Synthesis and Characterization of Star Polymers Made from Simple, Multifunctional Initiators

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Received April 29, 2002; Revised Manuscript Received August 19, 2002

ABSTRACT: A series of multifunctional molecules were synthesized, bearing either 4, 5, 6, or 10 sulfonyl chloride moieties, each capable of initiating atom transfer living radical polymerization. The general synthetic strategy was to prepare intermediates containing a plurality of phenyl groups and then chlorosulfonylate all of the available rings. These multifunctional initiators were used to synthesize star polymers via the "core-first" approach. Star polymers with relatively narrow molar mass distribution were successfully prepared, with a controlled number of arms and molar masses. The polymerization worked best with methacrylate esters and styrene, but acrylate esters polymerized very slowly under the reaction conditions employed. The number of arms in the polymers as a function of molar mass was determined by multidetector size-exclusion chromatography (SEC). Results of the arm number measurements by SEC were corroborated by experiments in which molar mass distributions were examined before and after the arms were cleaved chemically from the cores.

Introduction

There has been continuing worldwide research directed toward polymers with branched structures, because the presence of branches leads to significant modifications of physical properties.[1,2] For example, branched polymers generally exhibit lower solution and melt viscosities compared to linear polymers of the same molar mass, a characteristic that may help facilitate coating, extrusion, or other manufacturing processes. Hyperbranched and dendrimeric macromolecules, with their fractal structure and multitude of branches, have attracted the most attention in this field.[3−7] However, polymers with a small but controllable number of branches are also of interest because such materials may offer a practical compromise between physical toughness and ease of processing.

Star polymers, distinguished by a structure containing several chains radiating from a relatively compact core, represent a special case of branched polymers. Like dendrimers, they can possess a globular structure (at least for molecules containing a large number of relatively short arms) and have defined inner and peripheral groups. However, like hyperbranched polymers, their synthesis can be accomplished expeditiously. In the past, star polymers have been produced using living ionic polymerizations,[8−10] but of course, these reactions are demanding to carry out because of their sensitivity to air, moisture, and certain functional groups.

Star polymers can principally be synthesized in two different ways: "arm-first" and "core-first". The "arm-first" approach consists of reacting preformed, terminally functionalized polymer chains with a multifunctional quencher molecule that forms the core of the star. However, reaction of several polymer chains with a single core molecule is often difficult because of steric hindrance and can lead to stars with missing or unattached arms. A related approach involves reacting living chains with a multifunctional monomer such as divinylbenzene; however, this technique leads to a broad distribution of arm numbers. The alternative "core-first" approach involves growing polymers from a multifunctional initiator or precursor polymer. Here, the core reacts only with monomers, a less sterically demanding process. However, for ionic polymerizations the "core-first" approach requires the use of multiply charged initiators, which usually exhibit poor solubility.

It would be highly desirable to apply conventional free-radical polymerization to the synthesis of star polymers. Until recently, radical polymerization was not controllable, leading to chains with poorly defined lengths and end groups, unsuitable conditions for the synthesis of star polymers. Thanks to the progress in controlled radical polymerization techniques, it is now possible to avoid these problems. Chemistry developed in the past few years has been shown to produce, via a radical mechanism, polymers with narrow molar mass distribution and with predictable chain lengths,[11−14] the hallmarks of living polymerization. Moreover, block copolymers and other more complex chain architectures have been prepared using free radical polymerization, hitherto impossible feats. With regard to star polymers, a number of research groups have already synthesized these structures using living radical polymerization chemistry. Both the "arm-first"[15] and "core first"[16−21] approaches have been followed.

Our interest in star polymers was stimulated by the report of Percec et al. that sulfonyl halides are rapid and efficient initiators of atom transfer living radical polymerization.[22] Because aromatic sulfonyl chlorides are straightforward to prepare,[23,24] we reasoned that multifunctional versions of this initiating system might be useful for the synthesis of star polymers by the "core-first" method. Such multifunctional initiators would be uncharged and not be prone to the poor solubility often encountered with multifunctional ionic initiators. It might be possible to produce a wide variety of potentially useful macromolecules, ranging from simple star polymers with controlled number and length of arms to more complex structures such as star-block copoly-

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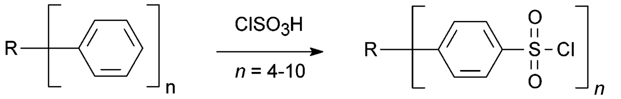
10.1021/ma0206570 CCC: $22.00

Scheme 1. Synthesis of Multifunctional Sulfonyl Chloride Initiators



mers, tapered star-block copolymers, core and arm functional materials, etc. Percec et al. had routinely synthesized linear polymers using difunctional sulfonyl chlorides as initiators[25] and more highly functionalized initiators for the preparation of star structures.[26,27]

We report herein our efforts in the synthesis of star homopolymers using simple, multifunctional aromatic sulfonyl chloride initiators. In addition, we describe a useful technique for the characterization of the number of arms in star polymers. Preliminary descriptions of this work have been communicated.[28,29]

Results and Discussion

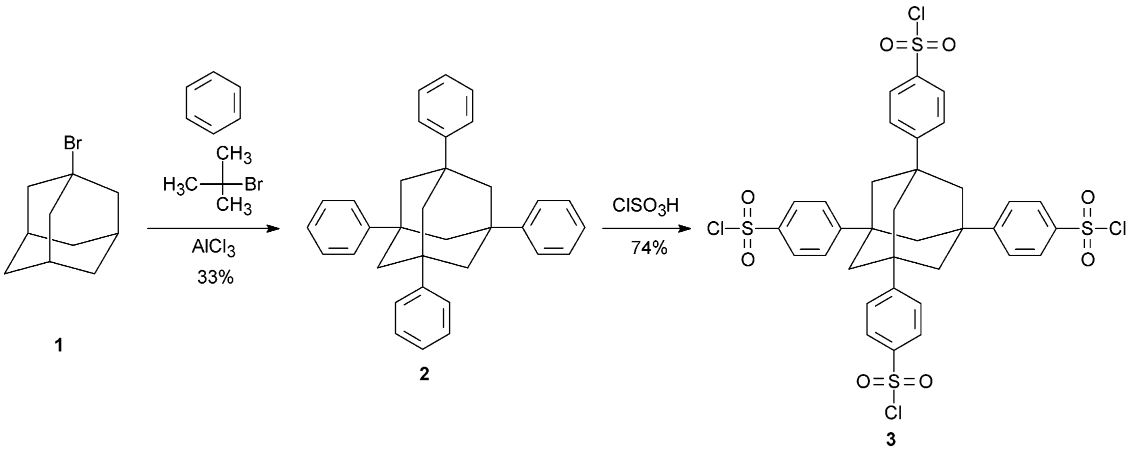
Initiator Syntheses. The overall scheme employed to synthesize multifunctional initiators was to prepare intermediates with a plurality of phenyl substituents and then apply electrophilic aromatic substitution to form chlorosulfonyl groups on each available ring (Scheme 1). In all cases, the predominant substitution pattern (determined by 500 MHz ^{1}H NMR) was *para*, but the unpurified products inevitably contained other isomers (*ortho* or *meta* placements). The presence of these regioisomers was confirmed by derivatization of the initiators with diethylamine and analysis of the resulting sulfonamides by HPLC/MS. These experiments separated several compounds of identical molecular mass in each unpurified sample. This technique could also be used to detect any partially reacted (or hydrolyzed) contaminants, because sulfonic acids do not undergo the derivatization reaction, leading to constituents with distinctly different molecular masses.

