Disulfonyl Chlorides: A Universal Class of Initiators for Metal-Catalyzed "Living" Diradical Polymerization of Styrene(s), Methacrylates, and Acrylates

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The principal requirement[1] for the wide application of any living polymerization process to the controlled synthesis of polymers with complex architecture[2] is a quantitative and faster initiation than propagation accessible with a large variety of functional initiators and applicable to more than one class of monomers. "Living" radical polymerization techniques presently available are limited to a specific monomer. For example, nitroxide-based initiators are efficient for styrene,[3] while organocobalt complexes are efficient for acrylates.[4] Metal-catalyzed "living" radical polymerization initiated with alkyl halides can be applied to styrene, [5a−c] methacrylates and acrylates.[5b−d] However, for this technique to generate a rate of initiation at least equal to propagation, the structure of the alkyl halide initiator should be adjusted for each class of monomers.[5] The only class of universal initiators which can be applied to metal-catalyzed "living" radical polymerization of styrene, methacrylates, and acrylates are arenesulfonyl chlorides.[6d] Soon after we discovered the heterogeneous and homogeneous "living" radical polymerization of styrene[6a−c] initiated with substituted arenesulfonyl chlorides, we reported their ability to control the polymerization of methacrylates[6c,d] and acrylates.[6d] Depending on the class of monomers used, the rate constants of initiation with substituted arenesulfonyl chlorides are from *five* to *three* orders of magnitude higher than the rate constants of propagation.[6d,e] This difference allows a complete separation of the initiation and propagation processes *via* temperature.[6d,e] This communication reports the application of this kinetic feature to diradical initiators and demonstrates that phenoxybenzene-4,4′-disulfonyl chloride (PDSC) represents the simplest disulfonyl chloride from a class of universal multifunctional initiators for the metal-catalyzed "living" polymerization of styrene(s), methacrylates, and acrylates.

Scheme 1 outlines the most representative kinetic steps of the "living" diradical initiation with phenoxybenzene-4,4′-disulfonyl chloride (PDSC).[7] On the basis of previous kinetic data we can assume the following: $k_{i3} \approx k_{i6} \approx k_{i9} \approx k_{-p1} > k_{i2} \approx k_{i5} \approx k_{i8} \approx k_{p2} > k_{i1} \approx k_{i4} > k_{i7} \gg k_{p1}$. Therefore, both sulfonyl chloride groups of PDSC should initiate before propagation occurs. Equations 7 and 8 are the least probable to occur. In this polymerization, the irreversible termination by combination (eq. 13) will not terminate the chain growth as in the monoradical process and therefore will not change the concentration of growing radicals *per* chain and the chain end functionality of the resulting difunctional polymer. When this reaction occurs, it will affect the polydispersity of the resulting polymers and increase the concentration of $CuCl_2$ present in the reaction system. Termination by disproportionation (not shown) also has a lower effect in the diradical process.

Table 1. Influence of Ligand Structure on the Experimental Rate Constant of Propagation (k_p^{exp}) and the Concentration of Propagating Radicals [P•] for the CuCl Catalyzed Polymerization of S (5.9 M), MMA (6.2 M), BMA (4.5 M), and BA (5.1 M) Initiated with MBSC and PDSC

M	I	ligand	[M]/[I]/[CuCl]/[lig] molar ratio	*T* (°C)	k_p^{exp} (10^{-3} s^{-1})	[P•] (10^{-7} mol/L)[c]
S	PDSC	bpy	200/1/2/6[a]	120	0.032	0.158
S	PDSC	bpy	200/1/2/6[a]	140	0.131	0.395
S	MBSC	bpy	100/1/1/3	120	0.047	0.231
S	MBSC	bpy	200/1/1/3	120	0.025	0.122
S	MBSC	bpy9	200/1/1/2[b]	120	0.019	0.091
MMA	PDSC	bpy	200/1/2/6[a]	90	0.376	2.320
MMA	PDSC	bpy	200/1/2/6[a]	140	2.305	5.811
MMA	MBSC	bpy	100/1/1/3	90	0.509	3.144
MMA	MBSC	bpy	100/1/0.5/1.5	90	0.317	1.958
MMA	MBSC	bpy	200/1/1/3	90	0.246	1.519
MMA	MBSC	bpy9	200/1/1/2[b]	90	0.020	0.123
BMA	PDSC	bpy	200/1/2/6[a]	90	0.251	
BMA	PDSC	bpy	200/1/2/6[a]	140	1.096	
BMA	MBSC	bpy9	200/1/1/2[b]	90	0.019	
BA	PDSC	bpy	200/1/2/6[a]	140	0.318	
BA	MBSC	bpy9	200/1/1/2[b]	140	0.005	

