Designing Functional Aromatic Multisulfonyl Chloride Initiators for Complex Organic Synthesis by Living Radical Polymerization

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ABSTRACT: The similarities and differences between sulfonyl chloride and alkyl halide initiators for metal-catalyzed living radical polymerizations are discussed. The differences in the rates of formation, reactivities, and reactions of primary radicals derived from sulfonyl halides and alkyl halides demonstrated the design principles for monosulfonyl and multisulfonyl chlorides that provided quantitative initiation and higher rates of initiation than of propagation. Multifunctional initiators with two, three, four, six, and eight sulfonyl chloride groups that produced perfect star polymers in 95% conversions were designed and synthesized on the basis of these principles. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 4776–4791, 2000

Keywords: living radical polymerization; multisulfonyl chloride initiators; reactivity; star polymers

INTRODUCTION

Scientists in the continuously growing field of polymer synthesis recognized long ago that living polymerizations[1] provide the most versatile method for the synthesis of well-defined polymers with controlled molecular weights and functional chain ends. The physical properties of polymers obtained by various living polymerization mechanisms (i.e., anionic, cationic, metathesis, coordinative, and radical) are different from those of the same polymers prepared by less controlled processes, such as the homologous chain polymerization reactions. Moreover, access to polymers with complex architectures through living polymerizations is opening a level of structural control that is competitive only with that generated via organic synthesis. From the synthesis of simple diblock copolymers to complex structures such as macrocyclic,[2] star,[3] and hyperbranched polymers,[4] the only limit is imagination. The design of reaction conditions and the optimization of yields for all the individual reaction steps involved in a living polymerization (i.e., initiation, propagation, and termination) are key parameters involved in the synthesis of any complex polymer architecture.

Metal-catalyzed living radical polymerizations (LRPs) are complementary to the stable free-radical polymerization mediated by nitroxide radicals.[5] Both polymerization processes require a suitable adjustment between the structure of the monomer, initiator, and atom or group of atoms that provide the reversible termination to gener-

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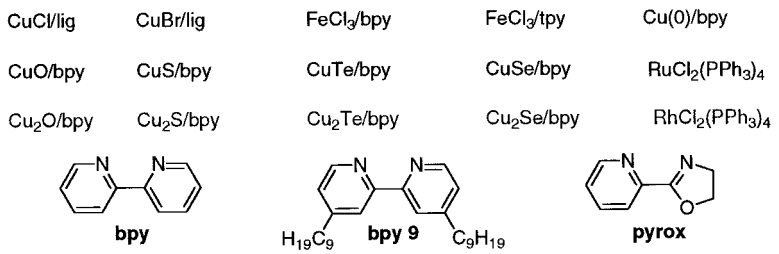


Scheme 1. Selected catalysts used for LRP.

ate a higher rate of initiation than propagation and a high initiator efficiency. Therefore, each process is restricted to the polymerization of selected classes of activated olefins. The complementarity of these two polymerization techniques has been used in the synthesis of hyperbranched polymers.[4]

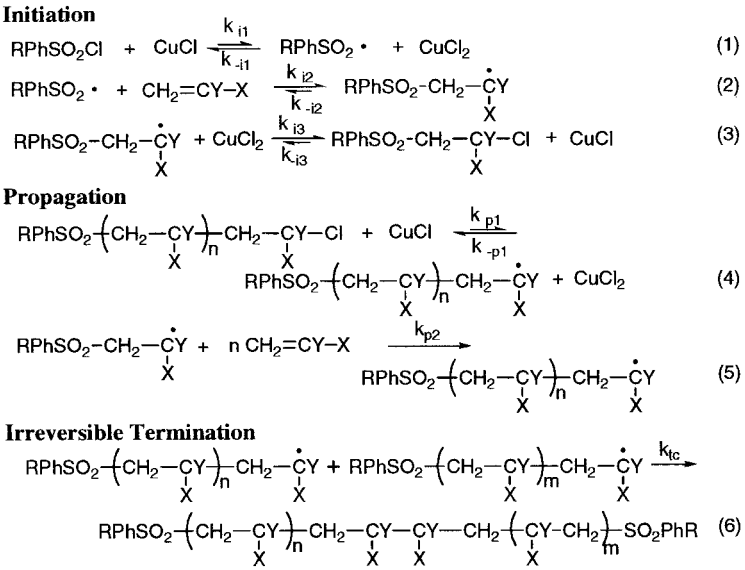
Publications on metal-mediated radical polymerizations initiated with alkyl halides, with unelucidated extents of control of each individual step, contributed to the present state of knowledge in the field of radical polymerization.[6] The groups of Sawamoto[7] and Matyjaszewski,[8] inspired by the landmark work of Otsu et al.,[6(g)] reported in 1995 the LRP of vinyl monomers initiated with alkyl halides. In the same year, we demonstrated that arylsulfonyl halides[9–15] and subsequently alkylsulfonyl[13–15(a)] and perfluoroalkylsulfonyl[16] halides represent a universal class of functional initiators[14] for heterogeneous[9–15,17] and homogeneous[10,14(a)] metal-catalyzed LRPs of styrene (S), methacrylates, and acrylates.

The catalytic systems used so far both with sulfonyl halide and alkyl halide initiators are based on various transition-metal salts (Scheme 1). The preferred ones in many laboratories are based on CuX and an organic ligand such as unsubstituted or 4,4′-disubstituted 2,2′-bipyridine (bpy). We demonstrated that Cu_2O, in conjunction with bpy, self-regulates in a phase-transfer-catalyst (PTC) process mediated by thermally stable multidentate acyclic neutral ligands, the LRP of S and methacrylates initiated with alkyl or arylsulfonyl chlorides.[15] This is the catalyst of choice for the synthesis of complex polymer architectures by LRP because it provides mild reaction conditions and a neutral or slightly basic reaction medium, useful for *in situ* acid-sensitive reactions. In contrast to Cu_2O LRP, CuCl LRP produces an acidic reaction medium. Less acidic and more soluble catalysts based on Cu^IX displaying increased rates of propagation were reported recently by our laboratory,[17] and their use for the synthesis of polymers with complex architecture is under investigation.

The monoaddition of sulfonyl and alkyl radicals to olefins and acetylenes followed by the transfer of a halide atom to the resulting radical is known as Kharasch addition or atom transfer radical addition (ATRA).[18] Unlike with carbon radicals, the addition of arylsulfonyl radicals to olefins is reversible,[19(c)] and this changes the overall kinetics of the initiation reaction. This equilibrium is determined by the nature of the substituent attached to the olefin and its ability to stabilize the resulting radical by resonance.[20]

The mechanism presented in Scheme 2 details the main steps involved in the metal-catalyzed LRP initiated with sulfonyl halides.[10] Initiation can be spontaneous or can be promoted by UV,[21] various sources of radicals,[22] or thermolysis,[22] and it is catalyzed by metals[23,34] that reduce the corresponding sulfonyl halide to a sulfonyl radical. Substituted and unsubstituted aryl and alkyl sulfonyl halides undergo bond homolysis, and the resulting electrophilic sulfonyl radicals subsequently add to substituted and unsubstituted olefins[22–24(a–c)] and acetylenes,[21] without[21–24(a–c)] and with[24(d)] the extrusion of SO_2 to yield the corresponding alkyl and vinyl halides. During propagation, depending on the nature of the substituent(s) present on the olefin, the resulting alkyl halides can undergo, under identical reaction conditions, addition to the same olefin.[25] More than one monomer addition followed by atom transfer is regarded as a side reaction (i.e., oligomerization) of ATRA.[18] The higher rate of propagation and broader molecular weight distribution in LRP are due to the increased number of monomer additions before each atom transfer step takes place.

