Macromolecules

Volume 25, Number 21 October 12, 1992

Hyperbranched Polyphenylenes†

Young H. Kim* and Owen W. Webster

Du Pont Central Research and Development, Wilmington, Delaware 19880-0328

Received November 4, 1991; Revised Manuscript Received June 12, 1992

ABSTRACT: Highly branched polyphenylenes were synthesized from AB_2 type monomers, e.g., 3,5-dibromophenylboronic acid (1A) and 3,5-dihalophenyl Grignard reagents (1B and 2). Monomers 1 and 2 were polymerized by Pd(0) and Ni(II) catalyzed aryl–aryl coupling reactions, respectively. Polymers obtained from 1 had molecular weights in the 5000–35 000 range with polydispersities less than 1.5. They are thermally stable to 550 °C and soluble in many organic solvents. ^{13}C NMR indicates about 70% branching efficiency. A T_g at 236 °C was observed, but the polymer was brittle and did not form films. The melt viscosity of polystyrene was reduced, and the modulus was improved as a bromo functional hyperbranched polymer was added. The bromo polymer was metalated with butyllithium. The resulting lithio polymer reacted with various electrophiles to provide polymers with other end groups which control solubility as well as thermal properties. Some of these derivatives were used as multifunctional initiators to prepare star polymers, for example, via ring-opening polymerization of propiolactone and anionic polymerization of methyl methacrylate.

Introduction

Branches in polymers, inadvertent or intentional, play important roles in determining their properties. The polymer viscosity, as well as density, can be affected by branching, as exemplified by various grades of polyethylenes.[1] Nature also employs branches in some polysaccharides and proteins for various reasons.[2] For example, whereas linear cellulose is quite insoluble, branched polysaccharides, such as glycogen, amylopectin, dextran, galactomannans, pectin, etc., are water soluble. These branched polysaccharides are nature's important energy-storaging materials.

Highly branched polymers, with branches at almost every repeat unit, have been a rather neglected subject until recently,[3] in part due to their poor mechanical properties. However, new classes of such substances have attracted increasing attention recently with the expectation that their unique spherical structures will impart unusual properties. These materials demonstrate characteristics such as supermolecular assembly[4] and micellar properties.[5]

This field has grown from two fundamentally different disciplines. On the one hand, well-characterized, highly branched small molecules, i.e., cascade compounds[6] and arborols,[7] etc., were grown into higher molecular weight molecules by stepwise synthesis. Both divergent[8] and convergent[9] synthetic approaches were employed. This method produces well-defined, large dendritic molecules whose structures can be extrapolated from that of the "core center" or building block. It also allows structural variation, as well as functional group variation.[9d,e] On the other hand, direct polymerization of AB_x type monomers, where x is 2 or greater, has also been pursued. Flory predicted that this type of monomer would produce highly branched polymers possessing one unreacted A functional group and $(x-1)n+1$ number of unreacted B functional groups at the surface of the polymer, where n is the degree of the polymerization (Scheme I).[10] There are very few literature references which implement this concept for synthesis. Highly branched polyesters were prepared by condensation polymerization in a single step from aliphatic dihydroxy monoacids[11a] or by thermal self-condensation of 3,5-bis(trimethylsiloxy)benzoyl chloride.[11b] Copolymers of 3,5-dihydroxybenzoic acid and *p*-hydroxybenzoic acid, which gave branched polyarylates, have also been reported.[12]

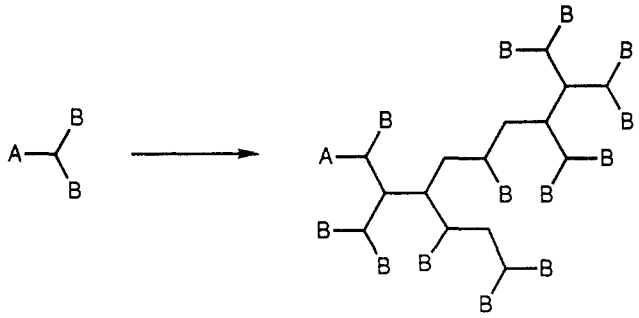
In addition to Flory's theoretical treatment of branched polymers, there have been a number of publications dealing with the theoretical aspects of these highly branched molecules.[13] Intriguing questions, such as the effect of steric crowding of the chains on the dimensional growth of the spherical macromolecules, have also been investigated.

We realized earlier that these highly branched polymers could be useful as polymer rheology control agents as well as spherical multifunctional macromonomers. In order to explore these ideas, we needed to prepare a hyperbranched polymer which not only was thermally and chemically robust under the testing conditions but also could be obtained rapidly in large quantity. The latter requirement led us to pursue the one-step polymerization of AB_x type monomers. We report here hyperbranched polyphenylenes which satisfy some of those research

* Author to whom correspondence should be addressed.
† Contribution No. 6061.

