Arenesulfonyl Halides: A Universal Class of Functional Initiators for Metal-Catalyzed “Living” Radical Polymerization of Styrene(s), Methacrylates, and Acrylates[†]

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

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

Received April 30, 1997

Abstract: The complex Cu(I)Cl/4,4′-dinonyl-2,2′-bipyridine (bpy9) catalyzes via a redox process the homogeneous “living” radical polymerization of styrene(s), methacrylates, and acrylates initiated with a variety of functional phenylsulfonyl chlorides. Polymers with narrow molecular weight distribution and molecular weights close to the theoretical ones are obtained from these three classes of monomers. Kinetics of propagation and initiation were performed with selected substituted phenylsulfonyl chlorides and with their monoadducts to monomer. Polymerizations follow first-order kinetics internally in monomer and externally in Cu(I)Cl while initiation is first order internally in initiator and in Cu(I)Cl concentrations. A catalyst concentration dependence of the optimum bpy9/Cu(I)Cl ratio which yields the largest rate constant of polymerization was observed. The apparent rate constants of propagation corrected for catalyst concentration are in the order: methacrylates > styrene > acrylates. This inversion from the classic dependence of the corresponding absolute rate constants (acrylates > methacrylates > styrene) was shown to be determined by a different steady-state concentration of propagating radicals which is in dynamic equilibrium with an extremely large excess of the corresponding dormant C−Cl species. The formation and the concentration of the radical species is determined by the C−Cl bond strength of the dormant species. Apparent rate constants of initiation corrected for catalyst concentration are in the order: styrene > methacrylates > acrylates. Within experimental error, initiation efficiency is 100% and the apparent rate constants of initiation are 4 (for styrene and methacrylates) and 3 or 2 (for acrylates) orders of magnitude higher than those of propagation. The absence of conjugation between the sulfonyl radical and its phenyl group generates a small effect of the phenyl group substituent on the rate constant of initiation. These results demonstrate that arenesulfonyl chlorides are the first *class of universal functional initiators* for the metal-catalyzed “living” radical polymerization of styrene(s), methacrylates, and acrylates. This discovery provides numerous fundamental and technological opportunities in the field of controlled radical polymerization and copolymerization, of well-defined functional polymers and copolymers with complex architecture, and of self-organized supramolecular systems based on them.

Introduction

Substituted and unsubstituted aryl- and alkylsulfonyl halides undergo bond homolysis, and the resulting sulfonyl radicals subsequently add to substituted and unsubstituted olefins[1−4] and acetylenes[5] without[1−3] and with extrusion of SO_2[2,4] to yield the corresponding alkyl and vinyl halides. This radical reaction (*initiation*) can be spontaneous, or be promoted by UV, various sources of radicals, or thermolysis,[3] and is catalyzed by metals[1,2,4,5] which can reduce the corresponding sulfonyl halide. Depending on the nature of the substituent(s) present on the parent olefin, the resulting alkyl halides can undergo, under related reaction conditions, addition to the same olefin (*propagation*).[6]

This sequence of reactions was recently exploited in our laboratory to generate a novel metal-catalyzed “living” radical polymerization (Scheme 1).[7−9] Although the propagation and

---

[†] Presented in part at the 36th International Symposium on Macromolecules, Seoul, Korea, August 4−9, 1996 (refs 9a,b) and the International Symposium on Advances in Free Radical Polymerization, San Francisco, CA, April 13−17, 1997 (ref 9c).

(1) For representative examples of Cu(I)-catalyzed addition of sulfonyl chlorides to olefins, see: (a) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**, 4962. (b) Orochov, A.; Asscher, M.; Vofsi, D. *J. Chem. Soc. B* **1969**, 255. (c) Sinnreich, J.; Asscher, M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1543. (d) Orochov, A.; Asscher, M.; Vofsi, D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1000. (e) da Silva Correa, C. M. M.; Waters, A. *J. Chem. Soc. C* **1968**, 1874.

(2) For selected examples of Ru(II)-catalyzed addition of sulfonyl chlorides to olefins, see: (a) Kamigata, N.; Sawada, H.; Kobayashi, M. *Chem Lett.* **1979**, 159. (b) Kamigata, N.; Sawada, H.; Kobayashi, M. *J. Org. Chem.* **1983**, *48*, 3793. (c) Kamigata, N.; Ozaki, J.; Kobayashi, M. *J. Org. Chem.* **1985**, *50*, 5045.

(3) For peroxide-induced addition of sulfonyl chlorides to olefins, see: Kharash, M. S.; Zavist, A. F. *J. Am. Chem. Soc.* **1951**, *73*, 964.

(4) For the Ru(II)-catalyzed addition of perfluoroalkanesulfonyl chlorides to olefins with extrusion of SO_2, see: Kamigata, N.; Fukushima, T.; Terakawa, Y.; Yoshida, M.; Sawada, H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 627.

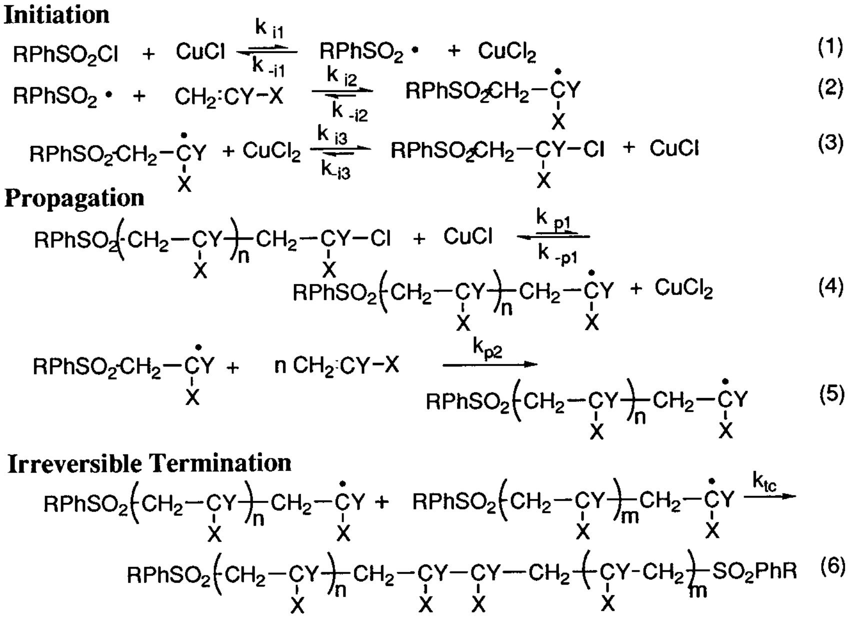
(5) For selected examples of Cu(I)-catalyzed addition of sulfonyl chlorides and bromides to olefins, see: (a) Amiel, Y. *Tetrahedron Lett.* **1971**, 661. (b) Amiel, Y. *J. Org. Chem.* **1974**, *39*, 3867. (c) For UV-initiated addition of sulfonyl iodides to acetylenes, see: Truce, W. E.; Wolf, G. C. *J. Org. Chem.* **1971**, *36*, 1727.

(6) For reviews discussing the monoaddition of alkyl halides to olefins and their telomerization, see: (a) Walling, C.; Huyser, E. S. *Organic Reactions*; Cope, A. C., Ed.; Wiley: New York, 1963; Vol. 13, p 91. (b) Freidlina, R. Kh.; Chukovskaya, E. C. *Synthesis* **1974**, 477. (c) Freidlina, R. Kh.; Velichko, F. K. *Synthesis* **1977**, 145. (d) Curan, D. P. *Synthesis* **1988**, 417, 489.

(7) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.

S0002-7863(97)01384-X CCC: $15.00

Scheme 1. Mechanism of “Living”Radical Polymerization Initiated with Substituted Phenylsulfonyl Chlorides



reversible termination steps of this polymerization are identical with the same steps in the “living” metal-catalyzed radical polymerization initiated with alkyl halides,[10−13] the initiation step of these two polymerizations differs substantially. First, the metal-catalyzed reduction of the substituted arylsulfonyl halides to the corresponding sulfonyl radical should be faster than that of the resulting alkyl halide, and therefore, they facilitate a higher rate of initiation than propagation. A quantitative and faster initiation than propagation is the primary requirement for the synthesis of polymers with narrow molecular weight distribution via a “living” polymerization. The quantitative and fast addition of sulfonyl radicals to activated olefins is assured by their extremely fast rate of formation and extremely low tendency to dimerization in comparison with carbon-based radicals.[1] Second, since the sulfonyl radical is not conjugated with the phenyl group, the nature of the substituent(s) on the arylsulfonyl halide should have relatively little effect on its rate of reduction and initiation.[1b] Third, the addition of arylsulfonyl radicals to olefins is reversible,[1c] and this changes the overal kinetic of initiation. Fourth, the equilibrium of the reversible addition of arylsulfonyl radical to olefins is determined by the nature of the substituent attached to the olefin and its ability to stabilize the resulting radical by resonance.[1a,14]

The monoaddition of sulfonyl and alkyl radicals to olefins and acetylenes followed by the transfer of the halide atom is known as Kharash addition[14a,c,15] or atom transfer radical addition (ATRA).[15] However, more than one radical addition followed by atom transfer is regarded as a side reaction (i.e., oligomerization) of ATRA. Since not only atoms (i.e., also groups of atoms) participate in this reaction and since the number of addition steps before atom transfer is not the most relevant issue in the control of the corresponding polymerization, to avoid confusion, we prefer to use the general name from the title of this paper[7−9,10,12] rather than ATRP[11] for this polymerization process. For example, a mechanistically related “living” radical polymerization to ATRP in which a noncatalyzed reversible termination is generated by a metal coordinated to a ligand (i.e., a noncatalyzed group transfer is generated via a coordinated metalloradical) is also available.[16] Other series of publications on metal-mediated radical polymerizations with unelucidated extends of control, initiated with alkyl halides, are classic pieces of work which contributed to the present state of knowledge in the field of radical polymerization.[17]

---

(8) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.

(9) (a) Barboiu, B.; Percec, V. *Abstracts of the 36th IUPAC International Symposium on Macromolecules*; Seoul, Korea, August 4−9, 1996; p 671. (b) Percec, V.; Barboiu, B.; Hill, D. H. *Abstracts of the 36th IUPAC International Symposium on Macromolecules*; Seoul, Korea, August 4−9, 1996; p 68. (c) Percec, V.; Barboiu, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 733.

(10) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3585.

(11) (a) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (b) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901. (c) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.

(12) Grannel, C.; Dubois, Ph.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1996**, *29*, 8576.

(13) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190.

(14) (a) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; p 223−228. (b) Daiton, F. S.; Ivin, K. J. *Nature* **1953**, *172*, 804. (c) Walling, C.; Huyser, E. S. in *Organic Reactions;* Cope, A. C., Ed.; Wiley: New York, 1963; Vol. 13, p 91.

(15) (a) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 4, pp 715 and 779. (c) Motherwell, W. B.; Crich, D. *Free Radical Reactions in Organic Synthesis*; Academic Press: London, 1992. (d) Minisci, F. *Acc. Chem. Res.* **1975**, *8*, 165.

(16) (a) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943. (b) Arvanitopoulos, L. D.; Greuel, M. P.; Harwood, H. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 549.

