Homogeneous Atom Transfer Radical Polymerization of Styrene Initiated by 1-Chloro-1-phenylethane/Copper(I) Chloride/Bipyridine in the Presence of Dimethylformamide

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ABSTRACT: Homogeneous atom transfer radical polymerization of styrene initiated with 1-chloro-1-phenylethane/CuCl/2,2′-bipyridine at 130 °C is easily achieved in the presence of a limited amount of dimethylformamide (∼10% v/v). The kinetics are in agreement with the accepted ATRP mechanism. For initial monomer-to-initiator ratios up to 400, the molar masses increase linearly with conversion and perfectly fit the calculated value for a controlled polymerization, and the results are still satisfactory up to a ratio of 650. For higher values of this ratio, the polymerization is no longer controlled, and this is attributed to thermal initiation, irreversible termination, and/or transfer.

Introduction

Although the control of anionic polymerization has been achieved as early as 1956 and that of the cationic polymerization in the 1980s, the control of radical polymerization has long seemed a far-fetched goal. The first breakthrough in this field was made by Otsu,[1] who used dithiocarbamate derivatives as initiators and first considered the possibility of a reversible termination. Many papers related to this method have been published since.[2–4] In the past 3 years, the control of radical polymerization became a fashionable topic, several methods of control have been proposed,[5] and reviews have been published.[6–8] One of the most promising methods has been proposed by Matyjaszewski and colleagues,[9] who coined for it the term atom transfer radical polymerization (ATRP). It is derived from redox atom transfer radical addition and polymerization, a topic thoroughly investigated by Vofsi and colleagues[10] and others[11,12] and used by Pietrasanta and colleagues[13,14] in the field of telomerization.

In atom transfer radical polymerization, initiation involves an equilibrium reaction between a halogenated derivative (e.g., alkyl halide or arylalkyl halide) with a copper(I) halide (in the presence of a ligand, essentially 2,2′-bipyridine) which yields the initiating radical and the oxidized copper derivative. A similar equilibrium is established between the growing radical and the halogen end-capped chain, which may be reactivated (reversible termination). In short, the control results from reversible end-capping of the growing chains:

$$P_nCl \ + \ CuCl \ \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} \ P_n^{\circ} \ + \ CuCl_2$$
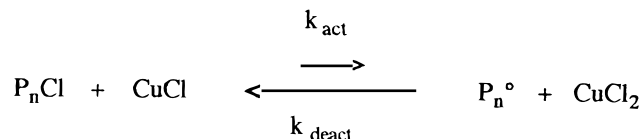
This initiating system allows to control the radical polymerization of a wide range of monomers. Besides, at the end of the polymerization, the chain end still contains an halogen atom which may be used to initiate another polymerization. Consequently, these systems provide an efficient tool for macromolecular engineering,

and the preparation of a wide range of copolymers has been reported: block, alternating and gradient copolymers, and hyperbranched polymers. The possibilities offered by ATRP have been recently reviewed by Matyjaszewski.[15]

However, when bipyridine is used as a ligand for the copper chloride, the ATRP medium is generally heterogeneous in the case of bulk polymerizations, as well as in most solvents. Substituted pyridines,[16,18] phenanthrolines,[19] pyridimines,[20] or multidentate amine ligands[21] can be used in order to obtain a homogeneous system. Some authors have used solvents such as diphenyl ether[17] and xylene[22] in the case of the polymerization of styrene and ethylene carbonate in the case of the polymerization of butyl acrylate,[23] but essentially as diluents without influence on the homogeneity of the medium.

It has been found in our laboratory that a homogeneous reaction medium is easily obtained using unsubstituted bipyridine (Bpy) in the presence of dimethylformamide (DMF, 10% v/v). In this paper, the polymerization of styrene initiated with 1-chloro-1-phenylethane (PECl) and copper(I) chloride in the presence of *N,N*-dimethylformamide is investigated. The possibilities and limitations of this system are discussed.

Experimental Section

Styrene (Acros, 99%) was distilled under reduced pressure from calcium hydride powder before use. Copper(I) chloride (Aldrich, 99.995%), 1-chloro-1-phenylethane (PECl, Acros, 99%), 2,2′-bipyridine (Bpy, Aldrich, 99+%), and *N,N*-dimethylformamide (DMF, Acros, 99+%) were used as received. Experiments with styrene purified under vacuum on sodium films led to similar results.

