Macromolecules **1998,** *31,* 4053−4056

Self-Regulated Phase Transfer of Cu$_2$O/bpy, Cu(0)/bpy, and Cu$_2$O/Cu(0)/bpy Catalyzed "Living" Radical Polymerization Initiated with Sulfonyl Chlorides[†]

V. Percec,* B. Barboiu, and M. van der Sluis

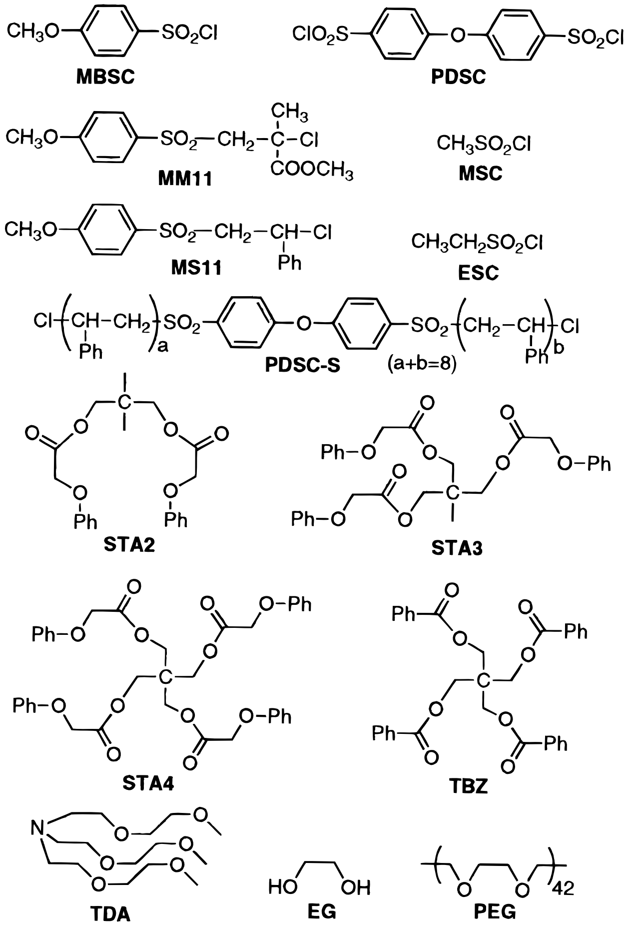
The W. M. Keck Laboratories for Organic Synthesis, Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

Received February 24, 1998
Revised Manuscript Received April 15, 1998

In 1995 we discovered that arylsulfonyl halides[1−4] and subsequently alkylsulfonyl halides[4] represent a universal class of functional initiators[5] for heterogeneous[1] and homogeneous[2,5] metal-catalyzed "living" radical polymerization of styrene(s), methacrylates, and acrylates.[5] This is due to a quantitative initiation with much faster rate than propagation,[5] regardless of the functional groups attached to the sulfonyl halide initiator.[4,5] Sulfonyl chlorides contrast with alkyl halide initiators whose structure should be tailored for each class of monomers in order to obtain a rate of initiation at least equal to that of propagation.[6] The large difference between the rates of initiation and propagation with sulfonyl chloride initiators[5] is of interest for the construction of polymers with well-defined and complex architecture.[7] The rational for this behavior and the mechanism of this reaction have been discussed elsewhere.[3,5] The catalytic systems used so far with both sulfonyl and alkyl halides initiators are based on various transition metal salts, the preferred one in many laboratories being based on CuX and an organic ligand such as unsubstituted and substituted 2,2′-bipyridine (bpy).[1−7]

This communication demonstrates that Cu$_2$O, Cu(0), and combinations of both in conjunction with bpy self-regulate in a phase transfer catalyzed (PTC) process mediated by thermally stable multidentate acyclic neutral ligands, including octopus-like compounds, poly(ethylene glycol) (PEG), and even ethylene glycol (EG),[8] the *in situ* generation of the CuCl/CuCl$_2$ catalyst to the extent that the control of this polymerization reaction approaches and exceeds that of the CuCl/bpy-based heterogeneous and homogeneous processes.[5] The experiments reported here were inspired by a review of Minisci,[9] which describes the accidental discovery of the FeCl$_2$-catalyzed Kharasch addition of alkyl halides to olefins during an attempt to perform radical polymerization of acrylonitrile in CCl$_4$ and CHCl$_3$ in a steel autoclave. The second source of inspiration was a series of publications by a Czech group that between 1974 and 1992 investigated metal oxides and zerovalent metals as catalysts in redox free radical additions to olefins.[10] An acceleration of the metal halides catalyzed polymerization in the presence of Cu(0) was published, without the authors being aware of related literature reports,[10] while this work was in progress.[11]

