

Metal Catalyzed Living Radical Polymerization of Acrylonitrile Initiated with Sulfonyl Chlorides

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ABSTRACT: Novel catalytic and initiating systems based on CuBr/2,2'-bipyridine (bpy), CuCl/bpy, Cu₂O/bpy, and CuO/bpy, in the presence of alkyl, alkylsulfonyl, and arenesulfonyl halides, for the living radical polymerization (LRP) of acrylonitrile (AN) are reported. The optimum combinations of catalyst and initiator are CuCl/bpy and 2-chloropropionitrile (CPN), CuCl/bpy and trichloromethanesulfonyl chloride (TCMSC), Cu₂O/bpy and 2-bromopropionitrile (BPN), Cu₂O/bpy and 4-methoxybenzenesulfonyl chloride (MBSC), and CuO/bpy and methanesulfonyl chloride (MSC). The first example of a three-arm star polyacrylonitrile (PAN) was synthesized by the LRP of AN using 1,1,1-tris(4-chlorosulfonylphenyl)ethane (3PSC) initiator, in the presence of Cu₂O/bpy catalyst.

Introduction

Metal catalyzed living radical polymerization (LRP) using the reversible termination concept^{1,2} has evolved into an important field of research. Polymers with controlled molecular weight (MW), narrow molecular weight distribution (MWD), and well-defined chain ends can be synthesized by this method from conventional vinyl monomers. Metal catalyzed LRP is a promising route to a variety of vinyl polymers with precise architecture since the catalyst is inexpensive, the rate of polymerization is fairly high, and the obtained polymers have well-defined chain ends, controlled MW, and narrow MWD. Two classes of initiators are used mostly: activated alkyl halides¹ and alkyl and arenesulfonyl halides.²

The first class of initiators contains compounds that mimic the structure of the propagating chain end obtained after the addition of the alkyl halide to the monomer. Consequently, the rates of initiation and propagation are of the same order of magnitude. Therefore, the MWD of the resulted polymers is broad in some cases. Moreover, the high reactivity of carbon center radicals favors side reactions such as termination by combination, disproportionation, or chain transfer during the initiation step, and the initiation efficiency can be lower than 1.0.

The second class of initiators, alkyl and aryl sulfonyl chlorides, was introduced by our group in 1995.² Sulfonyl radicals are more stable than carbon radicals, and thus they participate in a reduced number of side reactions. Sulfonyl chlorides generate in situ a monoadduct with a variety of vinyl monomers, and by contrast with alkyl halide initiators, they are considered universal.^{2e} Moreover, their rate of addition to the monomer is 2–4 orders of magnitude higher than the rate of propagation.^{2e} Therefore, the MWD of the resulting polymers is usually lower than that obtained when alkyl halides are used as initiators, and the initiation efficiency is 1.0 with a large group of functional initiators. As shown in Scheme 1 for the case of acrylonitrile (AN), a distinct feature of sulfonyl radicals vs alkyl radicals adding to activated vinyl monomers is the reversibility of the addition step (eq 2). The equilibrium constant of this step is monomer-dependent, and it controls indi-

rectly the concentration of radicals during the initiation step. Since, after adding to the monomer (eq 3), a carbon center radical is obtained upon activation, termination reactions (i.e., combination) occur and Cu(II) species accumulate in the system. The net result is that the type of initiator used will determine, via the amount of Cu(II) generated during initiation, the concentration of propagating radicals. The radical concentration determines both the rate of polymerization and the MWD of the resulting polymer, which depend therefore on the type of initiator used.

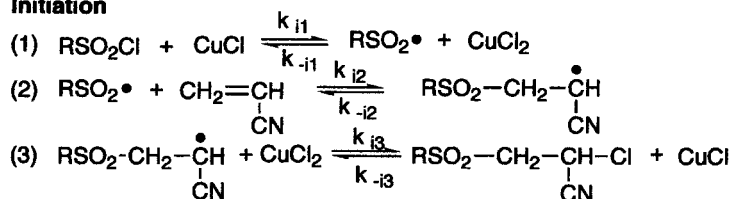
The metal catalyzed LRP initiated with sulfonyl halides was applied to styrenes, methacrylates, and acrylates.^{1,2} The most successful class of vinyl monomers for the LRP initiated with sulfonyl halides are methacrylates, followed by styrenes and acrylates. The radicals derived from acrylates are very reactive, and therefore, large amounts of termination occur during the early stages of the polymerization and produce a broad MWD polymer. The accumulated Cu(II) species dramatically reduce the rate of polymerization, generating a slow process.

LRP of AN represents a special challenge as this monomer tends to coordinate the catalysts and is not a solvent for its own polymer. The reactivity of the radical derived from AN is intermediary between acrylates and methacrylates, due to its conjugation with the cyano group. Polyacrylonitrile (PAN) synthesized by free radical polymerization is an important commercial polymer with a large array of uses. While many other monomers that can be polymerized by LRP can also be polymerized via other living methods, no living polymerization procedure is available for AN. It is therefore desirable to generate a LRP process for AN since this will open avenues for the synthesis of PAN with controlled chain ends and MW and narrow MWD as well as of polymers with more complex architecture based on AN.

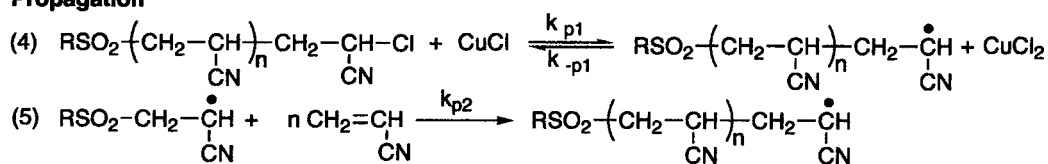
Preliminary studies on the LRP of AN initiated with alkyl halides and catalyzed by CuBr/2,2'-bipyridine (bpy), in ethylene carbonate (EC), were first reported by our group in 1996.³ Since then, other groups reported the synthesis of homopolymers or copolymers⁴ of AN using identical⁵ or similar⁶ conditions.

Scheme 1. Mechanism of Living Radical Polymerization of AN Initiated with Sulfonyl Chlorides

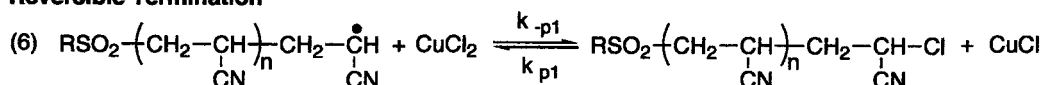
Initiation



Propagation



Reversible Termination

Table 1. Metal Catalyzed Living Radical Polymerization of AN^a Initiated with Alkyl Halides, Alkylsulfonyl Chlorides, and Arenesulfonyl Chlorides