Tetrafunctional Initiator 3 Based on Adamantane. This compound is notable for the three-dimensional (tetrahedral) disposition of its four chlorosulfonyl initiator groups and was prepared as shown in Scheme 2. 1-Bromoadamantane (**1**) was phenylated using excess benzene, *tert*-butyl bromide, and aluminum chloride according to the procedure of Newman[30] to produce tetraphenyladamantane **2**. (*Caution: this reaction is exothermic and should be performed in an oversized flask with an efficient reflux condenser to avoid accidental release of toxic benzene.*) Compound **2** is poorly soluble in most solvents; nevertheless, it could be recrystallized from boiling 1,2-dichlorobenzene. Compound **2** was successfully reacted with chlorosulfonic acid to provide the tetrasulfonyl chloride **3** following the procedure of Shen.[31] Compound **3** was found to be soluble in ketones such as cyclopentanone and was rather easily hydrolyzed. Analysis of unpurified **3** by HPLC/MS after derivatization with diethylamine indicated, in addition to the desired product, the presence of three minor isomers, along with three isomers of a related compound containing three sulfonyl chloride groups and one sulfonic acid. The predominance of an AA′BB′ peak grouping in aromatic region of the ^{1}H NMR spectrum of **3** is consistent with the major product being the all *para* isomer, as depicted.

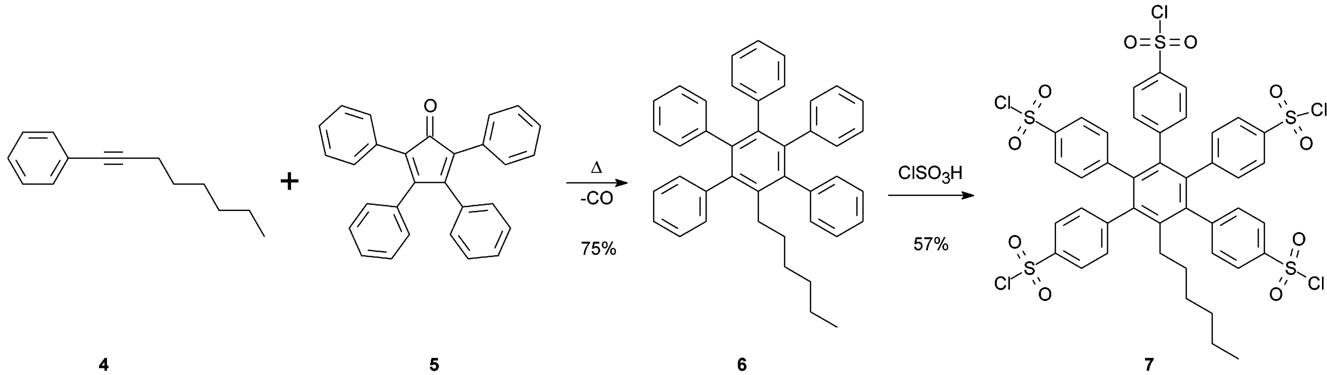
Pentafunctional Initiator 7. A core molecule containing five chlorosulfonyl groups was prepared in two steps (Scheme 3). First, a Diels−Alder reaction between 1-phenyl-1-octyne (**4**) and tetraphenylcyclopentadienone (**5**) was carried out. Under the reaction conditions, carbon monoxide was extruded spontaneously to produce hexylpentaphenylbenzene (**6**) in good yield. This intermediate was reacted with chlorosulfonic acid in dichloromethane to produce the 5-fold initiator **7**. This initiator could be purified by recrystallization from acetonitrile, in this way removing any partially hydrolyzed material and positional isomers. After derivatization of the purified product with diethylamine, only a single compound could be detected by NMR and FD/MS. **7** was soluble in ordinary solvents such as acetone, tetrahydrofuran, and dichloromethane.

Hexafunctional Initiator 9 Based on Hexaphenylbenzene. The synthesis of initiator **9** was analogous to the pentafunctional example **7**, above, except starting from commercially available hexaphenylbenzene (**8**, Scheme 4). (Hexaphenylbenzene is quite expensive and purchasable only in small quantities, but it can be conveniently synthesized on a large scale by Diels−Alder cycloaddition[32] of diphenylacetylene with tetraphenylcyclopentadienone, **5**, or by the cyclotrimerization[33] of diphenylacetylene using dicobalt octacarbonyl.) The chlorosulfonylation of **8** had been reported previously by Bergmann,[34] but with no details. We repeated this synthesis with excellent results. Analysis of the product **9** by 500 MHz NMR and by HPLC/MS demonstrated that the main product was the all *para* compound, but small quantities of other isomers were apparently also present. The other isomers are more soluble than the all *para* derivative and could be

Scheme 2. Synthesis of Tetrafunctional Initiator 3

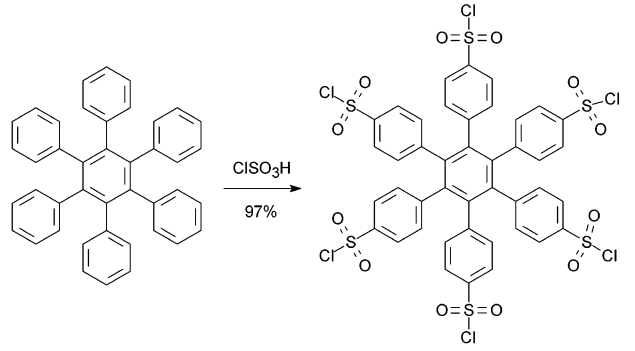


Scheme 3. Synthesis of Pentafunctional Initiator 7



4 **5** **6** **7**

Scheme 4. Synthesis of Hexafunctional Initiator 9



8 **9**

extracted away into acetonitrile. Compound **9** was further purified by recrystallization from nitromethane.

Decafunctional Initiator 12. To further increase the number of arms in a star polymer, we attempted to double the number of initiating sulfonyl chloride groups of the core molecule by formally linking two hexaphenylbenzene units together (Scheme 5). Decafunctional initiator **12** was prepared analogously to Scheme 3, starting with Hagihara coupling of 4,4′-diiodobiphenyl and phenylacetylene to produce diacetylene **10**, in a variation of the published procedure.[35] Compound **10** had been originally prepared[36] by a method involving pyrolysis at high temperature, but the modern palladium-catalyzed coupling chemistry used by Twieg et al.[35] and by us is unquestionably superior to the older one. Double Diels–Alder reaction of **10** with tetraphenylcyclopentadiene (**5**) produced the remarkable benzene dendrimer 2′,2′′′′,3′,3′′′′,5′,5′′′′,6′,6′′′′-octaphenyl-*p*-sexiphenyl (**11**), which had been prepared many years ago by a more circuitous route.[37,38] Compound **11** is more soluble than might be expected for such a rigid molecule, presumably because it adopts a twisted conformation. One might assume that the two inner benzene rings of **11** are too hindered to react with chlorosulfonic acid, but surprisingly we obtained the dibenzothiophene-1,1-dioxide derivative **12**, the structure of which was established by ^{1}H NMR and mass spectroscopy. This kind of cyclization reaction with chlorosulfonic acid had been reported to occur with simple biphenyl only under forcing conditions.[23] Unfortunately, **12** was poorly soluble, presumably caused by the rigid nature of the fused heterocycle at its center.

Decafunctional Initiator 15. To improve the solubility of **12**, it seemed advisable to introduce substituents to the molecule to lower its symmetry. We found that two methyl groups were sufficient to achieve this goal. Using 4-ethynyltoluene as starting material instead of phenylacetylene in an analogous reaction sequence led to the soluble 2′,2′′′′,3′,3′′′′,6′,6′′′′-hexaphenyl-5′,5′′′′-(4-methylphenyl)-*p*-sexiphenyl (**14**). It was still possible to sulfochlorinate the methyl-substituted phenyl rings, leading to the desired 10-fold initiator (**15**) (Scheme 6). The structure of **15** depicted in Scheme 6 indicates that the sulfonyl chloride groups on the tolyl rings are adjacent to the methyl groups, but we have no direct evidence for this specific regiochemistry. Despite its bridged central biphenyl unit, **15** proved to be soluble in methylene chloride and in THF.

