Metal-Catalyzed "Living" Radical Polymerization of Styrene Initiated with Arenesulfonyl Chlorides. From Heterogeneous to Homogeneous Catalysis

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For more than a decade "living"[1,2] polymerizations generated via the "iniferter" concept[3] provided the only approach, of very limited success, to controlled radical polymerization. More recently, radical polymerizations with reversible termination generated by nitroxide radicals,[4−8] various organometallic derivatives,[9] and metal-catalyzed atom transfer radical addition of alkyl halides[10,11] and arenesulfonyl chlorides[12] produced more successful approaches to this polymerization process. In a previous communication[12] we reported the redox initiation of "living" radical polymerization of styrene with arenesulfonyl chlorides catalyzed by Cu(I)/Cu(II). This polymerization proceeds by initiation via addition of the arenesulfonyl radical to styrene followed by reversible termination with the chlorine radical. The resulting polymers have a chain end derived from the arenesulfonyl radical and one containing a chlorine atom. Our first polymerization experiments were carried out with styrene in bulk in the presence of 2,2′-bipyridine (bpy) which complexes and subsequently *partialy solubilizes* the Cu(I)/Cu(II) catalyst. Therefore, the catalysis of this polymerization is, as in the case of the corresponding systems initiated with alkyl halides,[11] *heterogeneous*. Under our previous conditions we could not reach a very high monomer conversion and only incomplete kinetic data were obtained.[12]

The goal of this communication is to report our first results on the transformation of the catalysis process of this polymerization from *heterogeneous* to *homogeneous*. Experimental conditions and techniques are identical to those reported previously.[12] Four different approaches will be described: (i) polymerizations catalyzed by bpy/Cu(I)/Cu(II) performed in solution instead of bulk; (ii) solubilization of the bpy/Cu complex by attaching substituents in various positions of bpy; (iii) a combination of (i) and (ii); and (iv) the replacement of Cu-based catalyst with some soluble metal catalysts based on Rh, Ru, Pd, and Ni. These experiments will provide an estimate of the efficiency of atom transfer catalyzed organic reaction on the control of this polymerization process.

Figure 1 a−c presents the dependence of conversion and ln $[M]_0/[M]$, respectively, on time for the polymerization of styrene (Sty) initiated with *p*-methoxybenzenesulfonyl chloride (MSC), [Sty]/[MSC] = 100/1 (mol/mol), catalyzed in all cases by [bpy]/[CuCl] = 3/1 (mol/mol), in anisole, dioxane, and xylenes, respectively. These solvents were selected since they are efficient chain transfer agents in conventional free radical polymerizations.

Several important results were obtained from these experiments. The rate of polymerization in solution is lower than expected by taking into account the different monomer concentration and is affected by the nature of the solvent. The highest polymerization rate is in xylenes, followed by dioxane and anisole. Very high and even complete monomer conversions were obtained. A first order of reaction in monomer was observed in all cases. M_w/M_n values are not influenced by the nature of the solvent and vary from 1.3 to 1.5. Figure 2 plots the $M_{n,exp}$ versus $M_{n,th}$ for selected polymer samples obtained in these three solvents. All rates fall on a single line which demonstrates an identical initiator efficiency regardless of solvent (slope equal to 0.86). These results demonstrate the following: (a) the rate of initiation is higher than the rate of propagation; (b) no chain transfer to solvent takes place; (c) the nature of the solvent determines the concentration of the catalyst available in solution which in turn affects the rate of propagation; (d) initiation requires less catalyst than propagation and the concentration of catalyst available in these polymerization systems is higher than that required to provide a rate of initiation higher than that of propagation; (e) an increase in the amount of soluble catalyst via complexation and the use of a solvent enhance the efficiency of the metal-catalyzed atom transfer reaction and subsequently reduces the overall rate of polymerization.