The propagation and reversible termination steps of LRP initiated with sulfonyl halides and alkyl halides are identical.[26,27] However, the initiation step of these two polymerizations differs



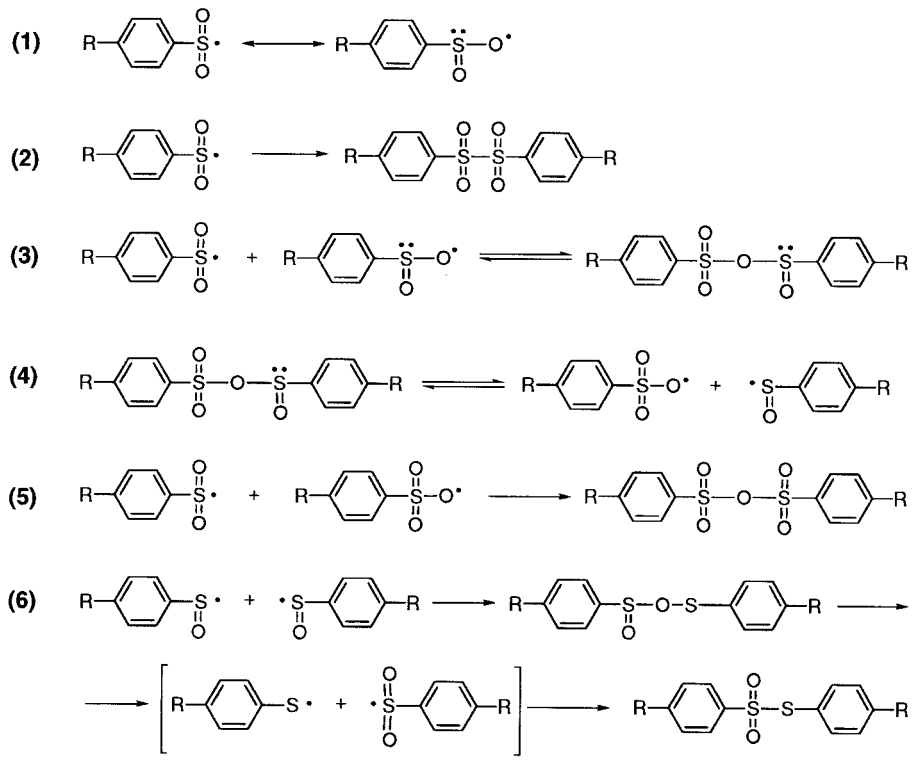
Scheme 2. Mechanism of the metal-catalyzed LRP initiated with arylsulfonyl chlorides.

substantially. The metal-catalyzed reduction of the substituted arylsulfonyl halides to the corresponding sulfonyl radicals is faster than that of the resulting alkyl halides, so arylsulfonyl halides facilitate a higher rate of initiation than propagation. A faster rate of initiation versus propagation is the primary requirement for the synthesis of polymers with narrow molecular weight distributions via LRP. A quantitative initiation is also the first step toward the elaboration of synthetic procedures required in the synthesis of complex organic molecules via LRP.

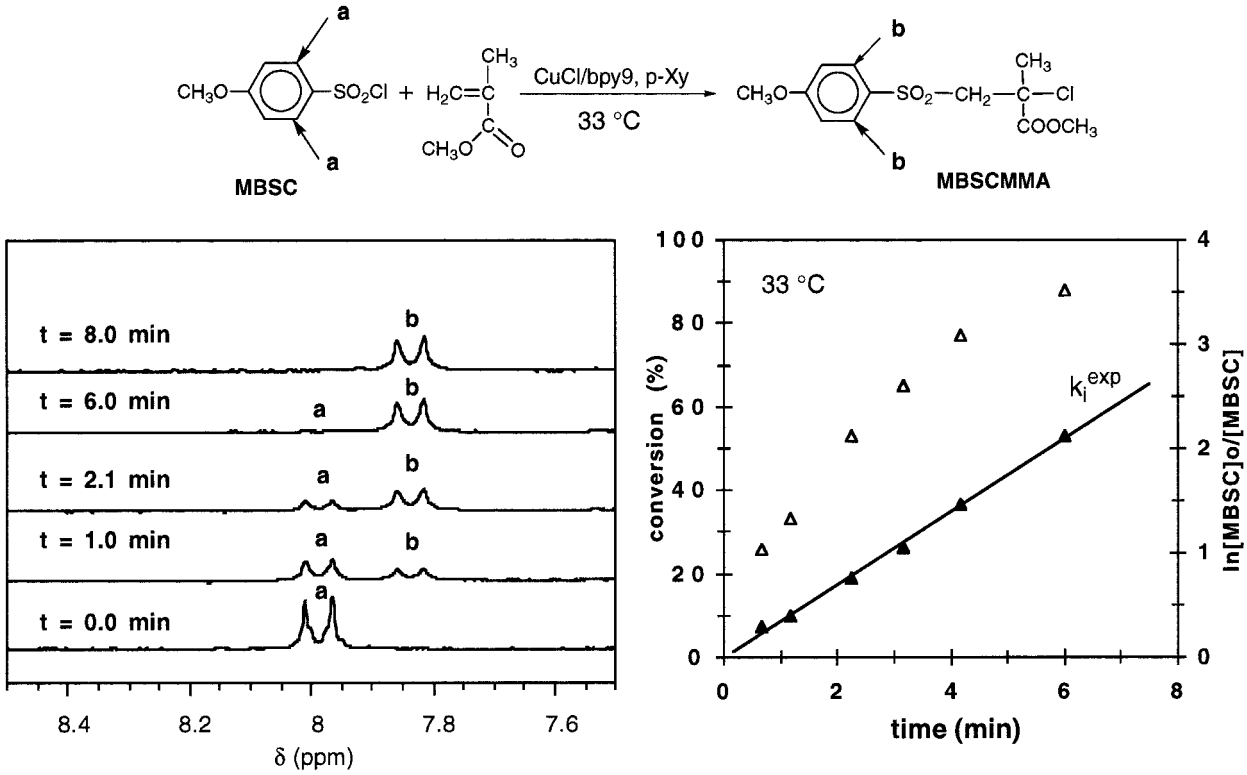
For sulfonyl halides, the sulfonyl radicals formed are more stable than the carbon-centered radicals obtained when alkyl halides are used as initiators.[14] The mechanism depicted in Scheme 3 shows the possible reaction products obtained from the sulfonyl radical dimerization.[28] Only disproportionation reaction products, as described by Scheme 3 (eq 4), were observed[28] in the absence of monomer. Although the sulfonyloxy radical can also initiate the polymerization, the sulfinyl radical does not act as an initiator.[28(d)] Their adduct sulfinylsulfonate (eq 3) also cleaves to regenerate sulfonyl radicals. The overall effect of these reactions is that, although the sulfonyl radicals do combine, their combination is reversible, so they become stable through this fast equilibrium. The mechanism of stabilization involves sulfinyl radicals that do not initiate or dimerize easily (eq 6). Therefore, we believe that they are persistent and accumulate. The concentration of sulfonyloxy radicals with which it is in equilibrium decreases, and the parent sulfonyl radical becomes persistent also.

For aromatic sulfonyl halides, the rate of the quantitative initiation is much faster than the rate of propagation,[14] regardless of the functional groups attached to the aromatic part of the sulfonyl halide initiator.[13] For sulfonyl chloride initiators, we directly measured both the rate constant of initiation {Scheme 4; k_i^{app} was derived[14] from the slope of $\ln([I]_0/[I])$ vs time} and the rate constant of propagation (k_p^{app}) and compared them at the polymerization temperature. For S and methyl methacrylate (MMA), k_i^{app} is four orders of magnitude higher than k_p^{app} ($k_i^{app}/k_p^{app} = 5.2 \times 10^4$ and 1.7×10^4, respectively). This difference decreases to almost three orders of magnitude ($k_i^{app}/k_p^{app} = 4.4 \times 10^3$) for butyl acrylate and two orders of magnitude ($k_i^{app}/k_p^{app} = 6.5 \times 10^2$) for methyl acrylate.[14]

In contrast, the structure of an alkyl halide initiator should be tailored for each class of monomers to obtain a rate of initiation at least equal to that of propagation. No experimental values of both initiation and propagation rate constants are available for alkyl halide initiators, so it is widely accepted that the two should have similar values. When alkyl halides are used as initiators, the initiation step is governed by the persistent radical effect.[29] The alkyl radicals formed during the