0024-9297/92/2225-5561$03.00/0

Scheme I[a]



[a] Number of unreacted A's: 1. Number of unreacted B's: (functionality - 2)DP + 1.

objectives.[14]

Results and Discussion

Polymer Synthesis. There has been a remarkable development during the last few decades in chemoselective aryl–aryl coupling reactions of aromatic halides and organometallics with transition-metal catalysts. For example, coupling reactions of arylboronic acids with aryl halides,[15] arylmagnesium halides with aryl halides,[16] and aryltrialkyltin compounds with aryl halides[17] are well recognized. We utilized these reactions for condensing polyhaloaromatic building blocks. The polyhaloaromatic substances were converted into AB_x type monomers by selective metalation of one of the halo functional groups in each monomer.

The arylboronic acid was prepared by monolithiation of 1,3,5-tribromobenzene[18] in ether at −78 °C with *n*-BuLi, followed by addition of the lithiate to a trimethyl borate solution in ether at −78 °C. Acidic hydrolysis followed by extractive workup provided the corresponding boronic acid (**1A**) in 50–80% yield. The boronic acid was found to convert to trimeric acid anhydride on heating or standing for a long period at room temperature. The yield in the polymerization declined as the amount of anhydride increased. Therefore, we usually did not attempt to purify the boronic acid nor dry it thoroughly but used it immediately for the polymerization. Since we are dealing with homopolymerization of **1A**, exact quantification of the monomer molarity is not essential. In another route to an AB_2 type monomer, the monolithiate was treated with an anhydrous $MgCl_2$ solution to form 3,5-dibromophenylmagnesium halide (**1B**).[19] The Grignard reagent **2** from 1,3,5-trichlorobenzene was best obtained by using activated magnesium.[20] Activated magnesium was obtained according to the known procedures, by treating $MgCl_2$ with either a K/Na (5:95) alloy or a mixture of KI and K in THF. Analysis of the chlorotrimethylsilane-quenched Grignard reagent indicated that most of the trichlorobenzene had reacted within 3 h. It also showed that selective monofunctionalization can be achieved even in the presence of excess Mg.

The phenylboronic acid, **1A**, was polymerized to a hyperbranched polyphenylene in a mixture of an organic solvent and an aqueous 1 N Na_2CO_3 solution in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium, under reflux similar to conditions reported by Suzuki.[15] Toluene, xylene, 1-methylnaphthalene, diphenyl ether, tetrachloroethane, and nitrobenzene were the organic solvents tested in this study. The molecular weight of the polymer depends on the organic solvent employed. Thus, polymers obtained in nitrobenzene had greater molecular weights than those obtained in other solvents (Table I). Since water and the corresponding organic solvent used formed an azeotropic mixture, the temperature of the reaction solution was around 90–95 °C regardless of the boiling point of the organic solvent.

Reaction in DMF[21] also gave a polymer at 100 °C with homogeneous or heterogeneous bases. This process, however, did not offer a substantial advantage over the original Suzuki's process. The solvating ability of the solvent seems to play an important role in the molecular weight control. The molecular weight can also be controlled by varying the temperature of the reaction. In tetrachloroethane, for example, polymers of $\bar{M}_n$ = 2000 and 4000 were obtained at room temperature and at reflux, respectively. Addition of more monomer at the end of polymerization did not increase the molecular weight of the polymer obtained nor did it give a bimodal molecular weight distribution. The polydispersities of the polymers prepared by this method were generally narrow. For a typical large batch run of 250-g scale, the yield from 1,3,5-tribromobenzene to the polymer was 65%. Polymer **3** was also obtained in THF from Grignard reagent **1B** with bis(triphenylphosphine)nickel chloride as the catalyst, in 40–80% yield. The advantage of this route is that large-scale runs can be easily made. This polymerization method gave polymers of $\bar{N}_n$ in the range of 2000–4000, often with a greater polydispersity than the boronic acid route. The polymer was soluble in THF during the polymerization; therefore, solubility is not a determining factor in the molecular weight control. One possible cause of molecular weight limitation is the loss of reactivity of the organometallic center by increased steric hindrance on molecular weight buildup. Another minor possibility is that the A functional group could be consumed by intramolecular cyclization. Since there is only one A group per polymer molecule, such cyclization would abort polymer growth by a step-polymerization mechanism. Polymer **4** was prepared similarly with a Ni(II) catalyst. The polymer was obtained as a white powder by precipitating it from the crude reaction mixture into petroleum ether or MeOH, followed by thorough washing. When nitrobenzene was used as the organic solvent, the organic layer was separated and concentrated under vacuum prior to precipitation. We found that Soxhlet extracting with THF was the most convenient method to separate the polymer from inorganic salts in large quantity.

de Gennes predicted that multiple-tiered perfectly branched polymers with flexible repeating units should have a maximum molecular weight.[13c] At this maximum molecular weight, the spherical growth of the polymer has reached a steric saturation point where further two-dimensional expansion by the branching monomers is prohibited. However, the repeat unit of our polymer is not flexible, and no definite saturation point could be predicted based on a molecular model.[5a] Furthermore, an NMR study showed that the branching was not complete (see below).