Scheme 1. Initiators and additives used for the metal-catalyzed "living" radical polymerization of styrene (S) and butyl methacrylate (BMA)



Scheme 1 shows the structures of the initiators and phase transfer catalysts (PTC) used. Table 1 summarizes selected experiments on the polymerization of butyl methacrylate (BMA). Cu$_2$O (entries 2, 11, 12, and 24) produces polymers with M_w/M_n as narrow as or even narrower than those obtained with homogeneous CuCl systems based on substituted bpy.[5] The k_p^{exp} is lower than that of the CuCl heterogeneous systems (entries 1, 9, and 23) and higher than that of the CuCl-based homogeneous systems.[5] In all cases an induction period (of 20−100 min) was observed (Figure 1a, entry 2, Table 1). This induction period can be eliminated by the use of a PTC such as TDA, EG, TBZ, STA4 and PEG (entries 3, 13−16, and 19, Table 1) (Scheme 1) (Figure 1c, entry 3, Table 1). Under these conditions k_p^{exp} becomes higher than that of the heterogeneous CuCl/bpy-catalyzed reaction and the molecular weight distribution, although slightly broader, remains in the range of values for homogeneous CuCl/substituted bpy-catalyzed systems[5] (Figure 1a,c, Table 1). Cu(0) provides the highest k_p^{exp} values (entries 4, 7, 20, and 25, Table 1). An induction period of 2−4 min was observed in many cases (Figure 1e). This induction can be removed by the use of a PTC (entries 5, 6, 21, and 22). The M_w/M_n values for Cu(0)-catalyzed polymerizations are close to those obtained in the CuCl/bpy heterogeneous systems. The initiation efficiency is about 1.0 with the exception of methanesulfonyl chloride (MSC) catalyzed by Cu(0)/bpy and of the experiments where EG was used as PTC. This is

---

[†] Dedicated to the 75th birthday of Professor H.-J. Cantow.

[*] Phone: (216) 368 4242. Fax: (216) 368 4202. E-mail: vxp5@po.cwru.edu.

S0024-9297(98)00286-1 CCC: $15.00

Table 1. Cu-, Cu_2O-, and CuCl-Catalyzed Polymerizations of Butyl Methacrylate (BMA) Initiated with *p*-Methoxybenzenesulfonyl Chloride (MBSC), Phenoxybenzene-4,4′-disulfonyl Chloride (PDSC), and Methanesulfonyl Chloride (MSC) at 120 °C in PhOPh ([BMA] = 4.5 M)

no.	initiator	cat./PTC	[M]/[I]/[cat.]/[bpy]/[PTC]	k_p^{exp} (h^{-1})	M_w/M_n	conv (%)	time (h)	init effic
1	PDSC	CuCl	200/1/2/6	1.95	1.27	94	1.8	0.99
2	PDSC	Cu_2O	200/1/2/6	1.34[b]	1.07	97	5.5	0.97[d]
3	PDSC	Cu_2O/EG	200/1/2/6/15	2.87	1.18	98	1.3	0.95
4	PDSC	Cu	200/1/2/6	4.21[b]	1.12	96	0.8	0.99[d]
5	PDSC	Cu/EG	200/1/2/6/15	5.37	1.46	97	0.7	0.68[d]
6	PDSC	Cu/STA4	200/1/2/6/0.5	8.20[b]	1.16	97	0.7	0.94[d]
7	PDSC	Cu coin	200/1/2/6	0.94[b]	1.14	93	2.8	0.98[d]
8	PDSC	Cu + Cu_2O	200/1/1/1/6	2.80[b]	1.16	93	1.1	0.97[d]
9	MBSC	CuCl	200/1/1/3	2.46[c]	1.22	98	3.2	0.99
10	MBSC	CuCl/STA4	200/1/1/3/0.5	4.04[c]	1.18	95	1.5	0.99
11	MBSC	Cu_2O	200/1/2/6	0.80[b]	1.09	95	4.0	0.99[d]
12	MM11[a]	Cu_2O	200/1/2/6	1.08[b]	1.10	98	4.5	0.97[d]
13	MBSC	Cu_2O/TDA	200/1/2/6/0.5	0.90	1.11	98	3.0	0.99[d]
14	MBSC	Cu_2O/TBZ	200/1/2/6/0.5	1.13	1.15	96	3.0	0.99
15	MBSC	Cu_2O/EG	200/1/2/6/15	2.13	1.16	96	1.5	0.85
16	MBSC	Cu_2O/PEG	200/1/2/6/15	1.90	1.19	94	1.5	0.99
17	MBSC	Cu_2O/STA2	200/1/2/6/1	1.31[b]	1.13	97	3.0	0.99[d]
18	MBSC	Cu_2O/STA3	200/1/2/6/0.5	1.93[b]	1.14	99	2.7	0.99
19	MBSC	Cu_2O/STA4	200/1/2/6/0.5	1.17	1.10	96	2.7	0.98
20	MBSC	Cu	200/1/2/6	3.11	1.26	95	1.0	0.99
21	MBSC	Cu/PEG	200/1/2/6/15	4.00	1.32	96	0.8	0.99
22	MBSC	Cu/STA4	200/1/2/6/0.5	4.67	1.28	97	0.7	0.99
23	MSC	CuCl	200/1/1/3	5.40[c]	1.27	95	1.0	0.99
24	MSC	Cu_2O	200/1/2/6	0.72	1.15	93	3.8	0.95
25	MSC	Cu	200/1/2/6	2.26	1.44	90	1.1	0.33