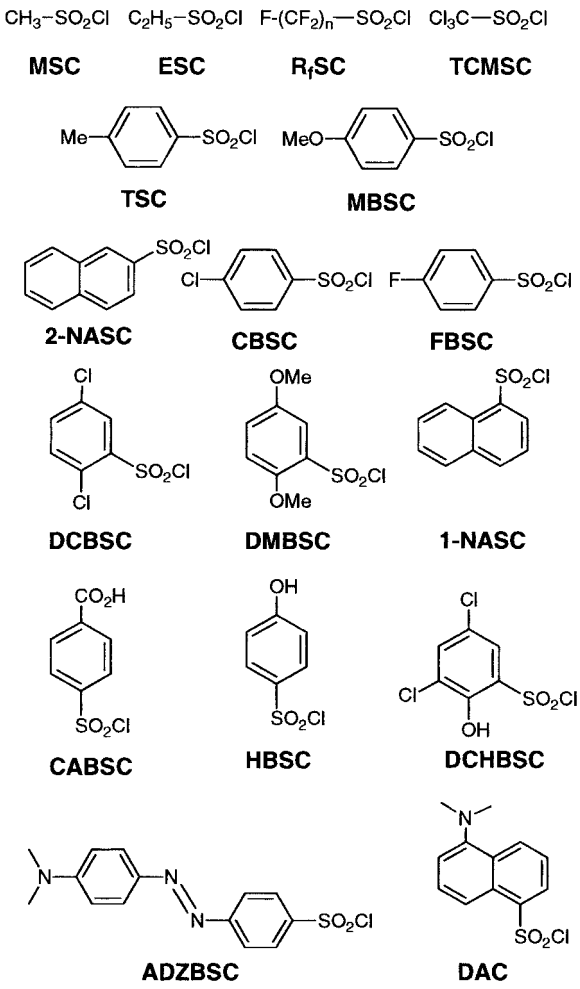
Scheme 3. Mechanism of the sulfonyl radical dimerization.



Scheme 4. Determination of k_i^{exp} in the LRP of MMA by ^{1}H NMR spectroscopy.

initiation step are very reactive and combine irreversibly to form stable dimers.[3(g)] This combination reaction decreases the initiator efficiency and creates excess Cu^{II} in the polymerization mixture.[3(g),27(b)] The formed Cu^{II} species decreases the dimerization rate, and the reaction attains a pseudoequilibrium Cu^{I}/Cu^{II} and a pseudosteady concentration of radicals for the rest of the propagation process. A too fast initiation with an alkyl radical will favor combination reactions, for example, low initiator efficiency, before the amount of Cu^{II} generated limits this side reaction. This process is present only in the early stages of propagation for the sulfonyl chloride initiators because during initiation reversible combination products (Scheme 3, eq 3) are formed. For sulfonyl halides, the extent of combination is much decreased versus alkyl halides because during the first propagation steps there is already excess Cu^{II} present from the initiation step. A slow initiation would overlap with the propagation, and the overall effect would be a broad molecular weight distribution because not all chains would be started at the same time. Therefore, it is only in the case of sulfonyl halide initiators that the large difference between the rates of initiation and propagation obtained is of interest for the construction of polymers with well-defined and complex architectures. Moreover, because the sulfonyl radical (a σ radical) is not conjugated with the aryl group, the electronic effects derived from different substituents attached to the phenyl ring affect the reactivity of the sulfonyl chloride group to a very limited extent.[19] Only a weak inductive effect from the substituents attached to the phenyl group was observed for model reactions for the arylsulfonyl chloride addition to vinyl monomers, as demonstrated by Hammett plots.[19(b)] This feature of the sulfonyl radicals translates into an extremely versatile methodology for chain-end functionalization of the polymers synthesized by substituted arylsulfonyl chloride-initiated LRP.[13]

In this article, we report a detailed investigation of the electronic and structural effects generated by the introduction of functional and/or multiple sulfonyl chloride groups on the initiation efficiency, side reactions, and rate of propagation observed in metal-catalyzed LRP systems initiated with functional aromatic monosulfonyl and multisulfonyl chlorides.



Scheme 5. Examples of functional alkyl and arylsulfonyl chloride initiators.

RESULTS AND DISCUSSION

Functional Monosulfonyl Chloride Initiators

Substituted arylsulfonyl chloride initiators (Scheme 5) were used in the LRP of S and MMA and showed similar rates of propagation and M_w/M_n (weight-average molecular weight/number-average molecular weight). Several synthetically useful groups with both electron-withdrawing and electron-donating character, —COOH, —PhOH, —NH_2, —$N(CH_3)_2$, —$COCH_3$, and —N=N—, were successfully introduced onto the polymer chain end.[13] The two catalysts used, Cu_2O and CuCl, in the presence of bpy showed a first order of reaction in monomer concentration {the linearity of $\ln([M]_0/[M])$ vs time}. In comparison, the Cu_2O catalyst [Fig. 1(a)] had an induction period because of its insolubility in the reaction mix-

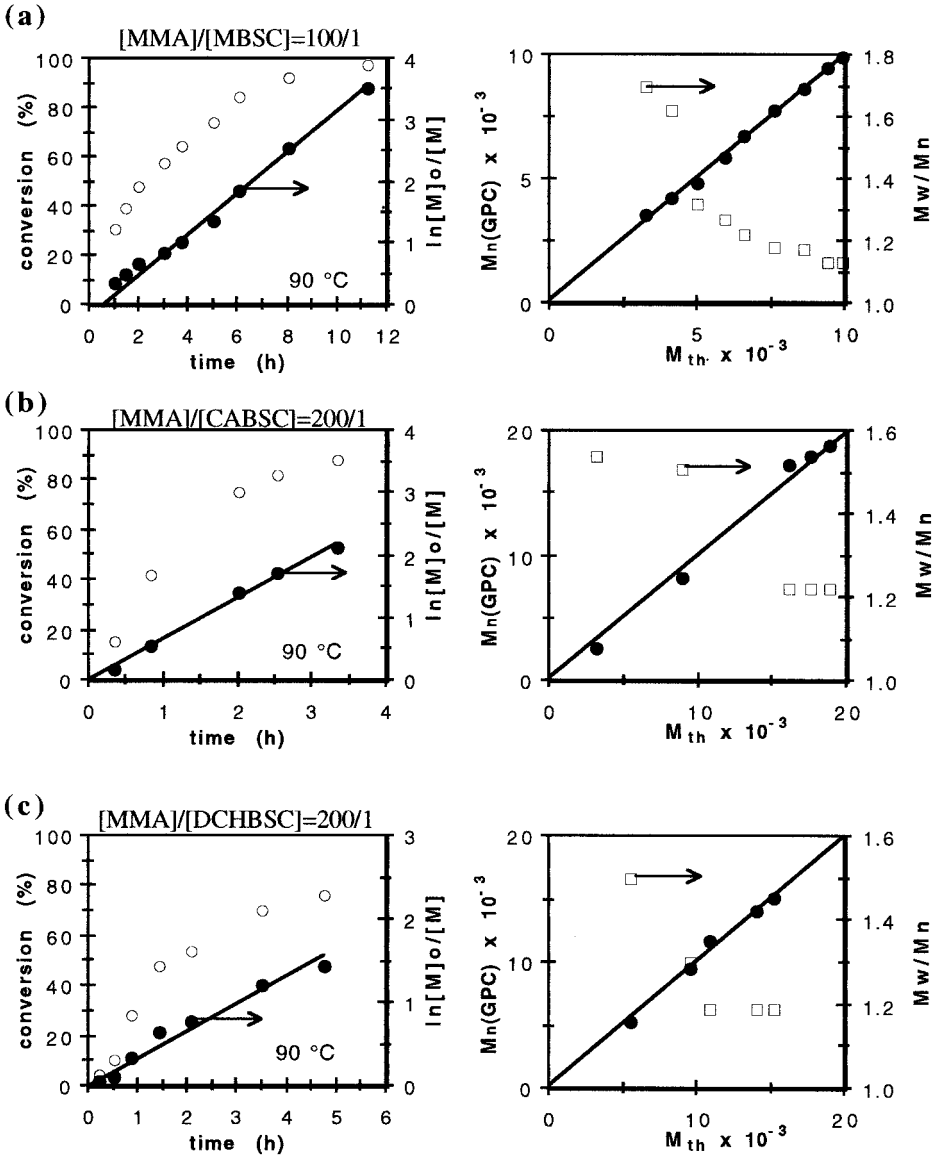
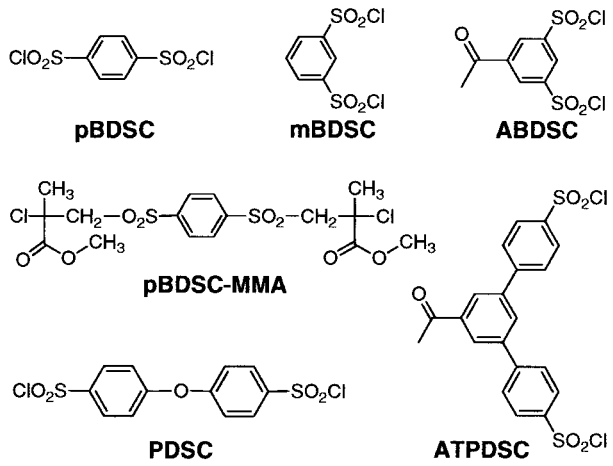