no.	initiator	catalyst	T (°C)	time (h)	conv (%)	GPC ^c		
						M _{th}	M _n	M _w /M _n
1	BPN	CuBr/bpy	60	3	52	3583	6000	1.19
2	BPN	CuBr/bpy	100	2	60	4134	5800	1.17
3	BPN	CuCl/bpy	100	2	60	4134	5000	1.15
4	BPN	CuO/bpy	100	6	59	4065	5800	1.16
5	BPN	Cu ₂ O/bpy	100	2	73	5030	8400	1.15
6	BPN ^b	Cu ₂ O/bpy	100	16	35	37100	38400	1.41
7	CPN	CuBr/bpy	100	2	67	4616	6700	1.16
8	CPN	CuCl/bpy	60	4	15	1034	2140	1.21
9	CPN	CuCl/bpy	80	4	40	2756	5040	1.20
10	CPN	CuCl/bpy	100	2	56	3858	6000	1.15
11	CPN	CuO/bpy	100	26	70	4823	22000	1.72
12	CPN	Cu ₂ O/bpy	100	26	60	4134	9400	1.35
13	TCMSC	CuCl/bpy	100	16	68	4685	5400	1.28
14	TCMSC	CuCl ₂ /bpy	100	24	56	3858	3370	1.28
15	TCMSC	Cu ₂ O/bpy	100	44	21	1447	1800	1.25
16	MSC	CuCl/bpy	100	16	68	4685	5440	1.28
17	MSC	CuO/bpy	100	9	45	3101	6900	1.17
18	MSC	Cu ₂ O/bpy	100	9	63	4341	10100	1.72
19	MBSC	CuCl/bpy	100	20	94	6477	10200	1.27
20	MBSC	CuCl ₂ /bpy	100	24	60	4134	7300	1.33
21	MBSC	Cu/bpy	80	20	2			
22	MBSC	Cu/CuCl ₂ /bpy	100	24	24	1654	2110	1.24
23	MBSC	CuO/bpy	100	6	54	3721	12200	1.51
24	MBSC	Cu ₂ O/bpy	100	2.5	71	4892	6700	1.37
25	MBSC ^b	Cu ₂ O/bpy	100	16	45	47700	25500	1.73

^a [AN] = 10.1 M, EC, [AN]/[I]/[Cat]/[bpy] = 130/1/0.3/0.6 molar ratios. ^b [AN] = 5.0 M, EC, [AN]/[I]/[Cat]/[bpy] = 2000/1/0.4/1.2 molar ratios. ^c From GPC analysis vs PEG standards.

We are reporting herein a novel LRP of AN based on the use of cuprous and cupric oxide catalysts in conjunction with monoalkylsulfonyl chlorides as well as mono- and multiarenesulfonyl chloride initiators and the synthesis of the first PAN with star architecture.

Results and Discussion

General Strategy. An overview of polymerization results obtained for selected initiators for the LRP of AN in the presence of different copper catalysts is presented in Table 1.

Reports on the use of CuO and Cu₂O for the addition of alkyl halides to olefins indicate that small amounts of CuCl form in situ.⁷ Our group reported for the first time the use of Cu₂O/bpy catalyst for the LRP of methacrylates and styrene.⁸ This catalyst generates slowly CuCl in situ, and side reactions are diminished

due to decreased radical generation determined by the small concentration of catalyst.

Traditional LRP catalysts, such as CuBr and CuCl, were compared to novel systems based on CuCl₂, Cu₂O, and CuO, for four classes of initiators in the LRP of AN. The more promising initiator-catalyst combinations were optimized, and the reaction kinetics were studied.

A. Alkyl Halide Initiators. Polymerization of AN using CuBr catalyst and 2-bromopropionitrile (BPN) as initiator lead to both rate and MWD increase with the amount of CuBr (Figure 1). Comparative kinetic studies using BPN initiator and CuBr catalyst in the LRP of AN, at two different [AN]/[BPN] ratios (i.e., 130 and 560), confirmed earlier observations that the curvature in the dependence of ln([M]₀/[M]) vs time (Figures 2 and 3) is due to loss of bromine chain ends.^{3,5,6} The molecular weight increases linearly with conversion up to a

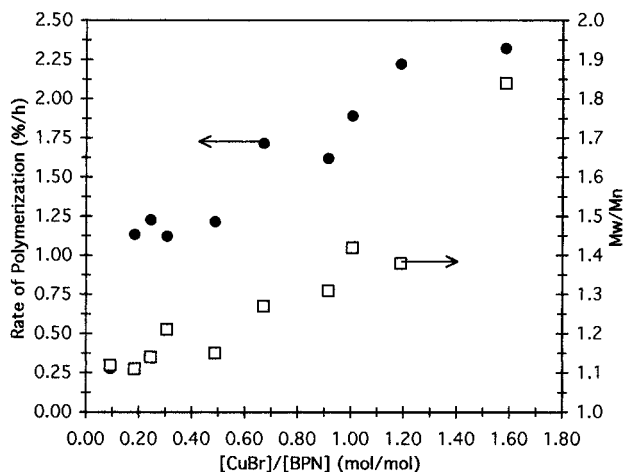


Figure 1. Dependence of rate of polymerization and M_w/M_n on catalyst concentration for the CuBr/bpy catalyzed living radical polymerization of AN initiated with 2-bromopropionitrile (BPN). Conditions: [AN] = 10.1 M, DMF, [AN]/[BPN] = 130/1 mol/mol, [CuBr]/[bpy] = 1/2 mol/mol, reaction temperature 60 °C.

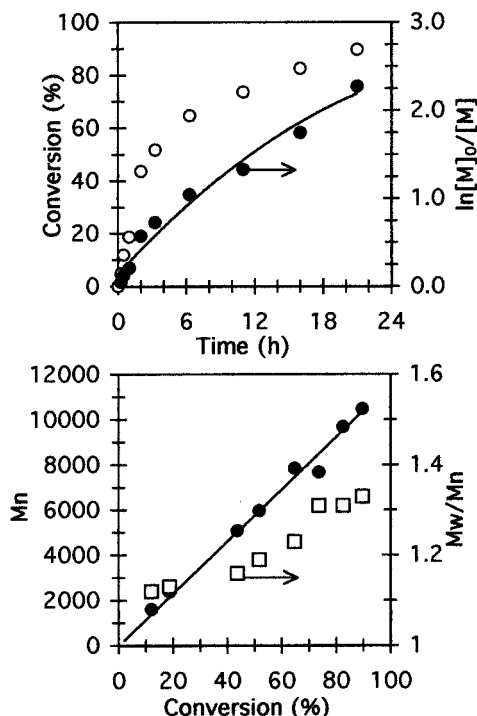


Figure 2. Living radical polymerization of AN catalyzed by CuBr/bpy and initiated with 2-bromopropionitrile (BPN). Conditions: [AN] = 10.1 M, EC, [AN]/[BPN]/[CuBr]/[bpy] = 130/1/0.3/0.6 molar ratios, reaction temperature 60 °C.

maximum M_n of 30 000 ($M_w/M_n = 1.18$). However, in this case, M_w/M_n also increases with conversion to values of 1.35 due to the presence of side reactions.⁶ Changing the catalyst to CuCl generates a PAN with a slightly narrower MWD (1.15) by exchanging some of the labile Br chain ends with the more stable Cl ones. A faster rate of polymerization and a narrower MWD than when CuBr is used as catalyst were observed during the BPN initiated LRP of AN catalyzed by Cu₂O/bpy. This system reduces the extent of side reactions as described previously.

More stable alkyl chloride initiators were used for the LRP of AN in the presence of copper catalysts (Table 1). The results for the 2-chloropropionitrile (CPN) initiated LRP of AN catalyzed by either CuBr or CuCl

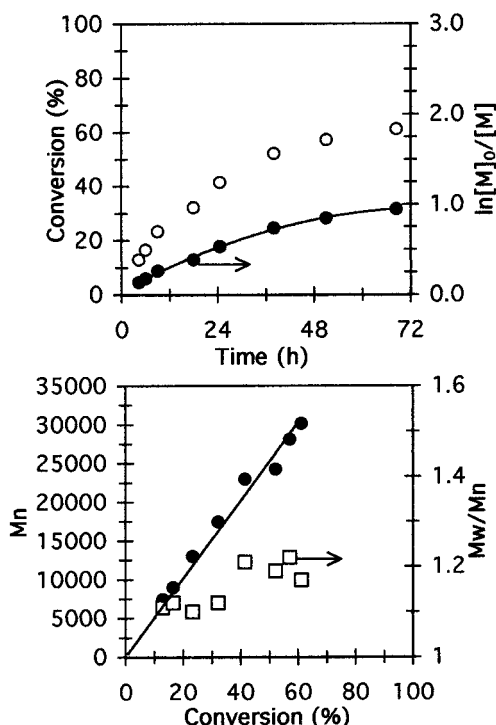


Figure 3. Living radical polymerization of AN catalyzed by CuBr/bpy and initiated with 2-bromopropionitrile (BPN). Conditions: [AN] = 7 M, EC, [AN]/[BPN]/[CuBr]/[bpy] = 560/1/0.3/0.6 molar ratios, reaction temperature 60 °C.

are almost identical. Increased polymerization temperature accelerates the polymerization and provides PAN with narrowed MWD. The CPN initiated LRP of AN catalyzed by Cu₂O/bpy affords 60% conversion in 26 h. By contrast, when 4-methoxybenzenesulfonyl chloride (MBSC) was used as initiator, under the same conditions, the same conversion was obtained in 2.5 h, while the M_w/M_n values are the same. However, the Cu₂O catalyzed, BPN initiated LRP of AN reached 73% conversion in 2 h, while M_w/M_n is only 1.15. Nevertheless, in this case, a bromine propagating chain end was responsible for the high rate of propagation.