Analysis of the Number of Arms in Star Polymers. Naturally, a key concern in any attempt to synthesize star polymers under controlled conditions is to determine whether the desired number of arms has been obtained. A convenient means for estimating the number of arms in the star polymers *as a function of molar mass* was developed, utilizing multidetector size-exclusion chromatography (SEC).[39]

Branched polymers occupy less volume in solution than linear polymers of the same molar mass. The number of arms in star molecules is commonly estimated from the molecular contraction factor, g,

$$g = \frac{\langle r_g^{\,2} \rangle_s}{\langle r_g^{\,2} \rangle_l} \quad \text{at the same M} \qquad (1)$$

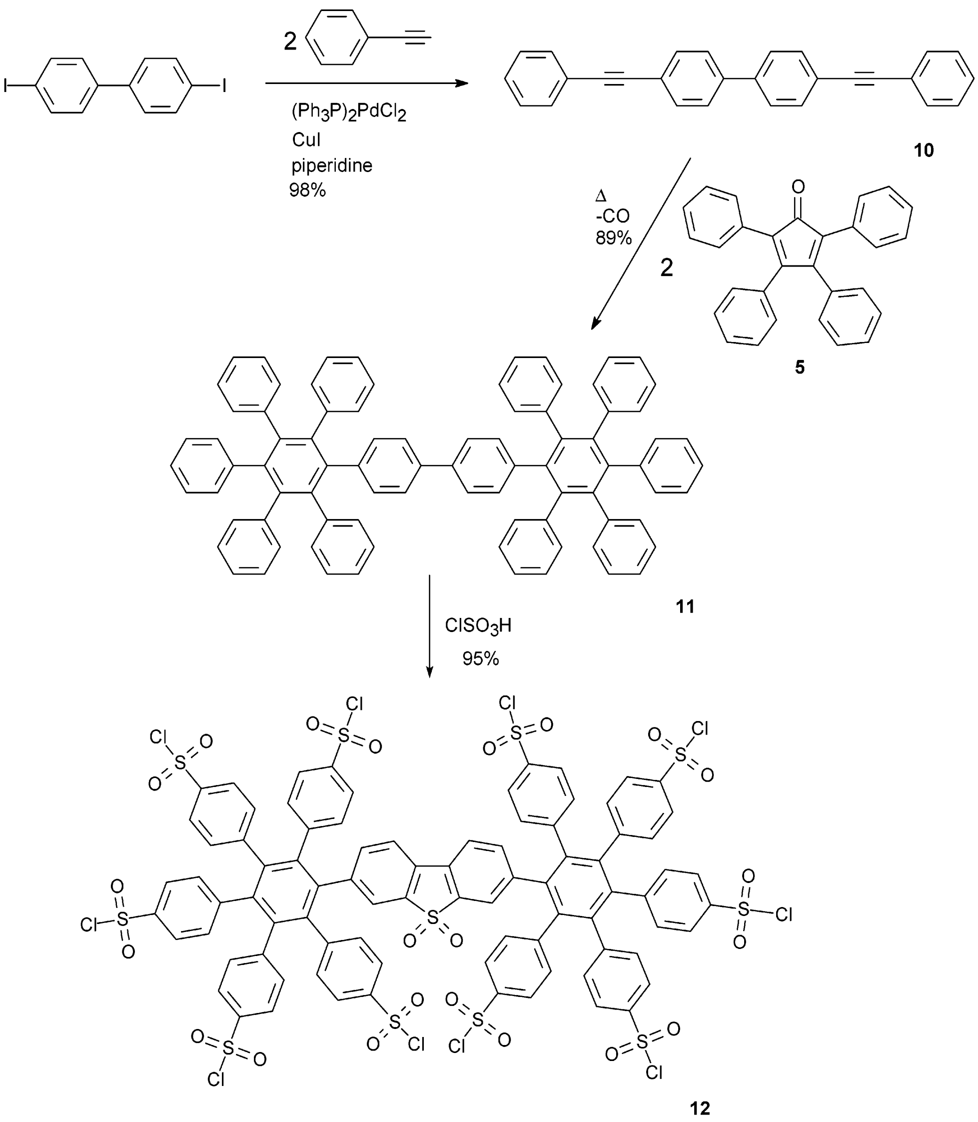
where $\langle r_g^{\,2} \rangle_s$ is the mean-square radius of the star polymer and $\langle r_g^{\,2} \rangle_l$ is the radius of a linear polymer of the same chemical composition and molar mass. The molecular contraction factor can be measured across the molar mass distribution by SEC with multiangle light scattering detection. However, root-mean-square radii are difficult to measure by light scattering for molecules with low specific refractive index increments (dn/dc) and radii between 10 and 20 nm, as is the case for many of the star molecules examined here. In this case, the ratio of hydrodynamic radii, r_h, is useful,

$$h = \frac{r_{h,s}}{r_{h,l}} \quad \text{at the same M} \qquad (2)$$

and is experimentally accessible through SEC intrinsic viscosity measurements (since $[\eta] \sim r_h^{\,3}$):

$$g' = h^3 = \frac{[\eta]_s}{[\eta]_l} \quad \text{at the same M} \qquad (3)$$

Scheme 5. Synthesis of Decafunctional Initiator 12



or from molar masses measured at equivalent hydrodynamic volume by light scattering,

$$g' = \left(\frac{M_l}{M_s}\right)_h^{\alpha+1} \quad \text{at equivalent volume} \tag{4}$$

where α is the Mark–Houwink exponent of the linear polymer.[40] Various relations of the form

$$g' = g^{\epsilon} \tag{5}$$

have been proposed, with the structure factor ϵ suggested to be in the range 0.5 for compact molecules such as some stars to 1.5 for long-chain branched structures at Θ conditions.[41,42] In a good solvent, the structure factor ϵ is close to 0.7, as found, for example, with polystyrene stars in THF.[43] Recent fits to experimental data suggest that a simple power law (eq 5) may not apply for a broad range of stars with differing numbers of arms.[44,45] A fit similar to that described in the literature[45,46] to data for compositionally different stars in various solvents,

$$g = [a + (1 - a)g'^{b}]g'^{c} \tag{6}$$

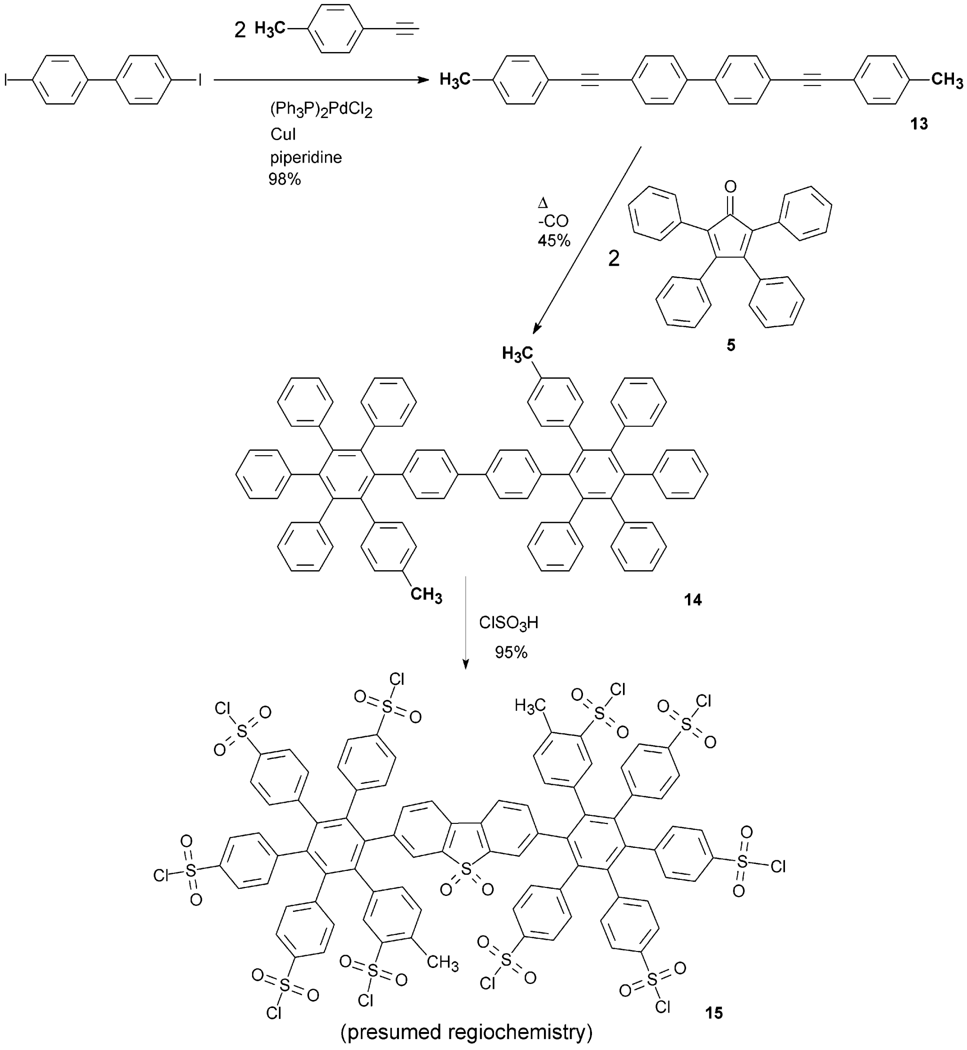
with $a = 0.2624$, $b = 1.088$, and $c = 0.6087$, was used in this work to avoid the use of ϵ and to cover a broad range of star structures. The number of arms, p, in regular (equal arm length) star molecules can then be related to the molecular contraction factor, g, by the solution of Zimm and Stockmayer:[47]