(17) For a series of kinetic investigations on the metal-catalyzed radical polymerization initiated with alkyl halides, see: (a) Bamford, C. H.; Eastmond, G. C.; Hargreaves, K. *Nature* **1965**, *205*, 385. (b) Bamford, C. H.; Hargreaves, K. *Nature* **1966**, *209*, 292. (c) For part 23 in the series initiated in refs 17a,b, see: Bamford, C. H.; Hughes, E. O. *Proc. R. Soc. London A* **1972**, *326*, 489. (d) Otsu, T.; Yamaguchi, M.; Takemura, Y.; Kusuki, Y.; Aoki, S. *Polym. Lett.* **1967**, *5*, 697, 835. (e) For part 6 of the series initiated by ref 17a see: Otsu, T.; Yamaguchi, M. *J. Polym. Sci.: Part A-1* **1969**, *7*, 387. (f) Iwatsuki, S.; Kasahara, H.; Yamashita, Y. *Makromol. Chem.* **1967**, *104*, 254. For the first claim of a metal-catalyzed living radical polymerization initiated with alkyl halides and the preparation of block copolymers, see: (g) Otsu, T.; Tazaki, T.; Yoshida, M. *Chem. Expr.* **1990**, *5*, 801. For reviews on organometallic derivatives of transition metals as initiators of free-radical polymerization, see: (h) Bamford, C. H. In *Reactivity, Mechanism and Structure in Polymer Chemistry*; Jenkins, A. D., Ledwith, A., Eds.; Wiley: New York, 1974; p 52. (i) Bamford, C. H. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon: Oxford, 1989, Vol. 3, p 123.

Metal-mediated "living" radical polymerizations[7−13,16] are complementary to "living" radical polymerization mediated with nitroxide radicals.[18] Both polymerization processes require a suitable adjustement between the structure of the monomer, initiator, and atom or group of atoms which provide the reversible termination to generate a higher rate of initiation than propagation or at least equal rates, and therefore, each process is restricted to the polymerization of selected classes of activated olefins. The complementarity of these two polymerization techniques has been elegantly demonstrated and exploited in the synthesis of polymers with complex architecture such as dendritic systems.[19]

We have reported "living" radical polymerization of styrene initiated with arenesulfonyl halides and catalyzed with various Cu, Rh, Ni, Pd, and Ru complexes under both heterogeneous and homogeneous conditions[7,8,9a] and also presented preliminary data on the "living" polymerization of methacrylates[9b,c] and acrylates[9c] catalyzed by soluble Cu complexes. "Living" Ru-catalyzed radical polymerization of methyl methacrylate initiated by sulfonyl chlorides was also recently reported by Sawamoto et al.[10b] in the presence of a Lewis acid activator.

The first goal of this publication is to demonstrate that substituted phenylsulfonyl chloride initiates the metal-catalyzed "living" radical polymerization of styrene, methacrylates, and acrylates under homogeneous conditions regardless of the nature of their substituent. The second goal is to report preliminary kinetic investigations which provide the first examples of rates and apparent rate constants of initiation and propagation for the "living" Cu(I)-catalyzed radical polymerization of styrene (S), methyl methacrylate (MMA), butyl methacrylate (BMA), methyl acrylate (MA), and butyl acrylate (BA) initiated with *various arenesulfonyl chlorides under homogeneous conditions*. These results will demonstrate that arenesulfonyl chlorides are *the first universal class of fuctional initiators* for the metal-catalyzed "living" radical polymerization of styrene(s), methacrylates, and acrylates since their initiation is quatitative and much faster than the propagation[20] regardless of the nature of the substituent present on the aryl group of the initiator and of the substituents of these three classes of monomers.

Results and Discussion

Demonstration of the "Living" Radical Polymerization and Determination of the Apparent Rate Constants of Propagation. Scheme 1 outlines the general mechanism for the metal-catalyzed "living" radical polymerization initiated with arenesulfonyl halides.[7,8] The expected trends of the equilibria in the reaction steps 1−5 from Scheme 1 are outlined with arrows. The basic polymerization concept used to provide a "living" radical polymerization[21] mediated by a reversible termination was advanced more than 15 years ago. The main requirements which were not met collectively until recently[7−13,16,18,19] are (a) a quantitative and faster rate of initiation than propagation; (b) a reversible termination providing a rapid exchange between covalent dormant and radical propagating species with its equilibrium shifted to dormant species; and (c) a reversible terminating atom or group which is not capable of initiation.

The first successful approach to the metal mediated "living" radical polymerization was accomplished by employing metalloradicals generated from organocobalt porphyrin complexes.[16a] Under these conditions, the "persistent radical effect" generated by the stable organocobalt radical suppresses the termination and chain transfer steps[22] and provides a "living" polymerization process. A related "living" radical polymerization process was elaborated by Sawamoto et al.,[10] Wang and Matyjaszewski,[11] and by us.[7−9] The first two research groups employed suitable activated alkyl halides[10,11] which either match the structure of the dormant chains or add to the olefin with a rate at least equal to propagation, while we used arylsulfonyl halides[7−9] as initiators to generate a metal-catalyzed "living" radical polymerization.

Scheme 2 outlines the synthesis of the monoadducts of 4-methoxybenzenesulfonyl chloride (MBSC) and 4-fluorobenzenesulfonyl chloride (FBSC) to MMA and S, respectively, under ATRA conditions to yield 1-(4-methoxybenzenesulfonyl)-2-chloro-2-(methyl)methyl propionate (MBSCMMA), 1-(4-fluorobenzenesulfonyl)-2-chloro-2-phenylethane (FBSCS), and 1-(4-methoxybenzenesulfonyl)-2-chloro-2-phenylethane (MBSCS) in 100% conversion. An excess of Cl^- was used in these experiments to suppress the oligomerization reaction.[1a] The chlorine group of the monoadduct FBSC was reduced with $Et_3SiH/PdCl_2$[23] to produce 1-(4-fluorobenzenesulfonyl)-2-phenylethane (FBSS). The monoadducts MBSCMMA and FBSCS were used to compare the rate of propagation of MMA and S, respectively, upon initiation with MBSC and FBSC with that of the reactions initiated with their corresponding monoadducts. These monoadducts were also used as model compounds in the kinetic experiments carried out to determine the apparent rate constants of initiation. FBSS was used to investigate the role of the SO_2 functional group in these radical polymerizations.

Table 1 summarizes selected examples of Cu(I)Cl-catalyzed polymerization experiments of S initiated with various *p*-substituted phenylsulfonyl chlorides, FBSCS, (1-chloroethyl)benzene (CEB), and a 1/1 molar ratio of CEB to FBSS at 120 °C. Bulk and diphenyl ether solution experiments are compared. CuCl was solubilized by complexation with 4,4′-dinonyl-2,2′-bipyridine (bpy9) (Scheme 3) which was shown previously to generate a homogeneous polymerization reaction.[7,8] The M_{th}-

---

(18) (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. US Patent 4,581, 429, 1985. (b) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (c) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185. (d) Hawker, C. J.; Barclay, G. C.; Dao, J. *J. Am. Chem. Soc.* **1996**, *118*, 11467. (e) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183. (f) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323. (g) Catala, J. M.; Bubel, F.; Hammouch, S. O. *Macromolecules* **1995**, *28*, 8441. (h) Fukuda, T.; Terauchi, T. *Chem Lett.* **1996**, 293.

(19) (a) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080. (b) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763. (c) Grubbs, R. B.; Hawker, C. J.; Dao, J.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 270.

(20) (a) Webster, O. W. *Science* **1991**, *251*, 887. (b) Sigwalt, P. *Makromol. Chem. Makromol. Symp.* **1991**, *47*, 179. (c) Penczek, S.; Kubisa, P.; Szymanski, R. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 77. (d) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359. (e) Szwarc, M. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 141. (f) Matyjaszewski, K.; Sigwalt, P. *Polym. Int.* **1994**, *35*, 1. (g) Matyjaszewski, K.; Pugh, C. In *Cationic Polymerizations*; Matyjaszewski, K., Ed.; Dekker: New York, 1996: pp 1 and 137.

(21) For pioneering examples of radical polymerization with reversible termination, see: (a) Borsig, E.; Lazar, M.; Capla, M.; Florian, S. *Angew. Makromol. Chem.* **1969**, *9*, 89. (b) Bledzki, A.; Braun, D. *Makromol. Chem.* **1981**, *182*, 1047. (c) Braun, D. *Macromol. Symp.* **1996**, *111*, 63. For the first model of "living" radical polymerization via thermal iniferters, see: (d) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127, 133. For a more recent publication from the same group, see (e) Endo, K.; Murata, K.; Otsu, T. *Macromolecules* **1992**, *25*, 5554. (f) Turner, S. R.; Blevins, W. R. *Macromolecules* **1990**, *23*, 1856. (g) Lambrinos, P.; Tardi, M.; Polton, A.; Sigwalt, P. *Eur. Polym. J.* **1990**, *26*, 1125. (h) Crivello, J. V.; Conlon, D. A.; Lee, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 1197, 1251. (i) For a recent review on thermal iniferters, see: Reghundhan Nair, C. P.; Clouet, G. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1991**, *C31*, 311.

(22) (a) Fischer, H. *J. Am. Chem. Soc.* **1986**, *108*, 3925. (b) Daikh, B. E.; Finke, R. E. *J. Am. Chem. Soc.* **1992**, *114*, 2938.

(23) Chatgilialoglu, C. *Organometallics* **1996**, *15*, 1508.

Scheme 2. Synthesis of 1-(4-Methoxybenzenesulfonyl)-2-chloro-2-(methyl)Methyl Propionate (MBSCMMA), 1-(4-Fluorobenzenesulfonyl)-2-chloro-2-phenylethane (FBSCS), 1-(4-Methoxybenzenesulfonyl)-2-chloro-2-phenylethane (MBSCS), and 1-(4-Fluorobenzenesulfonyl)-2-phenylethane (FBSS)

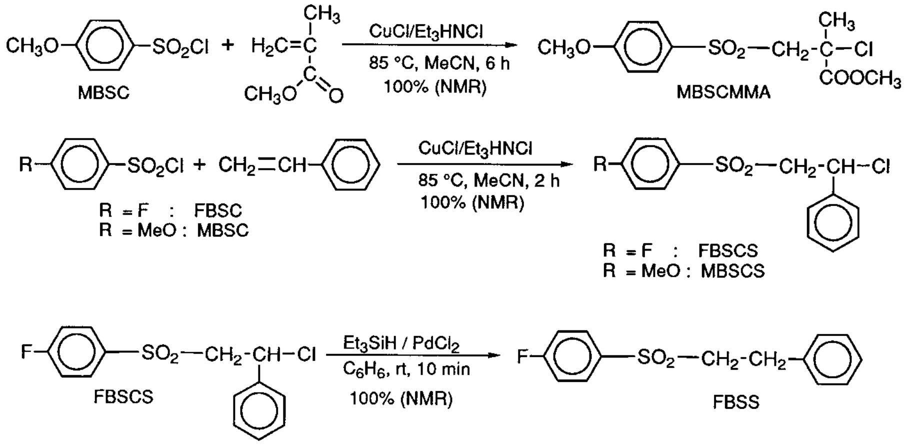


Table 1. Polymerization of Styrene (S) Initiated with Different *p*-Substituted Phenylsulfonyl Chlorides and Catalyzed by CuCl/bpy9[a]

initiator (I)	solvent	time (h)	convn (%)	M_{th}^{e}	GPC M_n	M_w/M_n
$FPhSO_2Cl$ (FBSC)	PhOPh	25	78	16224	16000	1.21
$FPhSO_2Cl$ (FBSC)	bulk	17	66	13728	11300	1.24
FBSCS[b]	PhOPh	93	96	19968	15000	1.20
FBSCS	bulk	14	72	14976	14800	1.22
CEB[c]	PhOPh	93	94	19552	14200	1.15
CEB	bulk	21	71	14768	13800	1.15
CEB/FBSS[d] (1:1)	PhOPh	93	91	18928	26000	1.16
CEB/FBSS (1:1)	bulk	21	68	14144	12600	1.20
$ClPhSO_2Cl$	PhOPh	25	71	14768	14250	1.28
$ClPhSO_2Cl$	bulk	17	67	13936	12440	1.20
$PhSO_2Cl$	PhOPh	25	71	16245	15320	1.27
$PhSO_2Cl$	bulk	17	68	14144	13550	1.33
$MePhSO_2Cl$	PhOPh	25	61	14591	15000	1.25
$MePhSO_2Cl$	bulk	17	67	15330	14500	1.39
$MeOPhSO_2Cl$	PhOPh	25	77	16016	15070	1.27
$MeOPhSO_2Cl$	bulk	17	67	15330	14800	1.29

[a] Reaction conditions: $[S]_{solution} = 5.77$ M; $[S] = 8.7$ M, [S]/[I]/[CuCl]/[bpy9] = 200:1:0.3:0.4 molar ratios; reaction temperature, 120 °C. [b] 1-(4-Fluorobenzenesulfonyl)-2-chloro-2-phenylethane. [c] (1-Chloroethyl)benzene. [d] 1-(4-Fluorobenzenesulfonyl)-2-phenylethane. [e] $M_{th} = 104 \times \text{convn} \times [M]_0/[I]_0 + M_{\text{chain ends}}$.