The tacticity of PAN synthesized by the CPN initiated LRP of AN in the presence of CuCl/bpy was determined by ¹³C NMR as shown in Figure 4. The calculated ratios mm/mr/rr = 28/50/22 are close to literature values⁹ for a PAN obtained by a free radical polymerization (24/55/21). Thus, the radical nature of the LRP of AN was indirectly demonstrated.

B. Perchloroalkylsulfonyl Chloride Initiators.

The LRP of AN initiated with trichloromethanesulfonyl chloride (TCMSC) and catalyzed by CuCl/bpy has a higher rate of polymerization and leads to PAN with a narrower MWD than that of PAN synthesized using any other sulfonyl chloride initiators, in the presence of CuCl/bpy (Table 1). Perhaloalkylsulfonyl radicals extrude SO₂ to give perhaloalkyl radicals, which in turn can add to olefins.^{2f} This result is consistent with other reports on the rates of addition of alkyl halides^{10a} vs alkylsulfonyl halides^{10b} to olefins. Direct evidence is obtained from the heteronuclear multiple bond correlation NMR (HMBC) spectra (Figure 5), which shows correlation peaks between the CCl₃ terminal (A), the CH₂ in the α position (C), and the CH in the β position (B), demonstrating the absence of the SO₂ group. In the TCMSC initiated, Cu₂O/bpy catalyzed LRP of AN, a conversion of only 21% in 44 h was obtained. This

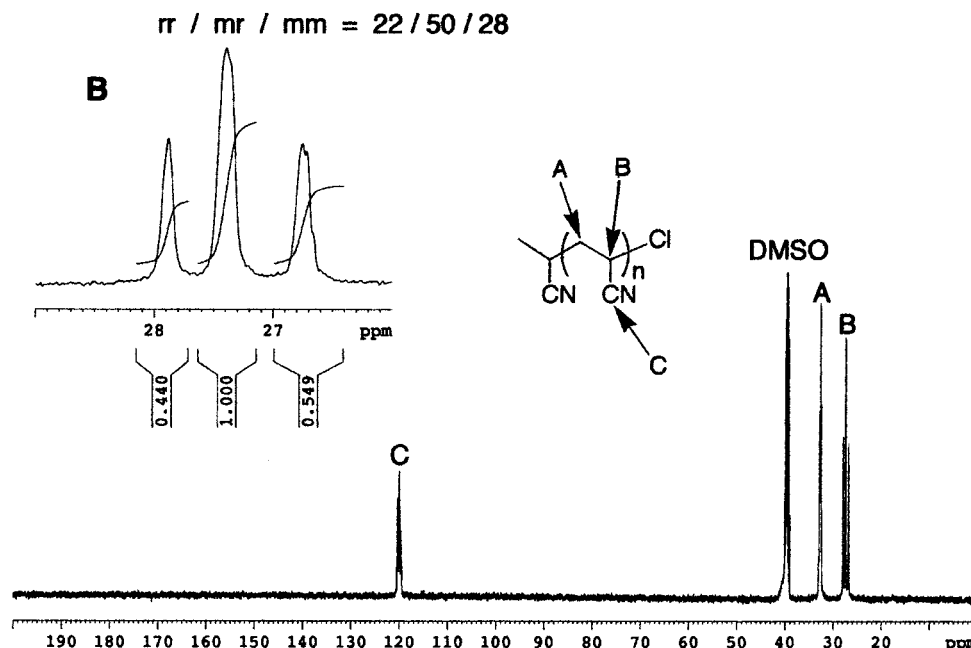


Figure 4. Determination of the tacticity of a 2-chloropropionitrile initiated PAN by ^{13}C NMR.

Table 2. Influence of [bpy]/[CuCl] on Conversion and M_w/M_n for the 4-Methoxybenzenesulfonyl Chloride Initiated Living Radical Polymerization of AN^a

no.	[bpy]/[CuCl]	conv (%)	M_{th}	M_n	M_w/M_n
1	1.6	76	4230	6500	1.32
2	2.1	78	4340	8200	1.41
3	3.0	75	4180	7200	1.64

^a Conditions: [AN] = 10.1 M, EC, [AN]/[MBSC]/[CuCl] = 100/1/0.2 molar ratios, reaction time 15 h, reaction temperature 100 °C.

supports that this initiator behaves as an alkyl chloride and not an alkylsulfonyl chloride. The polymerization of AN catalyzed by CuCl_2/bpy and initiated by TCMSC reached in 24 h almost the same conversion and M_w/M_n (conversion = 56%, M_w/M_n = 1.28) with the one initiated with MBSC (conversion = 60%, M_w/M_n = 1.33). Therefore, most likely due to a low radical concentration when CuCl_2 is used as catalyst, as reduced amounts of termination reactions take place, no significant initiator effect is observed.

C. Alkylsulfonyl Chloride Initiators. Contrary to perhaloalkylsulfonyl radicals, the very reactive alkylsulfonyl radicals do not extrude SO_2 .^{10b} In the methanesulfonyl chloride (MSC) initiated LRP of AN, the rate of polymerization decreases as a function of the catalyst used in the order $\text{Cu}_2\text{O} > \text{CuO} > \text{CuCl}$ (Table 1). This estimate is obtained on the basis of conversion per hour values calculated from the data in Table 1. An explanation may be that the extent of termination reactions may increase in the same order, as the solubility of the catalyst increases and more radicals are generated. A M_w/M_n value of 1.17 obtained for the CuO catalyst is comparable with the one obtained with the BPN/ CuBr system (Table 1).

D. Arenesulfonyl Chloride Initiators. Mechanistic investigations on the role of CuBr , CuCl , and CuCl_2 catalysts in the LRP of AN initiated with arenesulfonyl chlorides were performed in order to determine the influence of these species on the rate of polymerization and on the molecular weight distribution of the PAN (M_w/M_n). The CuCl/bpy catalyzed LRP of AN initiated

with MBSC showed that high conversion and narrow MWD are obtained at low catalyst concentrations (Figure 6). This is an interesting result since it is contrary to theoretical expectations, according to which the rate of polymerization should increase with the amount of catalyst due to increased radical concentration (Scheme 1, eq 4). It is possible that in the case of AN the amount of side reactions and the loss of chain ends increase with the increase in catalyst concentration since the radical concentration increases. This leads to a decrease in the rate of polymerization. On the basis of this result, one would expect that less soluble catalysts should actually provide a better control and a faster rate of polymerization in the case of the LRP of AN.

