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"Living" Radical Polymerization of Styrene Initiated by Arenesulfonyl Chlorides and $Cu^{I}(bpy)_{n}Cl$

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Free-radical polymerization with reversible termination has recently generated the longest waiting entry into the field of "living" [1] and/or controlled polymerization reactions.[2] The concept of radical polymerization with reversible termination has been, for many years, *relatively successful* only in the control of polymer molecular weight, chain ends,[3] and in the preparation of star, block, and graft copolymers.[3h] Probably, the most influential effort toward "living" free-radical polymerization was generated by using nitroxide-based radicals as reversible terminating agents since they provided the first examples of polymers with narrow molecular weight distribution.[4−8] Organometallic compounds such as cobalt complexes of porphyrin,[9a] dimethylglyoxime,[9b] and some organoaluminum[9c] derivatives represent the second class of compounds which yielded "living" radical polymerizations via reversible deactivation.

Recently, independent from each other, Sawamoto et al.[10a] reported "living" radical polymerization of methyl methacrylate initiated by $CCl_4/RuCl_2(PPh_3)_3$/MeAl(ODBP)$_2$, while Wang and Matyjaszewski[10b] that of styrene initiated by 1-phenylethyl chloride/CuCl/bpy. By analogy with the well-established metal-catalyzed halogen atom transfer radical addition (ATRA) of alkyl halides to alkenes, Wang and Matyjaszewski called their novel polymerization reaction "atom transfer radical polymerization" (ATRP).[10b] Sawamoto's polymerization reaction[10a] also proceeds by an ATRA mechanism.[12]

Metal-catalyzed halogen atom transfer radical addition systems were used as initiators for radical polymerizations almost simultaneous with the discovery of the organic reaction.[13] However, with the exception of a report which incorrectly claims a living radical polymerization,[13g] none of these old experiments demonstrated the *symptoms* of "living" and/or controlled polymerization.[13]

Besides alkyl halides, arenesulfonyl chlorides are known to be very efficient in metal-catalyzed ATRA reactions.[14] $Cu^{I}Cl$ and $Cu^{II}Cl_2$,[14a−d] $RuCl_2(PPh_3)_3$,[14e] and other transition metal complexes are efficient catalysts for the ATRA of arenesulfonyl chlorides to alkenes. Unfortunately, the use of arenesulfonyl chlorides in ATRA metal-catalyzed reactions is not mentioned in any of the classic reviews[11b,c] or more recent publications of this field.[15] Electrophilic sulfonyl radicals add reversibly and selectively to nucleophilic alkenes.[16] Therefore, "living" metal-catalyzed ATRP initiated with functional arenesulfonyl chlorides would provide a novel class of initiators useful for the preparation of homopolymers and copolymers with well-defined and dissimilar chain ends which cannot be introduced from alkyl chlorides, block and graft copolymers, and other polymers with more complex architecture.

Table 1. Bulk Polymerization of Styrene with Various *p*-R-Phenylsulfonyl Chlorides [(*p*RPhSC)/Cu(bpy)Cl = 1/1 (molar ratio) at 120 °C]

R	$[M]_0$/ [*p*RPhSC]$_0$	time, h	conv, %	% conv/h	$M_{n,th}$	$M_{n,exp}$	M_w/ M_n
NO_2	37.8	72	16.0	0.2	850	1460	1.60
H	50.1	4.5	72.0	16.0	3930	4900	1.63
F	39.4	5	88.7	17.7	3830	4300	1.80
Cl	49.1	4	74.6	18.7	4020	3900	1.50
CH_3	51.2	3.5	66.9	19.1	3750	3750	1.65
CH_3O	50.8	2.5	56.1	22.4	3170	4000	1.48

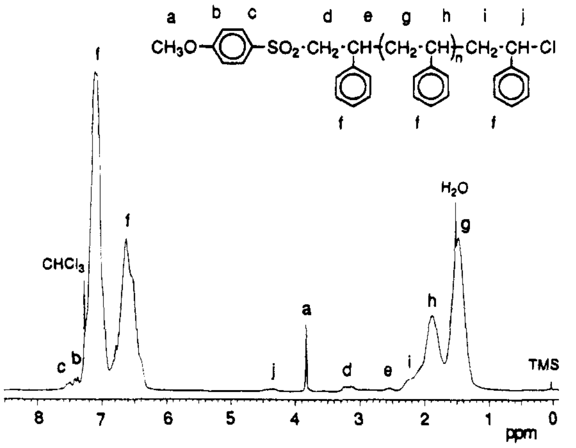

Figure 1. Representative 200 MHz ^{1}H NMR spectrum ($CDCl_3$, TMS) of polystyrene (M_n(GPC) = 3920, M_w/M_n = 1.49; M_n(NMR) = 4280).