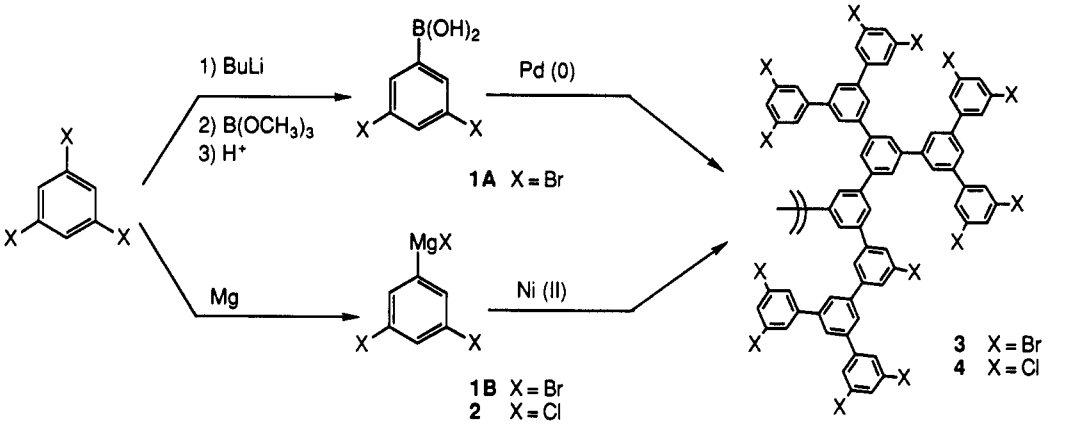
Polymer Characterization. The molecular weight of the polymer given throughout this paper is the GPC molecular weight calibrated against polystyrene standards and used only for a rough estimate. At the time of our investigation, no adequate GPC standards nor other methods were available to us for meaningful molecular weight measurement, and we did not pursue accurate molecular weight determination. It might suffice to mention that usually GPC measurements of branched polymers underestimate the true molecular weight.[9c] These polymers show good solubility in various solvents. Polymer **3** is freely soluble in *o*-dichlorobenzene (ODCB),

Table I
Effect of the Boronic Acid Coupling Reaction Conditions on the Molecular Weight of the Polymer

monomer	method[a]	polymerization conditions	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1A	A	xylene with a 1 N K_2CO_3 solution	3820	1.50
1A	A	1-methylnaphthalene with a 1 N Na_2CO_3 solution	6560	2.02
1A	A	phenyl ether with a 1 N Na_2CO_3 solution	5280	1.62
1A	A	tetrachloroethane with a 1 N Na_2CO_3 solution	4070	1.28
1A	A	same as above, but at room temperature	2000	1.38
1A	A	nitrobenzene with a 1 N Na_2CO_3 solution	32000	1.13
1A	A	dry DMF with a Na_2CO_3 powder	2000	1.38
1A	A	dry DMF with a tetraethylamine	2140	1.26
1B	B	anhydrous THF	3910	1.81
2	B	anhydrous THF	7590	2.3

[a] Method A: Pd(0)-catalyzed boronic acid coupling reaction.[15] Method B: Ni(II)-catalyzed coupling of phenyl Grignard compounds.[16]

Scheme II



tetrachloroethane, and THF. It is slightly soluble in toluene and benzene but practically insoluble in CH_2Cl_2 or $CHCl_3$. The high molecular weight polymer has a lower solubility than the low molecular weight polymer. Cooling a ca. 5 wt % clear solution of polymer 3 ($\bar{M}_n \approx 35\,000$) in THF to −78 °C results in precipitation, while a solution of polymer ($\bar{M}_n \approx 5000$) remains homogeneous. Polymer 4 is the most soluble, dissolving even in ethanol. The ^1H NMR spectra of these polymers show a broad peak between 7.0 and 8.5 ppm, in contrast to the highly symmetrical, single substance branched polyphenylenes.[9d,g] This broad, unresolved peak could be the result of the presence of various isomers. Elemental analysis of polymer 3 prepared by either method shows that they contained most of the bromine predicted from theory. Infrared spectra of these polymers show two characteristic peaks at 847 and 740 cm^{-1}, typical of 1,3,5-trisubstituted benzenes. The inherent viscosity of polymer with $\bar{M}_w = 5750$ ($c = 2$ g/dL, THF) was 0.031 dL/g. Elemental analysis of polymer 4 shows a lower amount of chlorine than expected, indicating possible reductive chlorine elmination during the polymerization.