Scheme 3. Synthesis of 4,4′-Dinonyl-2,2′-bipyridine (bpy9)

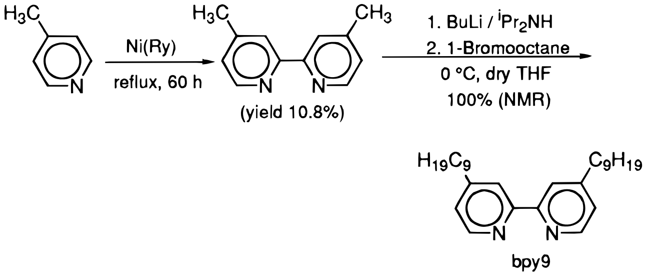


Table 2. Influence of X of X-$PhSO_2Cl$ Initiator on the CuCl/bpy9-Catalyzed Polymerization of MMA in *p*-Xylene[a]

substituent (X-)	convn (%)	M_{th}^{b}	^{1}H-NMR M_n	GPC M_n	M_w/M_n
MeO⁻	63	6500	6100	6200	1.16
F-	54	5600	5300	5800	1.15
Me-	73	7500	7900	7760	1.12
H-	50	5200	5400	5600	1.13

[a] Reaction conditions: [MMA] = 6.25 M; [MMA]/[$XPhSO_2Cl$]/[CuCl]/[bpy9] = 100:1:0.3:0.42 molar ratios; reaction temperature, 80 °C; reaction time, 74 h. [b] $M_{th} = 100.15 \times \text{convn} \times [MMA]_0/[XPhSO_2Cl]_0 + M_{\text{chain ends}}$.

(s) calculated according to a living polymerization reaction ($M_{th} = \text{conversion} \times FW_{monomer} \times [M]_0/[I]_0 + FW_{initiator}$) agree with the experimental values. As shown previously,[7,8] M_w/M_n values of the resulting polystyrene are broader for polymerizations carried out in bulk. As expected from the Hammett plot of the reaction of *p*-substituted phenylsulfonyl chloride with styrene in the presence of CuCl, various substituents in the para position of the sulfonyl radical do not exert an appreciable stabilizing influence on the resulting sulfonyl radical,[1a] and therefore, rates of polymerization by different *p*-substituted phenylsulfonyl chlorides are very close (Table 2). This is the result of the poor conjugation of the sulfonyl group with the benzene ring (i.e., arylsulfonyl radicals are σ radicals).[1a,24] This effect generates very important synthetic capabilities, since it allows the preparation of a large variety of chain ended functional polymers via this initiation process.[25]

Initiation with *p*-substituted phenylsulfonyl chlorides and their monoadduct to S (FBSCS) yield slightly broader M_w/M_n values than initiation with (1-chloroethyl)benzene (CEB). The elucidation of this difference requires further investigations. The presence or absence of FBSS during the polymerization initiated with CEB does not affect the M_w/M_n values. This demonstrates that SO_2 group does not influence this radical polymerization process, even if it can coordinate the catalyst.

Table 2 summarizes similar polymerization results performed with MMA at 80 °C in *p*-xylene. Lower M_w/M_n values are obtained in this case, and excellent agreement between M_{th} and experimental M_n for poly(MMA) are obtained in the temperature range from 60 to 120 °C (Table 3). It should be mentioned that the boiling point of MMA is 100 °C, and extremely good polymerization control is obtained at both 100 and 120 °C (Table 3).

Figure 1 presents selected examples of kinetic experiments which describe the dependence of conversion and $\ln[M]_0/[M]$ versus time (a, c, e) and respectively experimental M_n and $M_w/$

---

(24) (a) Fehnel, E. A.; Cormack, M. *J. Am. Chem. Soc.* **1950**, *72*, 1292. (b) Chatgilialoglu, C.; Lunazzi, L.; Ingold, K. U. *J. Org. Chem.* **1983**, *48*, 3588.

(25) (a) Percec, V.; Pugh, C. Oligomers. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, M. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1987; vol. 10, pp 432−463. (b) Percec, V.; Pugh, C.; Nuyken, O.; Pask, S. D. In *Macromonomers, Oligomers and Telechelics. In Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon: Oxford, 1989; Vol. 6, pp 281−357.

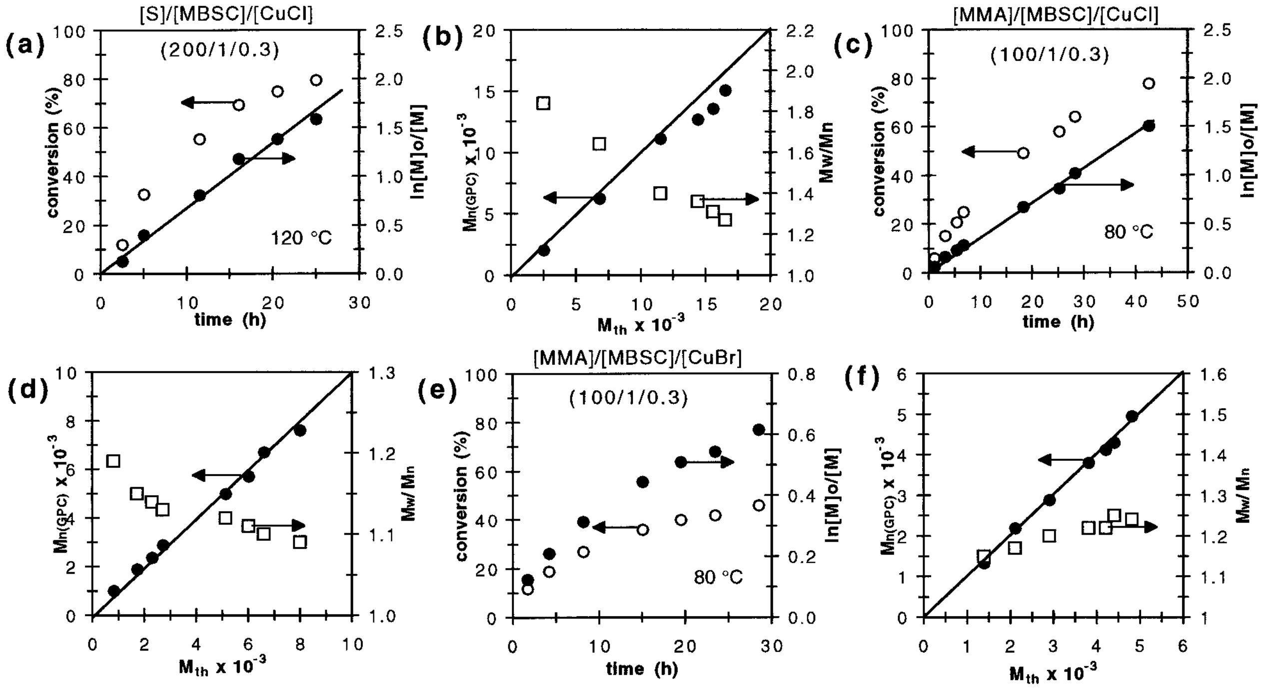


Figure 1. Selected kinetic plots for the CuX-catalyzed polymerization initiated with $MeOPhSO_2Cl$ (MBSC) of (a), (b) styrene (S), [S] = 5.77 M; [S]/[MBSC]/[CuCl]/[bpy9] = 200:1:0.3:0.42 molar ratios, at 120 °C in PhOPh; (c), (d) MMA, [MMA] = 6.25 M, [MMA]/[MBSC]/[**CuCl**]/[bpy9] = 100:1:0.3:0.42 molar ratios, at 80 °C in *p*-xylene; (e), (f) MMA, [MMA] = 6.25 M, [MMA]/[MBSC]/[CuBr]/[bpy9] = 100:1:0.3:0.42 molar ratios, at 80 °C in *p*-xylene.

Table 3. Influence of Temperature on the CuCl/bpy9-Catalyzed Polymerization of MMA Initiated with $MeOPhSO_2Cl$ in Bulk and Solution in *p*-Xylene[a]

temp (°C)	polym. condns.	time (h)	convn (%)	M_{th}[b]	GPC M_n	GPC M_w/M_n
60	bulk	120	82	8200	8200	1.18
60	*p*-xylene	69	18	1800	1900	1.14
80	bulk	72	80	8000	7960	1.21
80	*p*-xylene	74	63	6300	6200	1.18
100	bulk	18	61	6100	7770	1.35
100	*p*-xylene	42	75	7500	7500	1.14
120	*p*-xylene	6.3	57	5700	4060	1.21

[a] Reaction conditions: $[MMA]_{solution}$ = 6.25 M; [MMA]/[MBSC]/[CuCl]/[bpy9] = 100:1:1:2 molar ratios. [b] M_{th} was calculated as in Table 2.

M_n values versus M_{th} (which also demonstrate a linear dependence of M_n on conversion) (b, d, f) for the CuCl/bpy9-catalyzed polymerization of S (a, b) and MMA (c, d) initiated with $MeOPhSO_2Cl$ (MBSC) in *p*-xylene at 120 and 80 °C, respectively. These plots demonstrate that the rate of polymerization shows an internal first order in monomer concentration, a linear dependence of M_n with conversion, and a decrease in M_w/M_n with conversion. The perfect match between M_n and M_{th} demonstrate a 100% initiation efficiency. At high conversion, M_w/M_n values for polystyrene are approaching a value of 1.2, while for PMMA a value of 1.05 is obtained. All of these results demonstrate a "living" radical polymerization process.[20]

Figure 1e,f presents similar plots for the CuBr/bpy9-catalyzed polymerization of MMA initiated with MBSC under identical experimental conditions with those used for the polymerization catalyzed by CuCl/bpy9 (Figure 1c,d). Although a perfect control of M_n is observed also in this case, the rate of polymerization is not first order in MMA concentration and the M_w/M_n values increase with conversion. Since fast and constant exchange between dormant and radical species is controlling this polymerization, the results from Figure 1e,f suggest that an exchange of dormant chlorine chain end with bromine from CuBr occurs during this polymerization process. As a consequence, at higher conversions when the dormant chains contain Br groups, the equilibrium between dormant and radical species is shifted toward a higher concentration of radicals, and this provides an increase in polymer M_w/M_n values (Figure 1f).