The reaction mixtures were prepared in a glovebox, under magnetic stirring. The initiator was added last to a mixture of styrene, CuCl, Bpy, and DMF. Filtration of the dark brown solution in the glovebox showed that the CuCl/Bpy complex was completely solubilized. Samples of the stirred 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 cycles of cooling and thawing. The polymerizations were carried out in an oil bath at 130 °C, under magnetic stirring. The polystyrenes were recovered by precipitation in methanol and were pumped

Table 1. Influence of Dimethylformamide on the Kinetics of the Polymerization of Styrene[a]

DMF (vol %)	[DMF] (M)	[styrene] (M)	yield in 3 h	M_w/M_n
10	1.29	7.85	63	1.33
25	3.23	6.54	16	1.77
50	6.46	4.36	5	1.33

[a] $[PECl]_0 = [CuCl]_0 = \frac{1}{3}[Bpy]_0 = 2.27 \times 10^{-2}$ M; temperature = 130 °C.

overnight in a vacuum oven. The yields were calculated from the weight of recovered polymer.

The M_n of the polystyrenes 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 dual-detector system (UV detector and refractometer) with polystyrene standard calibration. The values of the reported polydispersities are calculated without correction for band spreading.

Results and Discussion

The CuCl/Bpy complex is only partially soluble in styrene at room temperature. In the presence of 10% DMF, mixtures of PECl, CuCl, and 2,2′-bipyridine ([PECl]:[CuCl]:[Bpy] = 1:1:3) in styrene yield a homogeneous red-brown solution at room temperature, although quasi-elastic light scattering measurements at room temperature still indicates the presence of trace amount of large aggregates (200−800 nm). However, it has been found that the addition to these solutions of small quantities of $CuCl_2$ (2.3×10^{-3} M) at room temperature leads to a pale green deposit which solubilizes at 130 °C. A reaction carried out at equimolar concentrations of initiating reagents ([PECl]_0 = [CuCl]_0 = 2.27×10^{-2} M), in the presence of DMF (10% v/v) but without Bpy, proceeds slowly (13% yield after 3 h.). The M_n of the polymer was 198 000, instead of 4700 for the controlled process, performed in the presence of Bpy. Therefore, DMF alone allows to operate under homogeneous conditions, but without any control of the polymerization. The influence of DMF concentration on the polymerization kinetics of the regular bipyridine ligated system is shown in Table 1, for a series of experiments at variable DMF-to-styrene ratio. The reaction rate (yield after 3 h) decreases when the DMF-to-styrene ratio increases and becomes negligible for a 1:1 v/v ratio. This may result not only from the corresponding decrease of styrene concentration but also from a possible competitive complexation or ligand exchange of the copper species by the DMF. Nevertheless, the M_n values are still in agreement with the calculated values for a controlled proces ($M_{n,exp} = 6600$; $M_{n,calc} = 5900$ for DMF = 25% v/v).

An ATRP of styrene at 130 °C initiated in the presence of 10% v/v DMF (1.29 M) with PECl and CuCl ([styrene]_0 = 7.86 M, [PECl]_0 = [CuCl]_0 = $\frac{1}{3}$[Bpy]_0 = 2.27×10^{-2} M) is fully controlled ($M_{n,expt} = 21\,400$; $M_{n,calc} = 22\,800$), and the polymerization proceeds through internal first-order kinetics with respect to styrene concentration, as expected for a polymerization involving a constant concentration of active species (Figure 1). The short induction period observed in Figure 1 is irreproducible and never longer than 1 h. The corresponding value of the apparent rate constant (d(ln[M])/d$t = k_p$[P$_n$°]) is 9.0×10^{-5} s^{-1}. This value is consistent with that reported by Matyjaszewski for the bulk polymerization of styrene in the presence of Bpy (k_p [P$_n$°] = 10^{-4} s^{-1}),[24] taking into account the lower concentration of PECl (2.27×10^{-2} M instead of 3.8×10^{-2} M) in our case. However, a higher value (k_p[P$_n$°] =
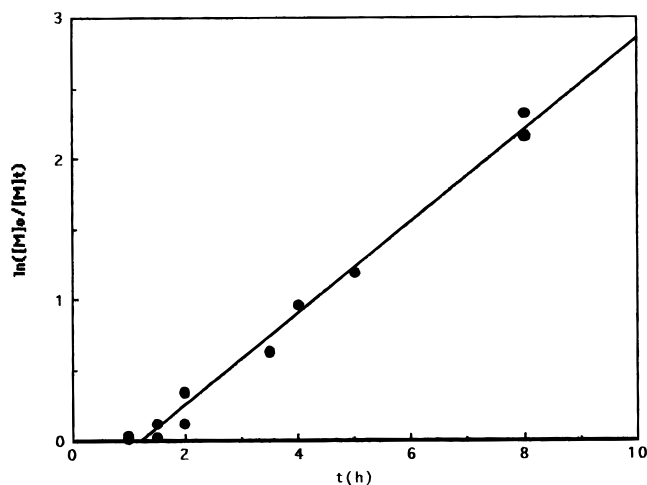

