Scope and Limitations of Functional Sulfonyl Chlorides as Initiators for Metal-Catalyzed "Living" Radical Polymerization of Styrene and Methacrylates

V. Percec,* H.-J. Kim, and B. Barboiu

The W. M. Keck Laboratories for Organic Synthesis, Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

Received September 16, 1997

Revised Manuscript Received November 6, 1997

Recently, we have demonstrated that functional arenesulfonyl chlorides represent the first class of universal initiators for monoradical[1,2] and diradical[3] metal-catalyzed "living" polymerization of styrene(s),[1−6] methacrylates,[3−6] and acrylates[3,5,6] (Scheme 1). This "universality" (i.e., quantitative and faster initiation than propagation for a variety of functional initiators and several classes of monomers) is facilitated by several particularities of the sulfonyl halides and of the corresponding sulfonyl radicals that make them behave differently from alkyl halides and the corresponding C-based radicals. They are as follows: (a) sulfonyl radicals form much faster than C-based radicals;[7] (b) the reactivity of sulfonyl radicals is much less affected by their substituent than that of C-based radicals;[8] (c) the addition of sulfonyl radicals to olefins is known to tolerate functional groups;[9] (d) the rate of addition of a sulfonyl radical to an olefin such as styrene is little affected by the substituents present on its side group (i.e., phenyl);[10] (e) sulfonyl radicals have an extremely low rate of dimerization by comparison with C-centered radicals, and in the presence of olefins they virtually do not dimerize;[11] (f) even if the addition of sulfonyl radicals to olefins is reversible,[9] under suitable reaction conditions they can add quatitatively to olefins.[3−6] These particularities facilitate a quantitative initiation, which depending on the class of monomers used, is from 5 (styrene) to 3 (methacrylates and acrylates) orders of magnitude faster than propagation.[4−6] Therefore, this "living" radical polymerization does not require a suitable initiator designed for each monomer in part, as is the case for the "living" radical polymerization mediated by nitroxides[12] and organocobalt complexes[13] and for the metal-catalyzed polymerization initiated with alkyl halides,[14,15] to generate an initiation faster or at least equal to propagation. The large difference between the rate of initiation and propagation accessible with sulfonyl halides allows a complete separation of initiation from propagation via temperature[4−6] and opens new possibilities for the synthesis of polymers with controlled architecture.[15] We have demonstrated that arenesulfonyl chlorides containing substituents with electronic character ranging from donor (*p*-methoxy, *p*-methyl) to acceptor (*p*-fluoro, -chloro, -nitro) act as universal initiators in this polymerization process.[1−6]

The goal of this communication is to explore the synthetic utility of functional arenesulfonyl chlorides containing substituents ranging from acidic and electrophilic (−COOH, −OH, halogen, −N═N−) to basic and nucleophilic (methoxy, $-N(CH_3)_2$), placed in the *para* and *ortho* positions of the sulfonyl chloride group, and to expand the scope of sulfonyl chlorides from arylsulfonyl chlorides to alkanesulfonyl chlorides as universal initiators for metal-catalyzed "living" radical polymerization of styrene and methacrylates.

Scheme 1. Mechanism of the "Living" Radical Polymerization Initiated with Substituted Sulfonyl Chlorides

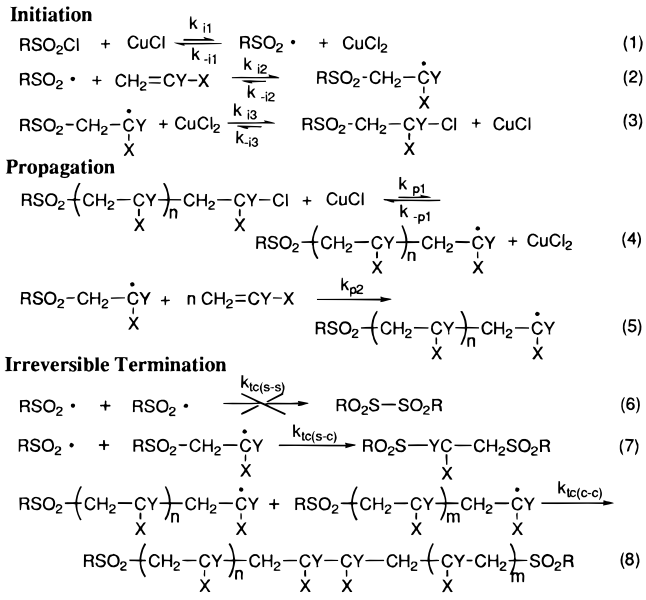

Chart 1. Structures of Sulfonyl Chlorides Used as Initiators in the CuCl/bpy-Catalyzed Radical Polymerization of Styrene, MMA, and BMA