In the MBSC initiated LRP of AN catalyzed by CuCl/bpy , a maximum rate of polymerization and the lowest MWD were observed at $[\text{CuCl}]/[\text{bpy}] = 1/1.6$ mol/mol (Table 2). The observed rate of polymerization (76% in 15 h) was lower than in the case when alkyl halides (i.e., CPN gives 56% in 2 h) were used as initiators in the presence of CuCl/bpy . Moreover, the MWD of the PAN obtained using MBSC as initiator (M_w/M_n = 1.32) was broader than the MWD of the PAN obtained using CPN as initiator (M_w/M_n = 1.15).

The effect of CuCl_2 resulted from termination reactions (Scheme 1) for the arenesulfonyl chloride initiated LRP of AN is shown in Figure 7. Contrary to data available for the LRP of AN when alkyl halides were used as initiators and CuBr_2 as catalyst,⁶ the polymerization occurs in the presence of pure CuCl_2 when arenesulfonyl halides are used as initiators. Though the rate of polymerization was much slower than in the presence of Cu_2O catalyst, and the MWD was broader, for low catalyst to MBSC ratios (i.e., 0.1), the result is almost identical with the CuCl/bpy system (Figure 6). The explanation could be that a conversion of Cu(II) to Cu(I) occurs during the initiation of the polymerization with arenesulfonyl halides,^{10b} while in the case of alkyl halides, this process does not take place.

The $\text{Cu}_2\text{O}/\text{bpy}$ catalyst provides both fast rate and narrow MWD for the LRP of AN initiated with MBSC

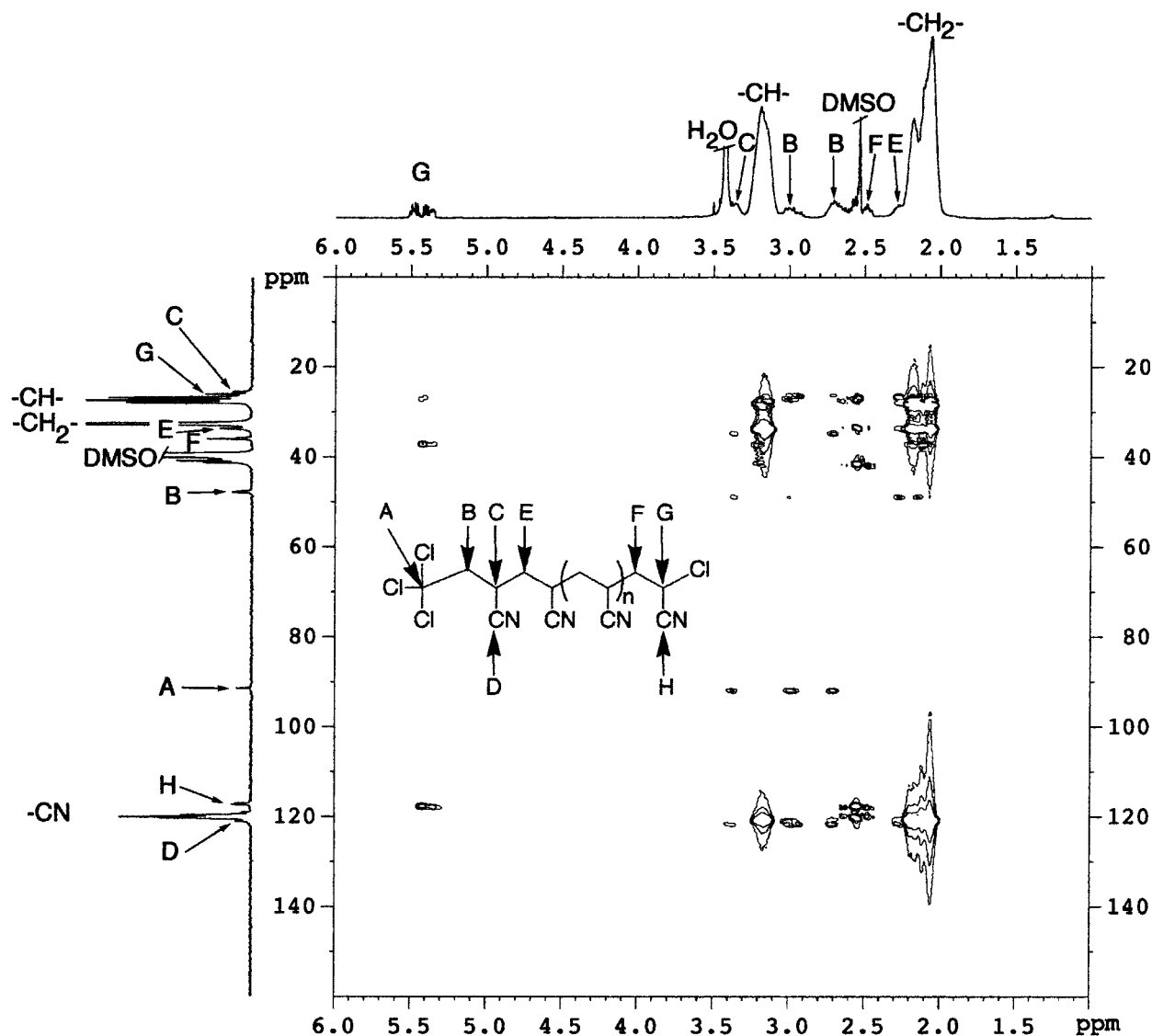


Figure 5. Structural analysis by 2D-NMR of a trichloromethanesulfonyl chloride initiated PAN.

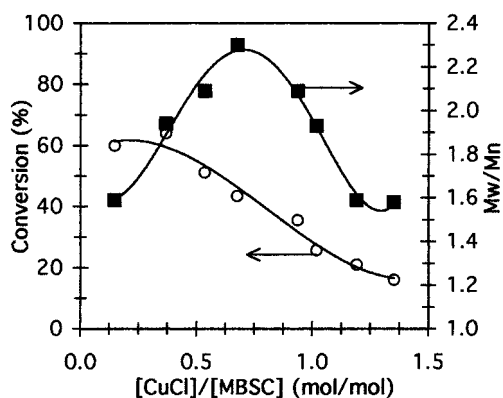


Figure 6. Dependence of conversion and M_w/M_n on catalyst concentration in the CuCl/bpy catalyzed living radical polymerization of AN initiated with 4-methoxybenzenesulfonyl chloride (MBSC). Conditions: [AN] = 10.1 M, [AN]/[MBSC] = 100/1 mol/mol, [CuCl]/[bpy] = 1/2 mol/mol, reaction time 24 h, polymerization temperature 100 °C.

in EC. This system was investigated using different solvents, such as *N,N*-dimethylformamide (DMF), propylene carbonate (PC), and mixtures EC/PC. The results in Table 3 demonstrate that only EC provides an increase in rate for the Cu₂O/bpy catalyst. This is in

Table 3. Solvents Tested for the Cu₂O/Bpy Catalyzed Living Radical Polymerization of AN Initiated with 4-Methoxybenzenesulfonyl Chloride^a

no.	solvent	time (h)	conv (%)	M_n	M_w/M_n
1	EC	2.5	55	19500	1.37
2	DMF	2.5	8	7100	1.23
3	PC	2.5	14	6500	1.18
4	PC/EC = 1/1 (v/v)	2.5	24	10200	1.22
5	PC/EC = 4/1 (v/v)	2.5	20	7800	1.36

^a Conditions: [AN] = 10.1 M, [AN]/[MBSC]/[Cu₂O]/[bpy] = 300/1/0.6/1.2 molar ratios, reaction temperature 100 °C.

line with previously reported data for the CuBr/bpy catalyzed LRP of AN where also EC provided the highest rate of polymerization.^{3,5,6}