If we consider an ideal, fully branched polymer with distinguishable tiers, which was prepared stepwise from 1,3,5-tribromobenzene as the zeroth tier core, the number of monomer units at the outermost tier is always double the number of monomer units in the next inner tier, since the number of the monomer units at the nth tier is $3 \times 2^{n-1}$.[8a] In this ideal case, only the phenyl groups at the outermost tier should contain bromide groups at the 3 and 5 positions, as shown in Scheme II. Since the conventional definition of a branching factor does not describe the architecture of these hyperbranched polymers, we defined a new "branching factor", which is equal to the mole fraction of fully branched monomer units. Thus, the branching factor for a fully branched polymer is assigned to be 1, and that of a linear isomer is 0. A fully branched high molecular weight polymer (DP: degree of polymerization >24) will have the population ratio of 1:4 between 4-carbons, which are in between two carbons attached to the bromine, and 1-carbons, which are connected to the phenyl ring (Figure 1). The ^{13}C NMR spectra of polymer 3 (Figure 2), where the peaks due to these two kinds of carbons are well separated, allow an estimation of the degree of branching. In order to avoid saturation, the NMR spectra were obtained with a 20-s pulse delay with NOE suppression. The relaxation times of the quaternary carbons were less than 5 s. The peaks between 133.0 and 134.0 ppm correspond to the 4-position carbons, and those between 140.0 and 145.0 ppm correspond to the 1-position carbons. This spectrum shows that a branching factor of 0.7 was achieved for polymer 3 when prepared from monomer 1A in a refluxing xylene and water mixture, whereas the polymer prepared from 1B has a 0.4 branching factor. This result indicates that the boronic acid coupling reaction is much less sensitive to the steric effects than the Grignard coupling reaction.

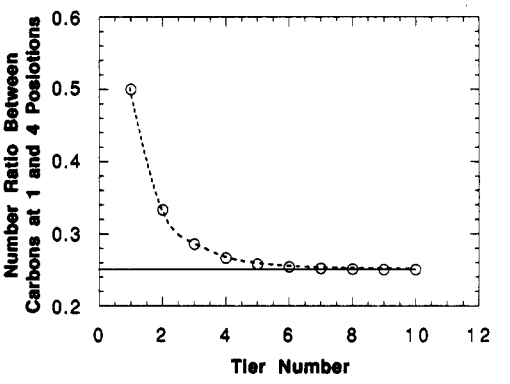


Figure 1. Relationship between the carbon number ratio of carbons at the 4 and 1 positions with respect to the number of tiers. The number of carbons at the 1 position equals that of the monomer at the outermost tier, $3 \times 2^{n-1}$, and the number of carbons at the 4 position is $1 + \sum 3 \times 2^n$.

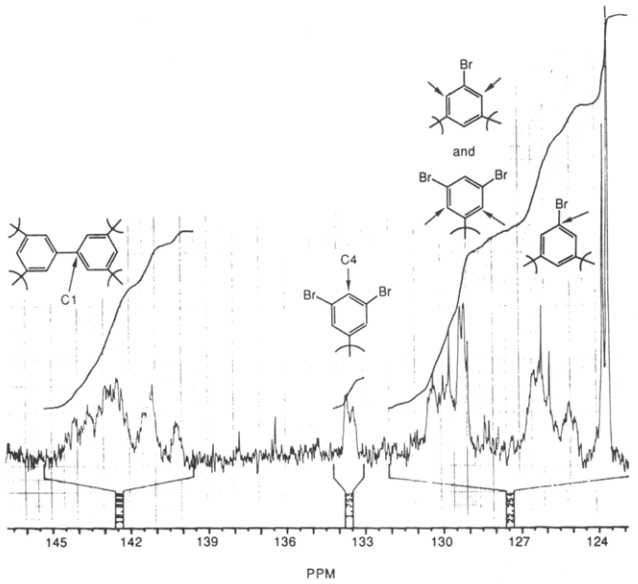


Figure 2. ^{13}C NMR of hyperbranched polyphenylene **3**. See text for conditions and interpretation.

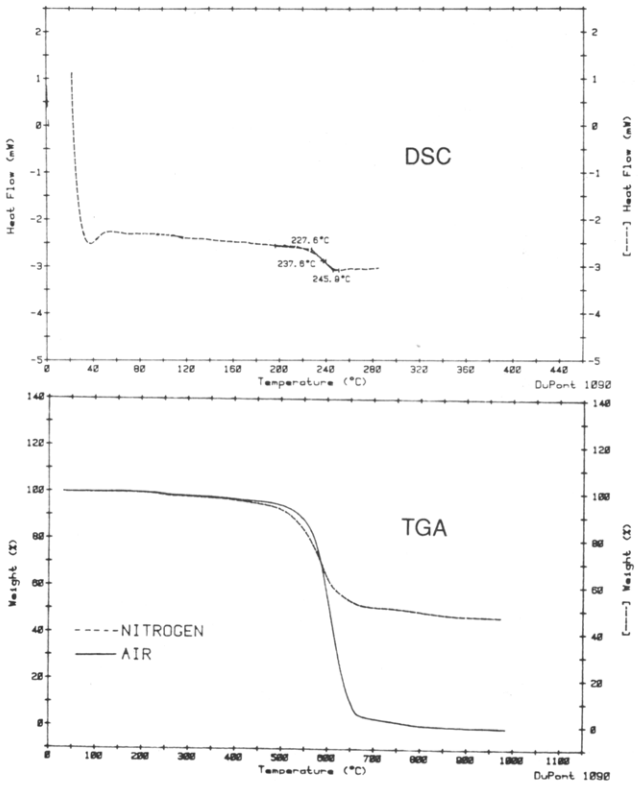


Figure 3. DSC and TGA of hyperbranched polyphenylene **3** at a 20 °C/min heating rate.