Figure 2a,b presents an example of kinetic plots for the CuCl/bpy9-catalyzed polymerization of MMA initiated with MBSC and its monoadduct to MMA (MBSCMMA), both at 80 °C. Within experimental error (estimated to be ±3% for k_p^{exp}), with the exception of M_w/M_n data, the two sets of results fall on the same plots. This demonstrates that rate of polymerization initiated by MBSC and MBSCMMA are identical and that within experimental error initiation efficiency is 100% in both cases. A definitive explanation of the difference between the two M_w/M_n on M_{th} trends (Figure 1b) requires further investigations.

Two selected kinetic plots for the CuCl/bpy9-catalyzed polymerization of butyl methacrylate (BMA) at 90 °C and butyl acrylate (BA) at 140 °C initiated with MBSC are presented in Figure 2c,d and Figure 2e,f, respectively. Both experiments demonstrate that substituted phenylsulfonyl chlorides provide a "living" radical polymerization of other methacrylates and also of acrylates. The main qualitative observation provided by these plots is that the rate of polymerization of acrylates is lower than that of methacrylates and that, at high conversion, M_w/M_n values of polymethacrylates are reaching values less than 1.1 while polyacrylates values of about 1.2.

The rate of monomer consumption in the propagation step (Scheme 1) is provided by eq 7.

$$R_p = -\frac{d[M]}{dt} = k_{p_2}[P^\bullet][M] \qquad (7)$$

Equation 8 expresses the steady-state assumption for the concentration of propagating radicals $[P^\bullet]$

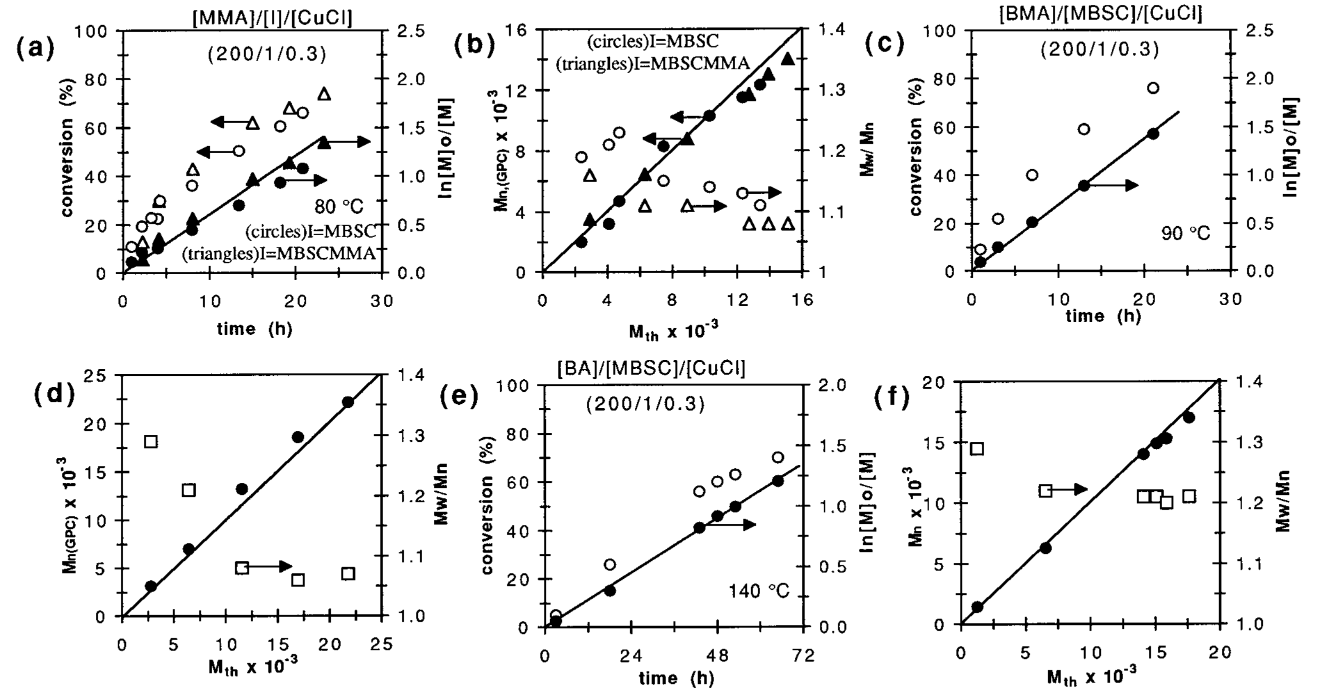


Figure 2. Selected kinetic plots for the CuCl-catalyzed polymerization of: (a), (b) MMA initiated with: (○) MBSC ([MMA] = 6.25 M, [MMA]/[MBSC]/[CuCl]/[bpy9] = 200:1:0.3:0.42 molar ratios, at 80 °C in *p*-xylene), (△) the MBSC adduct to MMA (MBSCMMA) ([MMA] = 6.25 M, [MMA]/[MBSCMMA]/[CuCl]/[bpy9] = 200:1:0.3:0.42 molar ratios, at 80 °C in *p*-xylene); (c), (d) BMA initiated with MBSC ([BMA] = 4.2 M, [BMA]/[MBSC]/[CuCl]/[bpy9] = 200:1:0.3:0.42 molar ratios, at 90 °C in PhOPh); (e), (f) BA ([BA] = 3.16 M, [BA]/[MBSC]/[CuCl]/[bpy9] = 200:1:0.3:0.42 molar ratios, at 140 °C in PhOPh).

$$\frac{d[P^\bullet]}{dt} = k_{p1}[PCl][CuCl] - k_{-p1}[P^\bullet][CuCl_2] = 0 \tag{8}$$

and therefore,

$$[P^\bullet] = \frac{k_{p1}[PCl][CuCl]}{k_{-p1}[CuCl_2]} \tag{9}$$

Substitution of eq 9 in eq 7 under the assumptions that the rate of initiation is higher than the rate of propagation and that the equilibrium between dormant and radical species is fast and shifted to dormant species (i.e., the reversible termination in eq 4 expressed by the equilibrium constant,

$$K_{p1} = \frac{[P^\bullet][CuCl_2]}{[PCl][CuCl]} = \frac{k_{p1}}{k_{-p1}} \tag{10}$$

$[PCl]=[I]_0$ and in eqs 5 and 7, $k_{p2}=k_p^{rad}$) yields eq 11.

$$R_p = -\frac{d[M]}{dt} = k_{p2}\frac{k_{p1}[CuCl][PCl]}{k_{-p1}[CuCl_2]}[M] \tag{11}$$

Since the rate of polymerization has been shown to be internally first order in monomer concentration, the left combination of parameters from the right side of eq 11 is equivalent to the slope of the semilogarithmic plots from Figures 1−3 and therefore, represents k_p^{exp}. This yields eq 12 which upon integration produces eq 13.

$$R_p = -\frac{d[M]}{dt} = k_p^{exp}[M] \tag{12}$$

$$\ln\frac{[M]_0}{[M]} = k_p^{exp}t \tag{13}$$

As it will be discussed later, the rates of propagation and initiation are externally approximately first order (~0.8) in CuCl concentration. The external order of the rate of propagation in initiatior concentration is about 0.4 ([M]/[I] = 150−2000). These deviations from an expected first order are most probable generated by the dependence of Cu(II)Cl_2 concentration on $[I]_0$, and their elucidation requires further investigations. Therefore, to compare the rate constants of propagation with those of initiation we need to correlate the newly defined apparent k_p^{app} and k_i^{app} to k_p^{exp} and k_i^{exp} via CuCl concentration, i.e.:

$$k_p^{exp} = k_p^{app}[CuCl] \tag{14}$$

$$k_i^{exp} = k_i^{app}[CuCl] \tag{15}$$

Since eqs 7 and 12 have the same meaning and k_{p2} in eq 7 is equal to k_p^{rad}, eq 16 holds.

$$k_p^{exp} = k_{p2}[P^\bullet] = k_p^{rad}[P^\bullet] \tag{16}$$

The other external orders of reaction which are not discussed here are part of the k_p^{app}. From eq 16, assuming that the reactivity of propagating radicals is not affected by the presence of the catalyst, we can calculate the steady-state concentration of propagating radicals from this polymerization process (i.e., eq 4) as the ratio between two rate constants (eq 17).

$$[P^\bullet] = \frac{k_p^{exp}}{k_p^{rad}} \tag{17}$$

The values of k_p^{exp} were calculated as the slopes of the semilogarithmic plots from Figures 1−3 while k_p^{rad} are the absolute rate constants of propagation of radical species available

Table 4. Comparison of Rate Constants of Initiation and Propagation (at Temperature *T*, °C) for the Homogeneous Solution Polymerization of MMA, S, MA, BA, and BMA Catalyzed by CuCl/bpy9 and Determination of the Reversible Termination Equilibrium Constant (K_e)

monomer (M)	MMA		S			MA	BA	BMA
solvent	*p*-xylene	*p*-xylene	*p*-xylene	PhOPh	PhOPh	*p*-xylene	PhOPh	PhOPh
initiator (I)	MBSC	MBSCMMA	MBSC	MBSC	$CH_3CHPhCl$[d]	MBSC	MBSC	MBSC
[I], polymerization, 10^{-2} M	3.12	3.12	5.77[i]	2.88	4.5	2.80	2.33	2.1
k_i^{app}, 10^{-3} M^{-1} s^{-1} (at 43 °C)[a]	116.0 (43)	*0* (43)	479.1 (43)	479.1 (43)	*0* (43)	8.66 (43)	2.65 (43)	23.0 (43)
k_i^{app}, 10^{-1} M^{-1} s^{-1} (at *T*)[a]	103.8 (80)	*0.0062* (*80*)	631.6 (130)	400.2 (120)	*0.0064* (120)	6.62 (90)	30.7 (140)	
k_p^{app}, 10^{-4} M^{-1} s^{-1} (at *T*)[b]	6.19 (80)	6.21 (80)	12.10 (130)	19.60 (120)	6.33 (120)	10.2 (90)[e]	6.97 (140)	27.54 (90)
k_p^{app} MMA, 10^{-4} M^{-1} s^{-1} (at *T*)	6.19 (80)	6.19 (80)	541.3 (130)	242.5 (120)	242.5 (120)	16.71 (90)	1162.4 (140)	16.71 (90)
k_p^{rad}, 10^3 M^{-1} s^{-1} (at 80 °C)[c]	1.31 (80)	1.31 (80)	0.66 (80)	0.66 (80)	0.66 (80)	40.35 (80)	27.83 (80)	
k_p^{rad}, 10^3 M^{-1} s^{-1} (at *T*)[c]	1.31 (80)	1.31 (80)	2.61 (130)	2.04 (120)	2.04 (120)	53.31 (90)	44.78 (140)	
10^7 K_e (at *T*)[f]	4.73 (80)	4.74 (80)	4.64 (130)	9.61 (120)	3.10 (120)	0.19 (90)	0.15 (140)	
[P•], 10^{-9} M[g]	4.87 (80)	4.88 (80)	8.83 (130)	9.13 (120)	13.96 (120)	0.18 (90)	0.12 (140)	
[P•], PMMA, 10^{-9} M (at *T*)[h]	4.87 (80)	4.87 (80)	308.4 (130)	81.77 (120)	127.6 (120)	9.62 (90)	205.1 (140)	

[a] $\ln([I]_0/[I]) = k_i^{exp}t = k_i^{app}[CuCl]t$; reaction conditions [MMA] = 3.12 M, [S] = 2.88 M, [MA] = 3.7 M, [BA] = 2.33 M, and [BMA] = 2.1 M, all in *p*-xylene, [M]/[MBSC]/[CuCl]/[bpy9] = 10:1:0.3:0.42 molar ratio. [b] $\ln([M]_0/[M]) = k_p^{exp}t = k_p^{app}[CuCl]t$; reaction conditions [MMA] = 6.25 M, [S] = 5.77 M, [BA] = 4.6 M, [BMA] = 4.2 M, [M]/[I]/[CuCl]/[bpy9] = 200:1:0.3:0.42 molar ratio. [c] MMA $k_p^{rad} = 10^{6.423}$ M^{-1} s^{-1} $\exp(-22.34$ kJ $mol^{-1}/RT)$; S $k_p^{rad} = 10^{7.63}$ M^{-1} s^{-1} $\exp(-32.51$ kJ $mol^{-1}/RT)$ (Both from ref 27a). MA $\ln k_p^{rad} = 20.72-3572/T$ (from ref 27b). BA $\ln k_p^{rad} = 13.51-1157/T$ (ref 27c). [d] Data from ref 28; reaction conditions [S] = 4.34 M; [(1-chloroethyl)benzene] = [CuCl] = [4,4′-di(5-nonyl)-2,2′-bipyridine]/2 = 0.045 M. [e] Value calculated from ref 29; reaction conditions [MA] = 11.2 M; [methyl 2-bromopropionate] = [CuBr]/2 = [di(*t*-Bu)bpy] = 0.1121 M. [f] $K_e = k_p^{app}/k_p^{rad}$ and the equivalent equilibrium reaction of the propagation step is $P \overset{K_e}{\rightleftharpoons} P^•$. [g] $[P^•] = k_p^{exp}/k_p^{rad} = K_e[CuCl]$. [h] [P•] for PMMA at *T* and with [CuCl]. [i] [S]/[MBSC]/[CuCl]/[bpy9] = 100:1:0.3:0.42.