Table 1 summarizes representative bulk polymerizations of styrene[17a] initiated with various para-substituted phenylsulfonyl chlorides (*p*RPhSC) catalyzed by the *in situ* prepared complex $Cu^{I}Cl$/2,2′-bipyridine (Cu(bpy)Cl). $M_{n,exp}$ values (determined by GPC with polystyrene standards) agree with the $M_{n,th}$ which were calculated by assuming that each polymer contains one phenylsulfonyl and one chlorine chain end $\{M_{n,th} = ([M]_0/[pRPhSC]_0) \times 104 \times \text{conv} + M_{pRPhSC}\}$. ^{1}H NMR spectra confirmed the structure of these polymers prepared with *p*-fluorobenzenesulfonyl chloride and *p*-methoxybenzenesulfonyl chloride initiators. Figure 1 presents the 200 MHz ^{1}H NMR spectrum of a representative polymer. The ratio between various integrals of the two chain ends demonstrated that the polymer contains only these two chain ends, and the M_n determined from the NMR spectrum agrees with the one determined by GPC. In the case of other initiators, the aryl group derived from arenesulfonyl chloride overlaps with the resonance of the phenyl groups of polystyrene. Previous experiments on CuCl-catalyzed ATRA of arylenesulfonyl chlorides to alkenes were carried out only in acetonitrile and in the absence of any added ligand.[14a−d] In the absence of this solvent, no reaction takes place. The experiments from Table 1 demonstrate that Cu(bpy)Cl, known previously to catalyze ATRA of alkyl chlorides to alkenes in bulk or in nonpolar solvents,[10b,15] also works extremely well in the reaction with arenesulfonyl chlorides.

Chain extension experiments were used to demonstrate the presence of benzyl chloride active chain end in these polymers. For example, 99 mg of polystyrene with M_n = 3750 (M_w/M_n = 1.60) was dissolved in 1.818 g of styrene and polymerized for 6 h at 140 °C with $Cu(bpy)_3Cl$. A polystyrene with M_n = 75 000 (M_w/M_n = 1.32) was obtained (88.8% conversion, $M_{n,th}$ = 61 323).

Figure 2a presents the dependence of $M_{n,exp}$ on conversion and Figure 2b the dependence $M_{n,exp}$ versus $M_{n,th}$ for two polymerizations performed with $[M]_0$/[*p*RPhSC]$_0$ = 100. In both sets of plots, polymers

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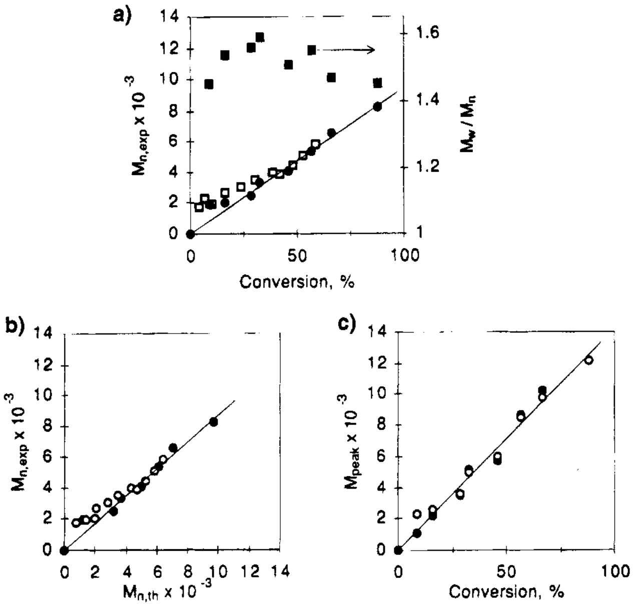


Figure 2. Dependence of $M_{n,exp}$ and M_w/M_n on conversion for bulk polymerization of styrene (a) with *p*RPhSC/CuCl/bpy (1/1/3 molar ratio) (R = Cl, □; R = OCH_3, ●; M_w/M_n, ■). $[M]_0/[p\text{RPhSC}]_0 = 100$, at 130 °C. (b) Dependence of $M_{n,exp}$ vs $M_{n,th}$ for the experiments in (a). (c) M_{peak} versus conversion for precipitated (○) and unprecipitated (●) samples of the experiments from (a) with R = OCH_3.