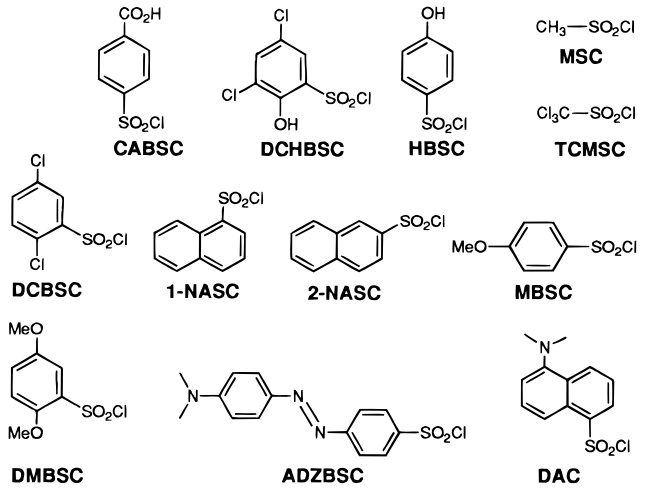

Chart 1 summarizes the group of initiators investigated in heterogeneous (CuCl/bpy, where bpy is 2,2′-bipyridine) metal-catalyzed "living" radical polymerization of styrene(s), methyl methacrylate (MMA), and butyl methacrylate (BMA). Plots of conversion and $\ln[M]_0/[M]$ in time were used to demonstrate a first order in monomer concentration of the rate of polymerization and to determine the experimental value k_p^{exp}. Plots of M_n(GPC) versus M_{th} (where $M_{th} = \text{conv} \times M_{ru} \times [M]_0/[I]_0 + FW_{initiator}$, where M_{ru} = repeat unit mass) and M_w/M_n versus M_{th} demonstrated a 100% initiation efficiency and a constant steady state concentration of radicals (i.e., extremely low extents of termination and chain transfer) through the polymerization process for all initiators shown in Chart 1 (Figures 1 and 2). The kinetic results not shown in these two figures are available in the Supporting Information. Table 1 summarizes M_w/M_n values obtained at the maximum conversion determined, k_p^{exp} values, and the steady state concentration of propagating radicals [P•], assuming that their reactivity is not affected by catalyst.