Figure 1. Homogeneous ATRP of styrene at 130 °C in the presence of DMF (10% v/v). First-order kinetics with respect to monomer. [Styrene]_0 = 7.85 M, [PECl]_0 = [CuCl]_0 = $\frac{1}{3}$[Bpy]_0 = 2.27×10^{-2} M.
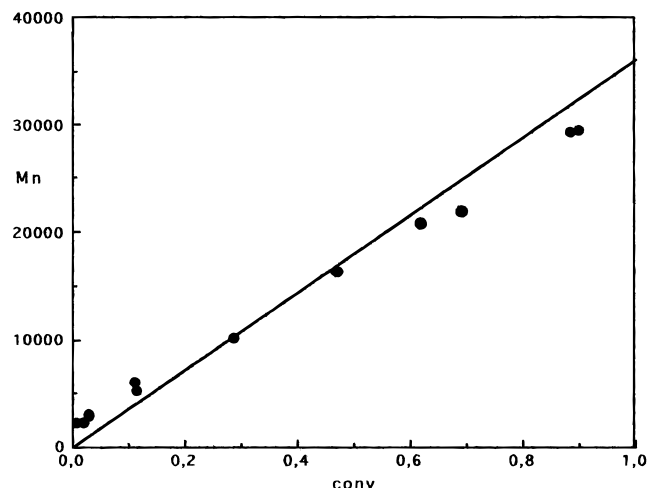

Figure 2. Homogeneous ATRP of styrene at 130 °C in the presence of DMF (10% v/v). Evolution of the M_n with conversion. [Styrene]_0 = 7.85 M, [PECl]_0 = [CuCl]_0 = $\frac{1}{3}$[Bpy]_0 = 2.27 $\times 10^{-2}$ M.

1.6×10^{-4} s^{-1}) has been found by this author in alkylbipyridine-based homogeneous solution at 110 °C[17] for a higher concentration of the initiating species ([CuBr] = 8.7×10^{-2} M at 110 °C). In the present case, assuming a propagation rate constant of 2600 L mol $^{-1}$ s^{-1} for styrene at 130 °C,[25] the concentration of active centers is about 3.5×10^{-8} mol L^{-1}.

The molar mass increases proportionally with conversion up to $M_n = 30\,000$ and agrees with the calculated value for a controlled process (DP$_n$ = ([M]_0 − [M]$_t$)/[I]_0), except for conversions lower than 10%, for which the M_n is slightly higher than the calculated value (Figure 2). This may be due to the fact that, at the beginning of the polymerization, the kinetic chain length l ($l = k_p$-[M]/k_{deact}[CuCl_2]) is high, given the high monomer concentration, and that a larger number of monomer units is added before reversible deactivation takes place. The polydispersity increases sharply at the beginning of the polymerization up to M_w/M_n =1.8 at 10% monomer conversion and decreases with conversion down to M_w/M_n = 1.4 at the end of the reaction (Figure 3). A possible explanation would be that, at the beginning of the polymerization, dead polymers chains are formed through irreversible termination reactions due to the
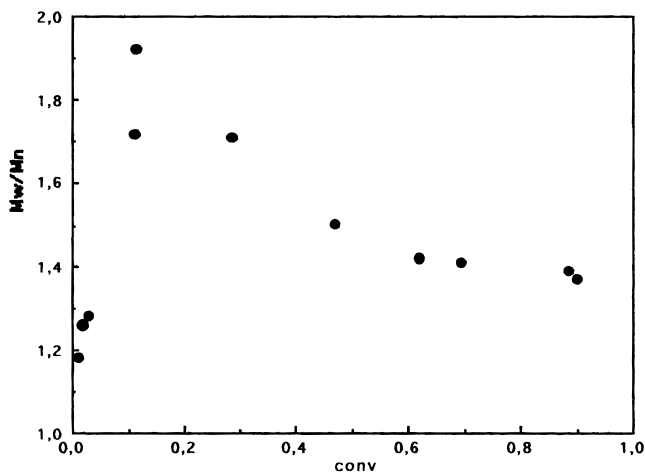
Figure 3. Homogeneous ATRP of styrene at 130 °C in the presence of DMF (10% v/v). Evolution of the polydispersity with conversion. $[Styrene]_0 = 7.85$ M, $[PECl]_0 = [CuCl]_0 = \frac{1}{3}[Bpy]_0 = 2.27 \times 10^{-2}$ M.