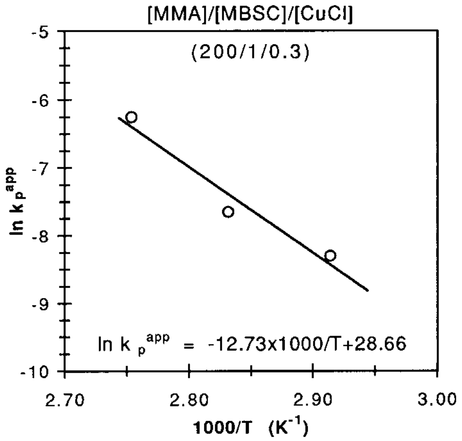


Figure 3. Arrhenius plot for the k_p^{app} of the CuCl/bpy9-catalyzed "living"radical polymerization of MMA initiated with $MeOPhSO_2Cl$ (MBSC) in *p*-xylene; [MMA] = 6.25 M, [MMA]/[MBSC]/[CuCl]/[bpy9] = 200:1:0.3:0.42 molar ratios.

in the literature.[27] The elaboration of the definitions for k_p^{app} and k_i^{app} will allow direct comparison of the rates of initiation and propagation.

Table 4 summarizes k_p^{app} for all monomers investigated. For the case of MMA, we have determined k_p^{app} at three different temperatures, and the Arrhenius plot from Figure 3 will allow the comparison of the k_p^{app} for all monomers; their discussion will be made later.

Figure 4a presents the plot ln k_p^{exp} vs ln [CuCl] for the case of MMA and S. The values of their slopes suggest that both rates of propagation are externally close to first order in CuCl. These data are in agreement with previously reported values for the metal-catalyzed polymerization of S initiated with CEB.[11c] Figure 4b shows that the external order of the rate of propagation for MMA in $[I]_0$ is 0.37.

Figure 4c shows the influence of the [bpy9]/[CuCl] ratio on k_p^{exp} values obtained for the polymerization of S and MMA. At 1:1 molar ratios of [MBSC]/[CuCl], k_p^{exp} values increase with [bpy9]/[CuCl] ratio until they seem to reach a plateau at [bpy9]/[CuCl] ≈ 2.0. These results are in agreement with previously reported data on the homogeneous polymerization of S initiated with CEB.[11c] However, when [MBSC]/[CuCl] = 1:0.3, k_p^{exp} has a maximum value at [bpy9]/[CuCl] = 1.3. This result suggests that the structure of the [bpy9]/[CuCl] catalyst is more complicated than considered,[11c] and in fact, a dynamic equilibrium between various complexes of various composition and reactivity mediates this polymerization. At low catalyst concentration (i.e., [MBSC]/[CuCl] = 1:0.3) a [bpy9]/[CuCl] = 1:1 complex seems to be more reactive than the [bpy9]/[CuCl] = 2:1 complex. The 1:1 complex provides the highest k_p^{app}. At high concentrations of catalyst (i.e., [MBSC]/[CuCl] = 1:1), the polymerization process may be dominated by the high concentration of the less reactive [bpy9]/[CuCl] = 2:1 catalyst. A more detailed investigation of the mechanism is in progress.

We have performed all of our propagation and initiation kinetic experiments with a ratio between initiator and catalyst equal to 1:0.3 and a ratio of ligand (bpy9) to catalyst 1.3:1. This provided a low rate of initiation which could be accessible experimentally at a reaction temperature where no propagation took place.

Determination of the Apparent Rate Constants of Initiation. The rate of consumption of the initiator was determined in the presence of a large excess of monomer. This assured a constant monomer concentration throughout the initiation experiment which minimizes its effect on k_i^{app} and simulates the polymerization conditions. When all reagents were mixed and degassed in a Schlenk tube as in the propagation experiments, the extent of initiation was high and in some cases even complete before the freeze−thaw process was over. Therefore, two Schlenk tubes containing MBSC and *p*-xylene and CuCl/bpy9, MMA, and *p*-xylene, respectively, were first degassed via three freeze−pump−thaw cycles and afterward the two contents were mixed via a syringe under Ar. The reaction mixture was sampled with a syringe directly into NMR tubes containing $CDCl_3$ and was analyzed by NMR in air. Oxygen from air terminated the radical reaction in all of these experi-

---

(26) (a) Takahara, Y.; Iino, M.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2268. (b) da Silva Corrêa, C. M. M.; Fleming, M. D. C. M.; Oliveira, M. A. B. C. S.; Garrido, E. M. J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1993.

(27) (a) IUPAC Commission on Polymer Characterization and Properties *Pure Appl. Chem.* **1996**, *68*, 1491. (b) Odian, G. *Principles of Polymerization*; Wiley: New York, 1991; p 275. (c) Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206.

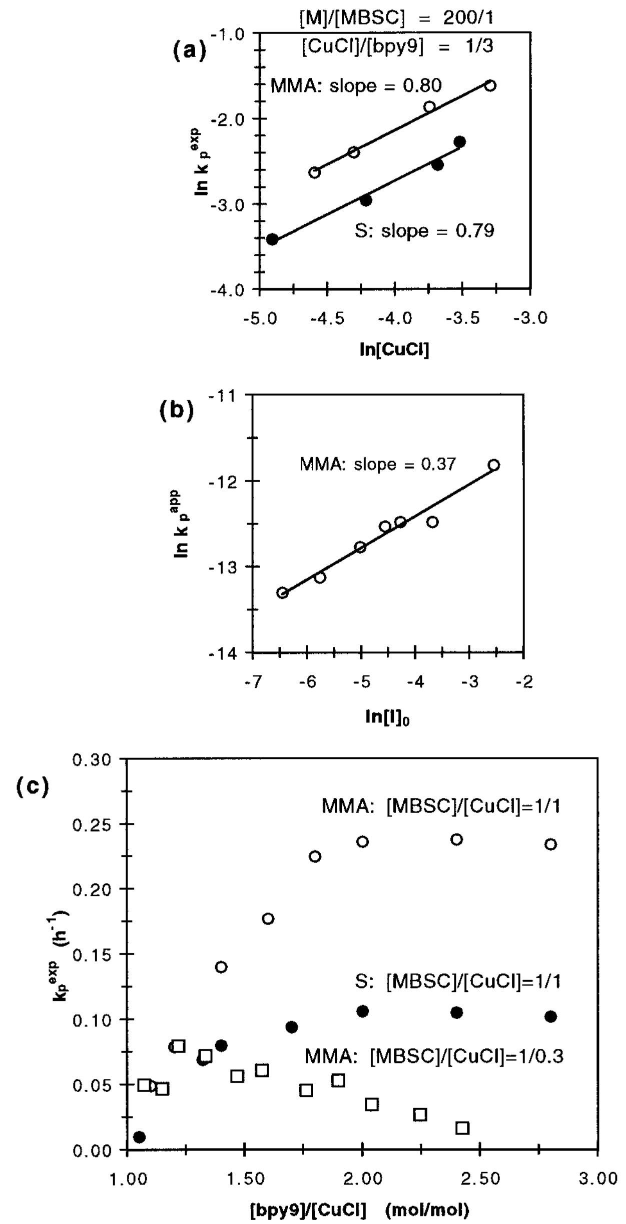


Figure 4. (a) Determination of the external order of reaction of the rate of propagation in catalyst concentration for the homogeneous radical polymerization initiated with $MeOPhSO_2Cl$ (MBSC), in *p*-xylene, of (○) MMA at 90 °C ([MMA] = 6.25 M, [MMA]/[MBSC] = 200:1 mol/mol, [CuCl]/[bpy9] = 1:2 mol/mol); (●) styrene (S) at 130 °C ([S] = 5.9 M, [S]/[MBSC] = 200:1 mol/mol, [CuCl]/[bpy9] = 1:2 mol/mol); (b) Determination of the external order of reaction of the rate of propagation in initiator concentration for the polymerization of MMA in *p*—xylene initiated with MBSC and catalyzed by CuCl/bpy9: [MMA] = 6.25 M, [CuCl]/[bpy9] = 1:1.3 molar ratio, 90 °C (c) The dependence of k_p^{exp} on the ligand/catalyst ratio ([bpy9]/[CuCl]) in the homogeneous radical polymerization initiated with $MeOPhSO_2Cl$ (MBSC) in *p*-xylene of MMA (90 °C, [MMA] = 6.25 M, using [MMA]/[MBSC]/[CuCl] = 200:1:1 (○) and, respectively, [MMA]/[MBSC]/[CuCl] = 200:1:0.3 (□) molar ratios) and of styrene (●) (130 °C, [S] = 5.9 M, [S]/[MBSC]/[CuCl] = 200:1:1 molar ratios).

ments. The integration of the doublet **a** from MBSC with that of doublet **b** from the model compound MBSCMMA and with that of *p*-xylene (internal standard) was used to provide conversion in time and the corresponding semilogarithmic plots. The rate of initiatior consumption was always equal to that of the formation of its monoadduct with the corresponding monomer. The experimental error for the k_i^{exp} values is ± 5%. Figure 5 illustrates an example of kinetic determination of the k_i^{exp} for the initiation step of CuCl-catalyzed polymerization of MMA initiated with MBSC at 33 °C in *p*-xylene. As observed from Figure 5, under these reaction conditions initiation of MMA with MBSC at 33 °C is quantitative, and the conversion is complete within 8 min. No polymerization of MMA takes place at this temperature. In all cases only the monoadduct of the MBSC with the corresponding monomer was formed and was quantitatively analyzed by a combination of ^1H NMR, GC, and HPLC experiments.