Other metals (Al, Fe) and ligands for Cu₂O were investigated in the LRP of AN initiated with MBSC (Table 4). The ligands used for Cu₂O were (i) bi- and tridentated aromatic ligands of similar electronic effect to bpy and (ii) aliphatic substituted amines. In terms of both rate of polymerization and narrow MWD, bpy was the best ligand for Cu₂O, while other ligands produced PAN with broader or multimodal MWD. Al and Fe catalysts, in the presence of bpy ligand, had lower rates of polymerization than Cu₂O. The MW of PAN was controlled for Fe(0)/bpy even if the M_w/M_n =

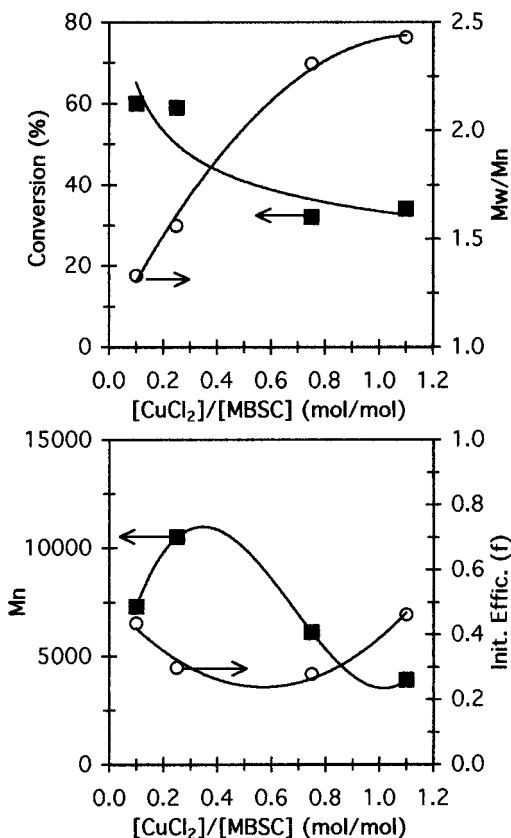


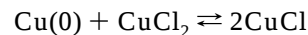
Figure 7. Dependence of conversion, M_w/M_n , and initiator efficiency (f) on catalyst concentration in the CuCl_2/bpy catalyzed living radical polymerization of AN initiated with 4-methoxybenzenesulfonyl chloride (MBSC). Reaction conditions: $[\text{AN}] = 10.1 \text{ M}$, EC, $[\text{AN}]/[\text{MBSC}] = 100/1 \text{ mol/mol}$, $[\text{CuCl}_2]/[\text{bpy}] = 1/1.5 \text{ mol/mol}$, reaction temperature 100°C , reaction time 24 h.

2.08 and uncontrolled for $\text{Al}(\text{O})/\text{bpy}$ while $M_w/M_n = 1.62$.

The ^1H NMR spectrum of a linear PAN obtained by MBSC initiated LRP is presented in Figure 8. Both chain ends are visible, and the functionality of this PAN sample, within experimental error, is 0.9. On the basis of the aromatic signals B and C in Figure 8, initiation from the sulfonyl chloride group was quantitative; the only potential loss of functionality occurs from the Cl chain end during polymerization. The calculated $M_{\text{NMR}} = 3002$ is within 7% of the theoretical value $M_{\text{th}} = 2798$. The MALDI-TOF analysis of a polymerization sample

of the same polymer reveals a perfect match between M_n and M_{th} (Figure 9). All four families of peaks (A, B, C, and D) are identified, and the presence of the MBSC initiator in each chain was demonstrated. Peaks corresponding to dehydrochlorination of the chain ends induced by the high laser intensity used in the MALDI^{5,6} were observed. No evidence for termination reactions was observed by MALDI-TOF. Interestingly, a small peak due to ionization of the PAN by Cu^+ ions from the unpurified polymerization mixture is observed. The most important information is, however, the comparison between the PAN molecular weight by MALDI ($M_{\text{MALDI}} = 2741$, almost equal to the theoretical value 2798) and by GPC analysis using poly(ethylene glycol) (PEG) standards ($M_n = 5240$, $M_w/M_n = 1.21$). The calculated overestimation factor of 1.87 should be applied to all the M_n and initiator efficiency (f) values reported in this paper since they were calculated vs PEG standards. A detailed discussion of the differences observed for the molecular weight of PAN, as determined by different techniques, is available.^{5,6}

LRP of AN using $\text{Cu}(\text{O})/\text{bpy}$ catalyst in conjunction with MBSC as initiator was much slower than that using CuCl/bpy under the same conditions (Table 1). This might be a consequence of increased amounts of CuCl present in the polymerization mixture presumably¹¹ due to the following disproportionation reaction:



On the basis of our previous experimental observations reported in Figures 6 and 7, that small amounts of CuCl or CuCl_2 are best in controlling the rate of polymerization and the M_w/M_n , the use of two copper oxides, Cu_2O and CuO , was of interest for the LRP of AN. Because of their reduced solubility, a low amount of CuCl catalyst is expected to be generated in situ and therefore be available during polymerization. Indeed, as seen in Figure 10, a fast rate of polymerization, narrow MWD, and good initiator efficiency are observed at low Cu_2O catalyst concentrations. In contrast, when CuO/bpy was used as catalyst, the polymerization rate increased with the catalyst concentration, while the MWD leveled at around 1.5 (Figure 11). On the basis of these results, $\text{Cu}_2\text{O}/\text{bpy}$ is the catalyst of choice for the arenesulfonyl chloride initiated LRP of AN.

Complete kinetic plots obtained for the LRP of AN initiated with MBSC and catalyzed by $\text{Cu}_2\text{O}/\text{bpy}$ are