S0024-9297(97)01375-2 CCC: $14.00

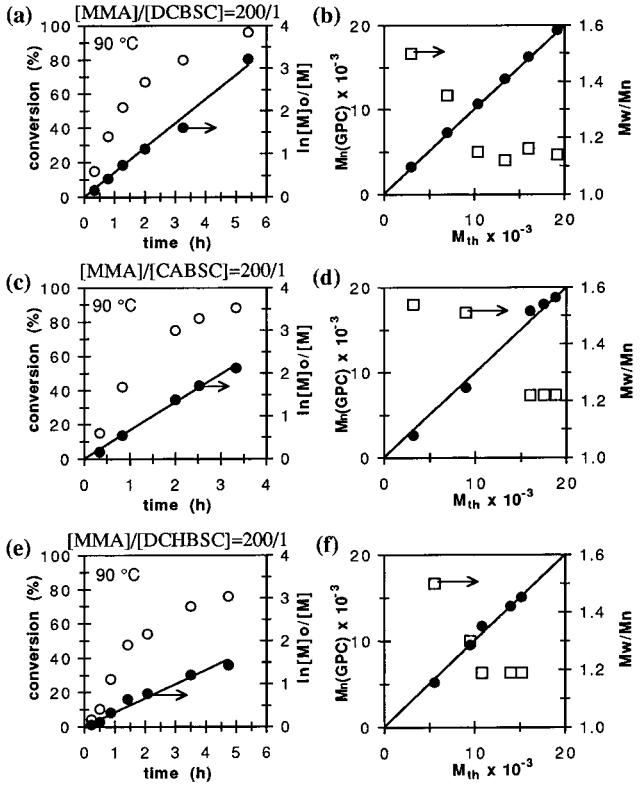

Figure 1. CuCl/bpy-catalyzed polymerization of MMA initiated with (a, b) DCBSC, (c, d) CABSC, and (e,f) DCHBSC in *p*-xylene. Reaction conditions: [MMA] = 6.2 M, [MMA]/[I]/[CuCl]/[bpy] = 200/1/1/3 molar ratio, reaction temperature 90 °C.

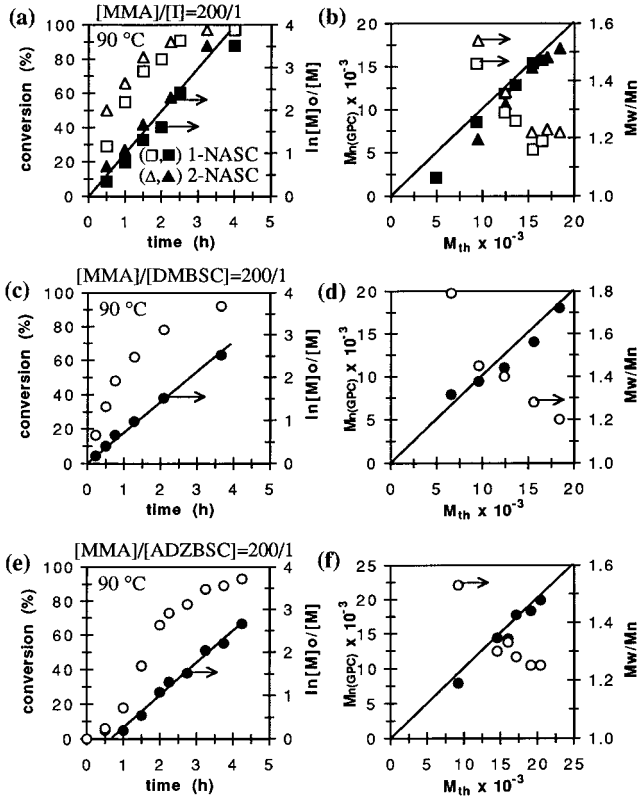

Figure 2. CuCl/bpy-catalyzed polymerization of MMA initiated with (a, b) 1-NASC (squares) and 2-NASC (triangles), (c, d) DMBSC, and (e, f) ADZBSC in *p*-xylene. Reaction conditions: [MMA] = 6.2 M, [MMA]/[I]/[CuCl]/[bpy] = 200/1/1/3 molar ratio, reaction temperature 90 °C.

The first rewarding result is that free carboxylic (CABSC) and phenol groups (DCHBSC and HBSC) placed in either the *para* or *ortho* positions to the sulfonyl chloride are tolerated by this polymerization process (Figure 1) without affecting its rate (Table 1).

The *ortho* substituent effect was tested by using both electron-withdrawing (chloro in DCBSC and phenol in DCHBSC) (Figure 1a,b,e,f) and electron-donating (methoxy in DMBSC) (Figure 2c,d) substituents. The same effect was investigated by using 1-NASC and 2-NASC as initiators (Figure 2a,b). No significant effect of *ortho* substitution on k_p^{exp} was observed (Table 1).

Figure 3 shows the ^{1}H-NMR spectrum of PMMA obtained by initiation with CABSC. The quantitative initiation can be estimated from the complete upfield shift of a′ and b′ from CABSC into a and b resonances after insertion of the initiator as a polymer chain end and from the agreement between the M_n(GPC) and M_n(NMR) = e/3 × 4/(a + b) × 100 + FW_{CABSC}. Changing the nucleophilic character of the aromatic ring attached to the sulfonyl chloride from DCBSC to 1- and 2-NASC, MBSC, and DMBSC also does not affect the "livingness" of this polymerization process.