Figure 1. Metal-catalyzed LRP of MMA initiated with functional monosulfonyl chlorides and catalyzed by (a) MBSC/Cu_2O, (b) CASC/CuCl, and (c) DHSC/CuCl at 90 °C. Reaction conditions: (a) [MMA] = 4.7 M, PhOPh, [MMA]/[MBSC]/[Cu_2O]/[bpy] = 100/1/2/4 molar ratio, and (b,c) [MMA] = 6.2 M, *p*-xylene, [MMA]/[I]/[CuCl]/[bpy] = 200/1/1/3 molar ratio.

ture[15] and also gave a longer reaction time. However, the final molecular weight distribution was much narrower: M_w/M_n = 1.12 versus 1.20. As proven by the points fitting the diagonal (efficiency = 100%) in the M_n versus the theoretical molecular weight, M_{th} ($M_{th} = FW_{mon} \times [M]_0/[I]_0$) plots in Figure 1(a–c), all initiators gave quantitative initiation regardless of the position of the substituent, that is, ortho or para to the sulfonyl chloride, and its electronic nature, that is, electron-withdrawing or electron-donating. This also demonstrates that steric hindrance makes no contribution or only a minor contribution to the reactivity of sulfonyl radicals.

Functional Disulfonyl and Trisulfonyl Chloride Initiators

The introduction of a second sulfonyl group in the initiator molecule was studied in detail to provide a



Scheme 6. Aryl disulfonyl chloride initiators.

rational approach to the design of functional multisulfonyl chloride initiators capable of quantitative and fast initiation from more than one sulfonyl group. Preliminary data from our group demonstrated that linear polymers with identical chain ends could by synthesized by LRP with a diphenyl ether-derived disulfonyl chloride di-initiator (PDSC; Scheme 6).[12] New disulfonyl chloride initiators were used as initiators for the LRP of MMA and S. The two sulfonyl chloride groups in *para*-benzenedisulfonyl chloride (Scheme 6; pBDSC) had different reactivities. Therefore, the polymers that resulted did not have narrow molecular weight distributions and controlled molecular weights. The sulfonyl chloride group was an extremely strong electron-withdrawing substituent (vs the SO_2CH_2— that resulted after addition to the monomer), and it affected the reactivity of the second sulfonyl chloride group. At first sight, this is an unexpected result because the sulfonyl radicals were not conjugated with the aryl group. We synthesized the monoadduct of pBDSC[30] to MMA (pBDSC-MMA) and used it as an initiator. This initiator generated poly(methyl methacrylate) (PMMA) with a controlled molecular weight and a narrow molecular weight distribution [Fig. 2(a)].

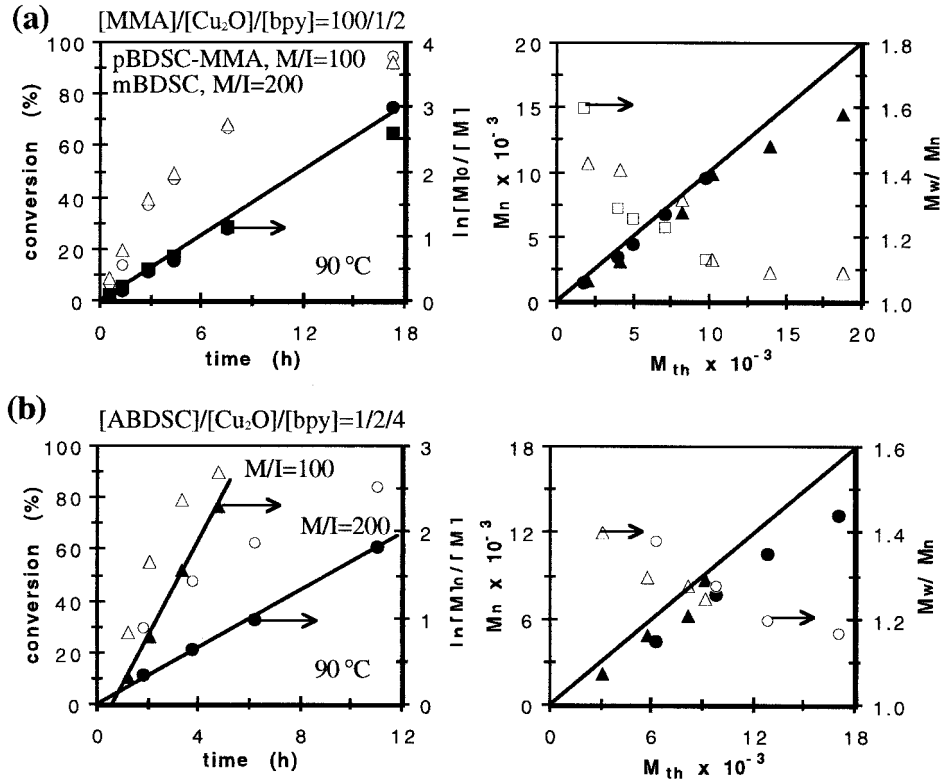


Figure 2. LRP of MMA catalyzed by Cu_2O/bpy in *p*-xylene and initiated with (a) mBDSC (▲; [MMA]/[mBDSC] = 200/1) and pBDSC-MMA (●; [MMA]/[pBDSC-MMA] = 100/1) and (b) ABDSC. Reaction conditions: (a,b) [MMA] = 6.2 M, 90 °C; (a) [MMA]/[Cu_2O]/[bpy] = 100/1/2 molar ratio; and (b) [MMA]/[ABDSC]/[Cu_2O]/[bpy] = 100/1/2/4 (▲) or 100/0.5/1/2 (●) molar ratios.

Table I. Metal-Catalyzed Living Radical Polymerization of Methacrylates[a] Initiated with Multisulfonyl Chloride Initiators

No.	Monomer	Initiator	Arms	Catalyst/Ligand	k_p^{exp} (h^{-1})	M_w/M_n	Conversion (%)	Time (h)	[M]/[—SO_2Cl]
1	MMA	MBSC	1	Cu_2O/bpy	0.33[e]	1.13	97	11	100
2	MMA	PDSC[b]	2	Cu_2O/bpy	0.19[e]	1.12	98	21	100
3	BMA	PDSC	2	Cu_2O/bpy	1.34[e]	1.07	97	5.6	100
4	MMA	mBDSC[b]	2	Cu_2O/bpy	0.15	1.09	92	17	100
5	MMA	ABDSC[c]	2	Cu_2O/bpy	0.47	1.25	90	4.7	50
6	MMA	ABDSC[b]	2	Cu_2O/bpy	0.17	1.17	84	11	100
7	MMA	pBDSC-MMA[c]	2	Cu_2O/bpy	0.17	1.13	95	17	50
8	MMA	ATPDSC	2	Cu_2O/bpy	0.18[e]	1.07	99	28	100
9	MMA	3PSC	3	Cu_2O/bpy	0.18[e]	1.06	98	22	100
10	MMA	3PMMA13	3	Cu_2O/bpy	0.19	1.07	98	21	100
11	BMA	ATSC	3	Cu_2O/bpy	1.20[e]	1.11	98	5.5	100
12	BMA	ATSC	3	Cu(0)/bpy	2.90[e]	1.27	98	1.6	100
13	BMA	STAR4[d]	4	CuCl/bpy	0.37	1.26	98	10.5	200
14	MMA	STAR4	4	Cu_2O/bpy	0.54	1.16	88	4.0	100
15	MMA	STAR4[d]	4	Cu_2O/bpy	0.29	1.20	90	8.0	200
16	MMA	C4	4	Cu_2O/bpy	0.37	1.13	95	8.0	100
17	MMA	C6	6	Cu_2O/bpy	0.59	1.16	92	4.3	100
18	MMA	C8[f]	8	Cu_2O/bpy	0.12	1.07	93	22	100

[a] Conditions: [MMA] = 4.7 M at 90 °C; [BMA] = 4.5 M at 120 °C; [M]/[—SO_2Cl]/[catalyst]/[bpy] = 100/1/1/2 molar ratio; PhOPh.
[b] Conditions: the same as those listed in footnote a, except [MMA] = 6.2 M.
[c] Conditions: the same as those listed in footnote b, except [M]/[—SO_2Cl]/[catalyst]/[bpy] = 50/1/1/2 molar ratio.
[d] Conditions: the same as those listed in footnote a, except [M]/[—SO_2Cl]/[catalyst]/[bpy] = 200/1/1/2 molar ratio.
[e] Induction period due to the absence of binding of the Cu_2O by the initiator.
[f] Conditions: the same as those listed in footnote a, except [M]/[—SO_2Cl]/[catalyst]/[bpy] = 100/1/0.5/1 molar ratio.