$$g = \frac{3}{p} - \frac{2}{p^2} \tag{7}$$

Molecular contraction factors, g', calculated via SEC viscometry (eq 3) and SEC light scattering (eq 4), gave results for the number of arms within ±1 of each other, and this is accepted as a minimum error for the analysis. It is recognized that a variety of complications in the SEC multidetector experiment, including axial dispersion and effects of interdetector volume, and the assumptions underlying eq 7 may contribute further to uncertainty, especially near the high and low limits of the molar mass distribution.

Synthesis and Characterization of Star Polymers. Polymerizations using multifunctional initiators containing either 4, 5, 6, or 10 initiating sites described above were carried out using ATRP. The monomers employed were styrene, methyl methacrylate, *n*-butyl

Scheme 6. Synthesis of Decafunctional Initiator 15



methacrylate, *tert*-butyl methacrylate, 2-ethylhexyl methacrylate, benzyl methacrylate, or methyl acrylate. The catalyst was copper(I) chloride in most cases, although copper(I) oxide was also used successfully. 2,2′-Bipyridine or 4,4′-dimethyl-2,2′-bipyridine were used as the ligand. Various solvents were examined, including sulfolane, phenyl ether, and cyclopentanone. Polymerization results varied significantly and unpredictably with solvent and ligand, for different combinations of initiator and monomer. In certain cases, little or no polymer was obtained, unexpectedly. These variations possibly reflected different solubilities and reaction rates for particular situations. A certain amount of trial and error was required in each case to determine conditions for obtaining narrow molar mass distributions, and some of these trials are shown in the tables below.

The observed variations may be related to the concentrations of various species during the early stages of the polymerization reaction. The copper(I)-catalyzed radical addition of the sulfonyl chloride to monomers is known to be extremely fast. In ATRP systems, the initial concentration of radicals might then be very high in certain circumstances, leading to a greater than normal occurrence of premature termination reactions such as coupling and disproportionation. Each termination event is accompanied by production of copper(II), which is a scavenger for the propagating radical. An abnormally high concentration of copper(II) is expected to inhibit polymerization. Therefore, the success of the title polymerization reactions may depend on the precise conduct of the synthetic procedure, for example, the rate and order of addition of the ingredients, the rate of dissolution of the initiator and metal complex, etc. This hypothesis is consistent with the observation that successful polymerizations were obtained more consistently using unsubstituted bipyridine, a ligand which leads to catalyst complexes with *decreased solubility*, thereby moderating the rate of radical initiation by slow dissolution at the onset of the polymerization.

Consistent with the assertion of Gnanou et al.,[16] the best molar mass control was obtained using high monomer concentrations and conversions below 70%. These conditions would be expected to minimize the occurrence of star−star coupling termination reactions.

A question that often arises with ATRP is the fate of the catalyst residues (copper salts in this case) after polymerization. We found that the procedure described by Matyjaszewski et al.[48] involving posttreatment of the reaction mixtures with ion-exchange resin drastically reduced the amount of residual copper species. For example, stirring a sample of a 5-arm star PMMA (see below) reaction mixture diluted in acetone with Dowex MSC-1 acidic ion-exchange resin reduced the copper concentration from 2200 to 25 μg/g, as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Table 1. Atom Transfer Radical Polymerization[a] with Tetrafunctional Initiator 3

monomer[b]	ligand[c]	I:C:L[d]	solvent concentration[e]	time (h)	yield (%)	$\bar{M}_w$ (SEC)[f]	$\bar{M}_w/\bar{M}_n$
MMA	MeBipy	1:2:4	sulfolane 1:1	0.83	95	231 000	1.75
MMA	MeBipy	1:2:4	sulfolane 1:0.5	2	31	52 900	1.46
MMA	MeBipy	1:2:4	sulfolane 1:2	2	63	124 000	1.87
MMA	MeBipy	1:0.3:1	cyclopentanone 1:1	3	70	23 600	1.69 bimodal
S	MeBipy	1:2:4	sulfolane 1:2	24	68	63 000	1.84 bimodal

[a] Conditions: CuCl catalyst, 4,4′-dimethyl-2,2′-bipyridine ligand, 90 °C; nitrogen atmosphere; 100:1 mole ratio of monomer to sulfonyl chloride groups. [b] Monomers: S = styrene; MMA = methyl methacrylate. [d] Mole ratio of sulfonyl chloride to copper halide to ligand. [e] Ratios are solvent:monomer (w/w). [f] Absolute weight-average molar mass from SEC viscometry and universal calibration.

Table 2. Atom Transfer Radical Polymerization[a] with Pentafunctional Initiator 7

monomer[b]	solvent[c]	I:C:L:M[d]	time (h)	yield (%)	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
MMA	sulfolane	1:2:4:100	0.6	41	52 600	2.89
MMA	cyclopentanone	1:2:4:100	1.25	33	25 900	1.70
MMA	Ph_2O	1:1:2[f]:350	2.5	80	62 100	1.22
MMA	Ph_2O	1:5:10:800	2.5	45	315 000	1.86
MMA	Ph_2O	1:4:8:800	1.0	43	331 000	1.44
MMA	Ph_2O	1:1:2:100	1.0	38	34 000	1.16
MMA	Ph_2O	1:1.1:2.4[f]:101	2.5	78	46 000	1.18
MMA	Ph_2O	1:7:14:1400	1.0	23	237 000	1.28
MMA	Ph_2O	1:0.8:1.6:150	0.3	1	37 200	1.08
tBuMA	Ph_2O	1:1:2.4:200	2.5	18	84 600	1.25
tBuMA	Ph_2O	1:1[e]:2.4[f]:76	2.2	70	76 200	1.17
MA	cyclopentanone	1:2:4:100	120	trace		
MA	DPGMA	1:2:4:100	48	0		
MA	Ph_2O[g]	1:1:2[f]:380	72	15	42 700	1.57
S	sulfolane	1:2:4:100	120	91	45 000	bimodal
S	Ph_2O[h]	1:1:2[f]:120	19.5	82	86 500	1.52
S	sulfolane	1:2:4:100	24	68	63 000	bimodal
S	cyclopentanone	1:2:4:100	48	98		very broad

[a] Conditions: catalyst = CuCl; ligand = 4,4′-dimethyl-2,2′-bipyridine; 90 °C; nitrogen atmosphere; 1:1 (w/w) monomer/solvent, unless otherwise noted. [b] Monomers: S = styrene; MMA = methyl methacrylate; MA = methyl acrylate; tBuMA = *tert*-butyl methacrylate. [c] Solvents: DPGMA = dipropylene glycol methyl ether acetate. [d] Mole ratio of sulfonyl chloride groups to metal catalyst to ligand to monomer. [e] Catalyst = Cu_2O. [f] Ligand = 2,2′-bipyridine. [g] Temperature = 100 °C. [h] Temperature = 120 °C.