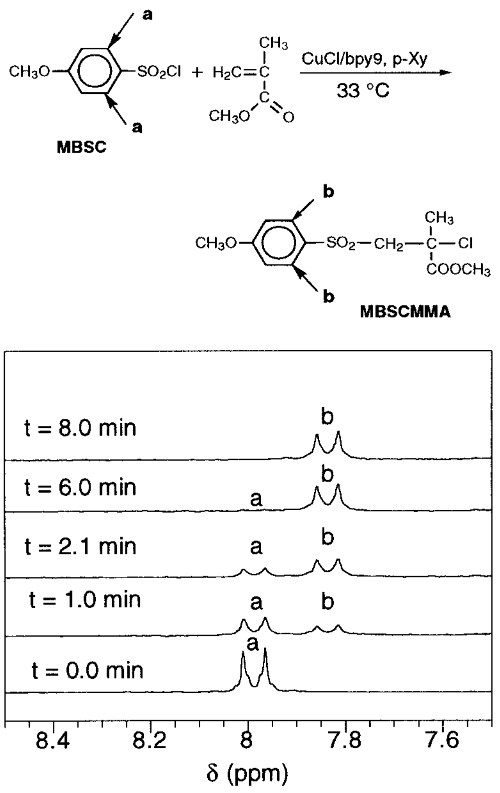


Figure 5. Determination of k_i^{exp} for the CuCl-catalyzed "living"radical polymerization of MMA initiated with MBSC in *p*-xylene at 33 °C ([MMA] = 3.12 M, [MMA]/[MBSC]/[CuCl]/[bpy9] = 10:1:0.3:0.42 molar ratios).

The rate of consumption of the $RPhSO_2Cl$ initiator is expressed[1b,d] by eq 18 which upon integration yields eq 19.

$$R_i = -\frac{d[RPhSO_2Cl]}{dt} = k_i^{app}[RPhSO_2Cl][CuCl] = k_i^{exp}[RPhSO_2Cl] \quad (18)$$

$$\ln\frac{[RPhSO_2Cl]_0}{[RPhSO_2Cl]} = k_i^{exp}t \quad (19)$$

Equation 18 does not assume an internal zero order of the rate of initiation in monomer or that the monomer is not part of the rate determining step, since it represents a simplified form of eq 20[1b,d] which was derived without assuming a rate-limiting step. A detailed discussion of the kinetic derivation of eq 20 is available in the Supporting Information. The meaning of k_i^{app} from eq 18 can be derived from eq 20.

$$R_i = \frac{k_{i1}[RPhSO_2Cl][CuCl]}{1 + \frac{\text{k-i1}(k_{-i2}/k_{i3} + [CuCl_2])}{k_{i2}[M]}} \quad (20)$$

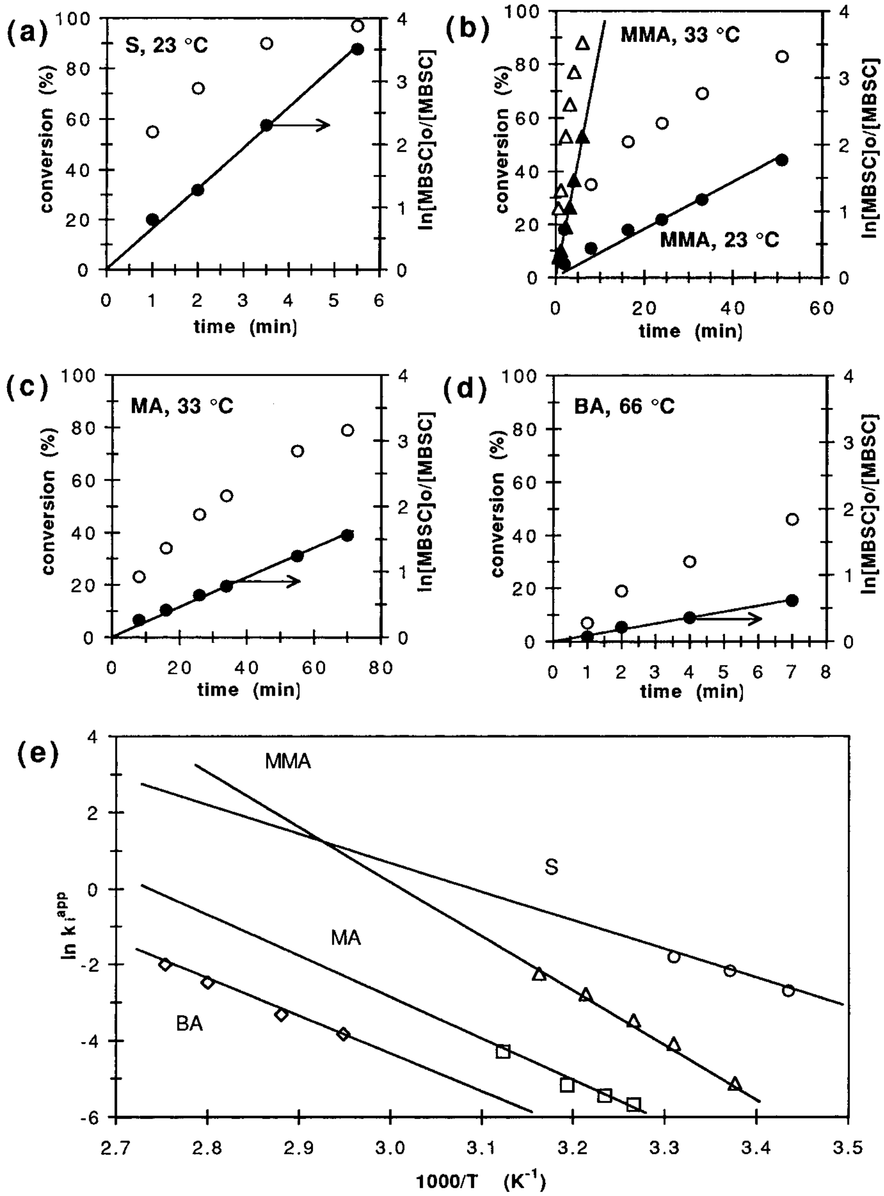


Figure 6. Selected plots for the CuCl-catalyzed "living"radical polymerization initiated with MBSC in *p*-xylene used in the determination of k_i^{exp} for (a) styrene (S) ([S] = 2.88 M); (b) MMA ([MMA] = 3.12 M); (c) MA ([MA] =3.7 M) and (d) BA ([BA] = 2.33 M). General reaction conditions: [M]/[MBSC]/[CuCl]/[bpy9] = 10:1:0.3:0.42 molar ratios (reaction temperatures are on the plots). (e) activation energy data in the case of **S** (E_a = 112.8 kJ/mol, ln *A* = 40.76); **MMA** (E_a = 59.5 kJ/mol, ln *A* = 21.88); **MA** (E_a = 80.7 kJ/mol, ln *A* = 25.96); **BA** (Ea = 79.0 kJ/mol, ln A = 24.12).

Figure 6 a−d presents selected kinetic experiments used for the determination of k_i^{exp} as slopes of the semilogarithmic plots for S, MMA, MA, and BA. These plots show that the rate of initiation is internally first order in [I]. Previously, it has been shown that rate of initiation is internally first order in catalyst.[1b] The corresponding Arrhenius plots are shown in Figure 6e. A qualitative inspection of this figure is instructive. The highest temperature at which the experimental rate constant of initiation of S could be determined under these conditions was 29 °C. At this temperature, the initiation was complete in about 3 min. Figure 6a shows the experiment carried out at 23 °C. Initiation of S is complete at this temperature in 6 min. At 23 °C, the initiation of MMA is complete in 80 min, while at 33 °C, it is complete in 12 min (Figure 6b). The initiation of MA and BA is slower than that of S and MMA. However, complete initiation occurs and was tested in all cases even when the kinetic plots do not show it (see the Supporting Information). The Arrhenius plots shown in Figure 6e allowed for the calculation of k_i^{exp} and k_i^{app} at various temperatures. Table 4 summarizes these results. These experiments as well as the one to be described below have demonstrated that the efficiency of initiation is 100%. Although it is well-known that phenylsulfonyl radicals may undergo small extents of other reactions,[1b,e] under our experimental conditions they do not take place in the presence of these three classes of olefins or occur below the level of detection by our experimental techniques. Even in the absence of olefins at 80 °C for 24 h, the reaction between MBSC and catalyst did not produce any product resulting from the homocoupling or disproportionation of sulfonyl radicals, thus demonstrating an extremely efficient cross-coupling between sulfonyl and Cl radicals.

However, the mechanism of initiation is more complex. Externally, the rate of initiation is second order in monomer concentration (for MMA and MA) and 0.1 order in CuCl concentration (for MMA)(Figure 7). This implies some kind of interaction between monomer and catalyst. Even if more

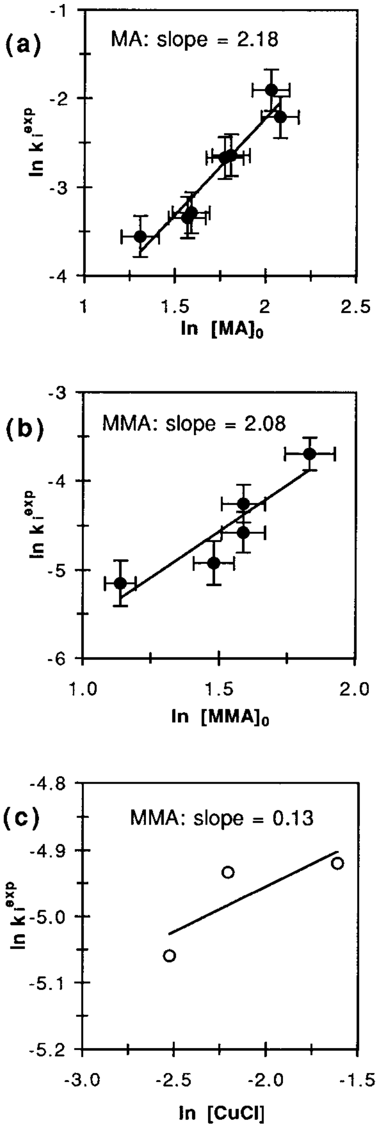


Figure 7. Determination of the external order of reaction of the rate of initiation of MA (a) and MMA (b) initiated with MBSC in *p*-xylene at 36 °C ([MBSC] = 0.3 M, [MBSC]/[CuCl]/[bpy9] = 1:0.3:0.42 molar ratios), and (c) determination of the external order of reaction of the rate of initiation of MMA with MBSC in CuCl concentration ([MMA] = 3.12 M, [MMA]/[MBSC] = 10:1 and [CuCl]/[bpy9] = 1:1.3 molar ratios, 32 °C).

Table 5. Comparison of Initiation Rate Constant Ratios for MMA, MA, BA, and BMA vs S in the Absence and Presence of Cu Catalysts[a]

ref	T (°C)	$k_{i,MMA}/k_{i,S}$	$k_{i,MA}/k_{i,S}$	$k_{i,BA}/k_{i,S}$	$k_{i,BMA}/k_{i,S}$
26a	0	0.08	0.012		
26b	25	0.1	0.020	0.035	0.07
present data[a]	25	0.070	0.011	0.0035	
present data[a]	43	0.24	0.018	0.0055	0.048

[a] Ratios are for k_i^{app} values calculated from the Arrhenius plots in Figure 6e.

kinetic studies are needed to elucidate the mechanism of this initiation, the ratio between various k_i^{app} reported here (with the exeption of BA) are in excelent agreement with data available in the literature,[26] even if the literature data were generated in the absence of CuCl (Table 5).