For the *meta*-benzenedisulfonyl chlorides from Scheme 6 (mBDSC and ABDSC[30]), the second sulfonyl chloride was so deactivated that a significant amount of side reactions occurred during polymerization, as evidenced by the curvature of M_n versus M_{th}. As shown in Table I, entries 2, 4, and 6, the LRPs of PDSC, mBDSC, and ABDSC had, within experimental error, the same rate constant of propagation, k_p^{exp}, as the concentrations of —SO_2Cl and the catalyst were identical. Attempts to synthesize, by standard literature procedures,[19(a)] the adduct of mBDSC to MMA produced a mixture of adduct and polymeric materials. This demonstrated that a large extent of side reactions occurred for this compound during activation by metal salts.

To confirm these unexpected results, a less conjugated, space-separated, disulfonyl chloride-functional (acetophenone) initiator (Scheme 6; ATPDSC) was synthesized[30] and compared to PDSC as an initiator in the LRP process (Fig. 3). We observe in Figure 3(b) versus Figure 3(a) that the induction period present when Cu_2O/bpy is used as a catalyst can be removed by the use of simple PTCs, such as ethylene glycol (EG). However, an increase in M_w/M_n from 1.07 to 1.18 is also observed. In Figure 3(c), a narrow molecular weight distribution (M_w/M_n = 1.07) and 100% initiator efficiency proved that reducing the conjugation in the ATPDSC initiator (the biphenyl group is only partially conjugated because it is twisted) and space-separating the sulfonyl chloride initiating groups opens the route to efficient multifunctional initiators for LRP. In addition, the acetophenone group from ATPDSC is useful for further chemical transformations.

The aniline-derived trichlorosulfonyl initiator (ATSC;[30] Fig. 4) provided the first surprise. As shown in Figure 4(a), in the presence of two Cu-based catalysts, this initiator gave well-controlled polymerizations with predetermined molecular weights and narrow molecular weight distributions (M_w/M_n as low as 1.12). Kinetically, as shown in Table I, entries 3 versus 11, under the same conditions this initiator had a similar rate constant of propagation with the PDSC initiator (k_p^{exp} = 1.2 vs 1.3 h^{-1}). The underestimation of the M_n by gel permeation chromatography (GPC) versus M_{th} was due to the presence of the three arms in the polymer. The cleavage of a polystyrene (PS) obtained by

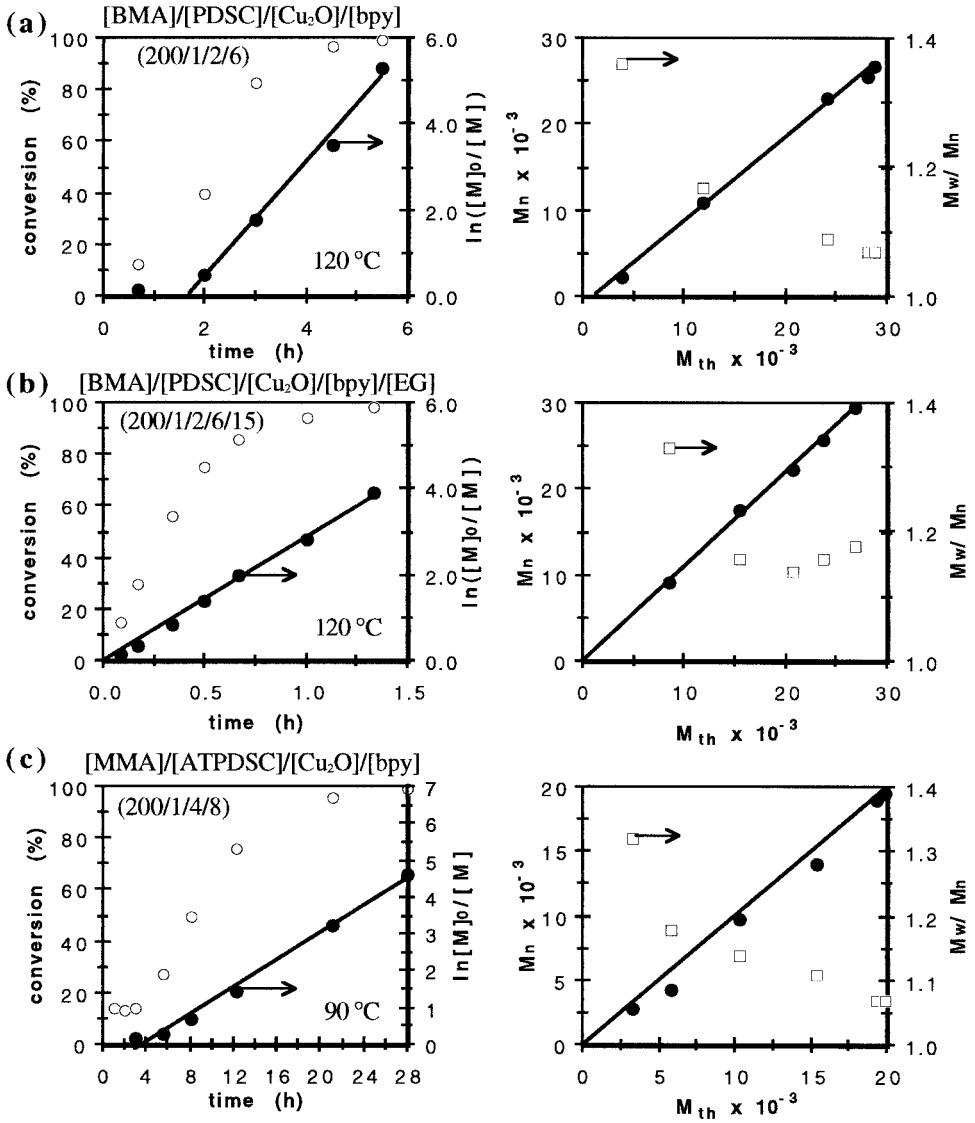


Figure 3. LRP of methacrylates catalyzed by Cu_2O/bpy in *p*-xylene initiated with (a,b) PDSC and (c) ATPDSC. Reaction conditions: (a–c) [BMA] = 4.5 M, [MMA] = 4.7 M; (a) [BMA]/[PDSC]/[Cu_2O]/[bpy] = 200/1/2/6 molar ratio, 120 °C; (b) [BMA]/[PDSC]/[Cu_2O]/[bpy] = 200/1/2/6 molar ratio, [PDSC]/[EG] = 1/15 mol/mol, 120 °C; and (c) [MMA]/[ATPDSC]/[Cu_2O]/[bpy] = 200/1/4/8 molar ratio, 90 °C.

LRP with this initiator under basic reaction conditions (Scheme 7) confirmed the presence of three arms (S usually gives broader molecular weight distributions under these LRP conditions, but PMMA is not stable under strong basic conditions). On the basis of kinetic results, we concluded that this initiator had three sulfonyl groups interacting. However, all of them initiated the polymerization with the same rate. This result could be explained by the fact that an —NH_2 group with a strong electron-donating effect was compensating for the electron-withdrawing effect of the sulfonyl chloride groups.