[a] Mono-adduct MBSC−MMA, see Scheme 1. [b] Induction period is present. [c] Refers to corrected k_p^{exp}; values from ref 5 have been multiplied by 2, assuming a first-order dependence in [CuCl]. [d] Deviation of M_n from M_{th}.

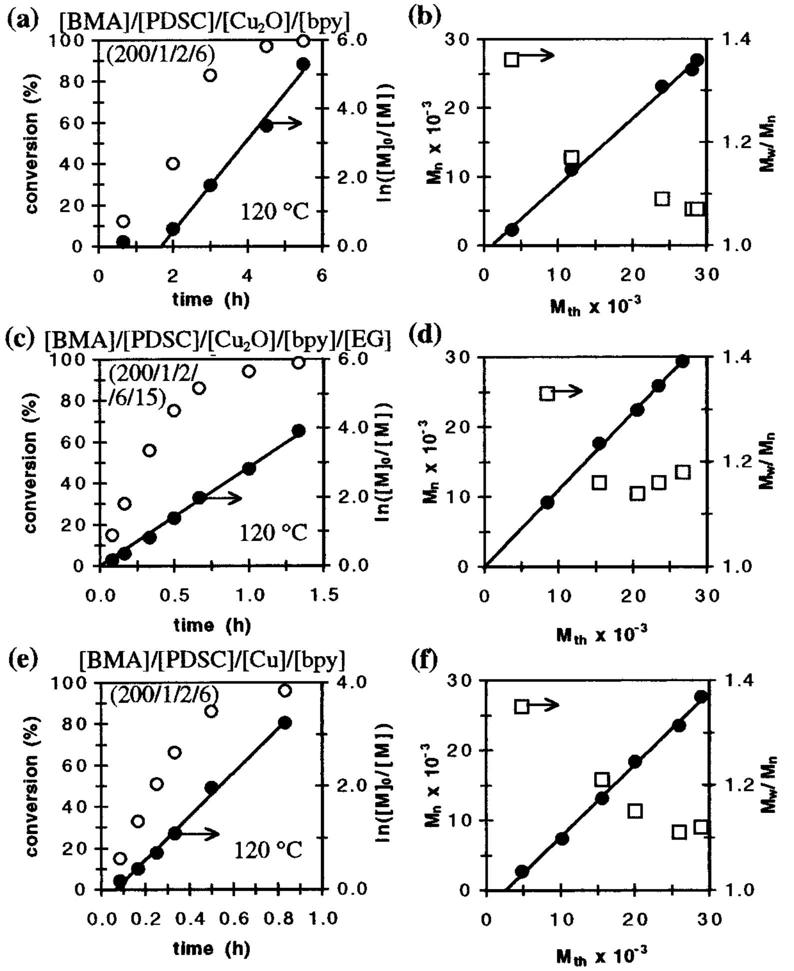


Figure 1. Kinetic plots for the heterogeneous diradical polymerization of BMA ([BMA] = 4.5 M) initiated with phenoxybenzene-4,4′-disulfonyl chloride (PDSC) and catalyzed by (a, b) Cu_2O; (c, d) Cu_2O and ethylene glycol ([Cu_2O]/[EG] = 2/15 molar ratio); and (e, f) Cu(0), all using [BMA]/[PDSC]/[cat]/[bpy] = 200/1/2/6 molar ratios at 120 °C in PhOPh.