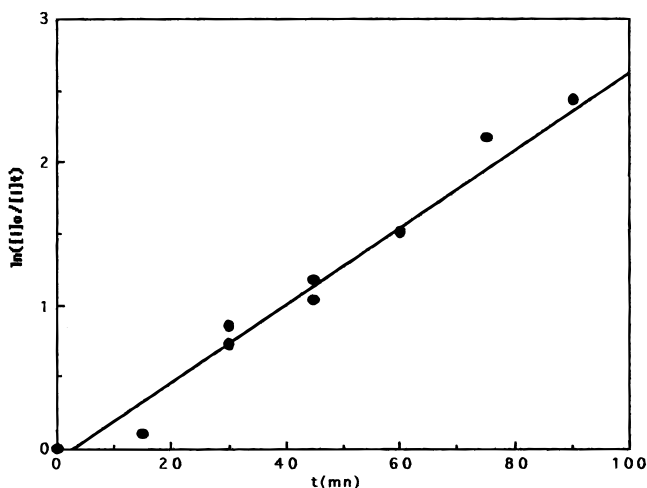**Figure 4.** Homogeneous ATRP of styrene at 130 °C in the presence of DMF (10% v/v). Kinetics of initiation. $[Styrene]_0 = 7.85$ M, $[PECl]_0 = [CuCl]_0 = \frac{1}{3}[Bpy]_0 = 2.27 \times 10^{-2}$ M.

high concentration of initiating radicals formed. Later on, but still at low conversions, the proportion of these dead chains is not negligible with respect to that of reactivable chains, and this broadens the molecular weight distribution. As the polymerization proceeds to higher conversion (higher than 10%), the proportion of dead chains formed becomes negligible and the polydispersity decreases, which implies that the deactivation rate is high with respect to propagation.

The rate of consumption of PECl has been followed by vapor-phase chromatography. The PECl is consumed according to first-order kinetics, and 92% of the PECl has disappeared, i.e., initiation is pratically complete after 90 min (Figure 4), which corresponds to 11% monomer conversion. Consequently, initiation is fast with respect to propagation, which is one of the prerequisites for a controlled polymerization. The initiation rate constant k_i for the consumption of PECl is 2×10^{-2} mol L^{-1} s^{-1}, considering that [CuCl] remains close to its initial value.

The occurrence of reversible deactivation has been evidenced by initiating the polymerization of styrene with a Cl-terminated polystyrene previously prepared by ATRP (precursor: $M_n = 2900$, $I_p = 1.29$). The reaction conditions were $[styrene]_0 = 7.85$ M and $[PS-Cl]_0 =$

Table 2. Chain Extension of a Polystyrene by ATRP[a]

reaction time (min)	yield (%)	M_n(expt)	M_n(calc)	M_w/M_n
240	57	29 500	31 340	1.64
480	88	48 300	47 130	1.49
900	92	52 400	49 135	1.36

[a] Initiator: chlorinated polystyrene. $M_n = 2900$; $M_w/M_n = 1.39$; $T = 130$ °C; $[styrene]_0 = 7.85$ M; $[PECl]_0 = [CuCl]_0 = \frac{1}{3}[Bpy]_0 = 1.63 \times 10^{-3}$ M; DMF = 10% v/v (1.29 M).
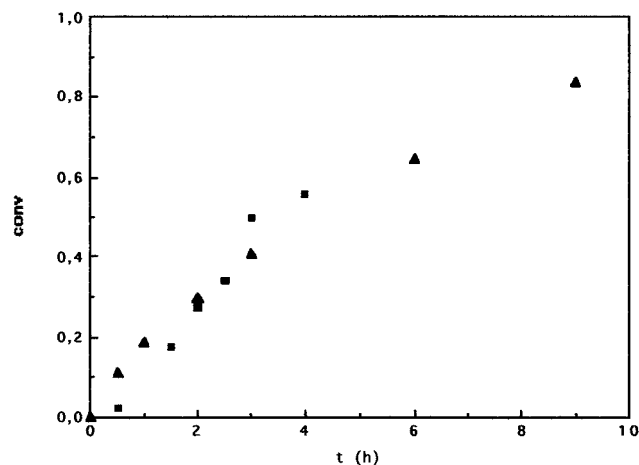

Figure 5. Kinetics of the thermally initiated polymerization of styrene at 130 °C: (■) bulk polymerization, $[styrene]_0 = 8.75$ M; (▲) polymerization in the presence of 10% v/v DMF, $[styrene]_0 = 7.85$ M.

$[CuCl]_0 = \frac{1}{3}[Bpy]_0 = 1.63 \times 10^{-2}$ M. The results in Table 2 show that the M_n of the polystyrene increases with reaction time and is in fair agreement with the calculated values. The M_n of the chain extended polystyrene was 52 400 (calculated value 49 135; $M_w/M_n = 1.36$), and the SEC traces of the polymers show that all the chains of polystyrene precursor have reacted. The polymerization of styrene is controlled under these conditions.

However, two side reactions—thermal initiation and transfer—may interfere with the controlled process.