Figure 2e,f shows the kinetic data for polymerization of MMA initiated with the very nucleophilic and basic ADZBSC. After a small induction period created by the limited solubility of this initiator in the reaction medium, a "living" polymerization process occurs. Interestingly, since this initiator is a dye, the resulting polymer is colored (orange to yellow). Its color is determined by the amount of initiator present at its chain end (i.e., its DP). Polymerization initiated with dansyl chloride (DAC) is slower and yields a polymer with a broader polydispersity (Table 1). No explanation for this behavior is available.

Table 1. Experimental Rate Constants of Propagation (k_p^{exp}) and the Concentration of Propagating Radicals ([P•]) for the CuCl/bpy-Catalyzed Radical Polymerization of S (5.9 M), MMA (6.2 M), and BMA (4.9 M) Initiated with Substituted Arenesulfonyl Chlorides[a]

M	I	M_w/M_n (conv, %)	T (°C)	k_p^{exp} (10^{-4} s^{-1})	[P•] (10^{-8} M)[b]
S	CABSC	1.38 (96)	130	0.50	0.19
S	DCHBSC	1.40 (85)	130	0.53	0.20
S	HBSC	1.53 (90)	130	0.36	0.14
S	MBSC	1.25 (93)	130	0.39	0.15
S	MSC	1.49 (89)	130	0.59	0.23
MMA	CABSC	1.22 (88)	90	1.83	0.70
MMA	DCHBSC	1.19 (76)	90	0.92	0.35
MMA	HBSC	1.27 (89)	90	1.50	0.57
MMA	TCMSC	1.21 (91)	90	1.50	0.57
MMA	DCBSC	1.14 (96)	90	1.58	0.61
MMA	1-NASC	1.19 (97)	90	2.44	0.94
MMA	2-NASC	1.22 (97)	90	2.97	1.14
MMA	MBSC	1.18 (94)	90	2.44	0.94
MMA	DMBSC	1.20 (92)	90	1.81	0.69
MMA	ADZBSC	1.25 (93)	90	2.08	0.80
MMA	DAC	1.60 (93)	90	0.54	0.21
MMA	MSC	1.35 (89)	90	2.87	1.10
BMA	CABSC	1.26 (92)	120	3.42	
BMA	MBSC	1.24 (98)	120	3.42	
BMA	MSC	1.27 (94)	120	7.50	

[a] [M]/[I]/[CuCl]/[bpy] = 200/1/1/3 molar ratio. [b] [P•] = k_p^{exp}/k_p^{rad}. For S: $k_p^{rad} = 10^{7.630}$ L mol^{-1} s^{-1} exp(−32.51 kJ mol^{-1}/RT). For MMA: $k_p^{rad} = 10^{6.423}$ L mol^{-1} s^{-1} exp(−22.34 kJ mol^{-1}/RT). From: IUPAC Commission on Polymer Characterization and Properties. *Pure Appl. Chem.* **1996**, *68*, 1491.

Finally, the polymerization of styrene, MMA, and BMA was initiated with methanesulfonyl chloride (MSC), and that of MMA, with trichloromethanesulfonyl chloride (TCMSC). The successful polymerization results summarized in Table 1 demonstrate the expansion of

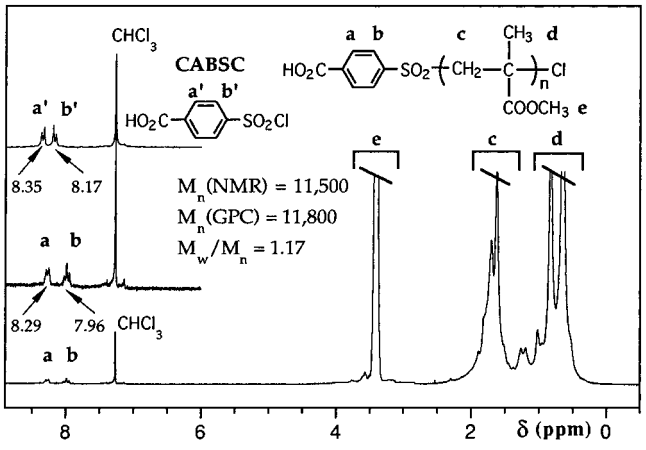

Figure 3. 200 MHz ^{1}H-NMR spectrum ($CDCl_3$, TMS, 20 °C) of PMMA obtained by CuCl/bpy-catalyzed radical polymerization of MMA initiated with *p*-carboxybenzenesulfonyl chloride (CABSC) in *p*-xylene (M_n(NMR) = 11 500, M_n(GPC) = 11 800, M_w/M_n = 1.17).

this class of initiators from arenesulfonyl chlorides to alkanesulfonyl chlorides.