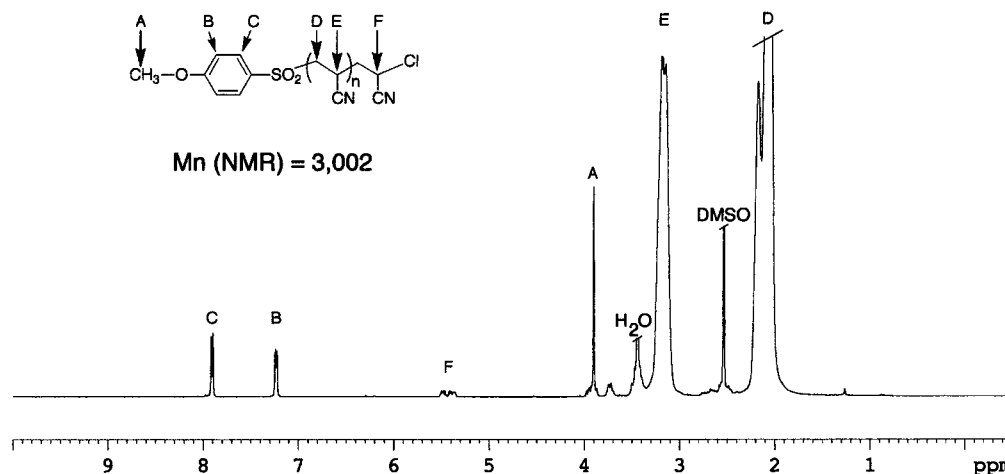
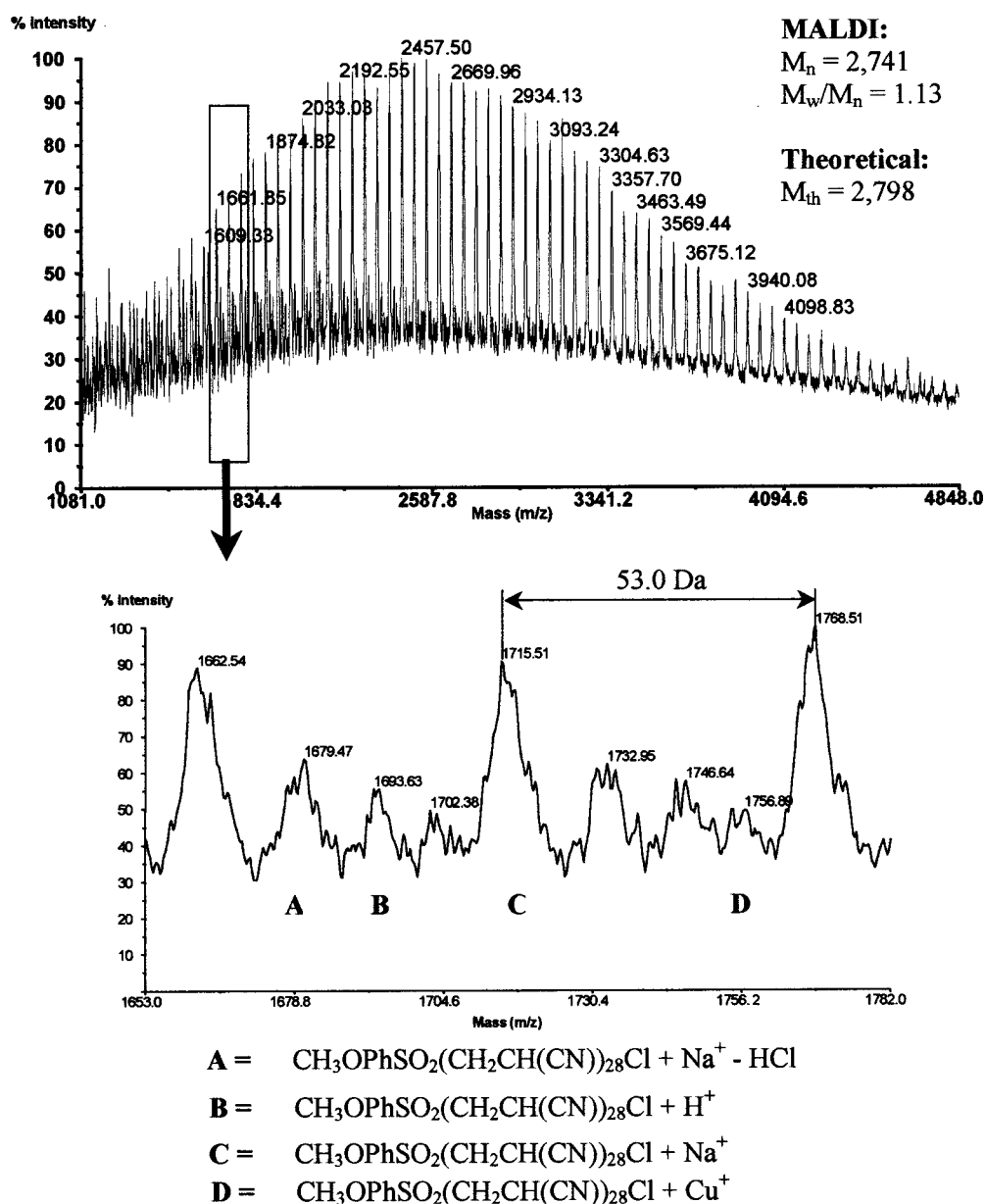


Figure 8. ^1H NMR spectral characterization of a PAN obtained by the $\text{Cu}_2\text{O}/\text{bpy}$ catalyzed living radical polymerization of AN initiated with 4-methoxybenzenesulfonyl chloride ($M_{\text{th}} = 2798$).

Table 4. Catalysts and Ligands Tested for the Metal Catalyzed Living Radical Polymerization of AN Initiated with 4-Methoxybenzenesulfonyl Chloride^a

no	cat	ligand	ligand structure	t ime (h)	conv (%)	M _{th}	M _n	M _w /M _n
1	Cu ₂ O	PMTA		2	12	756	2,700	1.43
2	Cu ₂ O	phen		2	69	4,347	11,300 (bimodal)	1.58
3	Al	bpy		16	32	2,016	39,000	1.62
4	Fe	bpy		16	54	3,402	6,600	2.08

^a Conditions: [AN] = 10.1 M, EC, [AN]/[MBSC]/[cat]/[lig] = 100/1/0.2/0.3 molar ratios, reaction temperature 100 °C.

**Figure 9.** MALDI-TOF analysis of a PAN obtained by Cu₂O/bpy catalyzed living radical polymerization initiated with 4-methoxybenzenesulfonyl chloride. Four distinct series of peaks (A, B, C, D) were identified.

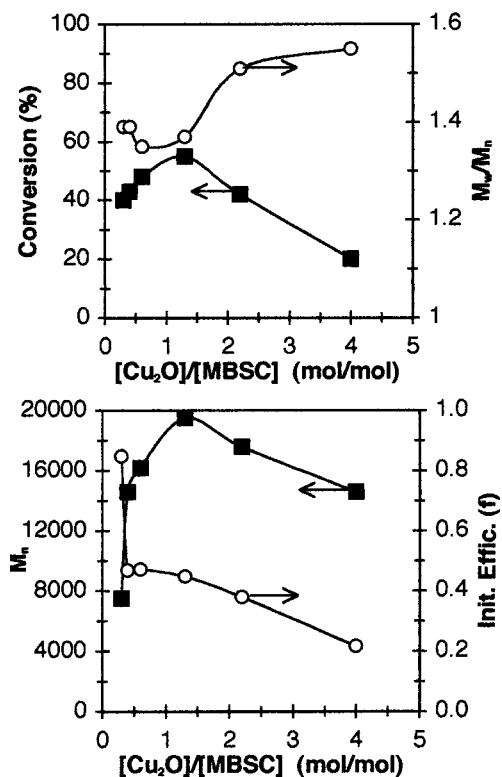


Figure 10. Dependence of conversion, M_w/M_n and initiator efficiency (f) on catalyst concentration in the Cu_2O/bpy catalyzed living radical polymerization of AN initiated with 4-methoxybenzenesulfonyl chloride (MBSC). Reaction conditions: $[AN] = 10.1$ M, EC, $[AN]/[MBSC] = 300/1$ mol/mol, $[Cu_2O]/[bpy] = 1/2$ mol/mol, reaction temperature 100 °C, reaction time 2.5 h.

presented in Figure 12. It is important to note that the reaction was first order in monomer up to high conversion (92%), while the MW increased linearly with conversion and MWD remained narrow (1.25–1.15). We have to mention that, starting at about 60% conversion, this polymerization proceeds in a gel state since the weight percent concentration of the monomer is 66%. Despite these heterogeneous polymerization conditions, conversion can reach almost 100%. Nevertheless, deviation from first order in $[AN]$ occurs only above 85% conversion. The observation that this polymerization takes place in a swollen gel state has important technological implications. This result shows a significant improvement vs previous results^{5,6} on alkyl bromide initiators and $CuBr$ or $CuCl$ catalysts, when large amounts of side reactions did not allow for a linear dependence of $\ln([M]_0/[M])$ with time, and the polymer MWD increased with conversion.