[a] Calculated at *T* (°C) using the Arrhenius parameters. [b] Data are from: Percec, V.; Barboiu, B. *Polym. Prepr.* **1997**, *38* (1), 733. [c] $[P^\bullet] = k_p^{exp}/k_p^{rad}$; for S, $k_p = 10^{7.630}$ L mol^{-1} s^{-1} exp(−32.51 kJ mol^{-1}/*RT*); for MMA, $k_p = 10^{6.423}$ L mol^{-1} s^{-1} exp(−22.34 kJ mol^{-1}/*RT*): IUPAC Commission on Polymer Characterization and Properties. *Pure Appl. Chem.* **1996**, *68*, 1491.

Table 2. [CuCl]/[bpy]-Catalyzed Polymerization of BMA Initiated with PDSC in Diphenyl Ether at 165 °C[a]

entry	exptl cond mixture/reaction[b]	reaction time (min)	conv (%)	M_{th}	M_n	M_w/M_n
1	freeze-thaw/Ar blanket	30	84	24 220	25 500	1.20
2	freeze-thaw/N_2 flow	27	82	23 670	25 000	1.19
3	Ar purged/Ar blanket	50	85	24 560	17 300	1.38
4	Ar purged/N_2 flow	40	83	23 940	15 000	1.39

[a] Reaction conditions: [BMA] = 5.14 M; [BMA]/[PDSC]/[CuCl]/[bpy] = 200/1/2/6 molar ratios. [b] Experimental conditions for the deoxygenation of the reaction mixture and for the polymerization reaction.

Figure 1 presents selected examples of kinetic experiments for the heterogeneous polymerization of styrene (S), butyl methacrylate (BMA), and butyl acrylate (BA) initiated with PDSC and catalyzed by CuCl/bpy. The dependence of conversion and ln$[M]_0/[M]$ *vs* time and M_n (GPC) *vs* M_{th} (M_{th} = conv × M_{ru} × $[M]_0/[I]_0$ + $FW_{initiator}$) (where M_{ru} = repeat unit mass) demonstrate a 100% initiation efficiency, a first order of the rate of polymerization in [M], and a constant steady state concentration of radicals through the polymerization process. At high conversion M_w/M_n values approach 1.2 for PS, 1.1 for PBMA, and 1.3 for PBA. These values are higher than those obtained in the homogeneous polymerization process.[6c,d] Figure 2 presents ^{1}H-NMR spectra of PMMA and PDSC together with their protonic assignments and the comparison of experimental M_n(NMR) (M_n(NMR) = 4e/3b × 100 + $M_{initiator}$) and M_n(GPC) values. The upfield shifts of signals a′ and b′ of PDSC into a and b in PMMA demonstrate the diradical polymerization process. Two polymerization experiments for BMA are plotted in Figure 1c. They demonstrate a ±3% reproducibility. As in the case of homogeneous polymerization experiments[6d] the rate of polymerization of S is lower than that of MMA, BMA, and BA, respectively (Table 1). Complete conversion for a molar ratio $[M]_0/[PDSC]_0$ = 200 (M_n depending on the M structure is 25 000−30 000) can be obtained within