Four-Arm Star Polymers. The polymers in this section are notable for the rigid tetrahedral disposition of their chain origins due to the adamantane core. The tetrafunctional initiator **3** was found to be soluble in warm cyclopentanone or sulfolane; therefore, polymerizations of MMA and styrene were attempted in these solvents (Table 1). Styrene and in one case MMA apparently polymerized by both controlled and uncontrolled mechanisms, producing a bimodal molar mass distribution consisting of one narrow fraction with 4-arm stars and a second broader fraction containing linear polymer unbound to the core (as determined by the lack of UV absorption in the SEC chromatogram of the MMA sample). This second fraction may be attributable to spontaneous thermal polymerization.

Much of the observed variation is thought to be caused by the high initial concentration of radicals in these polymerization reactions, as discussed above. In addition, initiator **3** is difficult to purify and is inevitably contaminated with impurities containing fewer than four sulfonyl chloride groups, either from incomplete reaction during synthesis or from hydrolysis during handling. These impurities may lead to polymers with missing arms. In addition, if the impurity contains a sulfonic acid, this group will not initiate an arm but remain attached to the polymer core as an ionic group. The presence of a small amount of charged polymer was evidenced by some prepeaks in SEC using THF as eluent, for samples not treated with ion exchange resin. However, in favorable cases, relatively narrow molar mass distribution polymers could be obtained, with close to the expected number of arms. For example, Figure 1 illustrates the "arm purity" of a sample of 4-arm star PMMA.

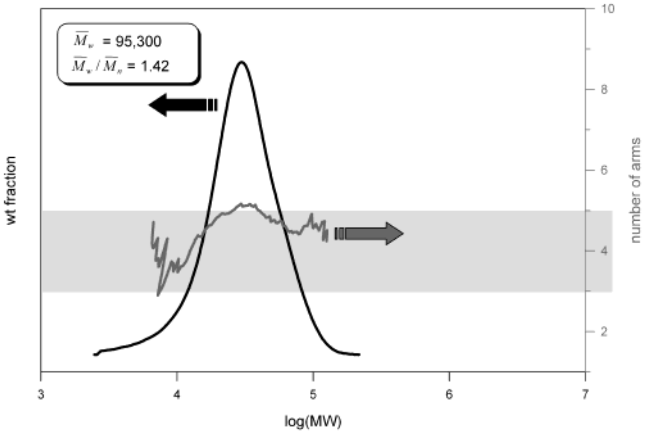


Figure 1. SEC and arm number determination for four-arm, adamantane-cored poly(methyl methacrylate). The shaded region represents the expected number of arms for this polymer, with an uncertainty of ±1.

Five-Arm Star Polymers. Methyl methacrylate, *tert*-butyl methacrylate, and styrene could be polymerized without difficulty with pentafunctional initiator **7**; however, methyl acrylate polymerized too slowly under the reaction conditions to be useful (Table 2). In favorable cases, star polymers with narrow molar mass distribution and controlled number of arms could be obtained (Figure 2). The details of the distribution of arms are typical of star polymers synthesized in this work. The lower molar mass fractions appear to contain fewer than the desired number of arms (five in this case), consistent with incomplete initiation from some of the core molecules or premature termination. The higher molar mass fractions appear to contain on

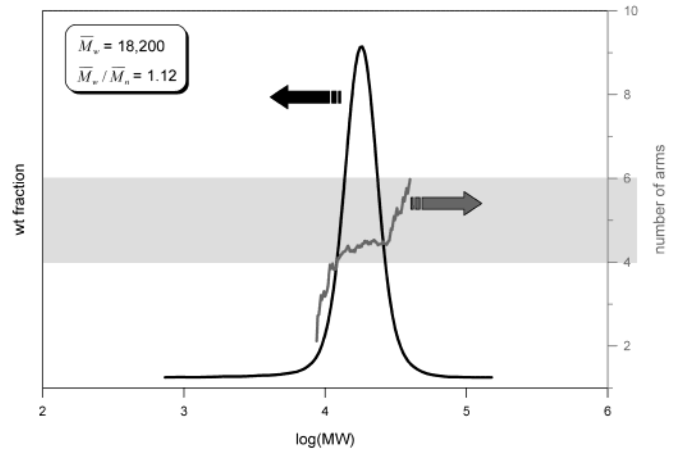


Figure 2. SEC and arm number determination for five-arm poly(methyl methacrylate). The shaded region represents the expected number of arms for this polymer, with an uncertainty of ±1.

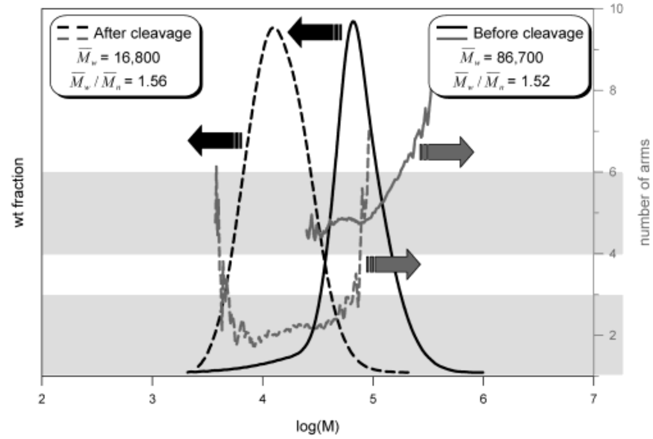


Figure 3. SEC and arm number determination for five-arm polystyrene before and after treatment with potassium *tert*-butoxide. The shaded region represents the expected number of arms for these polymers, with an uncertainty of ±1.

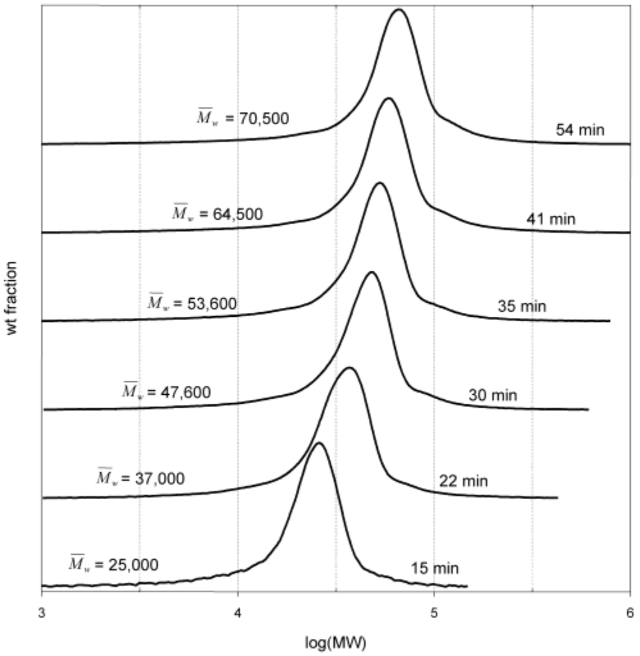


Figure 4. Polystyrene equivalent molar mass distribution during atom transfer polymerization of methyl methacrylate with hexafunctional initiator **9**. Conditions: solvent = sulfolane; catalyst = CuCl; ligand = 4,4′-dimethyl-2,2′-bipyridine; 1:2:4:100 mole ratio of sulfonyl chloride groups to CuCl to ligand to methyl methacrylate; 90 °C; nitrogen atmosphere; 1:1 (w/w) monomer/solvent. The reaction mixture was sampled by syringe during polymerization.

average more than five arms, indicative of some termination reactions by star−star coupling.