Thermal initiation of styrene polymerization is not negligible at 130 °C[26] and may take place concurrently with the catalyzed process. Thermal polymerizations of styrene either in the bulk at 130 °C ($[styrene]_0 = 8.75$ M) and in the presence of 10% v/v DMF take place at roughly the same rate (Figure 5) and yield similar molar masses. This shows that DMF alone does not inhibit the polymerization. A comparison of a thermally initiated polymerization in the presence of DMF with an ATRP experiment ($[PECl] = 2.27 \times 10^{-2}$ M) presenting roughly similar rates confirms that for the controlled process polystyrenes with the expected molar masses are obtained whereas for the pure thermal process much higher values practically independent of conversion are observed ($M_n = 170\ 000$) (Figure 6). This suggests that the catalyzed initiation is preponderant under the conditions of the ATRP experiment and that thermal initiation, which should add up to the catalyzed one, is apparently negligible.

Taking into account the respective molar masses at similar conversions of thermally and ATRP initiated polystyrenes, both prepared in the presence of DMF, the concentration of macromolecules resulting from thermal initiation (4×10^{-3} M) is approximately 15% of those resulting from the catalytic process (2.3×10^{-2} M). The
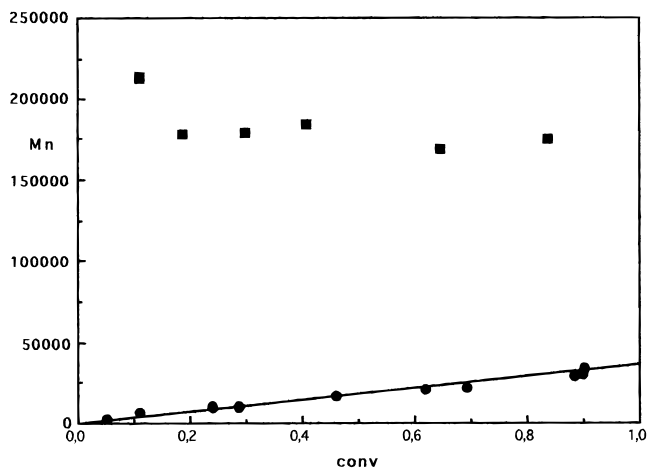
Figure 6. Comparison of thermally initiated and ATRP polymerizations at 130 °C. Evolution of the molecular weight with conversion. (■) Thermal initiation, bulk polymerization, [styrene] = 8.75 M. (▲) ATRP, $[styrene]_0 = 7.85$ M, $[PECl]_0 = [CuCl]_0 = \frac{1}{3}[Bpy]_0 = 2.27 \times 10^{-2}$ M, [DMF] = 1.29 M (10% v/v).

Figure 7. Polymerization of styrene by ATRP at 130 °C. Limit of the control of molar mass: evolution of M_n with conversion for different values of the ratio $[M]_0/[I]_0$ at constant styrene concentration. $[Styrene]_0 = 7.85$ M, $[PeCl]_0 = [CuCl]_0 = \frac{1}{3}[Bpy]_0.$ $[M]_0/[I]_0$: (△) 175, (▲) 350, (○) 650, (■) 1300, (□) 2600, (- - -) calculated values.

Figure 8. Homogeneous ATRP of styrene at 130 °C. Evolution of the apparent rate constant with the concentration of initiating species. [Styrene] = 7.85 M, $[PECl]_0 = [CuCl]_0 = \frac{1}{3}[Bpy]_0$, [DMF] = 1.29 M (10% v/v).

extra chains formed should undergo reversible deactivation by $CuCl_2$ simultaneously with those formed by catalyzed initiation. Thus, taking into account the chains formed by both thermal and catalytic initiation, the value of the M_n at complete conversion should be 31 000 instead of the calculated value of 36 000 for pure catalytic initiation. In the present case, this difference lies within the experimental error of SEC measurement and cannot be detected, but it may no longer be negligible at lower initiator concentrations.

To clarify this point, the influence of the concentration of the catalytic reagents on the kinetics of the polymerization and on the M_n of resulting polystyrenes has been investigated. A series of experiments have been carried out at variable concentration of initiator with a constant ratio of PECl, CuCl, and Bpy (1:1:3), in the presence of 10% v/v DMF.