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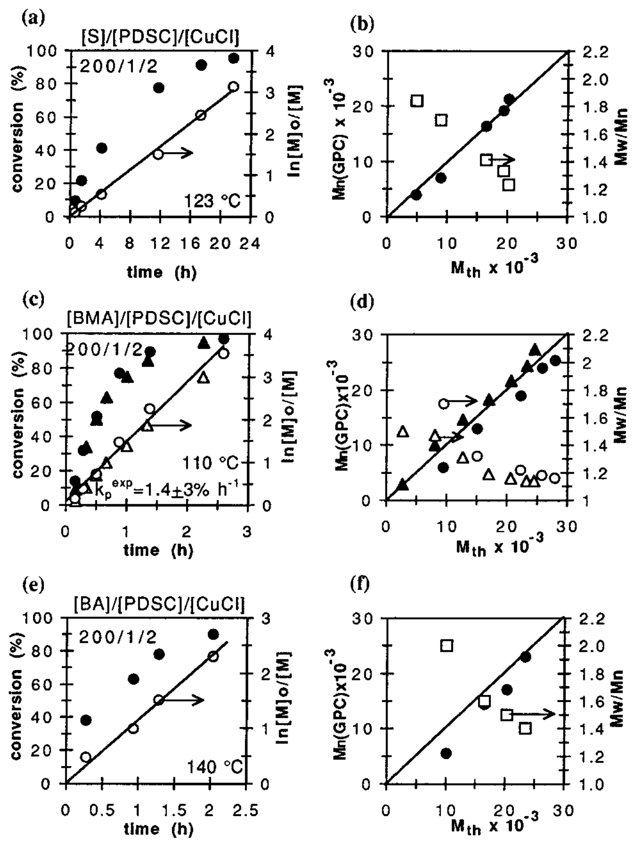


Figure 1. Kinetic plots for the CuCl/bpy-catalyzed heterogeneous diradical polymerization initiated with phenoxybenzene-4,4′-disulfonyl chloride (PDSC): (a, b) S ([S] = 5.9 M, *p*-xylene, 123 °C); (c, d) BMA ([BMA] = 4.5 M, PhOPh, 110 °C, duplicated experiment); (e, f) BA ([BA] = 5.1 M, PhOPh, 140 °C), all using [M]/[PDCS]/[CuCl]/[bpy] = 200/1/2/6 molar ratios.

less than 3 h for the polymerization of methacrylates and acrylates above 100 °C. Figure 3 shows experiments in which larger molar ratios $[M]_0/[PDSC]_0$, i.e., $[MMA]_0/[PDSC]_0 = 1000$ and $[BMA]_0/[PDSC]_0 = 2500$, were used. They demonstrate that this process can be controlled, at least, up to $M_n = 100\,000$ for MMA and $M_n = 300\,000$ for PBMA. The k_p^{exp} values obtained from polymerization experiments performed at several different temperatures were used to construct Arrhenius plots (S, $E_a = 94.51$ kJ/mol, $\ln A = 26.76$; MMA, $E_a = 45.23$ kJ/mol, $\ln A = 15.29$; BMA, $E_a = 36.74$ kJ/mol, $\ln A = 12.07$). The order of reaction in [CuCl] is 0.8 (Supporting Information).

Table 1 summarizes k_p^{exp} and $[P^\bullet]$ values calculated from the Arrhenius plots in Figure 5 of the Supporting Information for diradical polymerization of S, MMA, BMA, and BA initiated with PDSC. They are compared with the corresponding values obtained for the monoradical initiation experiments performed with *p*-methoxybenzenesulfonyl chloride (MBSC) under heterogeneous (CuCl/bpy)[6a] and homogeneous (CuCl/bpy9, where bpy9 is 4,4′-dinonyl-2,2′-bipyridine)[6b] catalyzed processes.[6d] Due to diradical *vs* monoradical processes, the results obtained with $[M]_0/[PDSC]_0 = 200$ should be compared with the results obtained with $[M]_0/[MBSC]_0 = 100$ since the theoretical DP *per* initiator (SO_2Cl) is 100 in both cases. The results from Table 1 are unexpected. For heterogeneous catalyzed polymerizations k_p^{exp} for $[M]_0/[PDSC]_0 = 200$ should be equal to that obtained for $[M]_0/[MBSC]_0 = 100$ and the corresponding value for the diradical process is always lower. However, the k_p^{exp} values for $[M]_0/[MBSC]_0 = 100$ are, as expected, about twice those obtained for $[M]_0/[MBSC]_0 = 200$. At the same time when the change from heterogeneous to homogeneous catalysis is made, the k_p^{exp} value decreases even more. Even under these conditions the diradical growth produces the same molecular weight polymer as the one generated from the monoradical growth in almost half of the reaction time. It is also interesting to observe from Table 1 that k_p^{exp} values for the diradical heterogeneous system at 140 °C obey the following trend: MMA > BMA > BA > S. For the homogeneous system[6c] the order is BMA > MMA > S > BA. The absolute k_p values for conventional radical polymerization follow the trend BA > MMA > S. The difference between conventional and the present radical polymerizations is due to different concentrations of propagating radicals.[6d] Finally, Table 2 summarizes several polymerizations of BMA carried out at reflux temperature (165 °C) in various open systems. These results also demonstrate an extremely good control of this polymerization.