Several bpy derivatives disubstituted with alkyl groups were investigated as complexing agents which produce more soluble Cu complexes than bpy/CuCl. 6,6′-Dioctyl-2,2′-bipyridine, 6,6′-bis[(dodecyloxy)[2,6-dimethylphenyl]-2,2′-bipyridine, and 4,4′-dimethyl-2,2′-bipyridine in conjunction with Cu^ICl and MSC did not yield "living" polymerizations. 4,4′-Dinonyl-2,2′-bipyridine (bpy9)[13] forms a very soluble complex with Cu^ICl, and a "living" polymerization results. The results of the polymerization of styrene initiated with MSC in xylenes and catalyzed with [bpy9]/[CuCl] = 2.3/1 (mol/mol), are plotted in Figure 1c. In this case the rate of polymerization (Figure 1d) is about half of that of the polymerization carried out with the unsubstituted bpy (Figure 1c), while the M_w/M_n values are lower (about 1.30) than those obtained with the heterogeneous catalyst (larger than 1.4). The efficiency of the initiation catalyzed with bpy9/CuCl is indentical to that of bpy/CuCl (Figure 2).

Besides Cu^ICl and $Cu^{II}Cl_2$,[14] $RuCl_2(PPh_3)_3$[15] is also efficient as a catalyst in the atom transfer addition of sulfonyl chlorides to olefins, while $NiCl_2(PPh_3)_2$,[16] $RhCl(PPh_3)_3$,[16] $Pd(OAc)_2-PPh_3$, and $PdCl_2(PPh_3)_2$[17] are known to catalyze the addition of alkyl halides to olefins. All these catalysts are soluble. $NiCl_2(PPh_3)_2$,[16] $Pd(OAc)_2/PPh_3/K_2CO_3$ or NaOAc, $PdCl_2(PPh_3)_2/K_2CO_3$ or NaOAc,[17] and *trans* -bis(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II)[18] yielded uncontrolled radical polymerizations of styrene with arenesulfonyl chlorides as initiators. $RuCl_2(PPh_3)_3$ and $RhCl(PPh_3)_3$ catalyzed the "living" polymerization of styrene initiated with MSC. The efficiency of initiation catalyzed by $RuCl_2(PPh_3)_3$ is lower (slope equal to 0.61) than that catalyzed by bpy/CuCl (slope equal to 0.86) (Figure 2). Figure 3 presents the influence of [catalyst]/[MSC] molar ratio on the M_w/M_n of polystyrene obtained in bulk at 130 °C with $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$, [bpy]/[CuCl] = 3/1 (mol/mol), and [bpy9]/[CuCl] = 2/1 (mol/mol). In all systems a mini-

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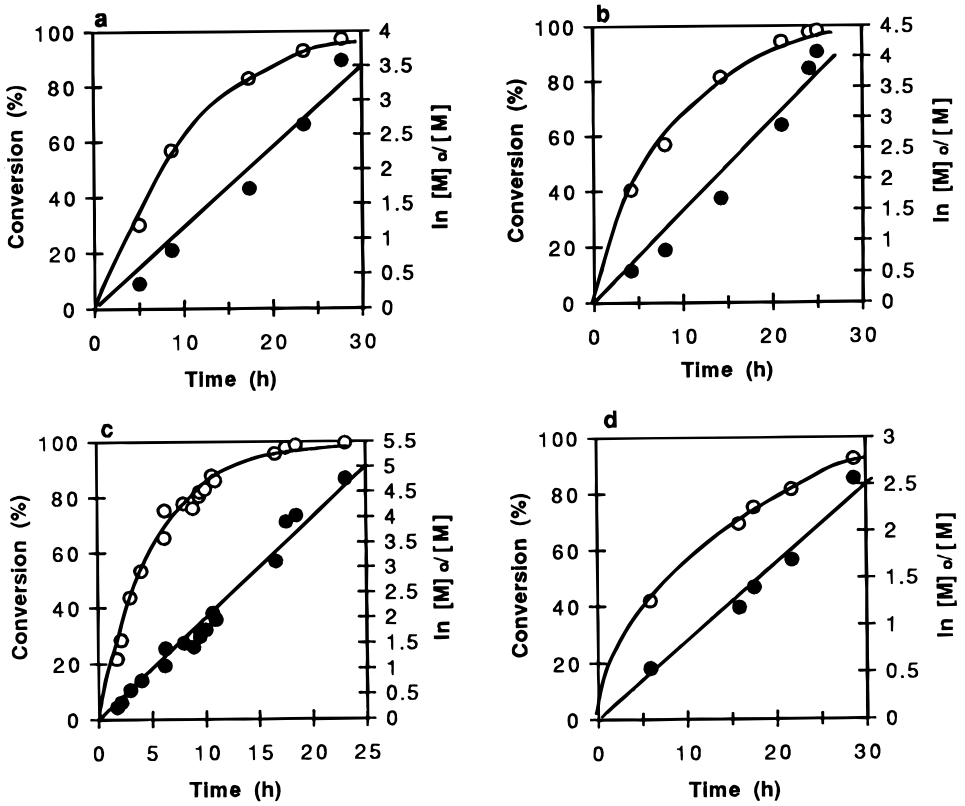