Hyperbranched polymer **3** shows no decomposition up to 550 °C in air but burns at 650 °C as observed by a TGA analysis. Under nitrogen, however, the polymer loses about 50% of its weight at 550 °C with the evolution of HBr, leaving a carbon-like residue (Figure 3). A large-scale thermolysis of polymer **3** at 600 °C gave 1 equiv of the acid in the off-gas, which was trapped in 1 N NaOH solution and back-titrated. The powder X-ray analysis of the residual carbon indicated it was an amorphous form, showing peaks at $2\theta = 22°$ (002 reflection) and 43° (100 reflection). The density, 2.0059, is between that of carbon and graphite.[22] Isothermal aging at 350 °C in air resulted in only 4.5% weight loss in 60 h. The polymer shows a T_g at 238 °C with a small heat capacity change, as observed in DSC, and does not show any melting point (Figure 3).

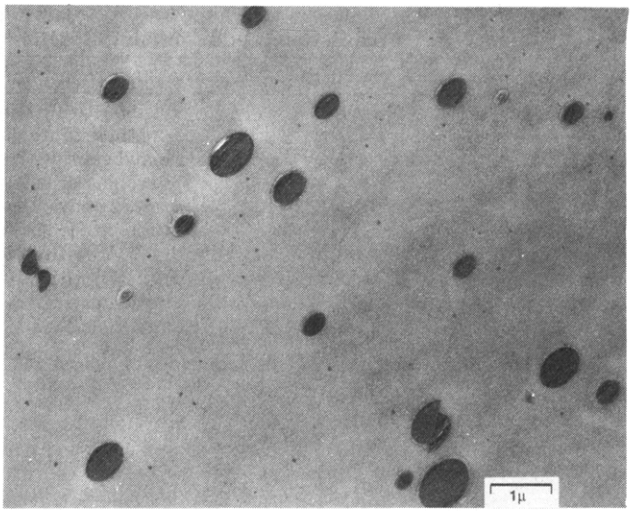


Figure 4. Transmission microgram of 5 wt % hyperbranched polyphenylene **3** in polystyrene. Note the bimodal distribution of the polymer **3**. The electron beam sensitivity of polymer **3** obstructed accurate size measurement of the smaller domain.

The molecular weight of the polymer, in the range of $\bar{M}_n$ = 2000–35 000, did not influence the T_g. Even segmental crystallization must be prohibited by a steric effect of neighboring branches and/or by an inability to peak regularly, owing to the existence of the numerous isomers. Similar, interchain entanglement is highly unlikely; thus, these polymers do not form stable films from solution or under a hot press.

Blending with Other Polymers. Molecular modeling of the polymer reveals a large number of empty cavities between branches. The existence of molecular complexation in the cavities was confirmed by an NMR study of a water-soluble version of polymer **3** with *p*-toluidine.[5a] Such interaction in a polymer containing aromatic groups causes a reversible physical cross-linking of the polymer chain. On the other hand, in the molten state where such static interaction would not be sustained, a spherically shaped hyperbranched polymer could affect the rheology of a matrix polymer. Polystyrene was chosen to test this hypothesis. The polymers can be blended either in solution or in the melt. A blend of up to 2% of polymer **3** mixed with polystyrene appeared clear, although turbid blends were obtained with larger amounts of **3**. The T_g's of polymer blends with up to 30% of polymer **3** did not change from that of pure polystyrene. Low-angle X-ray diffraction and TEM (Figure 4) analysis of the 5% blend shows that there are bimodal distributions of polymer **3** domains, with a small amount in 10-nm domains and a larger portion in 1-μm size domains. The 400-MHz ^1H NMR spectrum of the mixture of polystyrene and polymer **3** in $CDCl_3$ showed no significant changes in chemical shifts for either polymer, except a small degree of peak broadening in the polystyrene benzylic protons.

In spite of this evidence of poor mixing, some noticeable changes in the properties of polystyrene were found in rheology and in thermal stability. Two polystyrene blends, one with 5% of polymer **3** and the other with 0.1%, were prepared for the rheology study (Table II). In comparison to the 0.1% blend (control), the melt viscosity of the 5% blend was lowered to about 50% at 180 °C and 80% at 120 °C. The effect is greater at higher temperatures and higher shear rates. The addition of polymer **3** also seems to improve the thermal stability of polystyrene. When the molten polymer was kept at 180 °C for 20–30 min, the melt viscosity of the 0.1% blend increased about 3-fold, which is equivalent to an increase of 1.38 times $\bar{M}_n$ due to

Table II
Effect of Hyperbranched polymer 3 on the Melt Viscosity of Polystyrene Determined by Capillary Rheometery