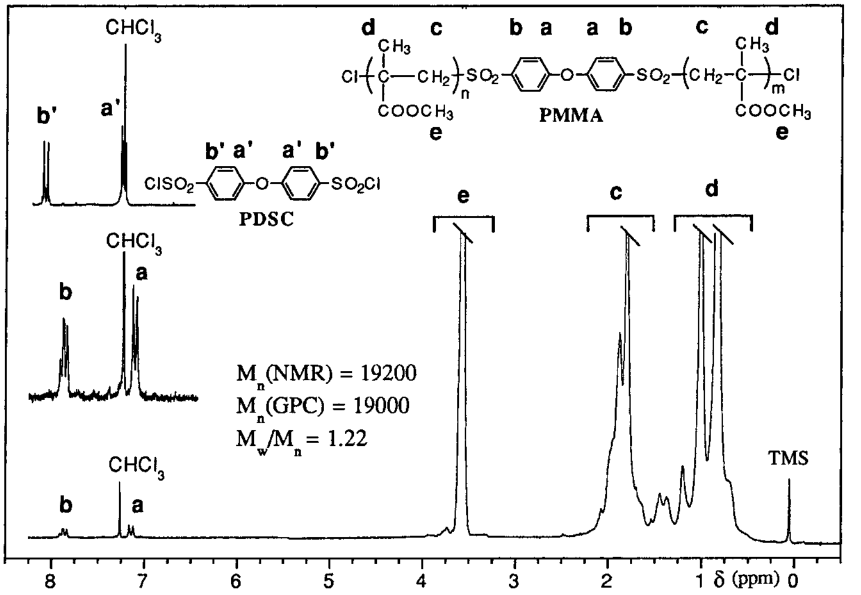
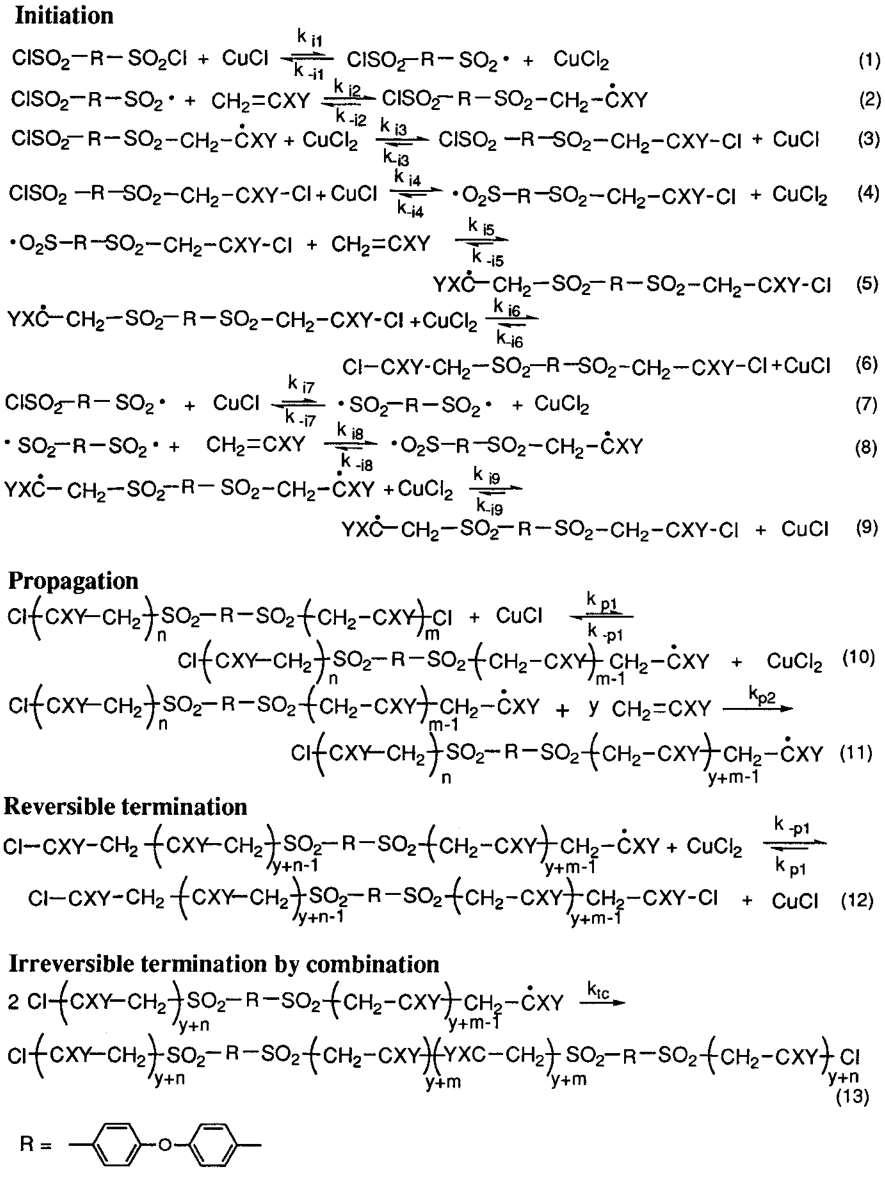


