.72$ mol L^{-1}; +: polymerization in the presence of 10% DMF; $[\text{styrene}]_0 = 7.86$ mol L^{-1}; $[\text{DMF}]_0 = 1.28$ mol L^{-1}; △: polymerization in the presence of DMF and CuCl; $[\text{styrene}]_0 = 7.86$ mol L^{-1}; $[\text{DMF}]_0 = 1.7$ mol L^{-1}; $[\text{CuCl}]_0 = [\text{bipy}]_0/3 = 2.27 \times 10^{-2}$ mol L^{-1}.

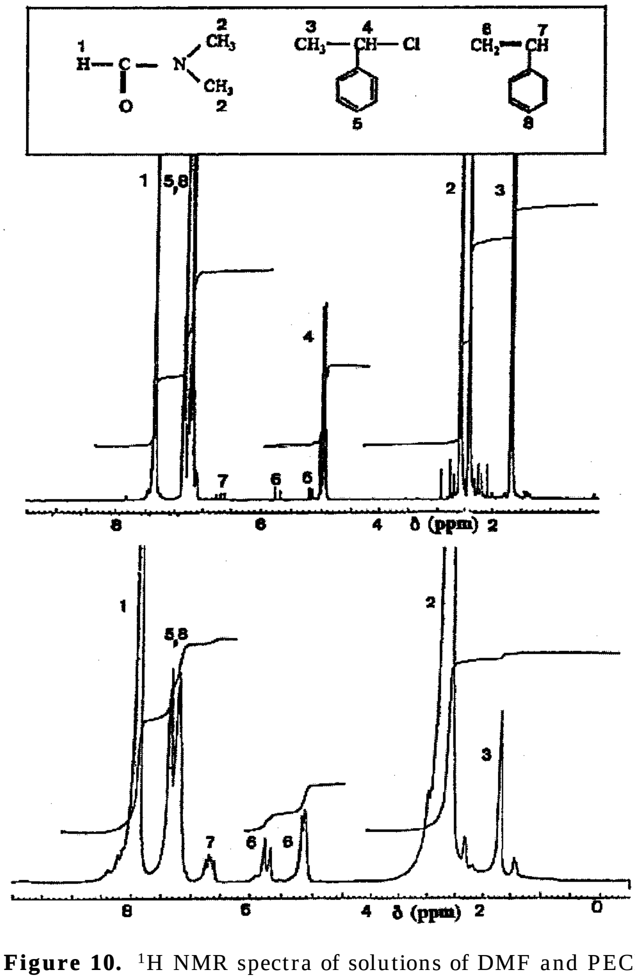

Figure 10. ^{1}H NMR spectra of solutions of DMF and PECl in deuterated toluene after 10 h heating at 130 °C. Upper graph: $[\text{DMF}]_0 = 1.28$ mol L^{-1} (10% v/v); $[\text{PECl}]_0 = 9.9 \times 10^{-1}$ mol L^{-1}. Lower graph: $[\text{DMF}]_0 = 6.46$ mol L^{-1} (50% v/v); $[\text{PECl}]_0 = 9.9 \times 10^{-1}$ mol L^{-1}.

Table 2. Evolution of the Concentration of $CuCl_2$ Formed after 60 mn of Reaction and of the Ratio $[PECl]_0/[CuCl_2]$ for Different Initial Concentrations of PECl[a]

$[PECl]_0$ (10^2 mol L^{-1})	$[CuCl_2]$ (10^2 mol L^{-1})	$[PECl]_0/[CuCl_2]$
3.77	2.1	1.79
7.46	4.1	1.82
10.1	5.0	2.02

[a] $[\text{CuCl}]_0 = [\text{bipy}]_0/3 = 4.5 \times 10^{-2}$ mol L^{-1}. $T = 130$ °C.

decomposition of PECl is enhanced in the presence of large amounts of DMF but that this reaction remains negligible within the time scale of our polymerizations in the presence of 10% v/v DMF.

Thus, the experimental zero order with respect to PECl cannot be ascribed to side reactions. This order of reaction implies that in the relationship giving the concentration of propagating species:

$$[P_n°] = K_e \frac{[\text{PECl}][\text{CuCl}]}{[\text{CuCl}_2]} \tag{7}$$

the $[PECl]/[CuCl_2]$ ratio is independent of the initial concentration of PECl, at least in the range of concentrations investigated. This has been experimentally verified by measuring by ESR the concentration of $CuCl_2$ present after 60 mn. (i.e., when initiation is nearly complete) in solutions with variable concentrations of PECl, the concentrations of styrene, CuCl, and bipy being kept constant. It appears from Table 2 that the $[PECl]_0/[CuCl_2]$ ratio measured after 60 min is nearly constant (although with a slight increase), when the initial PECl concentration varies from 3.8×10^{-2} to 10^{-1} mol L^{-1}. During the initiation period, primary radical termination yields 2 equiv of $CuCl_2$ per termination process, and the major part of $CuCl_2$ is formed during initiation. After the initiation phase, when the initiator is completely consumed, termination between primary radicals no longer takes place, and the rate constant for irreversible termination between growing chains is 1 order of magnitude lower than that of termination between primary radicals. Reversible termination becomes predominant and controls the polymerization. Therefore, the amount of $CuCl_2$ present is approximately proportional to the intial PECl concentration, even if small increments are produced afterward through irreversible termination.

Conclusion

A kinetic study of the ATRP of styrene at 130 °C has been carried out. The equilibrium constant for the reversible termination and the activation and deactivation constants have been measured. Thermal initiation takes place at 130 °C, but its incidence is negligible in the range of initiator concentrations higher than 2×10^{-2} mol L^{-1}, and MALDI-TOF data showed that initiation involves a PECl molecule.

The reaction order with respect to CuCl is nearly one. But an apparent zero-order dependence of the reaction rate with respect to the initiator concentration has been found, which disagrees with some of the few published kinetic analyses concerning ATRP. This is not due to the presence of the 10% v/v DMF used to operate in homogeneous conditions and is to be compared with the rather low order (0.19) resulting from Matyjaszewski's modeling.[10] Given the narrow range of concentration investigated, it is possible that the real value might be sligthly positive. The most simple explanation for this result, which has been checked experimentally, is that the $[PECl]/[CuCl_2]$ ratio remains approximately constant, the concentration of $CuCl_2$ formed being proportional to the initial concentration of PECl.

Although Fischer's treatment gives an accurate description of an ATRP process, the simplified treatment satisfactorily describes the reaction for practical purposes (prediction of molar masses and synthesis of block copolymers).

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