		PS with 0.1 wt % polymer 3		PS with 5.0 wt % polymer 3	
shear rate (1/s)	temp (°C)	contact time (min)	viscosity (Pa·s)	contact time (min)	viscosity (Pa·s)
3.3	150	23	39310	18	31620
	180	25	34220	18	11720
	220	24	14080	20	3941
131.6	150	14	5517	7	2785
		34	4738	20	2388
	180	6	1758	5	982
		28	5267	20	958
	220	6	573	5	500
		22	1819	23	504
3289	150			19	401
	180	26	241	21	65
	220	12	166	12	98

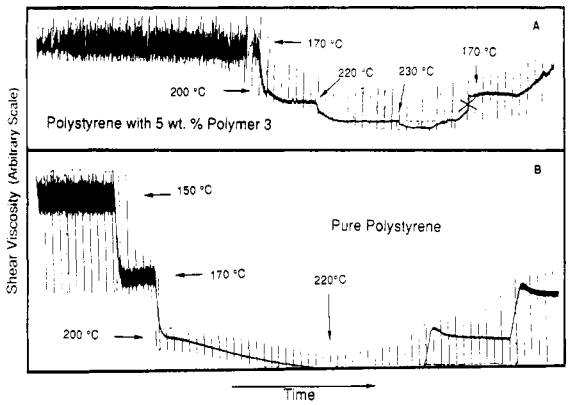


Figure 5. Torque viscosity of polystyrene in the molten state: (a) A blend of 5 wt % polymer 3 with uninhibited polystyrene. (b) Pure uninhibited polystyrene.

thermal chain transfer. The melt viscosity of the 5% blend did not show this behavior. In a separate experiment where a molten mixture of the 5% blend was sheared in a mixer, the melt viscosity (measured as the torque pressure of the Brabender mixer screw) did not change even at 220 °C in 4 h. The same experiment with pure polystyrene showed a drastic viscosity reduction at 220 °C (Figure 5). A GPC analysis of the resulting polymer showed that the molecular weight of polystyrene (2.6×10^5) was decreased to 24% (0.6×10^5) of its original value after 4 h at 220 °C, but it maintained 65% of its molecular weight (1.7×10^5) at 230 °C with 5% of polymer **3**.

The effect of a hyperbranched polymer on the mechanical properties of polystyrene blends was studied using a solution blended sample which was injection molded into $^1/_8$-in. wide flex and tensile bars at 180 °C with 50 psi back-pressure. The blend with 2% of the polymer **3** showed no difference in the flexural modulus compared to polystyrene, but an improvement in the initial modulus (24% increase) with a concomitant sacrifice in the maximum strength (15% decrease) was realized (Table III). The weak cross-linking of polystyrene by polymer **3** through aryl–aryl interaction might be responsible for the high initial modulus.

Chemical Modification of Polymer 3. The halogen functional groups in the polymer are mostly at the polymer surface and can be chemically modified. This functionalization allows conversion of polymer **3** or **4** into "multifunctional initiators" or macromonomers.

Since polymer **3** shows excellent solubility in THF, lithiation with alkyllithium reagents was studied. Polymers prepared using xylene as the organic solvent were

Table III
Mechanical Properties of Polystyrene and 2 wt % Polymer 3 Blended Polystyrene[a]

		PS	PS with 2 wt % polymer 3
tensile test	initial modulus (kpsi)	384	476
	strength at break (psi)	7983	6786
	elongation at break (%)	2.5	3.1
flexural test	flexural modulus (kpsi)	468	473
	strength at yield (kpsi)	13.8	13.8

[a] Sample size: width, $^1/_2$ in.; thickness, $^1/_8$ in. Temperature: 25 °C. Crosshead speed: 0.5 in./min.

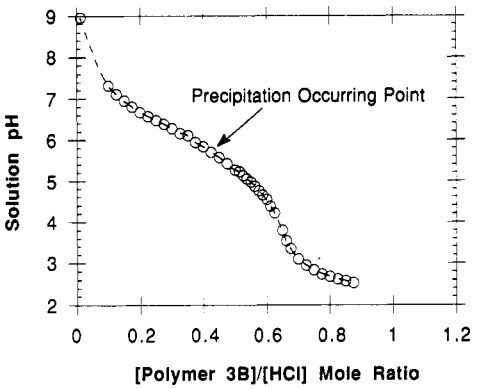


Figure 6. Titration curve of crude polymer **3B** with 0.1 N HCl.

used for the functionalization. Polymers prepared using high boiling organic solvents needed extraordinary care to remove the trapped solvents, which could interfere with derivatization. The lithiate **3A** is insoluble in THF but stable for many hours at −78 °C. When it was warmed to room temperature, an intractable material was obtained. In a small-scale reaction, the lithiation yield was shown to be over 90% by quenching the anion with chlorotrimethylsilane. When the anion was quenched with methanol or acetonitrile, IR peaks at 700 and 779 cm^{-1} due to monosubstituted benzene appeared, in addition to the peaks at 867 and 766 cm^{-1} corresponding to trisubstituted benzene in almost the same intensities.