Another trisulfonyl chloride initiator (3PSC) with a nonconjugated structure was synthesized[30] and used successfully for the LRP of MMA [Fig. 4(b)]. It is noteworthy for 3PSC and its adduct to MMA (3PMMA13) that the rate constant of propagation (k_p^{exp}), M_n, and molecular weight distribution dependencies were identical between them and fit the data for the ATPDSC initiator under identical reaction conditions (Table I, entries 8–10). The removal of the induction period usually associated with the use of Cu_2O/bpy as a catalyst was due to the binding effect created by

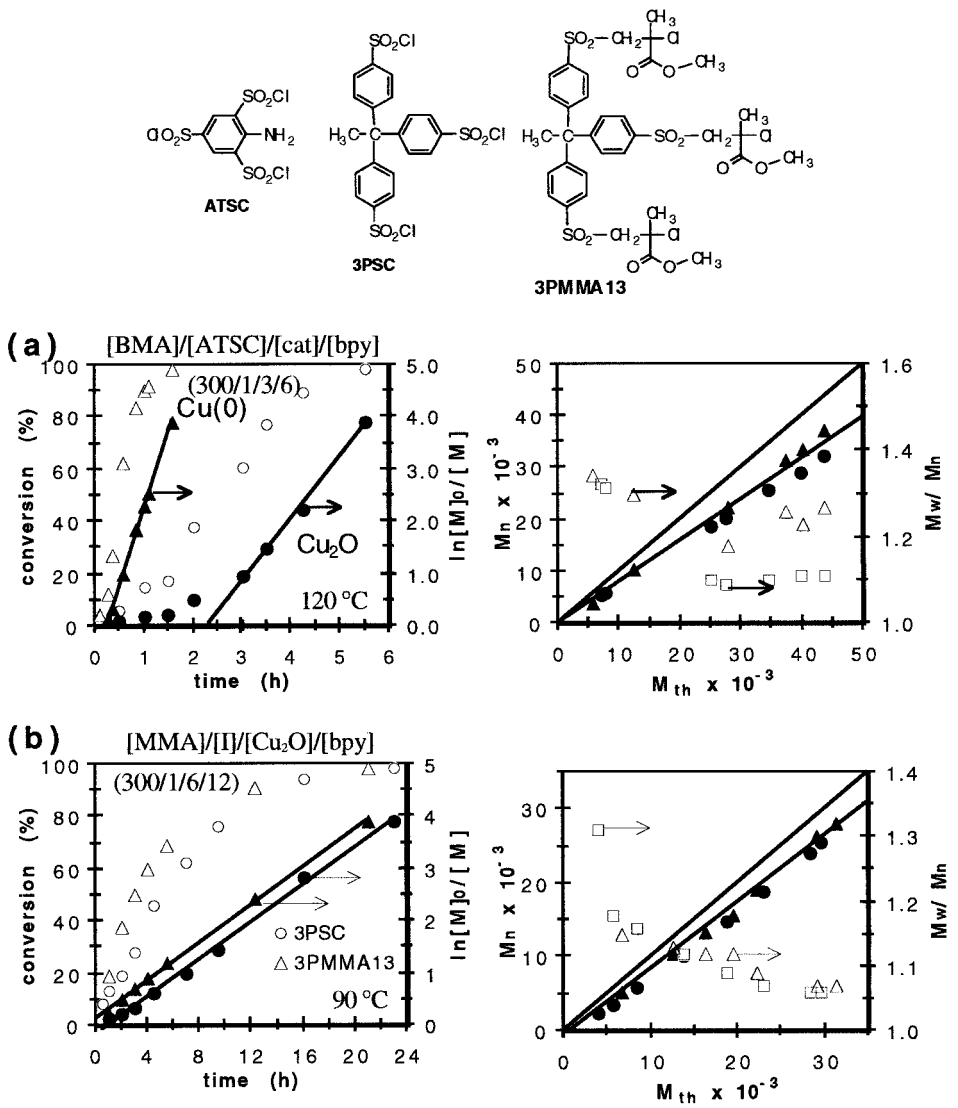


Figure 4. LRP of methacrylates (a) initiated with ATSC and catalyzed by Cu/bpy (▲) or Cu_2O/bpy (●) and (b) initiated with 3PSC (●) or its adduct to MMA, 3PMMA13 (▲), and catalyzed by Cu_2O/bpy. Reaction conditions: (a) [BMA] = 4.5 M, PhOPh, [BMA]/[ATSC]/[catalyst]/[bpy] = 300/1/3/6 molar ratio, 120 °C and (b) [MMA] = 4.7 M, *p*-xylene, [MMA]/[I]/[Cu_2O]/[bpy] = 300/1/6/12 molar ratio, 90 °C.

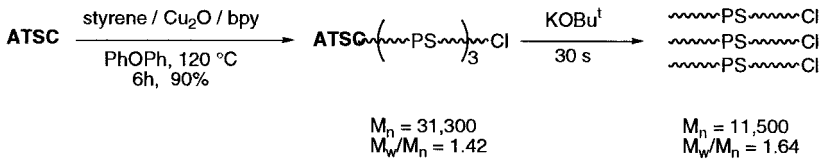
the large adduct molecule 3PMMA13. This effect was similar to other reported PTCs[17] [i.e., EG in Fig. 3(b)], although no broadening of the molecular weight distribution was observed.

In conclusion, to design initiators with multiple sulfonyl chloride groups, we need to consider the following strategic options:

1. Decrease the conjugation between the sulfonyl chloride groups.
2. Eliminate the conjugation between the sulfonyl chloride groups.
3. Compensate the strong electron-withdrawing effect of the sulfonyl chloride group by strong electron-donating groups (i.e., —NH_2, —OCH_3).

Tetrasulfonyl, Hexasulfonyl, and Octasulfonyl Chloride Initiators

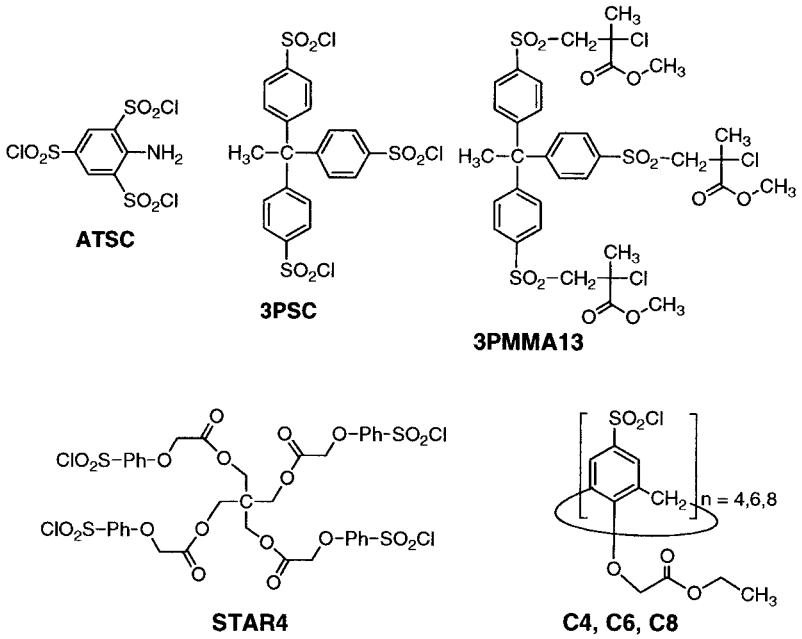
A tetrasulfonyl chloride initiator with a nonconjugated structure (STAR4; Scheme 8) was synthesized[30] and used for the CuCl/bpy-catalyzed LRP of *n*-butyl methacrylate (BMA) [Fig. 5(a)] and the



Scheme 7. Synthesis of a three-arm star PS by LRP initiated from ATSC and the cleavage of its three PS arms.

Cu_2O/bpy-catalyzed LRP of MMA and S [Fig. 5(b,c)]. This initiator had the same PTC effect noted previously for EG and 3PMMA13; that is, it removed the induction period associated with the use of Cu_2O/bpy as a catalyst. Polymers with well-controlled molecular weights and M_w/M_n as low as 1.18 were obtained. The cleavage of the STAR4 initiator core for a PMMA (Scheme 9) and a PS (Scheme 10) demonstrated the tetrafunctionality of the initiator and, therefore, the equal reactivity of all initiating groups. In both cases, M_n per cleaved arm was about one-quarter of the M_n of the star polymer, and the molecular weight distribution of the cleaved arms was within the range of values obtained with monofunctional initiators.