To test the accuracy of the SEC method for determining the number of arms, a nominal five-arm sample of polystyrene was examined before and after treatment with potassium *tert*-butoxide, a reagent that cleaves the arms from the core without changing the molar mass or chemical constitution of the arms (Figure 3).[49] After cleavage, the $\bar{M}_w$ of the polymer was reduced by a factor of 5.16, yet the distribution remained relatively narrow. The SEC arm number estimation for the cleaved sample demonstrated that this material consisted almost entirely of linear strands, depicted in the figure as two arms. (Of course, a “2-armed” star is indistinguishable from a linear chain.)

Six-Arm Star Polymers. The six-arm polymers were derived from **9**, a planar, hexagonal core based on hexaphenylbenzene. The hexafunctional initiator **9** is poorly soluble in common solvents; however, we discovered that sulfolane (tetrahydrothiothene-1,1-dioxide) could be used successfully in certain cases. The typical procedure was to predissolve the initiator **9** in hot sulfolane, cool the solution to room temperature, add the catalyst, ligand, and monomer, deaerate the resulting solution, and conduct the polymerization at 90 °C for several hours. In this way, 6-arm acrylic polymers such as PMMA could be prepared. Unfortunately, this procedure failed for styrene, because the initiator **9** precipitated from the sulfolane solution when this nonpolar monomer was added, and it did not redissolve upon heating to the reaction temperature.

The living character of the polymerization reaction is illustrated by the data shown in Figure 4. The molecular size increased as a function of reaction time, as expected for a living polymerization, and the bulk of the distribution remained relatively narrow. However, the occurrence of some termination reactions is evidenced by the growth of a shoulder in the high equivalent molar mass region as the reaction proceeded and the monomer was consumed.

The utility of the arm number determination technique is further illustrated by the analyses depicted in Figure 5. An ATRP of MMA initiated by **9** was analyzed after 1 h, at which point the molar mass distribution was narrow, and the polymer contained approximately the expected number of arms. However, when the reaction mixture was held for a total of 12 h, termination by star−star coupling apparently occurred, leading to a broad high MW tail that contained many more than six arms. Remarkably, this sample remained perfectly soluble, despite its very high molar mass.

When conducted under optimized conditions, the polymerization of methacrylic esters with initiator **9** gave rise to narrow molar mass distribution polymers with the expected number of arms. Such a result is depicted in Figure 6 for poly(*n*-butyl methacrylate).

Ten-Arm Star Polymers. Figure 7 illustrates the results for a polymerization of methyl methacrylate using the decafunctional initiator **15** conducted in phenyl ether solvent with CuBr catalyst and 2,2′-bipyridyl ligand. The molar mass distribution is broader than other examples, indicative of the increased prob-

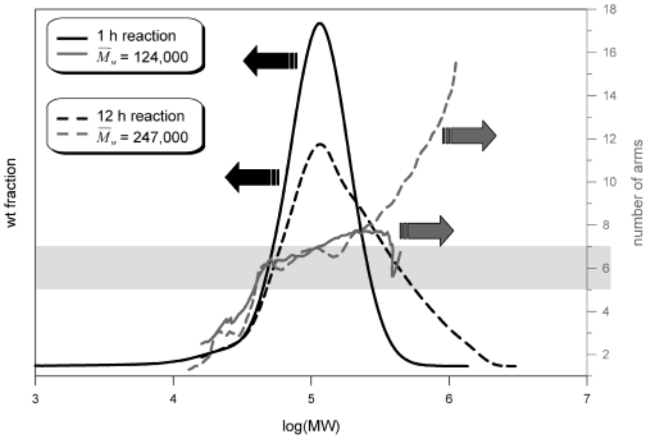


Figure 5. SEC and arm number determination for six-arm poly(methyl methacrylate) prepared using hexafunctional initiator **9** after 1 and 12 h reaction times. The shaded region represents the expected number of arms for this polymer, with an uncertainty of ±1.

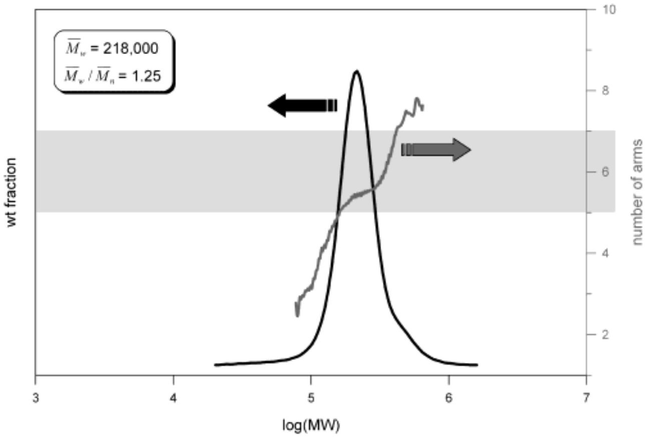


Figure 6. SEC and arm number determination for six-arm poly(*n*-butyl methacrylate). The shaded region represents the expected number of arms for this polymer, with an uncertainty of ±1.

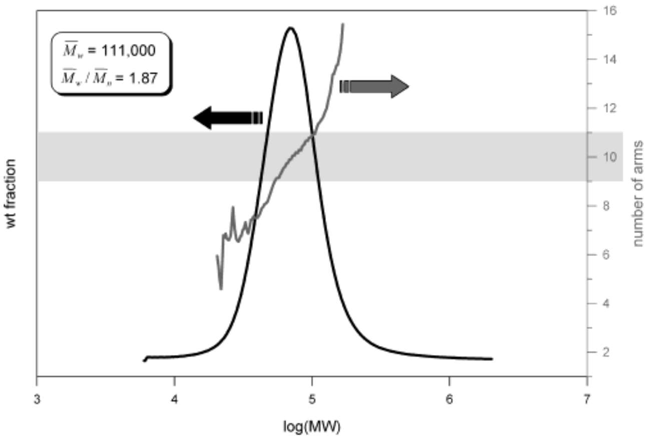


Figure 7. SEC and arm number determination for 10-arm poly(methyl methacrylate). The shaded region represents the expected number of arms for this polymer, with an uncertainty of ±1.

ability of termination reactions for molecules containing a larger number of growing arms.[16] As in other polymerizations in this study, the lower molar mass fractions contained fewer than 10 arms, consistent with the failure of some arms to grow, or premature termination. Similarly, the higher molar mass fractions contained more than 10 arms, presumably caused by star–star coupling. Nevertheless, most of the molar mass distribution appeared to contain approximately 10 arms, the expected number.

Conclusions

We were successful in preparing multifunctional compounds containing 4–10 initiating sites for ATRP. The most significant limitation of the syntheses was the difficulty in purifying the moisture-sensitive multiple sulfonyl chloride compounds. In fact, polymers with optimum structural homogeneity were obtained when starting with the purest possible cores.

Reaction conditions were developed that allowed for the preparation of star polymers with moderately narrow molar mass distributions and a controlled number of arms, using multifunctional ATRP initiators. Nevertheless, there remain uncertainties in the course of the polymerization reaction, especially at early stages, that require further experimentation. For example, the effects of rate of addition and solubility of the various reagents may be crucial to the success of the polymerizations. Recent studies[16] indicate that the concentration of polymer and extent of reaction play important roles in the occurrence of star–star coupling reactions that lead to high molar mass tails in the distribution.

The development of a SEC method for determining the number of arms as a function of molar mass was the key to characterizing the polymers synthesized and to understanding the mechanism of their formation. The technique is still being refined, possibly providing improved accuracy in the wings of the distribution. In addition, it may be possible to deconvolute the distribution of arms for each molar mass “slice” and provide information on the polydispersity of arms rather than a simple average at a given molar mass.

Because the polymer arms still contain halide end groups even after isolation, they can be reinitiated with fresh charges of monomer, catalyst, and ligand to prepare star-block copolymers. A number of examples of such polymers have been prepared and will be described in a separate report. The physical properties of star polymers, in bulk, as polymer blends, or in solution are of interest. Research in this area is in progress and will be reported in due course.