The lithiate anion reacts with various electrophiles. Treating the lithiate with dry CO_2 gave carboxylate **3B**, which is water soluble. In order to avoid possible cross-linking by multiple addition of the lithiate to the carbonyl group, the lithiate slurry was cannulated to the CO_2 solution in THF. The conversion from the bromine group to the carboxylate group was 70–80%. An aqueous solution containing more than 50 wt % of the carboxylate polymer did not show much change in viscosity. The micellar properties of this polymer have been reported.[5a] The acidity of the carboxy groups seems to be in the normal range for aromatic carboxylic acids as indicated from the titration curve of crude **3B** with 0.1 N HCl (Figure 6). The acid form of this polymer is water insoluble but soluble in THF.

The degree of functionalization was based on ^{1}H NMR integration and elemental analysis. Since the lithiation usually does not take place in quantitative yield, due to limited solubility of the lithiate **3A**, the chemically modified polymers were never obtained as pure species. ^{1}H NMR integration was used to estimate the conversion yield, in examples where the derivative contains a functional group which exhibits a ^{1}H NMR peak well separated from the aromatic peaks (see, for example, Figure 7). In other cases, elemental analysis was used to estimate the conversion yields. Linear iteration of the observed compositions with theoretical compositions for the expected

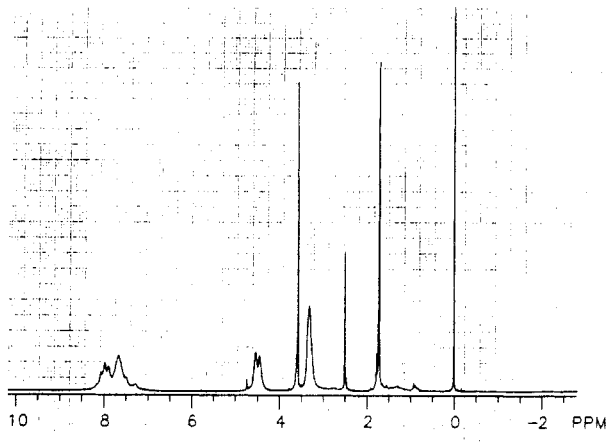
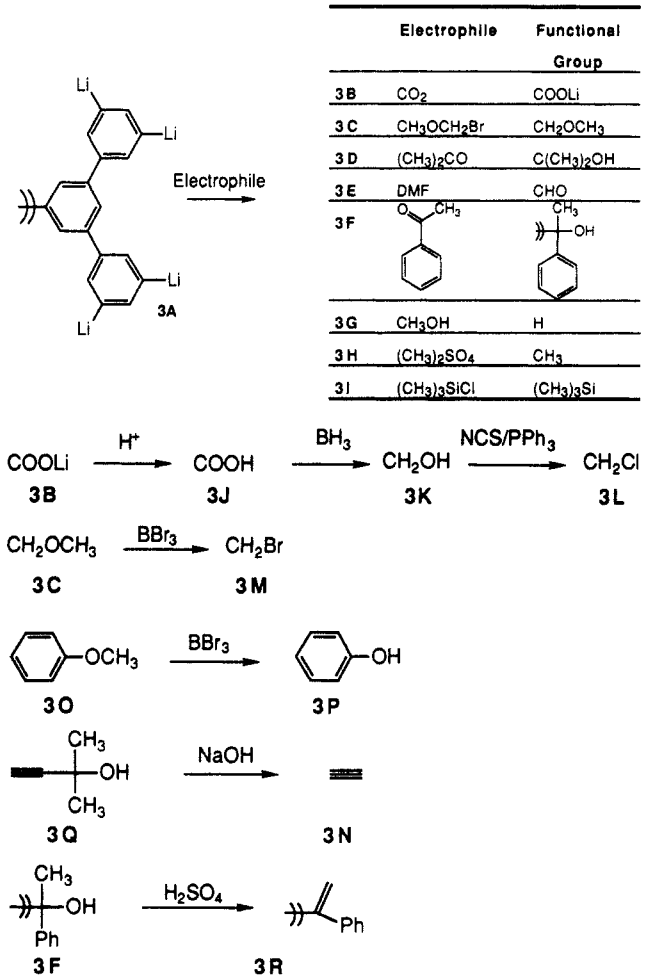


Figure 7. ^{1}H NMR of **3C** at 300 MHz in THF-d_8.

Scheme III



product and those of polymer **3** gave conversion yields which were in fair agreement with those obtained by the NMR method. The elemental analysis of derivatives from the large-scale reactions showed that usually 70–80% of the bromine had exchanged.