Figure 1. Plots of conversion (%) and ln $[M]_0/[M]$ versus reaction time for the polymerization of styrene with *p*-methoxybenzenesulfonyl chloride (MSC) as initiator at 130 °C ([Sty]/[MSC]/[CuCl] = 100/1/1 (mol/mol/mol), [Sty] = 5.77 mol/L): (a) solvent anisole, catalyst [bpy]/[CuCl] = 3/1 (mol/mol); (b) solvent dioxane, catalyst [bpy]/[CuCl] = 3/1 (mol/mol); (c) solvent xylenes, catalyst [bpy]/[CuCl] = 3/1 (mol/mol); (d) solvent xylenes, catalyst [bpy9]/[CuCl] = 2.3/1 (mol/mol).

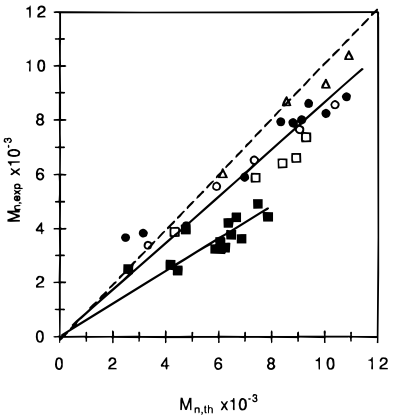

Figure 2. Plots of $M_{n,exp}$ (GPC) versus $M_{n,th}$ for styrene polymerization using *p*-methoxybenzenesulfonyl chloride as initiator ([MSC] = [CuCl] = 57.7 × 10^{-3} mol/L) and 130 °C (for solution, [Sty] = 5.77 mol/L): (○) solvent: anisole, catalyst [bpy]/[CuCl] = 3/1 (mol/mol); (△) solvent dioxane, catalyst [bpy]/[CuCl] = 3/1 (mol/mol); (●) solvent: xylenes, catalyst [bpy]/[CuCl] = 3/1 (mol/mol); (□) solvent xylenes, catalyst [bpy9]/[CuCl] = 2/1 (mol/mol); (■) bulk, $[RuCl_2(PPh_3)_3]$ = 20 × 10^{-3} mol/L.

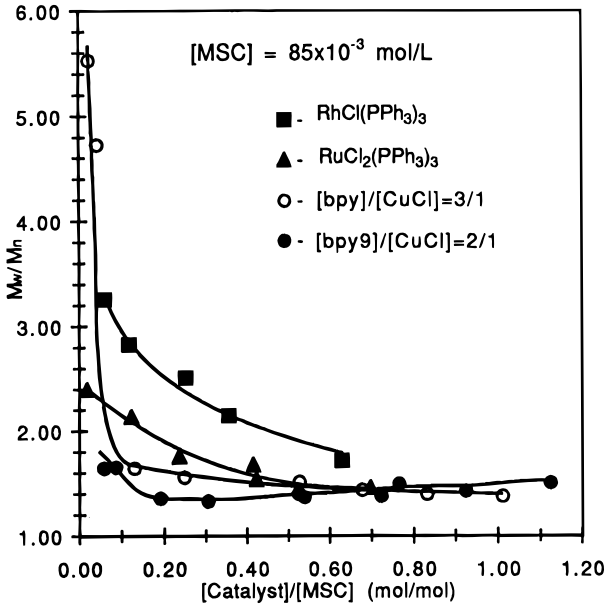

Figure 3. Influence of catalyst nature and concentration on the M_w/M_n of polystyrene obtained in bulk polymerization at 130 °C using MSC as initiator and [Sty]/[MSC] = 100/1 (mol/mol).