Comparison of the Apparent Rate Constants of Propagation and Initiation. The absolute rate constants of propagation for MMA,[27a] S,[27a] MA,[27b] and BA[27c] are available in the literature and are also tabulated at the polymerization temperature in Table 4. Lets us first remember that in radical polymerizations the rate constants of propagation for acrylates are higher than those for methacrylates, which are higher than that for styrene[27] (Table 4). The k_i^{app} values from line 2 of Table 4 were all calculated from their Arrhenius plots (Figure 6e) at 43 °C and can be used to compare different monomers from this line. This comparison demonstrates that the order of k_i^{app} is S > MMA > BMA > MA > BA. In Table 4 we list the k_p^{app} values of MMA (line 5) calculated from the Arrhenius plot in Figure 3 at the temperature T at which the k_p^{app} values for S, MA, BA, and BMA determined experimentally are available in line 4. These data can be compared from each column. The k_i^{app} values from line 3 of Table 4 are calculated at the same temperature T with k_p^{app} from line 4. This provides access to the comparison of k_i^{app} with k_p^{app} at the same temperature T (on columns). The values of k_i^{app} at T from second and fifth columns of line 3 (in italics) are assumed to be equal to their k_p^{app} since the structure of the initiator and of the growing dormant chain are identical. Contrary to the absolute rate constants known from literature,[27] the highest k_p^{app} is for methacrylates, which in the case of MMA is 12.4 times larger in PhOPh and 44.9 times larger in *p*-xylene than that of styrene when MBSC was used as initiator. This difference is due to different reaction conditions (solvent, concentration of initiator, catalyst, and temperature). Presently, we do not know if the nature of the solvent has any effect on the apparent rate constants of initiation and propagation. The k_p^{app} value for S is three times larger than that reported for the CuCl-catalyzed polymerization initiated with CEB.[28] This is due to different catalyst, ligand, and initiator concentrations. The k_p^{app} values of MMA and BMA are also larger than those of MA and BA. Therefore, while the trend for the absolute rate constant (k_p^{rad}) (line 6) is acrylates > methacrylates > styrene, the trend for the k_p^{app} (lines 4 and 5 on columns) is methacrylates > styrene > acrylates. This inversion is explained below.

The concentrations of propagating radicals [P•] calculated with eq 17 are reported in the line 9 of Table 4. The steady concentration of propagating radicals in these polymerizations ranges from 10^{-8} to 10^{-10} mol/L. The values of [P•] for MMA (line 10) calculated at temperature T at which values for other monomers are available on line 9 can be compared on columns. This can rank [P•] at the same temperature, i.e., MMA > S > MA > BA. They demonstrate that C−Cl bond strength of the dormant species determines the radical concentration. Therefore, the highest [P•] is for MMA followed by S and acrylates. This trend explains the inversion in the k_p^{app} values and might be generated by a combination of C−Cl bond strength and Cu(I)/Cu(II) steady concentration.

Finally, the most important discussion of this series of experiments refers to the k_i^{app} and k_p^{app} values (lines 3 and 4 of Table 4). In the cases of S and MMA, k_i^{app} is 4 ($k_i^{app}/k_p^{app} = 5.2 \times 10^4$ and 1.7×10^4, respectively) orders of magnitude higher than k_p^{app}. This difference decreases to almost 3 (4.4×10^3) for BA and 2 (6.5×10^2) orders of magnitude for MA.

This extremely large difference between the much higher rates of initiation versus propagation is extremely rewarding since it demonstrates that substituted phenylsulfonyl chlorides are providing the first class of *universal functional initiators* for the "living" radical polymerization of styrene(s), methacrylates, and acrylates. At the same time they provide the first example of universal functional initiators which can initiate the "living"

---

(28) Xia, J.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (2), 513.

polymerization of these three classes of monomers regardless of the polymerization mechanism used. The initiation with arenesulfonyl chlorides containing phenol, carboxylic acid, and amino groups will be reported in a paper dedicated to the preparative applications of this class of initiators.[29]

While "living" radical polymerization of styrene was previously mediated by nitroxide stable radicals[18] and by metal-catalyzed polymerization initiated with various alkyl halides,[11] that of acrylates was most conveniently accomplished with organocobalt-coordinated stable radicals,[16] and with few activated alkyl bromides which match the structure of the growing chain.,[28,30,31] The most efficient initiators for the metal-catalyzed "living" radical polymerization of methacrylates are substituted phenylsulfonyl chlorides,[9,10b] although selected activated alkyl bromides and chlorides were also successfully used.[11,12,13]

In view of the immense technological interest in the controlled polymerization of styrene, methacrylates, and acrylates and of the research efforts dedicated to the development of various polymerization techniques for the controlled polymerization of methacrylates and acrylates,[20a,31,32] the results reported in this paper are extremely rewarding. The discovery that substituted phenylsulfonyl chlorides which is one of the commodities of any organic chemistry laboratory initiate with 100% efficiency and with a rate from 2 to 4 orders of magnitude higher than the rate of propagation the metal-catalyzed "living" radical polymerization of styrene(s), methacrylates, and acrylates opens new and numerous fundamental and technological opportunities in this field, since they can be used to synthesize controlled chain-ended functional polymers and copolymers with linear and more complex architecture and self-organized supramolecular systems based on them.[32] Research on the elaboration of novel catalysts which can control the polymerization rate and on the elucidation of this polymerization mechanism is in progress.

Experimental Section

Materials. All materials, unless otherwise noted, were purchased from Aldrich. The monomers (99 to 99+% purities) were first distilled from CaH_2 and then were passed through a basic Al_2O_3 chromatographic column (flash). The arenesulfonyl chloride initiators (Lancaster, 98%) were recrystallized from hexanes. CuCl (Fisher, 96%) was purified by grinding and stirring with H_2SO_4 (1 N), followed by filtration and succesive washing with glacial HOAc (four times), EtOH, and Et_2O. The white CuCl powder was dried at 100 °C for 30 min and stored in an airtight bottle.[33] 2,2′-Bipyridine (bpy) (99+%), CuBr (99.999%), diphenyl ether (99+%), acetonitrile (99%), triethylammonium hydrochloride (Et_3HNCl, 98%), *n*-butyllithium (1.6 M in hexanes), 1-bromooctane (Acros, 99%), and (1-chloroethyl)benzene (TCI America, 97%) were used as received. *p*-Xylene and benzene (both 99%) were shaken with concentrated H_2SO_4, washed with water, dried on $MgSO_4$, distilled from sodium/benzophenone, and stored on molecular sieves (5 Å). THF was dried over molecular sieves, and then freshly distilled from sodium/benzophenone. Raney Ni (50% slurry) was dried under vacuum (2 mmHg) for 2 h and at 100 °C (0.5 mmHg) for 2 h. The flask was filled with Ar and closed in order to avoid any contact with air, which may result in an explosion. 4-Methylpyridine (98%) was stirred with KOH (4 h), fractionated under vacuum (bp 55−56 °C), and finally bubbled for 30 min with N_2. Diisopropylamine (99%) was distilled from CaH_2 (bp 127 °C).

Techniques. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian Gemini 200 spectrometer at 20 °C in $CDCl_3$ with tetramethylsilane (TMS) internal standard. Melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. The HPLC and GPC analysis were obtained with a Perkin-Elmer Series 10 high-pressure liquid chromatograph equipped with an LC-100 column oven (40 °C), a Nelson Analytical 900 Series integrator data station, a Perkin-Elmer LC-15B UV Detector (254 nm), and a Perkin-Elmer LC-25 RI Detector. The HPLC column was PL gel (5 μm, 100 Å) while the GPC had two columns AM gel (10 μm, 500 Å and 10 μm, 10^4 Å). THF was used as eluent at a flow rate of 1 mL/min. Number and weight average molecular weights were determined from calibration plots constructed with polystyrene and poly(methyl methacrylate) standards (RI detector only).

Synthesis of Monoadducts and Ligands. Synthesis of 1-(4-Methoxybenzenesulfonyl)-2-chloro-2-(methyl)methyl Propionate (MBSCMMA). A mixture of MMA (1 mL, 9.3 mmol), *p*-methoxybenzenesulfonyl chloride (1.5 g, 7.2 mmol), Et_3NHCl (31 mg, 0.23 mmol), CuCl (11 mg, 0.11 mmol), and CH_3CN (1 mL) in a 25 mL Schlenk tube was degassed and then filled with N_2.[1a] The Schlenk tube was fitted with a small condenser and heated to reflux for 6 h. After this time, part of the solvent (50%) was removed by distillation and replaced by MeOH. On cooling, the reaction mixture crystallized. The product was filtered, recrystallized twice from MeOH, and dried under vacuum to yield 1.3 g (45%) of white crystals of 99% purity (HPLC) (mp 72−73 °C): ^{1}H NMR δ 2.00 (s, 3H, CCH_3), 3.72 (d, 1H, SO_2CH_2CCl, $J = 14$ Hz), 3.81 (s, 3H, $COOCH_3$), 3.87 (s, 3H, CH_3OPh), 4.11 (d, 1H, SO_2CH_2CCl, $J = 14$ Hz), 7.01 (d, 2H, *m* to SO_2, $J = 8.8$ Hz), 7.81 (d, 2H, *o* to SO_2, $J = 8.8$ Hz); ^{13}C NMR δ 26.78 (CCH_3), 53.67 ($COOCH_3$), 55.78 (CH_3OPh), 62.36 (CH_2CCl), 65.70 (SO_2CH_2CCl), 114.59 (*o* to MeO), 130.27 (*m* to MeO), 131.79 (*p* to MeO), 164.10 ($COOCH_3$), 169.19 (*p* to SO_2). Anal. Calcd for $C_{12}H_{15}ClO_5S$: C, 46.98; H, 4.93. Found: C, 46.75; H, 5.03.

Synthesis of 1-(4-Methoxybenzenesulfonyl)-2-chloro-2-phenylethane (MBSCS). A mixture of S (2.6 mL, 22.7 mmol), *p*-methoxybenzenesulfonyl chloride (4 g, 20.1 mmol), Et_3NHCl (48 mg, 0.35 mmol), CuCl (22 mg, 0.22 mmol), and CH_3CN (1 mL) in a 25 mL Schlenk tube was degassed and then filled with N_2.[1a] The Schlenk tube was fitted with a small condenser and heated to reflux for 2 h. After this time, part of the solvent (50%) was removed by distillation and replaced by MeOH. On cooling, the reaction mixture crystallized. The product was filtered, recrystallized twice from MeOH, filtered, and dried under vacuum to yield 2.06 g (40%) of white crystals of 99.9% purity (HPLC) (mp 77−79 °C): ^{1}H NMR δ 3.77−4.00 (m, 2H, SO_2CH_2CHCl), 3.86 (s, 3H, CH_3OPh), 5.32 (d of t, 1H, $SO_2CH_2CHPhCl$, $J_d = 2$ Hz, $J_t = 6.9$ Hz), 6.90 (d, 2H, *m* to SO_2, $J = 9.1$ Hz), 7.25 (m, 5H, Ph-), 7.67 (d, 2H, *p* to SO_2, $J = 9.1$ Hz); ^{13}C NMR δ 55.34 ($CHClPh$), 55.80 (H_3COPh), 64.27 (SO_2CH_2), 114.43 (*o* to CH_3O), 127.22 (*p* to CHCl), 128.99 (*m* to CHCl), 129.20 (*o* to CHCl), 130.45 (*m* to CH_3O), 130.61 (*p* to CH_3O), 138.68 (*C* connecting Ph to CHCl), 163.89 (*p* to SO_2).