E. Synthesis of Three-Arm Star PAN. The synthesis of PAN with complex architecture, such as three-arm star PAN, is presented in Scheme 3. Fast and quantitative initiation is the requirement for multiple initiators used in the synthesis of star polymers via living polymerizations. The three-arm star PAN was obtained from the 1,1,1-tris(4-chlorosulfonylphenyl)ethane¹³ (3PSC) initiated LRP of AN, in the presence of Cu_2O/bpy catalyst. Chain-ends analysis, determination of MW ($M_{NMR} = 1030$), as well as demonstrating the absence of dehydrochlorination of the three-arm star PAN was performed by 1H NMR analysis (Figure 13). On the basis of the aromatic signals observed (B and C), quantitative initiation from sulfonyl chloride groups occur in this case, similar to the initiation from MBSC,

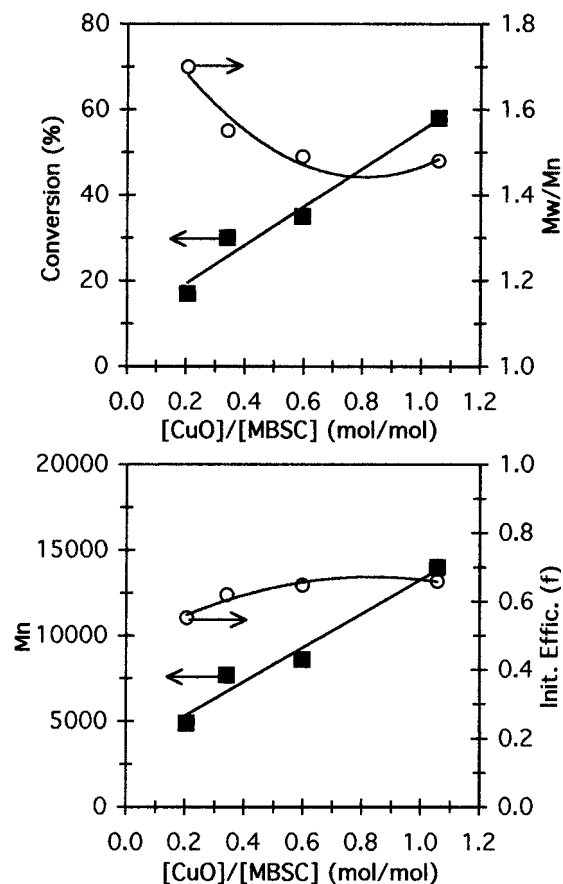


Figure 11. Dependence of conversion, M_w/M_n and initiator efficiency (f) on catalyst concentration in the CuO/bpy catalyzed living radical polymerization of AN initiated with 4-methoxybenzenesulfonyl chloride (MBSC). Reaction conditions: $[AN] = 10.1$ M, EC, $[AN]/[MBSC] = 300/1$ mol/mol, $[CuO]/[bpy] = 1/1.5$ mol/mol, reaction temperature 100 °C, reaction time 4 h.

as observed in Figure 8 (signals B and C). The more complex pattern of the aromatic region observed in Figure 13 is due to restricted rotation of the phenyl rings. All molecular weight peaks observed by MALDI-TOF demonstrate the presence of the initiator and are grouped in three series (A, B, C), as presented in Figure 14. M_n determined by MALDI indicates an average of five monomer units per arm. On the basis of the $[AN]/[3PSC]$ ratio and the obtained conversion, the PAN should have an average of four monomer units per arm. This difference can be attributed to underestimating the conversion due to the fractionation of the low MW PAN during precipitation. Peaks corresponding to dehydrochlorination of the chain ends induced by the high laser intensity used in the MALDI,^{5,6} and addition of Na^+ or K^+ ions, are present. As this sample was purified, the Cu^+ ionized series observed for MBSC initiator (D, Figure 9) is missing. The distance between peaks from the same series corresponds to the molecular weight of AN monomer (53.1 Da).

Conclusions

The optimum combinations of catalysts and initiators obtained for the LRP of AN are $CuCl/bpy$ and CPN, $CuCl/bpy$ and TCMSC, Cu_2O/bpy and BPN, Cu_2O/bpy and MBSC, and CuO/bpy and MSC. These systems represent a dramatic improvement in terms of rate of polymerization, chain-end functionality, and reduced amount of side reactions over the alkyl bromide/ $CuBr$ /

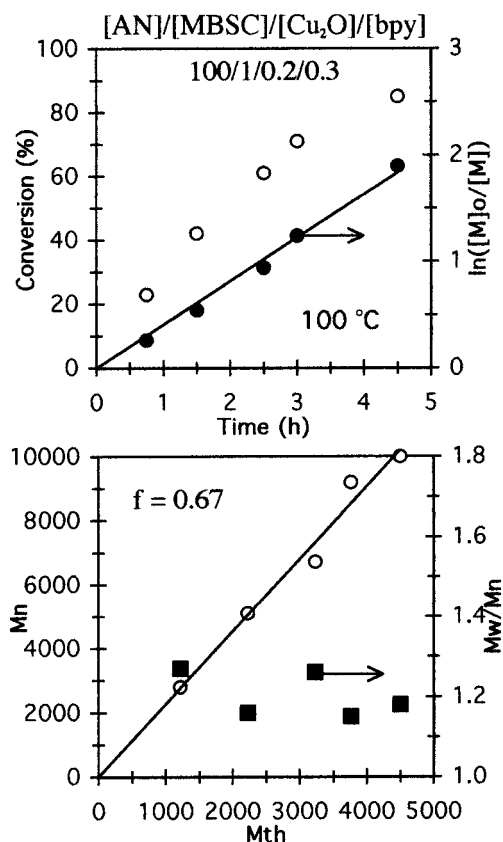
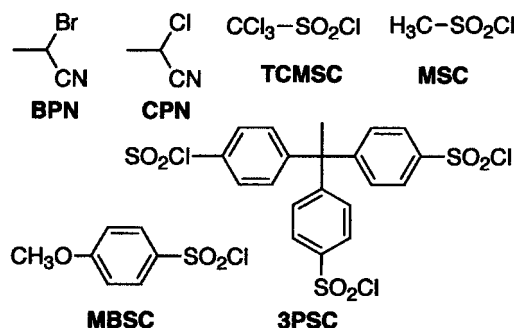


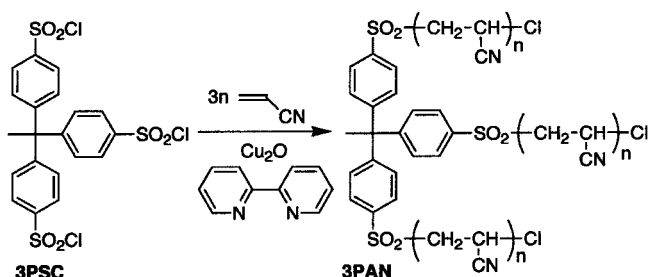
Figure 12. Cu_2O/bpy catalyzed living radical polymerization of AN initiated with 4-methoxybenzenesulfonyl chloride (MBSC). Reaction conditions: $[AN] = 10.1$ M, EC, $[AN]/[MBSC]/[Cu_2O]/[bpy] = 100/1/0.2/0.3$ molar ratios, reaction temperature 100 °C.

bpy system as reported both in the current article and in previous publications.^{5,6} This can be best concluded by comparing Figures 2, 3, and 12 from this article. Alkyl and arenesulfonyl chlorides are efficient initiators for the LRP of AN in the presence of copper oxide catalysts. The first three-arm star PAN was synthesized

Scheme 2. Initiators Used for the Living Radical Polymerization of AN



Scheme 3. Synthesis of a Three-Arm Star PAN by Living Radical Polymerization



by the LRP of AN using a triarenesulfonyl chloride (3PSC) initiator, in the presence of Cu_2O/bpy catalyst. NMR and MALDI analyses of this polymer demonstrated the star architecture generated by quantitative initiation from the arenesulfonyl chloride groups and the good control of the MW provided by the cuprous oxide catalyst.

Experimental Section

Techniques. Gel permeation chromatography (GPC) analysis was performed using a Shimadzu high-pressure liquid chromatography system containing a LC-10AT pump, a CTO-10A column oven (45 °C), and a RID-10A RI detector coupled to a Nelson Analytical 900 series integrator data station.