Table 2. Cu-, Cu_2O-, and CuCl-Catalyzed Polymerizations of S Initiated with *p*-Methoxybenzenesulfonyl Chloride (MBSC), Phenoxybenzene-4,4′-disulfonyl Chloride (PDSC), Methanesulfonyl Chloride (MSC), and Ethanesulfonyl Chloride (ESC) at 120 °C in PhOPh ([S] = 5.9 M)

no.	initiator	cat./PTC	[S]/[I]/[cat]/[bpy]/[PTC]	k_p^{exp} (h^{-1})	M_w/M_n	conv (%)	time (h)	init effic
1	MBSC	CuCl	200/1/1/3	0.18[b]	1.36	92	28	0.99
2	MBSC	Cu	200/1/2/6	0.17[c]	1.35	80	6.0	0.70
3	MBSC	Cu/STA4	200/1/2/6/0.5	0.20[c]	1.18	92	11	0.65
4	MBSC	Cu_2O/PEG	200/1/2/6/15	0.09	1.37	94	32	0.99
5	MS11[a]	Cu	200/1/2/6	0.73	1.55	96	4.5	0.74
6	PDSC	CuCl	200/1/2/6	0.12	1.22	96	22	0.99
7	PDSC	Cu_2O	200/1/2/6	0.28	1.24	80	6.0	0.99
8	PDSC-S[a]	Cu_2O	200/1/2/6	0.14	1.22	97	24	0.99
9	PDSC	Cu	200/1/2/6	0.69	1.33	88	3.0	0.99
10	PDSC	Cu/PEG	200/1/2/6/15	0.70	1.40	92	3.5	0.71
11	MSC	Cu	200/1/2/6	0.43	1.22	96	8.0	0.69
12	ESC	Cu	200/1/2/6	0.32[c]	1.43	91	6.8	0.40

[a] Adduct initiator-S, see Scheme 1. [b] Refers to corrected k_p^{exp}; values from ref 5 have been multiplied by 2, assuming a first-order dependence in [CuCl]. [c] Initial acceleration is present.