mum concentration of catalyst is required to obtain low values of M_w/M_n. Both M_w/M_n values and the rate of polymerization decrease with the increase in catalyst concentration. This demonstrates that the lowest M_w/M_n values are obtained at the highest rate of exchange between the dormant and active species. If we consider that the values of M_w/M_n are determined by the catalyst efficiency, the least efficient catalyst is $RhCl(PPh_3)_3$ followed by $RuCl_2(PPh_3)_3$, bpy/CuCl, and bpy9/CuCl. [Catalyst]/[MSC] molar ratios as low as 0.05 are required for bpy9/CuCl to produce M_w/M_n values of 1.6, while a ratio of 0.3 produces M_w/M_n = 1.3 . Higher molar ratios of bpy9/CuCl do not decrease M_w/M_n . Equivalent M_w/M_n values can be obtained with $[RuCl_2(PPh_3)_3]$/[MSC] = 0.7 (mol/mol). Due to its high molecular weight, at this concentration the Ru-based catalyst approaches the weight concentration of the monomer. Therefore, for both price and quantity reasons the Ru catalyst becomes less practical in the range of concentrations when it becomes efficient.

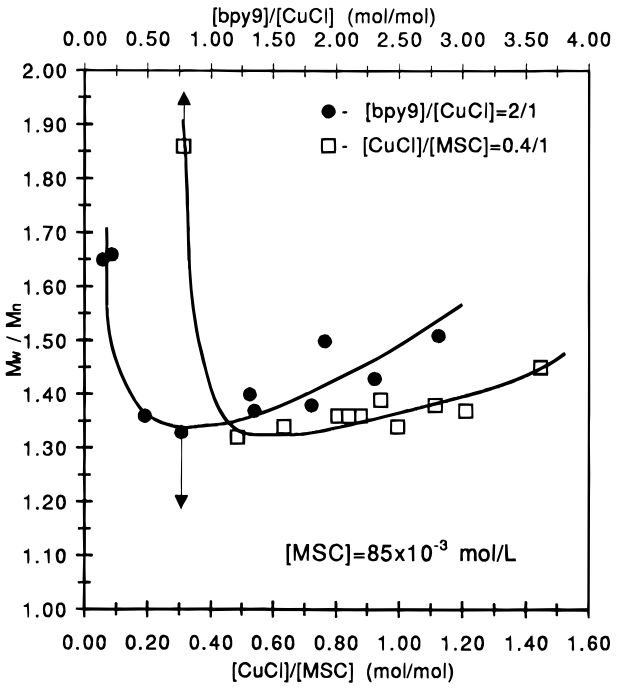

Figure 4. Influence of the molar ratios [CuCl]/[MSC] (at [bpy9]/[CuCl] = 2/1 (mol/mol)) and of [bpy9]/[CuCl] (at [CuCl]/[MSC] = 0.4/1 (mol/mol)) on the M_w/M_n of polystyrene obtained in bulk at 130 °C with [MSC] = 85 × 10^{-3} mol/L.

Figure 4 plots the influence of the molar ratios [bpy9]/[CuCl] and [CuCl]/[MSC] on the M_w/M_n values of polystyrene obtained in bulk at 130 °C. In both cases there is an optimum value. Decreasing the molar ratios of [bpy9]/[CuCl] below 0.5 and of [CuCl]/[MSC] below 0.2 produces larger polydispersities, and the polymerization starts to become uncontrollable. These results are consistent with those in Figure 3; i.e. both suggest that a minimum amount of catalyst is required to control this polymerization process. However, increasing the amount of catalyst above a certain concentration creates a larger concentration of radicals which propagate and consequently broadens the polydispersity (Figure 4). Finally, the most efficient homogeneous catalyst for the atom transfer radical addition to olefins known to date is from the class of bis(*ortho*-chelated)-arylnickel compounds of the type Ni{$C_6H_3(CH_2NRR')_2$-2,6}X.[19] We have synthesized the corresponding catalyst with R = R′= CH_3 and X = Br,[19c] and although its efficiency in the organic reaction (i.e., initiation step) is extremely high, it did not produce a "living" polymerization since it decomposes at the polymerization temperature (higher than room temperature) in a very short time.

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