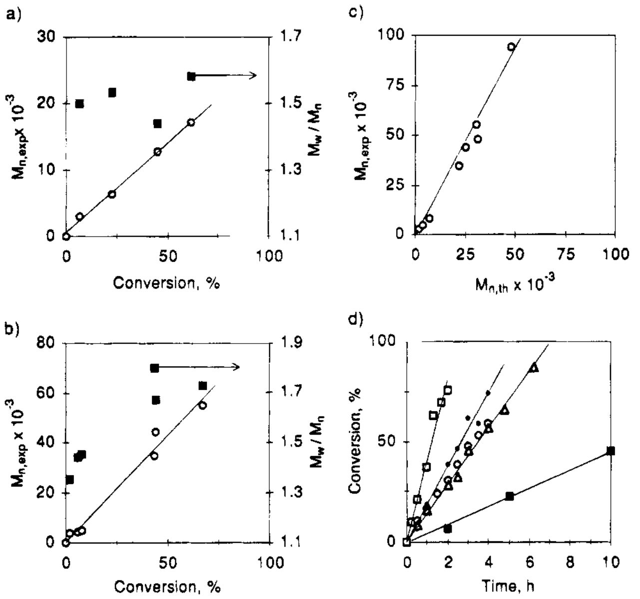
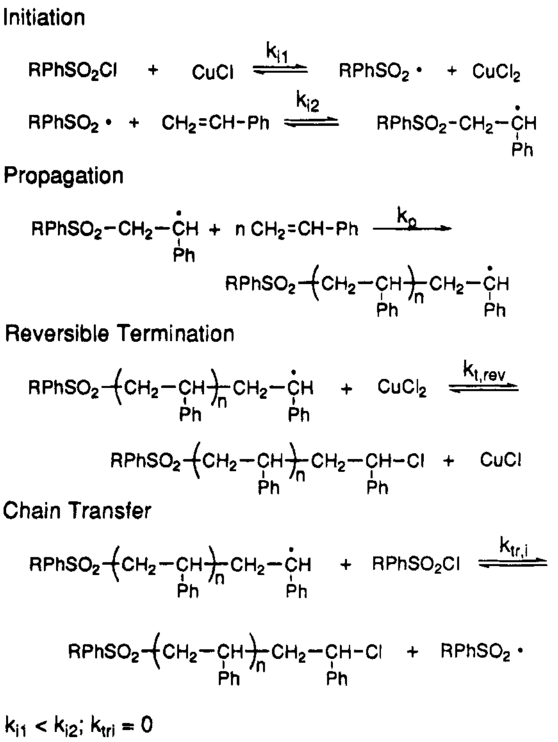


Figure 3. Dependence of $M_{n,exp}$ and M_w/M_n on conversion for bulk polymerization of styrene (a) with *p*CH_3OPhSC/CuCl/bpy (1/1/3 molar ratio) ($[M]_0/[pCH_3OPhSC]_0 = 300$, at 130 °C) and (b) with *p*CH_3OPhSC/CuCl/bpy (1/1/1 molar ratio) ($[M]_0/[pCH_3OPhSC]_0 = 500$, at 140 °C). (c) Dependence of $M_{n,exp}$ vs $M_{n,th}$ for selected polymerizations carried out with *p*RPhSC/CuCl/bpy (1/1/1 molar ratio) at 135 °C. (d) Dependence of conversion on time for selected polymerization experiments. ClPhSC/CuCl/bpy (1/1/1 molar ratio), $[M]_0/[ClPhSC]_0 = 50$: (□) at 140 °C; (●) at 120 °C. RPhSC/CuCl/bpy (1/1/3 molar ratio), $[M]_0/[RPhSC]_0 = 100$: (○) R = Cl at 130 °C; (△) R = OCH_3 at 130 °C. (■) CH_3OPhSC/CuCl/bpy = 1/1/3 (molar ratio), $[M]_0/[CH_3OPhSC]_0 = 300$, at 130 °C.

precipitated from THF solution into methanol were used. The deviation from linearity at low molecular weights is due to fractionation.[17b] The plots from Figure 2c (i.e., M_{peak} vs conversion for fractionated and unfractionated polymers) demonstrate the fractionation of polystyrene samples with $M_n \le 2200$ during the precipitation process.[17c] Figures 3a and b show the linear dependence of M_n versus conversion for two series of experiments carried out with $[M]_0/[p\text{RPhSC}]_0 = 300$ (R = OCH_3) and 500 (R = Cl), while Figure 3c shows the agreement between $M_{n,exp}$ and $M_{n,th}$ obtained from a large variety of experiments. The linear increase of $M_{n,exp}$ with conversion indicates the high efficiency of arenesulfonyl chloride initiators and a constant number of chains. The molecular weight distributions are narrower than expected for a conventional radical polymerization. High conversions are obtained within relatively short reaction times (about 4 h) when polymers with DP = 100 are aimed at (Figure 3d). Regardless of the ratio between Cu^ICl and bpy, the catalyst is not completely soluble in the reaction mixture.

Scheme 1



Based on the mechanism suggested for the metal-catalyzed ATRA, we propose the polymerization mechanism outlined in Scheme 1. The lowest rate constant of the initiation process is k_{i1}.[14b] In the presence of CuCl, the chain transfer to *p*RPhSC is absent[14a] and therefore, the equilibrium of the reversible termination with $CuCl_2$ determines the overall rate of this redox polymerization. The main difference between the present polymerization and that reported previously by Wang and Matyjaszewski[10b] consists in the initiation step, and this might complicate the polymerization kinetics (Figure 3d). However, the range of functional groups which can be introduced as chain ends of polystyrene from arenesulfonyl chlorides opens a large variety of previously unexplored synthetic capabilities for this and other polymers.

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