The evolution of the molar mass with conversion at variable initiator concentrations for $[M]_0 = 7.85$ M shows the progressive incidence of thermal initiation as the $[M]_0/[I]_0$ ratio increases, i.e., when $[I]_0$ decreases (Figure 7). For the two lower ratios (175 and 350), the experimental points fairly fit the calculated values (dotted lines), and the process is fully controlled. In the case of a $[M]_0/[I]_0$ ratio of 650, a slight discrepancy, with M_n lower than the calculated values at high conversions, shows that thermal initiation as well as irreversible termination is no longer negligible. The discrepancy is much more apparent for $[M]_0/[I]_0 = 1300$, but the M_n increases with conversion due to the presence of still enough $CuCl_2$ to allow the reversible termination of chains formed either thermally or through catalyzed initiation. For $M]_0/[I]_0 = 2600$, there is no more control, which means that thermal initiation largely takes over. Thus, it appears clearly that the control of bulk ATRP of styrene at 130 °C is dependent upon the $[M]_0/[I]_0$ ratio, the deviation from the calculated M_n vs conversion plots becoming significant for values of the ratio of about 600. That limits the range of molar mass that can be expected under perfectly controlled conditions at 130 °C to a maximum value of 40 000.

The apparent rate constant obtained from the first-order kinetic plots for the consumption of styrene increases roughly linearly when the concentration of
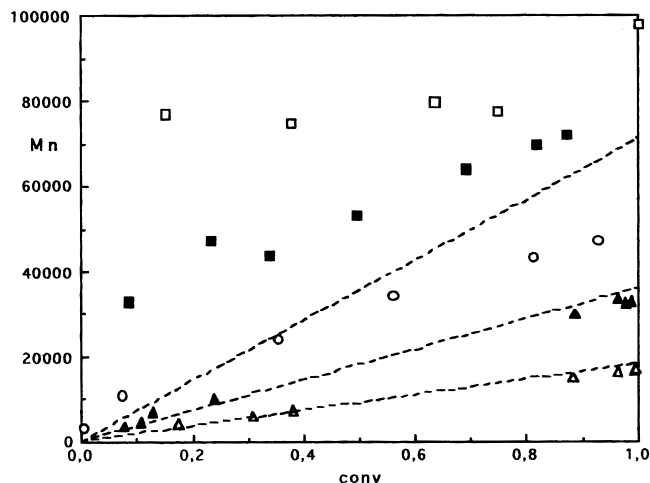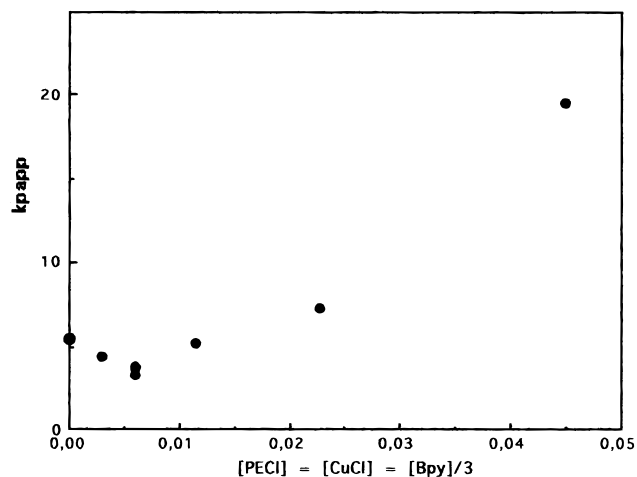
both initiating reagents ($[PECl]_0 = [CuCl]_0$) increases from 6×10^{-3} to 4.5×10^{-2} M (Figure 8). This would mean that in this concentration range the reaction rate should be independent of one of these components. A series of separate experiments at constant $[CuCl]_0$ and variable $[PECl]_0$ concentrations show that the apparent rate constant (i.e., $[P_n°]$ at equilibrium) is independent of the concentration of PECl for $[PECl]_0 < 4 \times 10^{-2}$ M (Figure 9). We are presently investigating the influence of the CuCl concentration. Preliminary results agree with a first order with respect to CuCl, but these experiments need to be confirmed.

For pure thermal initiation at 130 °C in the presence of DMF, the apparent propagation rate constant is 5.4×10^{-5} s⁻¹, and it slightly decreases in the presence of concentrations of PECl/CuCl lower than 6×10^{-3} M. It seems that the presence of small amounts of initiating reagents decreases the stationary concentration of radicals observed in the pure thermal process. A possible explanation might be that, at these very low concentrations of PECl and CuCl, the ATR initiation rate is drastically reduced or even suppressed, whereas
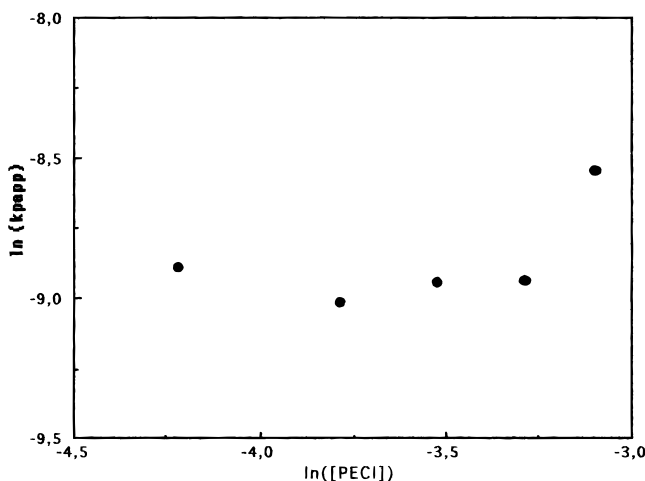
Figure 9. Homogeneous ATRP of styrene at 130 °C. Dependence of the kinetics on the concentration of PECl. $[Styrene]_0$ = 7.85 M, $[CuCl]_0 = {}^1/_3[Bpy]_0 = 4.5 \times 10^{-2}$ M, $[DMF]$ = 1.29 M (10% v/v).