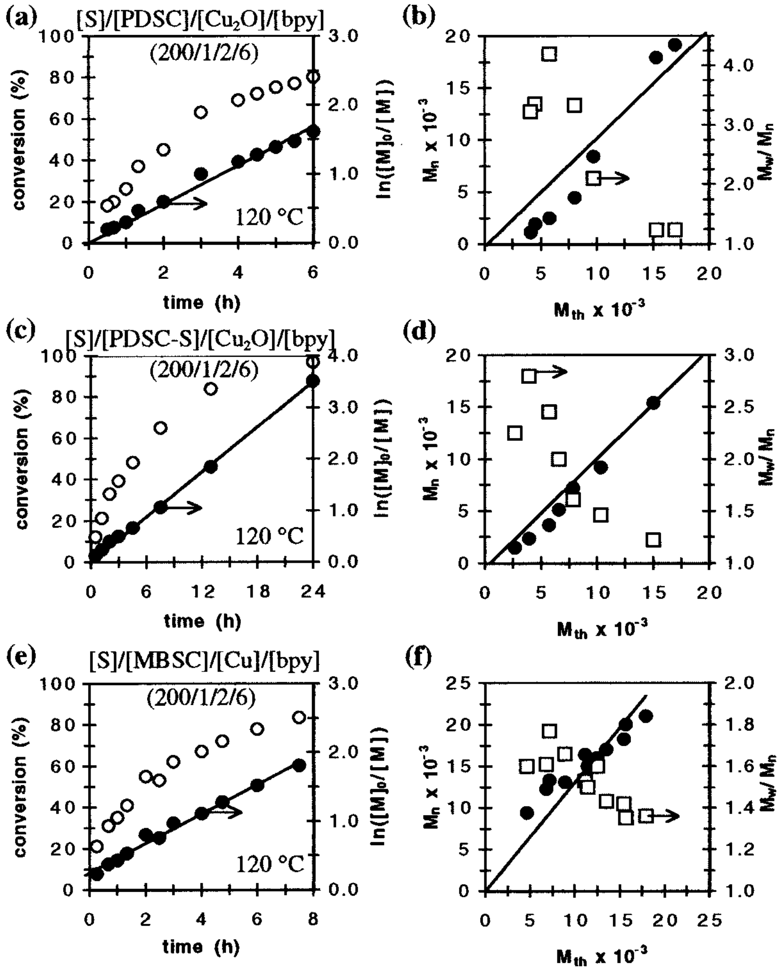


Figure 2. Kinetic plots for the metal-catalyzed heterogeneous radical polymerization of S ([S] = 5.9 M) (a, b) initiated with: phenoxybenzene-4,4′-disulfonyl chloride (PDSC) and catalyzed by Cu_2O, (c, d) initiated with isolated PDSC−S oligomer (M_n = 1100, M_w/M_n = 1.20) and catalyzed by Cu_2O, and (e, f) initiated with 4-methoxybenzenesulfonyl chloride (MBSC) and catalyzed by Cu(0), all using [S]/[I]/[cat]/[bpy] = 200/1/2/6 molar ratios at 120 °C in PhOPh.

due to a partial initiator extraction from the polymerization solution in a second immiscible EG liquid phase.

Polymerization of styrene (S) with the same initiators is summarized in Table 2. Cu_2O (entries 4, 7, and 8) provides the best control of this polymerization (*i.e.*, lowest M_w/M_n) although with a lower rate than Cu(0)-based catalysts (entries 2, 3, 5, and 9−12). The k_p^{exp} values for both Cu_2O- and Cu(0)-catalyzed reactions (entries 2−4 and 7−12) are higher than those obtained for homogeneous[5] and heterogeneous (entries 1 and 6) polymerizations. An initial acceleration period is observed for the MBSC/Cu(0)/bpy system (entry 2). This acceleration is not observed when initiation is carried out with MS11 (entry 5), under the same conditions. No acceleration is observed when PDSC is used as initiator for the polymerization of S in the presence of Cu(0) or Cu_2O (entries 7, 9, and 11).

Figure 2a shows kinetic plots for the polymerization of S initiated with PDSC/Cu_2O/bpy (entry 7, Table 2). GPC traces of this experiment are shown in Supporting Figure 26a. We can observe an initial jump in the molecular weight of the polymer (at 18% conversion)

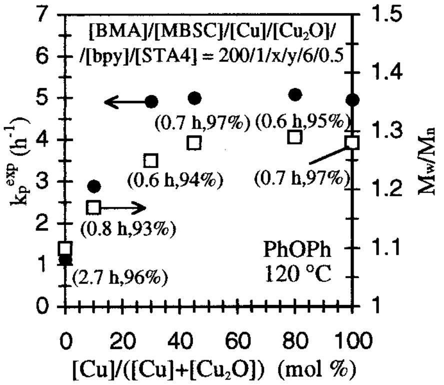


Figure 3. "Living" radical polymerization of BMA initiated with 4-methoxybenzenesulfonyl chloride (MBSC) and catalyzed by mixtures Cu/Cu_2O/bpy in the presence of STA4. Reaction conditions: [BMA] = 4.5 M, [BMA]/[MBSC]/[Cu(0)]/[Cu_2O]/[bpy]//[STA4] = 200/1/x/y/6/0.5 molar ratios, $x + y = 2$, reaction temperature 120 °C in PhOPh.

that is presumably due to the absence of $CuCl_2$ in the reaction mixture (*i.e.*, absence of reversible termination). Above this conversion the reaction becomes controlled, and at 80% conversion, $M_w/M_n = 1.24$ (entry 7, Table 2) (Figure 2a). The oligomer obtained at 18% conversion was separated, characterized (PDSC−S, see Scheme 1), and used as initiator in a new polymerization experiment (Figure 2c,d, entry 8 in Table 2). The same kinetic trend as with PDSC was observed. Figure 2e,f shows the polymerization of S with MBSC/Cu/bpy (entry 2, Table 2). A very fast polymerization occurs at short reaction times (initial acceleration). This suggests again the absence of $CuCl_2$ in the reaction mixture in the early stages of the polymerization.