In conclusion, the experiments reported here have demonstrated a remarkable synthetic utility for functional aromatic and aliphatic sulfonyl chlorides as initiators in the metal-catalyzed "living" radical polymerization of styrenes and methacrylates. Since aromatic and aliphatic sulfonyl chlorides tolerate a variety of functional groups in their structure and maintain quantitative and faster initiation than propagation for styrene and methacrylates, they provide a much broader versatility for chain end functionalization by initiation than alkyl halide initiators.[14] However, even if the initiation is faster than the propagation, the nature of the initiator affects the k_p^{exp} values (Table 1), most probably by small extents (less than detectable by the analytical techniques used) of side reactions (for example, the irreversible termination in the initiation step eq 7, Scheme 1, etc.) which subsequently creates an excess of $Cu^{II}Cl_2$ that controls the steady state concentration of [P•] in the polymerization process.

Acknowledgment. Financial support from the National Science Foundation (DMR-9708581), a fellowship from BP for B.B., and an unrestricted faculty award from DuPont are gratefully acknowledged.

Supporting Information Available: Characterization techniques, syntheses of CABSC and HBSC, an example of a kinetic experiment, determination of k_p^{exp} from polymerization experiments, and five figures containing 13 kinetic plots (9 pages). See any current masthead page for ordering and Internet access instructions.

References and Notes

(1) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.
(2) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.
(3) Percec, V.; Kim, H.-J.; Barboiu, B. *Macromolecules* **1997**, *30*, 6702.
(4) (a) Percec, V.; Barboiu, B.; Hill, D. H. *Abstracts of the 36th IUPAC International Symposium on Macromolecules*, Seoul, Korea, August 4−9, 1996; Polymer Society of Korea: Seoul, 1996; p 68. (b) Barboiu, B.; Percec, V. *Abstracts of the 36th IUPAC International Symposium on Macromolecules*, Seoul, Korea, August 4−9, 1996; Polymer Society of Korea: Seoul, 1996; p 671.
(5) Percec, V.; Barboiu, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 733.
(6) Percec, V.; Barboiu, B.; Kim, H.-J. *J. Am. Chem. Soc.*, in press.
(7) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**, 4962.
(8) Orochov, A.; Asscher, M.; Vofsi, D. *J. Chem. Soc. B* **1969**, 255.
(9) Sinnreich, J.; Asscher, M. *J. Chem. Soc. Perkin Trans. 1* **1972**, 1543.
(10) Orochov, A.; Asscher, M.; Vofsi, D. *J. Chem. Soc. Perkin Trans. 2* **1973**, 1000.
(11) da Silva Corrêa, C. M. M.; Waters, W. A. *J. Chem. Soc. C*, **1968**, 1874.
(12) (a) Kazmaier, P. M.; Daimon, K; Georges, M. K.; Hamer, G. K.; Veregin, R. P. N. *Macromolecules* **1997**, *30*, 2228. (b) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323.
(13) Wayland, B. B.; Pozmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.
(14) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901. (c) Grannel, C.; Dubois, Ph.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1996**, *29*, 8576. (d) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules*, **1997**, *30*, 2190. (e) Haddleton, D. M.; Waterson, C.; Derrick, P. J.; Jasieczek, C. B.; Shooter, A. J. *Chem. Commun.* **1997**, 683. (f) Haddleton, D. M.; Clark, A. J.; Crossman, M. C.; Duncalf, D. J.: Heming, A. M.; Morsley, S. R.; Shooter, A. J. *Chem. Commun.* **1997**, 1173.
(15) (a) Fréchet, J. M. J.; Hemni, M.; Gitsov, I.; Aoshima, S.; Leduc, S.; Grubbs, R. B. *Science* **1995**, *269*, 1080. (b) Grubbs, R. B.; Hawker, C. J.; Dao, J.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 270.

MA971375G