Figure 10. ATRP of styrene at 130 °C. Incidence of transfer to monomer on the molar mass. $[Styrene]_0$ = 7.85 M, $[PECl]_0$ = $[CuCl]_0 = {}^1/_3[Bpy]_0 = 1.2 \times 10^{-2}$ M; T = 130 °C; $[DMF]$ = 1.29 M (10% v/v); (- - -) calculated plot for a controlled polymerization; (—) calculated curve taking transfer into account ($C_M = 3 \times 10^{-4}$); (●) experimental points.

termination by $CuCl_2$ (deactivation of thermally initiated radicals) still remains rapid. The presence of trace amounts of $CuCl_2$ as impurity in the CuCl and slowly consumed during the polymerization could justify the observed minimum for $k_{p,app}$ (and thus for $[P_n^\circ]$) on Figure 8, as the catalytic system now essentially acts as a terminating agent.

Transfer reactions can also take place if the active center in ATRP has the same structure as that involved in conventional radical polymerization. The incidence of transfer to monomer on the molar mass is negligible for experiments carried out at low $[M]_0/[I]_0$ ratios but becomes important at high $[M]_0/[I]_0$ ratios. The value of the transfer constant to styrene at 130 °C is $C_M = 3 \times 10^{-4}$,[27] and for the polymerization of styrene in the presence of 10% DMF ($[M]_0$ = 7.85 M), the concentration $[N]_{tr}$ of chains formed by transfer at complete conversion should be 2.35×10^{-3} M ($[N]_{tr} = k_{trM}[M]_0/k_p$). Consequently, for an initial concentration of PECl ($[PECl]_0$ = 2.27×10^{-2} M) and for complete conversion, about 10% of the macromolecules should be formed by transfer and the M_n should be 10% lower than the calculated value. In the considered case, the difference may still lie within the experimental error in the SEC measurement of M_n, but for higher $[M]_0/[I]_0$ ratios (e.g., 1000), the deviation from the calculated M_n (23%) should be detectable.

Figure 10 shows the evolution of the theoretical M_n with conversion for a unperturbed ATRP process and when the incidence of transfer ($k_{trM}/k_p = 3 \times 10^{-4}$) is taken into account, together with the experimental values for ATRP initiated with 1.2×10^{-2} M PECl. Transfer induces a slight deviation from the calculated values, but at high conversion the experimental molar masses are even lower than those calculated taking transfer into account. This suggests that in this case both thermal initiation and additional transfer take part in the process. Similar results are obtained for $[PECl]_0$ = 6×10^{-3} M. This is still more evident in the case of a lower initiator concentration ($[PECl]_0 = 3 \times 10^{-3}$ M), for which there is no more control as M_n is practically independent of conversion (Figure 7). In this last case, it can be reasonably considered that thermal initiation is predominant.

The main feature of ATRP is the dynamic equilibrium between CuCl and $CuCl_2$. At low temperature (below 80 °C), $CuCl_2$ acts as an inhibitor of radical polymeri-
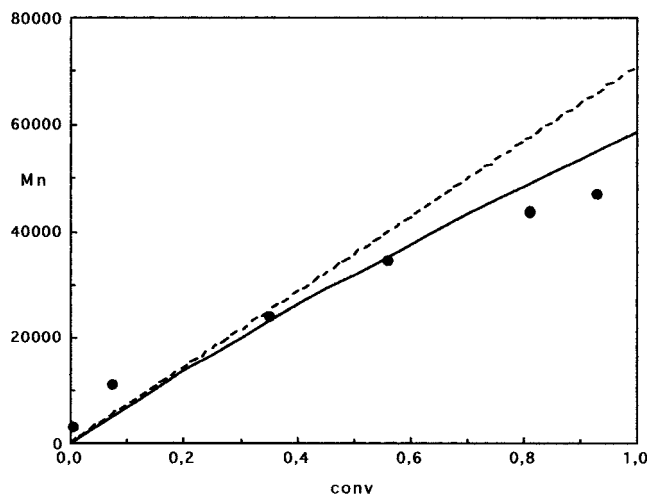
zation by irreversibly terminating the growing chains via a stable carbon–chlorine bond[28] which can only be broken at high temperature. For thermally initiated polymerizations at 130 °C, $CuCl_2$ reversibly deactivates the chains formed by thermal initiation. To investigate the role of $CuCl_2$, the polymerization of styrene by thermal initiation has been carried out in the presence of variable amounts of $[CuCl_2]_0$ (2×10^{-3} and 5×10^{-3} M), in the presence of 2.6×10^{-2} M Bpy and 10% v/v DMF.