Figure 2. 200 MHz ^{1}H-NMR spectrum ($CDCl_3$, TMS, 20 °C) of PMMA obtained by CuCl/bpy-catalyzed diradical polymerization of MMA initiated with PDSC in *p*-xylene.

Scheme 1. Mechanism of the CuCl/bpy-Catalyzed "Living" Diradical Polymerization Initiated with Phenoxybenzene-4,4′-disulfonyl Chloride (PDSC).



The results reported here are demonstrating the universality of disubstituted arylenesulfonyl chlorides as diradical initiators for living radical polymerization of styrene(s), methacrylates, and acrylates. Previously, the only two classes of diradical initiating systems available were based on dinitroxide[3b,c] and α,α′-halogeno-*p*-xylene.[5g] Both were efficient only for the polymerization of styrene. Kinetic experiments on both homogeneous and heterogeneous diradical and multiradical initiating systems and their use in the synthesis of polymers and copolymers with more complex architecture are in progress.

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Supporting Information Available: Text giving characterization techniques, synthesis of PDSC, and an example of kinetic experiment and figures containing 26 kinetic plots (9 pages). See any current masthead page for ordering and Internet access instructions.

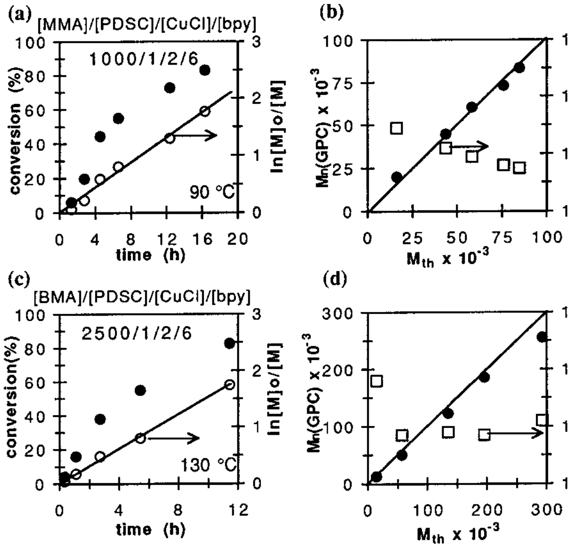

Figure 3. CuCl/bpy-catalyzed diradical polymerization initiated with PDSC: (a, b) MMA ([MMA] = 5.16 M, *p*-xylene, [MMA]/[PDSC]/[CuCl]/[bpy] = 1000/1/2/6 molar ratios, 90 °C); and (c, d) BMA ([BMA] = 4.5 M, PhOPh, [BMA]/[PDSC]/[CuCl]/[bpy] = 2500/1/2/6 molar ratios, 130 °C).

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