These results can be explained as follows. In the initial stages of the polymerization both Cu_2O and Cu form the true CuCl catalyst by a mechanism that is not yet elucidated.[10b] The formation of CuCl is slower in the case of Cu_2O than in the case of Cu. This explains the longer induction period for Cu_2O and the initial acceleration of Cu-catalyzed reactions. CuCl/bpy is solubilized by various PTCs in a similar way substitution of bpy with alkyl groups does.[5] However, the PTC solubilizes the overall CuCl/bpy and $CuCl_2$/bpy complexes.[8] The detailed mechanism of this new PTC process requires investigation. In the case of Cu(0)-catalyzed reactions, $CuCl_2$ generated by initiation, propagation, and a small extent of irreversible termination is maintained to a minimum by reduction to CuCl with Cu(0),[10c] and this provides a very fast rate of polymerization. However, larger M_w/M_n values are obtained. In the case of Cu_2O, most probably, no reduction of $CuCl_2$ occurs. Still, the concentration of CuCl generated during the Cu_2O initiation is lower than that produced by Cu(0) and, therefore, the very small concentration of propagating radicals suppresses the rate of irreversible termination more than in the case of CuCl- and Cu(0)-catalyzed reactions. The overall result is that these heterogeneous reaction mixtures produce a homogeneous polymerization reaction that self-controls the amount of CuCl catalyst generated by its very slow formation (in the case of Cu_2O), by reduction of $CuCl_2$ (in the case of Cu(0)), and/or by a combination of both.

As summarized in Figure 3, mixtures of Cu_2O and Cu(0) provide the simplest and the most convenient method to control the rate and M_w/M_n in these polymerizations. Because very small amounts of catalyst are needed for controlling the polymerization, Cu_2O, Cu(0), and various Cu alloys can be used as powder, films, wires, coins (entry 7, Table 1), etc. Preliminary experiments with Cu(0)[12] and Cu_2O of various activities have shown that the surface area of the catalyst is the most significant parameter that controls the rate of these polymerizations. Combinations of unsubstituted bpy with PEG as PTC provide the most efficient ligand for this novel self-regulated Cu_2O/Cu(0)-catalyzed "living" radical polymerization, which provides polymers with narrower M_w/M_n than the homogeneous process[5] and higher rates than the heterogeneous process.[3,4]

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: Experimental conditions and techniques, synthesis of **STA2**, **STA3**, and **STA4**, and kinetic plots for the data in Tables 1 and 2, of conversion in time, and of M_n vs M_{th} (16 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) Percec, V.; Kim, H.-J.; Barboiu, B. *Macromolecules* **1997**, *30*, 8526.
(5) Percec, V.; Barboiu, B.; Kim, H.-J. *J. Am. Chem. Soc.* **1998**, *120*, 305.
(6) (a) Kato, M.; Kamigato, 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.; Waterson, C.; Derrick, P. J.; Jasieczek, C. B.; Shooter, A. J. *Chem. Commun.* **1997**, 683.
(7) (a) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080. (b) Grubbs, R. B.; Hawker, C. J.; Dao, J.; Frechet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 270.
(8) (a) Heimann, U.; Herzhoff, M.; Vögtle, F. *Chem. Ber.* **1979**, *112*, 1397. (b) Soula, G. *J. Org. Chem.* **1985**, *50*, 3717. (c) Vögtle, F.; Weber, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 753. (c) Menger, F. M. *Top. Curr. Chem.* **1986**, *136*, 2.
(9) Minisci, F. *Acc. Chem. Res.* **1975**, *8*, 165.
(10) (a) Hájek, M.; Silhavy, P.; Málek, J. *Tetrahedron Lett.* **1974**, *36*, 3193. (b) For the reactivity scale of various metal oxides and induction see: Hájek, M.; Silhavy, P.; Málek, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 3488 and 3502. (c) For ranking ligands for CuCl, Cu_2O, and Cu(0) catalysts, rate increases in the Cu(0)-catalyzed process due to the reduction of excess $CuCl_2$ generated via combination and disproportionation, and UV acceleration see: Hájek, M.; Silhavy, P. *Collect. Czech. Chem. Commun.* **1983**, *48*, 1710. (d) For an innersphere pathway via a presumably coordinated radical see: Hájek. M.; Silhavy, P.; Spirková, B. *Collect. Czech. Chem. Commun.* **1990**, *55*, 2949.
(11) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348.
(12) Kórösy, F. *Nature* **1947**, *160*, 21.

MA980286G