First, in both cases, an induction period is observed (1 h for $[CuCl_2]_0 = 2 \times 10^{-3}$ M and 5 h for $[CuCl_2]_0 = 5 \times 10^{-3}$ M). The $CuCl_2$/Bpy complex alone is not completely soluble in styrene at 130 °C. The solutions present a greenish suspension and turn to a brown solution as the $CuCl_2$ solubilizes. This shows that the $CuCl_2$ is progressively transformed into CuCl. A stoichiometric amount of PS–Cl is simutaneously formed, and the composition of the medium then corresponds to that of a regular ATRP experiment with similar concentrations of PECl, P_n°, CuCl, and $CuCl_2$. During the induction period, the macromolecules formed through thermal initiation are terminated by the $CuCl_2$. The polymerization starts only when $CuCl_2$ and is nearly completely converted into CuCl.

Second, for the two thermally initiated polymerizations performed in the presence of $CuCl_2$ (2×10^{-3} and 5×10^{-3} M) the experimental M_n and their evolution with conversion (Figure 11) are close to those observed in ATRP experiments for the lowest initiator concentrations ($[PECl]$ = $[CuCl]$ = 3×10^{-3} and 6×10^{-3} M, Figure 7). This shows that this increase of molar masses is significant and that the chains formed are reactivated by the CuCl formed during the induction period.

Conclusion

The complexes of copper(I) chloride with unsubstituted 2,2′-bipyridine are soluble in styrene at room temperature in the presence of limited amounts of dimethylformamide (~10% in volume), and the polymerization of styrene initiated with 1-chloro-1-phenylethane can be carried out under homogeneous conditions at 130 °C. Initiation is fast and quantitative. Control of
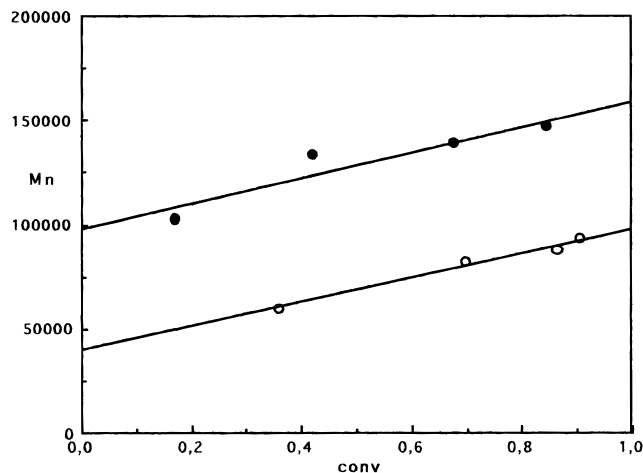
Figure 11. Thermal polymerization of styrene in the presence of CuCl$_2$ and Bpy: partial control of the molar masses. Evolution of the M_n with conversion. [Styrene]$_0$ = 7.85 M, [Bpy] = 6.8 × 10^{-2} M, [DMF] = 1.29 M (10% v/v); T = 130 °C; (●) [CuCl$_2$]$_0$ = 2 × 10^{-3} M; (○) [CuCl$_2$]$_0$ = 5 × 10^{-3} M.

the molar masses is achieved up to M_n = 40 000 (i.e., for a [M]$_0$/[I]$_0$ ratio of about 400) and is still satisfactory up to M_n = 70 000. The polydispersity decreases with conversion, in agreement with the ATRP process. However, for higher [M]$_0$/[I]$_0$ ratios, thermal initiation interferes with the catalyzed process, and control of molar masses is progressively lost, due to the interference of thermal initiation and of transfer. This is in agreement with the fact that, in this range of initiator concentrations, the observed external reaction order with respect to PECl is zero, due to concurrent thermal initiation.

The main limitation of this system is due to the incidence of thermal initiation, at the rather high temperatures necessary for catalytic initiation by chlorinated derivatives. The results should be improved by using brominated initiating reagents instead of chorinated ones, in the presence of DMF. This would allow one to operate in homogeneous systems at lower temperatures and would significantly reduce the incidence of thermal initiation.

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