Synthesis of 1-(4-Fluorobenzenesulfonyl)-2-chloro-2-phenylethane (FBSCS). A mixture of S (2.6 mL, 22.7 mmol), *p*-fluorobenzenesulfonyl chloride (4 g, 20.5 mmol), Et_3NHCl (48 mg, 0.35 mmol), CuCl (22 mg, 0.22 mmol), and CH_3CN (1 mL) in a 25 mL Schlenk tube was degassed and then filled with N_2.[1a] The Schlenk tube was fitted with a small condenser and heated to reflux for 2 h. After this time, part of the solvent (50%) was removed by distillation and replaced by MeOH. On cooling, the reaction mixture crystallized. The product was filtered, recrystallized twice from MeOH, filtered, and dried under vacuum to yield 3.7 g (62%) of white crystals of 99.9% purity (HPLC) (mp 86−87 °C): ^{1}H NMR δ 3.93 (m, 2H, SO_2CH_2CHCl), 5.35 (d of t, 1H, $SO_2CH_2CHPhCl$, $J_d = 2$ Hz, $J_t = 7$ Hz), 7.08 (t, 2H, *m* to SO_2, $J = 8$ Hz), 7.26 (m, 5H, Ph-), 7.76 (m, 2H, *p* to SO_2); ^{13}C NMR δ 55.14 ($CHClPh$), 64.11 (SO_2CH_2), 116.44 (d, *o* to F, $J = 22.8$ Hz), 127.22 (*p* to CHCl), 128.99 (*m* to CHCl), 129.30 (*o* to CHCl), 131.11 (d, *m* to F, $J = 9.8$ Hz), 135.24 (*p* to F), 138.25 (*C* connecting Ph to

---

(29) Percec, V.; Kim, H.-J.; Barboiu, B. *Macromolecules* **1997**, *30*, 8526.

(30) Paik, H.-J.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (2), 274.

(31) (a) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34* (2), 243. (b) Yasuda, H.; Yamamoto, K.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908. (c) Boffa, L. S.; Novak, B. M. *Macromolecules* **1994**, *27*, 6993. (d) Zagala, A. P.; Hogen-Esch, T. E. *Macromolecules* **1996**, *29*, 3038. (e) Aida, T.; Inoue, S. *Acc. Chem. Res* **1996**, *29*, 39.

(32) (a) Percec, V., Tirrell, D. A., Eds. *New Macromolecular Architecture and Supramolecular Polymers, Macromolecular Symposium*; Hüthig and Vepf Verlag: Heidelberg, 1994; Vol. 77. (b) Percec, V.; Lando, J. *Polymers, Materials for the 21st Century, Macromolecular Symposium*; 1995; Vol. 98.

CHCl), 165.80 (d, *p* to SO_2, $J = 257.4$ Hz). Anal. Calcd for $C_{14}H_{12}ClFO_2S$: C, 56.28; H, 4.05. Found: C, 56.48; H, 4.26.

Synthesis of 1-(4-Fluorobenzenesulfonyl)-2-phenylethane (FBSS). To a mixture of 1-(4-fluorobenzenesulfonyl)-2-chloro-2-phenylethane (0.3 g, 1 mmol) in C_6H_6 (2 mL) was added, at 23 °C, Et_3SiH (0.2 g, 1.7 mmol) and a catalytic amount of $PdCl_2$ (3 mg).[23] After stirring for 10 min, conversion was 100% (NMR). C_6H_6 was distilled under vacuum, the crude product was recrystallized three times from hexanes, and the catalyst was removed by passing through an Al_2O_3 column to yield 0.25 g white crystals (85%) of 99.9% purity (HPLC) (mp 67−68 °C): ^{1}H NMR δ 3.05 (m, 2H, $SO_2CH_2CH_2$Ph), 3.37 (m, 2H, SO_2CH_2-CH_2Ph), 7.12 (d, 2H, *m* to SO_2, $J = 6.7$ Hz), 7.25 (m, 5H, Ph-),7.95 (m, 2H, *o* to SO_2); ^{13}C NMR δ 28.81 (CH_2Ph), 57.69 (SO_2CH_2), 116.67 (d, *o* to F, $J = 23$ Hz), 126.80 (*p* to CH_2CH_2), 128.17 (*o* to CH_2CH_2), 128.70 (*m* to CH_2CH_2), 130.86 (d, *m* to F, $J = 9.6$ Hz), 134.98 (*p* to F), 137.13 (*C* connecting Ph to CHCl), 165.69 (d, *p* to SO_2, $J = 260.8$ Hz). Anal. Calcd for $C_{14}H_{13}FO_2S$: C, 63.62; H, 4.96. Found: C, 63.66; H, 5.00.

Synthesis of 4,4′-Dimethyl-2,2′-bipyridine. In a 1500 mL reaction flask fitted with condenser and inert gas inlet/outlet containing Raney Ni (78 g) degassed and maintained under Ar was carefully introduced 700 mL of degassed 4-methylpyridine.[34] The mixture was refluxed for 60 h, the solution was then decanted, and the Ni catalyst rinsed with boiling C_6H_6 (2 × 100 mL). C_6H_6 and unreacted 4-methylpyridine were distilled off under vacuum (0.5 mmHg), and the remaining solid then crystallized. The yellow crude crystals were first recrystallized from 400 mL of toluene and then from 1200 mL of EtOH (95%) to give 72 g (11%, lit.[34] 30%) of white crystals (mp 171−173 °C (lit.[34] 172−173 °C): ^{1}H NMR δ 2.41 (s, 6H, CH_3), 7.11 (d, 2H, positions 5, 5′, $J = 4.7$ Hz), 8.20 (s, 2H, positions 3, 3′), 8.51 (d, 2H, positions 6, 6′, $J = 4.7$ Hz); ^{13}C NMR δ 21.09 (CH_3), 121.91 (*p* to Py), 124.56 (*o* to Py), 147.99 (*p* to N), 148.84 (*o* to N), 155.96 (*C* from bridge). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.56. Found: C, 78.20; H, 6.57.

Synthesis of 4,4′-Dinonyl-2,2′-bipyridine. This compound was synthesized by a modified literature procedure.[35] In a 500 mL three-necked flask equipped with septum and dropping funnel maintaned under N_2 were placed diisopropylamine (14 mL, 0.08 mol) and 30 mL of THF. The mixture was cooled to 0 °C, and BuLi (1.6 M, 50 mL, 0.08 mol) was added dropwise. The solution was stirred for 1 h at 0 °C, and 4,4′-dimethyl-2,2′-bipyridine (5.52 g, 0.03 mol) dissolved in 150 mL of THF was added dropwise. The resulting orange suspension was stirred for 3 h at 0 °C, and 1-bromooctane (14 mL, 0.08 mol) dissolved in 20 mL THF was added dropwise while the temperature was maintaned at 0 °C. The resulting dark green solution was stirred for 3 h, quenched with 10 mL MeOH, poured onto ice-water (20/80 v/v), extracted with Et_2O, and concentrated to a yellow oil using a rotary evaporator. The crude product was recrystallized from 20 mL of hexanes giving a first fraction of white crystals. The mother liquor was concentrated and mixed with an equal volume of EtOH, giving a second fraction of crystals while cooling in the freezer. In this manner, 7.9 g (64%) of product was obtained. The pure product was obtained after three recrystalizations from EtOH (6.58 g, 54%) (purity (HPLC) 99.99%, mp 58−59 °C): ^{1}H NMR δ 0.87 (t, 6H, CCH_3, $J = 6.5$ Hz), 1.25 (m, 24H, Py-$CH_2CH_2(CH_2)_6CH_3$), 1.68 (m, 4H, Py-CH_2CH_2-), 2.68 (t, 4H, Py-CH_2CH_2-, $J = 7.4$ Hz), 7.12 (d, 2H, positions 5,5′, $J = 4.7$ Hz), 8.23 (s, 2H, positions 3,3′), 8.55 (d, 2H, positions 6,6′, $J = 4.8$ Hz); ^{13}C NMR δ 14.08 (-CH_3), 22.65−35.55 (alkyl tails), 121.30 (*p* to Py), 123.85 (*o* to Py), 148.93 (*o* to N), 152.85 (*p* to N), 156.18 (*C* from bridge). Anal. Calcd for $C_{28}H_{44}N_2$: C, 82.29; H, 10.85, N, 6.85. Found: C, 81.89; H, 10.98, N, 6.64.

Typical Procedure for Polymerization Kinetics. The monomer (MMA, 2 mL, 18.7 mmol), solvent (*p*-xylene, 1 mL), initiator (MBSC, 19 mg, 0.092 mmol), catalyst (CuCl, 4 mg, 0.04 mmol), and ligand (bpy9, 22 mg, 0.054 mmol) were weighted directly in a 25 mL Schlenk tube. The mixture was degassed by four freeze−pump−thaw cycles and the tube was filled with Ar and heated to the polymerization temperature. The sidearm of the tube was purged with N_2 for at least 5 min before it was opened to remove samples at determined times using an airtight syringe. Samples were diluted with $CDCl_3$ in NMR tubes, and the conversion was measured by ^{1}H NMR spectroscopy. Part of the solution was then injected in a GPC column eluted with THF, and the molecular weight was measured versus PS standards using a UV detector (254 nm). In this case, the phenylsulfonyl chain end derived from the initiator is responsible for the UV absorption. Samples were also run by using an RI detector, and molecular weights were calculated using a calibration made with PMMA standards. The molecular weight determined by both detectors were identical. This demonstrates that all polymer chains contained the substituted phenylsulfonyl chain end.

Typical Procedure for Initiation Kinetics. Solutions of initiator and monomer were prepared in two Schlenk tubes. The first solution contained the initiator (4-methoxybenzenesulfonyl chloride, MBSC, 287 mg, 1.39 mmol) in 1.5 mL *p*-xylene. The second solution contained the monomer (MMA, 0.5 mL, 4.67 mmol), catalyst (CuCl, 17 mg, 0.17 mmol), and ligand (4,4′-dinonyl-2,2′-bipyridine, 84 mg, 0.21 mmol) in solvent (*p*-xylene, 0.5 mL). Both solutions were degassed by four freeze−pump−thaw cycles, and the tubes were then inserted in a thermostated (±0.5 °C) oil bath at the desired reaction temperature.

At the initial time, 0.5 mL of initiator solution was transferred into the Schlenk tube containing the monomer and the reaction starts instantly. At given times, samples are removed through the septum using an airtight syringe and dilluted 10 times with $CDCl_3$ directly in the NMR tube. After reaction is over, the samples were analyzed by ^{1}H NMR for initiator consumption and, simultaneously, adduct initiator−monomer formation, using *p*-xylene as internal standard. The NMR signals used in the calculation were the doublet at 7.98 ppm ($J = 8.5$ Hz) for MBSC, the doublet at 7.84 ppm ($J = 8.5$ Hz) for the adduct (MBSCMMA), and the singlet of the *p*-xylene at 7.07 ppm.

General Comments on this Polymerization Technique. For preparative purposes this polymerization can be carried out with unpurified reagents (i.e., catalyst, monomer, and solvents as received) under a blancket of N_2 or Ar. However, an induction period due to the presence of traces of O_2 from air or inhibitor from monomer will be observed. Also, the molecular weight distribution can be broader. This polymerization is not sensitive to moisture but is sensitive to O_2 and radical inhibitors. Therefore, we recommend that the monomer be passed at least through an Al_2O_3 column (to remove the inhibitor) and the system should be maintained O_2 free via any suitable experimental technique.

Acknowledgment. Financial support from the National Science Foundation (DMR-97-08581), a fellowship from BP for B.B., and an unrestricted faculty award from DuPont are gratefully acknowledged.

Supporting Information Available: Kinetic derivations, kinetic plots, and tables with rate constants for the initiation and propagation steps of the “living” radical polymerization of S, MMA, BMA, MA, and BA (11 pages). See any current masthead page for ordering and Internet access instructions.

JA9713845

---

(33) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

(34) Noltes, J. G.; Bos, K. D. Kraaijkamp, J. G. *Synth. Commun.* **1979**, *9* (6), 497.

(35) Garelli, N.; Vierling, P. *J. Org. Chem.* **1992**, *57*, 3046.