Experimental Section

Analyses. NMR measurements were carried out at 300 MHz on a Varian VXR-300S spectrometer or at 500 MHz on a Varian Unity 500 spectrometer. Field desorption mass spectrometry (FD-MS) was performed with a Varian MAT model 731 instrument. Electrospray mass spectrometry (ES-MS) was performed on a Micromass Platform II instrument. Sample injections were made from solutions into a flowing stream of 45% methanol, 45% acetonitrile, and 10% 0.05 M ammonium acetate solution, buffered to pH 4.65. The mass to charge (*m*/*z*) ratios of the ions were then determined utilizing a quadrupole mass spectrometer which was scanned from 65 to 2000 amu, alternately scanning in positive and negative mode once per second. Analysis for residual copper in the polymers was conducted by inductively coupled plasma atomic emission spectroscopy (ICP-AES), after digestion of the samples in a mixture of sulfuric and nitric acids. Samples for HPLC/MS analyses were derivatized as follows: A mixture of 4.0 mg of the sample and 0.5 mL of dry diethylamine was mixed by sonication for 5 min. The resulting sample was then diluted with 3.5 mL of dry acetonitrile and analyzed directly. HPLC/MS analyses were performed on a Perkin-Elmer Sciex 365 triple quadrupole mass spectrometer. The instrument was operated in the single quad mode, scanning from 70 to 3000 mass units. The sample was introduced into a Turbo Ion Spray (nebulization assisted electrospray) ionization source. The HPLC separation was performed on a HP1100 HPLC with a quaternary pump employing a proportioning valve, an autosampler, and a full diode array detector. The separation was a reversed phase method using a Keystone Betasil Phenyl 2.0 mm by 15 cm column and a flow rate of 400 μL/min. A gradient was used to effect the separation. The A phase was 0.1% formic acid in water, and the B phase was acetonitrile. The gradient started at 90% A/10% B and was programmed linearly to 100% B in 20 min. The column effluent was taken directly from the diode array detector into the mass spectrometer.

1,3,5,7-Tetraphenyladamantane (2). This compound was synthesized according to the literature.[30] The product was obtained as white needles in 45% yield after purification by recrystallization from boiling 1,2-dichlorobenzene. ^{1}H NMR ($CDCl_3$): δ 3.45 (s, 12 H), 8.51 (t, 4 H), 8.64 (t, 8 H), 8.76 (d, 8 H).

1,3,5,7-Tetrakis(4-chlorosulfonylphenyl)adamantane (3). This compound was synthesized according to the literature.[31] Purification was effected by precipitation from tetrahydrofuran into excess hexanes. ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 12 H), 7.73 (d, 8 H), 8.08 (d, 8 H). ES-MS *m*/*z* 893$^-$ (M + OAc$^-$). FD-MS showed a complicated cluster of ions centered near *m*/*z* 830$^+$. HPLC/MS after derivatization with diethylamine showed the molecular ion at *m*/*z* 980$^+$, along with small impurity signals with molar mass corresponding to one (925$^+$) or two (870$^+$) sulfonic acid groups.

1-Phenyl-1-octyne (4). A mixture of 95.0 g (0.466 mol) of iodobenzene, 100 mL of piperidine, and 400 mL of acetonitrile was deaerated by sparging with nitrogen for 30 min. Bis(triphenylphosphine)palladium(II) chloride (3.27 g, 0.0047 mol) and copper(I) iodide (0.44 g, 0.0023 mol) were added, and the mixture was stirred mechanically while continuing sparging for 15 min. 1-Octyne (56.4 g, 0.512 mol) was deaerated separately in the same way and then added to the stirred reaction mixture under nitrogen at room temperature. The resulting mixture was stirred mechanically and warmed at 65 °C for 24 h, during which time it turned from yellow to brown. The mixture was cooled to room temperature and treated with 200 mL of 10% aqueous HCl and 300 mL of ligroin. The organic layer was separated, and the aqueous layer was further extracted three times with 300 mL each of ligroin. The combined extracts were dried ($MgSO_4$), filtered, passed through a short column of silica, and concentrated to deposit a light brown oil. The product was purified by distillation at reduced pressure to afford 68.9 g (79%) of a gold oil; bp 68−102 °C/0.05 mm. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3 H), 1.3 (m, 4 H), 1.5 (m, 2 H), 1.6 (m, 2 H), 7.25 (m, 3 H), 7.40 (m, 2 H).

1-Hexyl-2,3,4,5,6-pentaphenylbenzene (6). A 100 mL round-bottom flask was charged with 2.5 g (0.013 mol) of 1-phenyl-1-octyne (**4**), 6.0 g (0.16 mol) of tetraphenylcyclopentadienone (**5**), and 2.0 g of benzophenone. The system was degassed and then filled with nitrogen. The mixture was heated for 2.5 h at 250 °C. The purple reaction mixture was cooled to room temperature and then dissolved in toluene. The product was precipitated in excess methanol, filtered, and dried to provide 5.47 g (75%) of a white solid. ^{1}H NMR ($CDCl_3$): δ 0.65 (t, 3H), 0.8 (m, 4 H), 0.97 (q, 2 H), 1.23 (q, 2 H), 2.31 (m, 2 H). FD-MS *m*/*z* 512 (M$^+$).

1-Hexyl-2,3,4,5,6-penta(4-chlorosulfonylphenyl)benzene (7). A 250 mL round-bottom flask was charged with 2.0 g (0.004 mol) of 1-hexyl-2,3,4,5,6-pentaphenylbenzene (**6**) and 50 mL of dichloromethane. Chlorosulfonic acid (15 mL) was added to the stirred reaction mixture at room temperature via an addition funnel. The reaction mixture turned purple immediately and then clear orange after 1 h. The reaction mixture was stirred at room temperature for 1 day and poured onto crushed ice. The layers were separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to deposit a light-gray solid. The product was recrystallized from acetonitrile to provide 1.39 g (57%) of a white powder. ^{1}H NMR ($CDCl_3$): δ 7.96 (d, $J = 10$, 4 H), 7.66 (m, 6), 7.41 (d, $J = 10$, 4 H), 7.08 (m, 6 H). FD-MS *m*/*z* 1034 (M$^+$). HPLC/MS after derivatization with diethylamine showed the molecular ion at *m*/*z* 1344$^+$, along with small impurity signals with molar mass corresponding to one (1289$^+$) or two (1234$^+$) sulfonic acid groups and also some dimerized species (2480$^+$).

1,2,3,4,5,6-Hexakis(4-chlorosulfonylphenyl)benzene (9). This compound was synthesized by a variation of the literature procedure.[34] A 500 mL round-bottom flask was charged with 11.7 g (0.022 mol) of hexaphenylbenzene (**8**) and 180 mL of dichloromethane and placed in an ice bath. Chlorosulfonic acid (90 mL) was added to the stirred reaction mixture via an addition funnel. Upon addition of the acid, the reaction turned immediately purple and then dark brown. The flask was purged with nitrogen and allowed to return to room temperature. After 1 day, the reaction was carefully poured onto crushed ice, which resulted in the precipitation of a yellow solid. The solids were filtered and dissolved in acetone. The acetone solution was dried ($MgSO_4$) and evaporated to dryness. The product was recrystallized from dry nitromethane to provide 8.5 g (73%) of light pink crystals. ^{1}H NMR (acetone-d_6): δ 7.77 (d, $J = 8.7$, 2 H), 7.54 (d, $J = 8.9$, 2 H). ES-MS *m*/*z* 1184$^-$ (M + OAc$^-$).