Initiators with four, six, and eight noninteracting sulfonyl chloride groups attached on calixarene cores (Scheme 8) were synthesized[30] and tested for the LRP of MMA. Kinetic results presented in Figure 6 prove their PTC effect on Cu_2O/bpy (previously discussed) and also an excellent capability to avoid chain-breaking reactions (i.e., termination by combination) up to conversions as high as 95%. This result was extremely rewarding because it has been reported[3(e,g,h)] that the synthesis of star polymers by LRP with alkyl halide initiators had a limiting conversion of 38% if no radical termination by combination reactions were to be observed. Our result proves unequivocally that because of the absence of side reactions, arylsulfonyl chlorides are indeed the initiators of choice for the synthesis of polymers with complex architectures by LRP. Figure 7 shows size exclusion chromatography (SEC) traces from a kinetic experiment using C8 [Fig. 6(c)] and demonstrates that with this octasulfonyl chloride initiator, conversions up to 93% with no significant termination by combination can be obtained.



Scheme 8. Trisulfonyl, tetrasulfonyl, hexasulfonyl, and octasulfonyl chloride initiators with equal reactivity of the sulfonyl chloride groups.

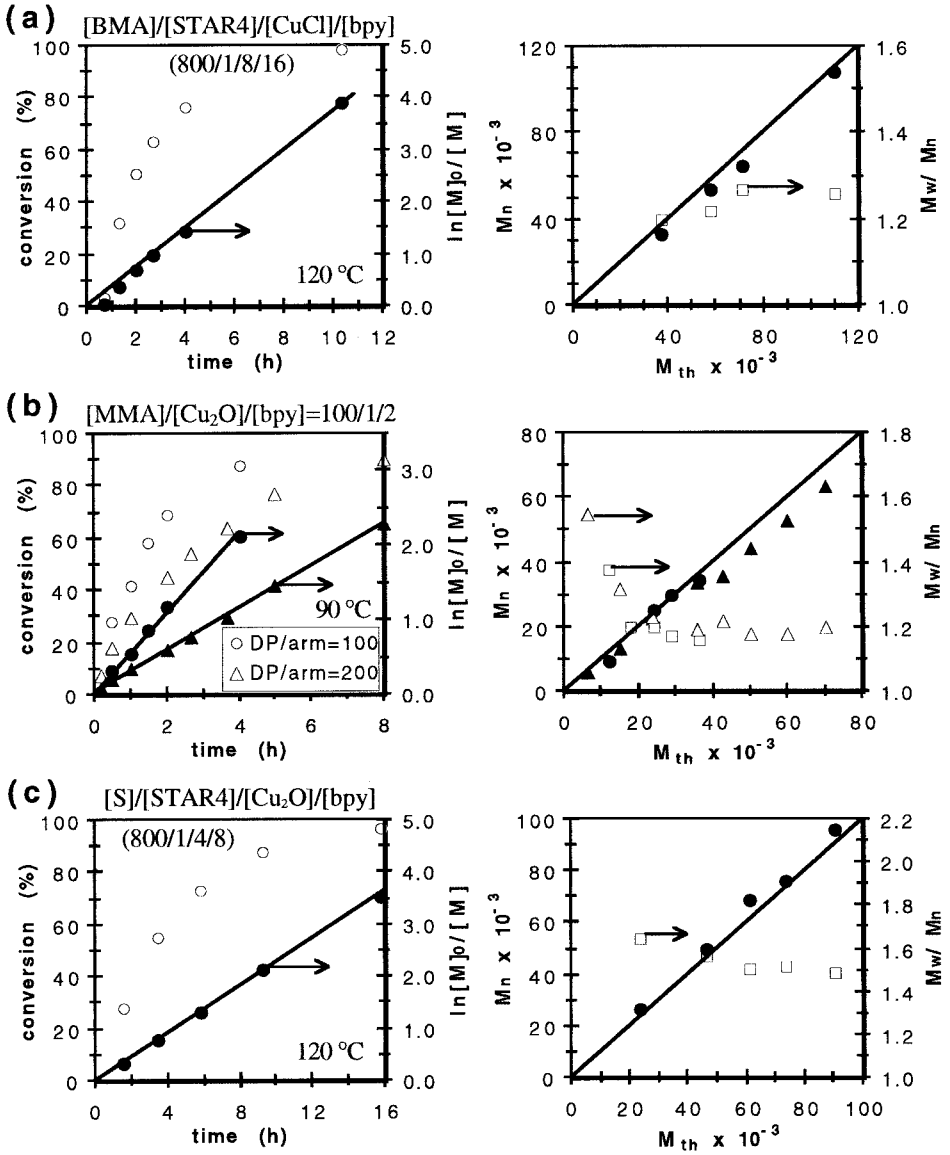
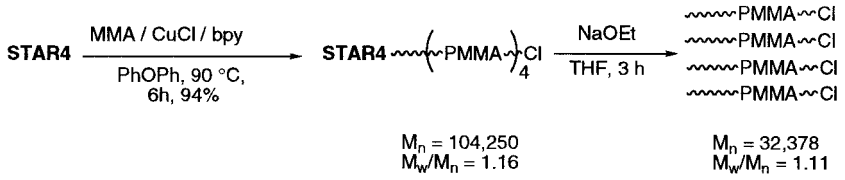
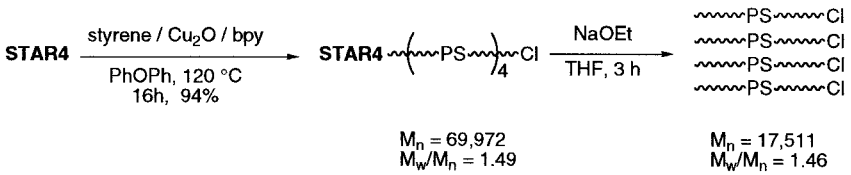


Figure 5. Metal-catalyzed LRPs initiated with STAR4 for (a) BMA, with CuCl/bpy as a catalyst; (b) MMA, with Cu_2O/bpy as a catalyst; and (c) S, with Cu_2O/bpy as a catalyst. Reaction conditions: (a) [BMA] = 4.5 M, *p*-xylene, [BMA]/[STAR4]/[CuCl]/[bpy] = 800/1/8/16 molar ratio, 120 °C; (b) [MMA] = 4.7 M, PhOPh, [MMA]/[Cu_2O]/[bpy] = 100/1/2 molar ratio, 90 °C, (l) [MMA]/[STAR4] = 100/1 mol/mol, and (s) [MMA]/[STAR4] = 200/1 mol/mol; and (c) [S] = 4.4 M, PhOPh, [S]/[STAR4]/[Cu_2O]/[bpy] = 800/1/4/8 molar ratio, 120 °C.



Scheme 9. Synthesis of a four-arm star PMMA by LRP initiated from STAR4 and the cleavage of its four PMMA arms.



Scheme 10. Synthesis of a four-arm star PS by LRP initiated from STAR4 and the cleavage of its four PS arms.

EXPERIMENTAL

Materials

All materials, unless otherwise noted, were purchased from Aldrich and used as received. All monomers (≥99% purity) were passed through a basic Al_2O_3 chromatographic column (flash). CuCl (Fisher; 96%) was purified by grinding and stirring with H_2SO_4 (1 N), followed by filtration and successive washing with glacial acetic acid