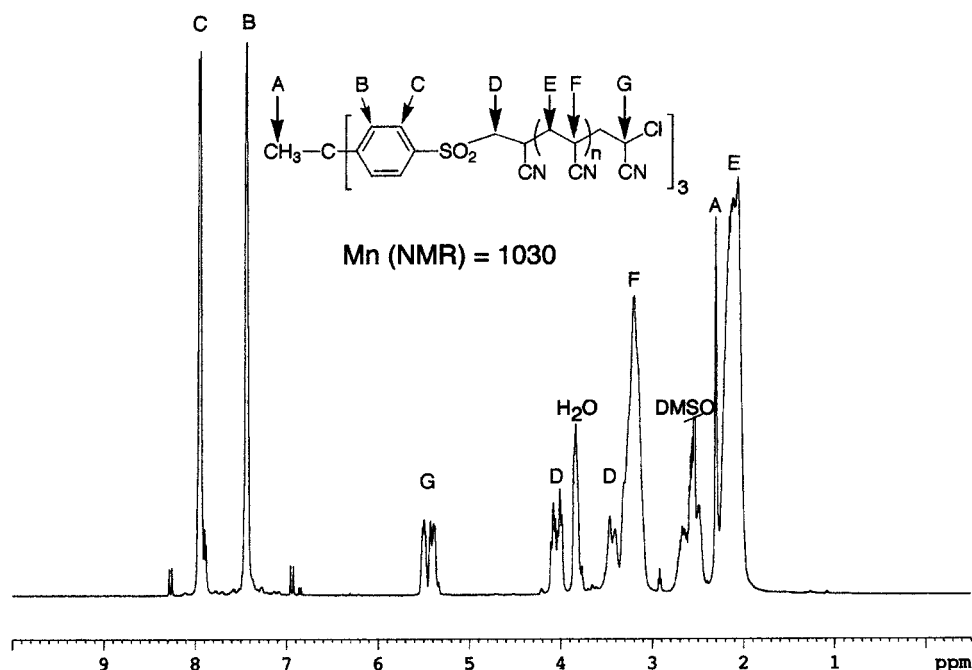


Figure 13. 1H NMR spectral characterization of the three-arm star PAN.

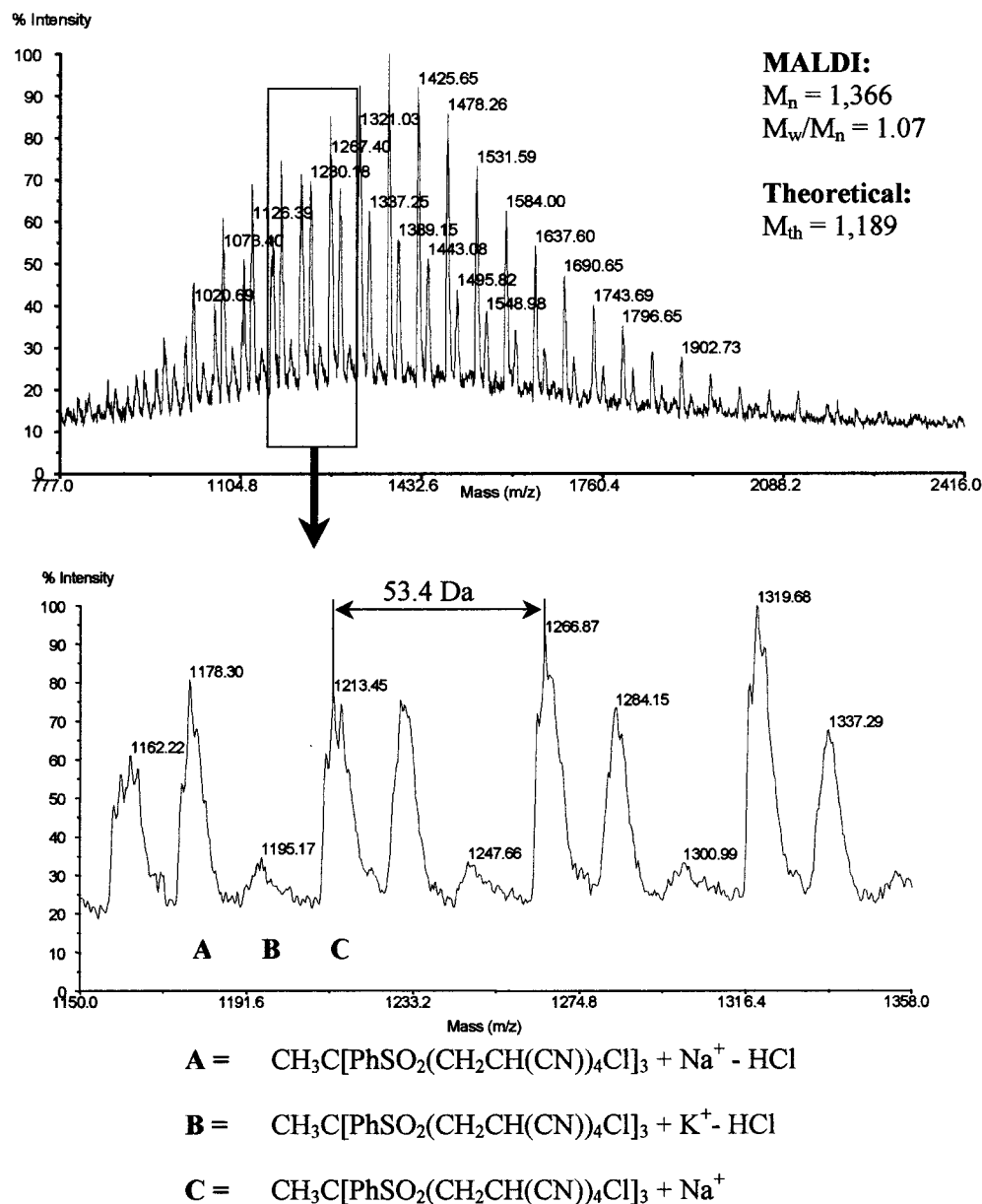


Figure 14. MALDI-TOF analysis of the three-arm star PAN.

working with the Perkin-Elmer Turbochrom 4 software. The GPC setup had a guard column and two 25 cm AM gel columns (10 μm , 500 Å and 10 μm , 10 000 Å). *N,N*-Dimethylformamide (Aldrich, HPLC grade) 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 poly(ethylene glycol) standards (American Polymer Standards Corp.). ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DRX500 at 27 °C in $\text{DMSO}-d_6$. MALDI analysis was performed on a Voyager-DE (Applied Biosystems) with a 337 nm nitrogen laser (pulse width, 3 ns), accelerating potential of 24 kV, positive ionization. The sample preparation was done as reported in the literature.¹²

Materials. All materials, unless otherwise specified, were purchased from Aldrich and were used as received. Acrylonitrile (AN) was purified by flash chromatography using basic alumina. 4-Methoxybenzenesulfonyl chloride (MBSC) (99%, Lancaster) was recrystallized twice from hexanes. 1,1,1-Tris-(4-chlorosulfonylphenyl)ethane (3PSC) was synthesized as previously described.¹³

Typical Polymerization Procedure. A 25 mL Schlenk tube was charged with bpy (0.033 g, 0.21 mmol), Cu_2O (0.020 g, 0.014 mmol), AN (1.0 mL, 0.8 g, 15.2 mmol), EC (0.5 mL), and MBSC (0.031 g, 0.15 mmol). The tube was sealed (rubber

septum secured with a screw cap) and immediately frozen in a liquid nitrogen bath. The solution was degassed by four freeze–pump–thaw cycles and was placed under an argon atmosphere. The reaction tube was then maintained at 100 °C under stirring. After 2.5 h the tube was depressurized, and the content was diluted with 4 mL of DMF. When the mixture become a homogeneous solution, slightly acidic methanol (15 mL) was added to precipitate the polymer (PAN). The precipitate was filtered and dried to yield 0.57 g of PAN (conversion = 72%, $M_n = 6700$, and $M_w/M_n = 1.37$).

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