4,4′-Bis(phenylethynyl)biphenyl (10). A mixture of 12.0 g (0.030 mol) of 4,4′-diiodobiphenyl, 150 mL of piperidine, and 200 mL of acetonitrile was deaerated by sparging with argon, and 0.40 g (0.6 mmol) of bis(triphenylphosphine)palladium dichloride and 0.25 g (1.3 mmol) of copper(I) iodide were added. To the resulting stirred solution at room temperature was added 6.04 g (0.059 mol) of phenylacetylene via a syringe. The reaction mixture was held at room temperature for 30 min and heated at 60 °C for 3 h. The precipitated product was collected by filtration of the cooled reaction mixture and was washed successively with acetonitrile and dichloromethane until the solid was colorless. Yield: 8.5 g (81%). FD-MS *m*/*z* 354$^+$ (M$^+$).

2′,2′′′′′,3′,3′′′′′,5′,5′′′′′,6′,6′′′′′-Octaphenyl-*p*-sexiphenyl (11). A mixture of 5.00 g (0.014 mol) of 4,4′-bis(phenylethynyl)biphenyl (**10**), 10.85 g (0.028 mol) of tetraphenylcyclopentadienone (**5**), and 10 g of benzophenone was heated under argon at 280 °C for 3 h. The reaction mixture was cooled to room temperature, slurried in 500 mL of dichloromethane, and filtered. The collected product was washed successively with dichloromethane and acetone until the filtrate was colorless. The product was purified by extraction with boiling benzonitrile for 30 min, followed by cooling to room temperature and filtration. Yield: 14.0 g (93%). FD-MS *m*/*z* 1067$^+$ (M + H$^+$).

3,3′-Bis(2,3,4,5,6-penta(4-chlorosulfonylphenyl)phenyl)-dibenzothiophene-1,1-dioxide (12). A suspension of 2.0 g (1.9 mmol) of 2′,2′′′′′,3′,3′′′′′,5′,5′′′′′,6′,6′′′′′-octaphenyl-*p*-sexiphenyl (**11**), 5 mL of chlorosulfonic acid, and 20 mL of dichloromethane was stirred at room temperature for 3 days. The reaction mixture was diluted with 20 mL of nitromethane, and the precipitated product was filtered. The product was washed successively with nitromethane and acetonitrile. Yield: 2.5 g (65%). HPLC/MS after derivatization with diethylamine showed the molecular ion at *m*/*z* 2498$^+$ (M + NH_4^+), along with small impurity signals with molar mass corresponding to one (2444$^+$, M + NH_4^+) or two (2389$^+$, M + NH_4^+) sulfonic acid groups.

1,1′-4,4′-Bis((4-methylphenyl)ethynyl)biphenyl (13). A solution of 4,4′-diiodobiphenyl, 12.0 g, 9.030 mol), bis(triphenylphosphine)palladium dichloride (0.70 g, 0.01 mol), and copper(I) iodide (0.200 g, 0.001 mol) in 200 mL of piperidine was deaerated by sparging with argon. The solution was stirred and cooled in an ice bath, and 4-ethynyltoluene (6.04 g, 0.059 mol) was added via a syringe. The reaction mixture was allowed to warm gradually to room temperature and held for 12 h. The precipitated product was collected by filtration and washed successively with methanol, water, and again with methanol. The product was dried in vacuo and obtained in quantitative yield. FD-MS *m*/*z* 382$^+$ (M$^+$).

2′,2′′′′′,3′,3′′′′′,6′,6′′′′′-Hexaphenyl-5′,5′′′′′-(4-methylphenyl)-*p*-sexiphenyl (14). A mixture of 1,1′-4,4′-bis((4-methylphenyl)ethynyl)biphenyl (**13**, 4.05 g, 0.011 mol), tetraphenylcyclopentadienone (**5**, 8.79 g, 0.023 mol), and 5 g of benzophenone.

The system was degassed, filled with argon, and heated at 270 °C for 12 h. The reaction mixture was cooled to room temperature, slurried in 200 mL of THF, and filtered. The precipitated product was washed with dichloromethane until it was nearly white and then dried in vacuo. Yield: 9.0 g (75%). ^{1}H NMR ($C_6D_5NO_2$, 130 °C): δ 1.89 (s, 6 H), 6.64 (d, 4 H), 6.80 (m, 12 H), 6.88 (m, 16 H), 6.97 (d, 4 H), 7.08 (m, 20 H).

3,3′-Bis(1-(3-chlorosulfonyl-4-methylphenyl)-3,4,5,6-tetra(4-chlorosulfonylphenyl)-phenyl)dibenzothiophene-1,1-dioxide (15). A solution of 2.00 g (2.0 mmol) of 2′,2⁗,-3′,3⁗,6′,6⁗-hexaphenyl-5′,5⁗-(4-methylphenyl)-*p*-sexiphenyl (**14**) in 20 mL of chlorosulfonic acid was stirred at room temperature for 4 h. The olive-brown reaction mixture was poured into 200 mL of dichloromethane to precipitate the product. The precipitate was filtered, washed with water, and dried in vacuo to provide 2.5 g (65%) of a tan powder. ^{1}H NMR (acetone-d_6): δ 2.50 (m, 6 H), 7.33 (br m, 4 H), 7.50 (br m, 22 H), 7.75 (br m, 16 H), 8.00 (br m, 2 H). HPLC/MS after derivatization with diethylamine showed the molecular ion at m/z 2524$^+$ (M + NH_4^+).

Size Exclusion Chromatography. Molar mass distributions and numbers of arms were determined by multidetector SEC. Detectors were arranged in series in the following order: 757 Spectroflow spectrophotometric detector (UV), Precision Detectors PD2020 15° and 90° light scattering (LS) detector, Viscotek H502A differential viscometer (DV), and Waters 410 differential refractive index (DRI) detector. The columns, LS, DV, and DRI detector temperatures were maintained at 35.0 ± 0.1 °C. Specific refractive index increments (dn/dc) calculated from the integrated DRI response and the mass of sample injected were comparable to values for the linear homopolymers. The eluent was HPLC-grade uninhibited tetrahydrofuran, delivered at a nominal flow rate of 1.0 mL/min. Flow rate corrections were made from the retention volume of acetone, added to the sample solvent at a concentration of 0.2% (v/v). Columns were three Plgel mixed-C (Polymer Laboratories), 7.5 × 300 mm. A universal calibration curve was constructed using 16 narrow molar mass distribution polystyrene standard (Polymer Laboratories) ranging from MW 580 to 2 300 000. Samples were injected in a volume of 100 μL at a concentration of 1.5 mg/mL.

Typical Polymerization Conditions. The following procedure for 6-arm poly(methyl methacrylate) initiated with **7** is typical of the polymerization reactions employed. A heavy-walled glass tube with a sidearm and stopcock was charged with 0.059 g (0.034 mmol) of initiator **7**, 0.018 g (0.18 mmol) of copper(I) chloride, 0.054 g (0.35 mmol) of 1,1′-bipyridine, and 5.8 g (68 mmol) of methyl methacrylate dissolved in 6.2 mL of phenyl ether. The contents of the flask were degassed under vacuum, blanketed with nitrogen, and sealed. The green and heterogeneous mixture became brown and homogeneous upon heating. The reaction was held at 90 °C for 30 min. As the vessel cooled, the original green color returned, and a small amount of precipitate was observed in the viscous polymer gel. The product was diluted with acetone and stirred with DOWEX MSC-1 (H$^+$) resin for a few minutes at room temperature to remove the catalyst and ligand. The polymer was precipitated into excess methanol, collected, and dried. Finally, the polymer was reprecipitated from tetrahydrofuran into excess methanol, filtered, and dried overnight in a vacuum oven.

Acknowledgment. We acknowledge the contributions of Linda Burns for FD-MS measurements, William Smith and Robert Saccante for HLPC/MS measurements, Kim Le, and Trevor Bryan for SEC measurements and determinations of the number of arms on the star polymers, and Moi Leong for ICP-AES determination of copper residues in the polymers, all members of the Eastman Kodak Company Analytical Technologies Division. We thank Prof. Virgil Percec of the University of Pennsylvania (and his research group) for advice concerning this polymerization technique and for allowing A.K. to perform experiments in his laboratory. We also thank Dr. Robert B. Grubbs of Dartmouth College for information concerning the *tert*-butoxide cleavage reaction.

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MA0206570