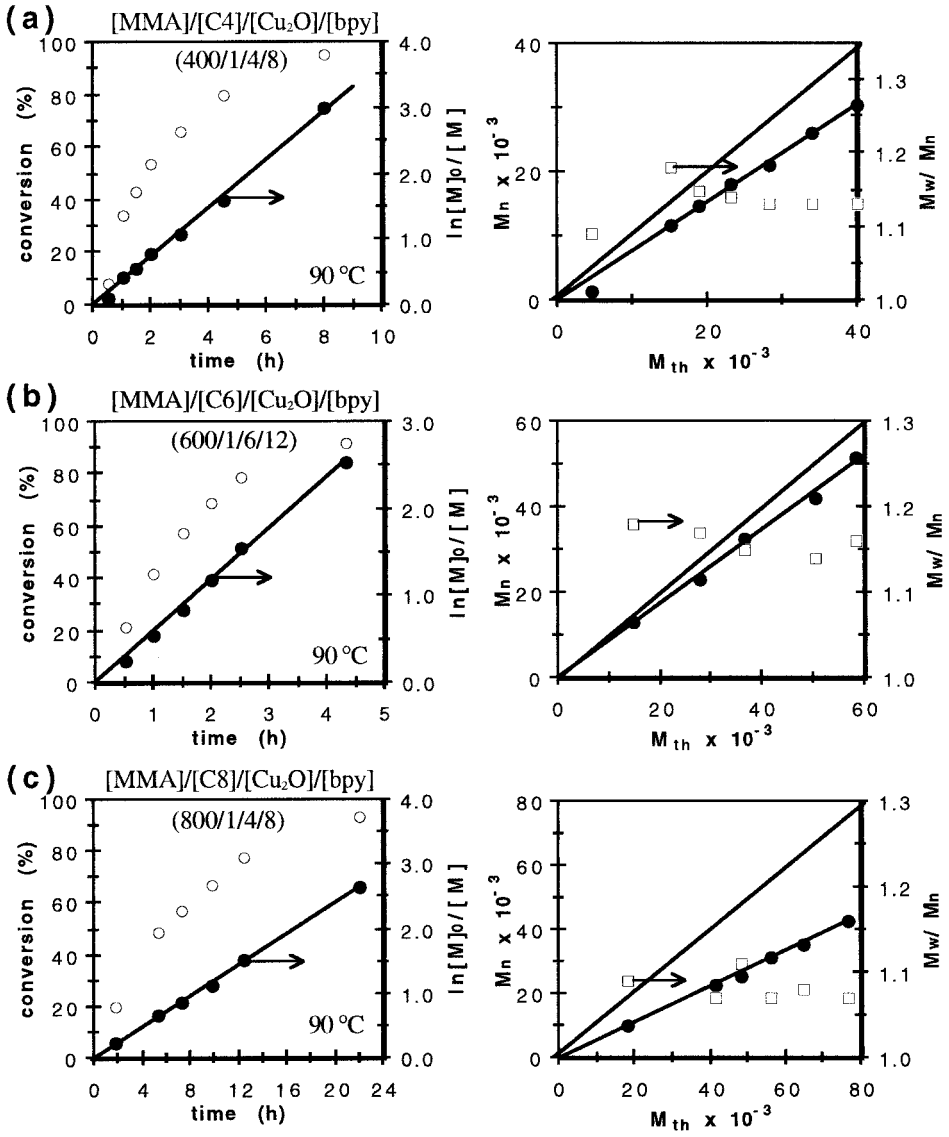


Figure 6. Cu_2O/bpy-catalyzed LRP of MMA initiated with chlorosulfonyl calix[*n*]arenes: (a) C4, $n = 4$; (b) C6, $n = 6$; and (c) C8, $n = 8$. Reaction conditions: (a–c) [MMA] = 4.7 M, 90 °C; (a,b) PhOPh, [MMA]/[—SO_2Cl]/[Cu_2O]/[bpy] = 100/1/1/2 molar ratio; and (c) *p*-xylene, [MMA]/[—SO_2Cl]/[Cu_2O]/[bpy] = 100/1/0.5/1 molar ratio.

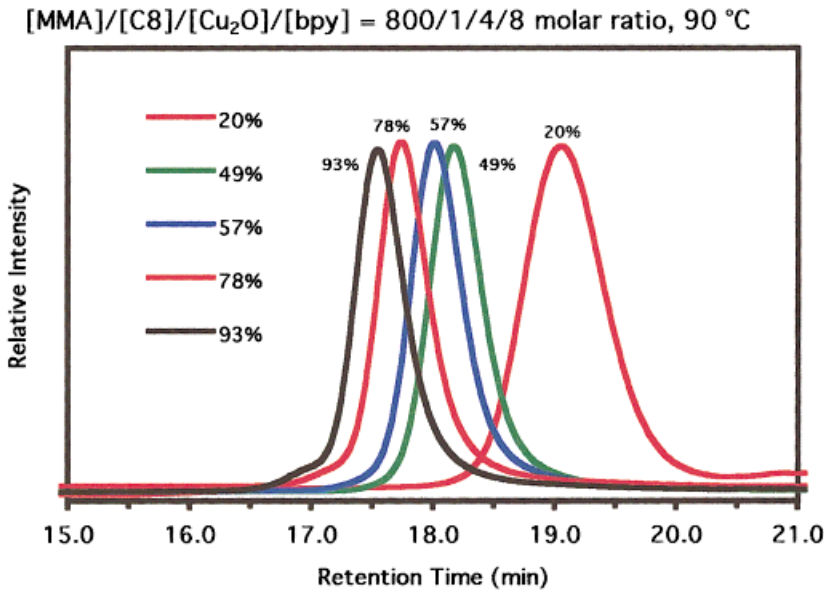


Figure 7. SEC traces for the Cu_2O/bpy-catalyzed, C8-initiated LRP of MMA.

(four times), ethanol, and diethyl ether. The white CuCl powder was dried at 100 °C for 30 min and stored in an airtight bottle. Copper(I) oxide (≥95%) was used as received from Alfa

Characterization 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 as an internal standard. Melting points were determined with a Thomas–Hoover capillary melting-point apparatus and are uncorrected. High-pressure liquid chromatography (HPLC) and GPC analyses were obtained with a PerkinElmer series 10 high-pressure liquid chromatograph equipped with an LC-100 column oven (40 °C), a Nelson Analytical 900 series integrator data station, a PerkinElmer 785A ultraviolet–visible detector (254 nm), and a Varian STAR 9040 refractive index detector. The HPLC column was PL gel (5 μm, 100 Å), whereas for GPC, there were two columns of AM gel (10 μm, 500 Å and 10 μm, 10^4 Å). Tetrahydrofuran (THF; Fisher; HPLC-grade) was used as an eluent at a flow rate of 1 mL/min. Relative M_n's and M_w's were determined from calibration plots constructed with PS standards.

Typical Procedure for Polymerization Kinetics

The monomer (MMA, 2 mL, 18.7 mmol), solvent (diphenyl ether, 2 mL), initiator (C4, 53.1 mg, 0.045 mmol), catalyst (Cu_2O, 23.6 mg, 0.16 mmol), and ligand (bpy, 50 mg, 0.32 mmol) were weighted directly into a 25-mL Schlenk tube. The mixture was degassed by four freeze–pump–thaw cycles, filled with Ar, and heated to the polymerization temperature. The side arm of the tube was purged with N_2 for at least 5 min before it was opened for the removal of samples at determined times with an air-tight syringe. Samples were diluted with $CDCl_3$ in NMR tubes, and the conversion was measured by ^{1}H NMR spectroscopy. Then, part of the solution was injected into a GPC column eluted with THF, and the molecular weight was measured versus PS standards with a UV detector (254 nm) and versus PMMA standards with a refractive index detector. In this case, the phenylsulfonyl chain end derived from the initiator was responsible for the UV absorption.

Arm Cleavage of ATSC-Initiated PS

Three-arm star ATS(PS-Cl)$_3$ (30 mg, 1 mmol, 3 mmol of SO_2, M_n = 31,300, M_w/M_n = 1.42) was mixed in a test tube with potassium *tert*-butoxide (30 mg, 270 mmol). The reagents were melted to a dark-brownish solid by the brief application (30 s) of a hot-air gun. The residue was dissolved in CH_2Cl_2, washed with water, dried ($MgSO_4$), and evaporated to dryness. GPC analysis showed the product had M_n = 11,500 and M_w/M_n = 1.64. Heating the polymer without a base gave a multimodal product, M_n = 13,400 and M_w/M_n = 3.01.

Arm Cleavage of STAR4-Initiated PMMA

STAR4-PMMA (500 mg, 5 mmol, 20 mmol SO_2, M_n = 104,250, M_w/M_n = 1.16) was dissolved in 25 mL of THF. At room temperature, $NaOCH_2CH_3$ (0.1 g, 2 mmol) was added. The entire mixture was stirred for 2 h at room temperature. GPC analysis showed the product had M_n = 32,378 and M_w/M_n = 1.11.

Arm Cleavage of STAR4-Initiated PS

STAR4-PS (500 mg, 5 mmol, 30 mmol SO_2, M_n = 69,972, M_w/M_n = 1.49) was dissolved in 25 mL of THF. At room temperature, $NaOCH_2CH_3$ (0.1 g, 2 mmol) was added. The entire mixture was stirred for 2 h at room temperature. GPC analysis showed the product had M_n = 17,511 and M_w/M_n = 1.46.

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