Reaction of **3A** with bromomethyl methyl ether gave the methoxymethyl derivative (**3C**) in about 70% (NMR analysis) or 80% (elemental analysis) conversion. The list of electrophiles used, and the resulting functional groups is shown in Scheme III. For some nucleophiles, conversion to the expected functional groups was rather poor. For example, the formyl group (**3E**) was produced in about 30% efficiency by reacting **3A** with DMF. Similarly, the polymer can be modified by coupling reactions. Reaction of *p*-methoxyphenylmagnesium bromide with a Ni(II) catalyst gave **3O** in high coupling yield, which is soluble in CH_2Cl_2 and $CHCl_3$ but not in ether or hexane. The intensity ratio of the methoxymethyl peak to the aromatic peaks by ^{1}H NMR suggests that 67% of the bromine groups were converted to methoxy groups. Pd(0)-catalyzed coupling[23] to 2-methyl-3-butyn-2-ol gave an acetylene derivative **3Q**. In certain cases, the polymer reactivity seems to be enhanced when a small amount of the bromide groups had reacted with the reagent. For instance, in the reaction of 2-methyl-3-butyn-2-ol with $\bar{M}_n$ = 3500 polymer **3**, in which about 35% of the bromine reacted as estimated from the ^{1}H NMR spectrum, GPC showed two peaks in about a 6 to 4 ratio (Figure 8). Such accelerated reactivity of a partially converted polymer could be one characteristic of highly branched materials. Wooley et al. also reported[9a] that when a fourth-generation monofunctional wedge containing benzylic bromide was reacted with a hypercore with six phenolic coupling sites to make a higher generation dendrimer, only the starting material and the final hexasubstituted dendrimer were observed in GPC experiments, indicating that the di-, tri-, tetra-, or pentasubstituted dendrimers have a much higher reactivity than the hypercore in substitution reactions. The authors speculated that such behavior may be due to local polarity or "microenvironmental effects" favoring coupling of the dendrimeric wedges to the more lipophilic partly substituted cores rather than to their more hydrophilic unsubstituted or less substituted counterparts.

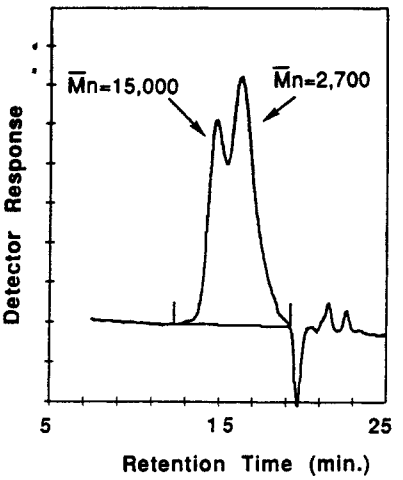
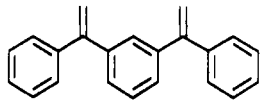


Figure 8. GPC of partially reacted 3-hydroxy-3-methylbutynated polymer **3Q**.

The initial functional groups formed by polymer modification can be converted to other groups via standard chemical manipulations. The carboxy functional groups were reduced with borane in THF to give the hydroxymethyl derivative (**3K**). Treatment of the hydroxymethyl derivative with a mixture of *N*-chlorosuccinimide and triphenylphosphine gave the chloromethyl derivative (**3L**), a useful macroinitiator. Alternatively, the bromomethyl derivative can be prepared in two steps from the methoxymethyl derivative with excess BBr_3 in CH_2Cl_2 or with PBr_3 in toluene. Another potential macroinitiator, **3R**, was prepared by dehydration of **3F** in toluene with sulfuric acid as catalyst. This polymer showed a T_g at 71 °C and an endotherm at 160 °C in the first DSC scan, but in the second scan only a T_g was found at 96 °C. It appears that the endotherm is due to evaporation of a trapped solvent. This polymer migrates well on a silica gel TLC with CH_2Cl_2 as an eluent, so that purification by column chromatography was possible. This product is a multifunctional analogue of 1,3-bis(1-phenylvinyl)benzene (*MDDPE*), which is a convenient difunctional initiator for anionic



1,3-bis(1-phenylvinyl)benzene (MDDPE)

polymerizations in hydrocarbon solvents.[24] The GPC molecular weight of **3R** was almost twice that of the starting polymer **3**. Cleavage of the methyl ether group of the *p*-anisole derivative of **3O** with BBr_3 in CH_2Cl_2 at low temperature gave **3P**, and cleavage of the acetone protecting group from 2-methyl-3-butyn-2-ol of **3Q** with KOH to give **3N** also proceeded smoothly.

Properties such as the solubility and the T_g of the polymers were greatly affected by the terminal functional groups (Table IV). Several derivatives, such as those containing *p*-methoxyphenyl, phenyl-α-vinyl, and hydroxymethyl groups, are CH_2Cl_2 soluble. The hydroxymethyl derivative requires a small amount of a hydrogen bond donor solvent to be solubilized. Derivatives with nonpolar groups are soluble in ether. These high solubilities can be explained by two synergistic properties of these polymers, namely, lack of crystalline packing and complexation of the solvent in the cavities. Polymers with nonpolar terminal groups, such as CH_3 and $Si(CH_3)_3$, show much lower T_g's than polymer **3**. Polymers with polar groups, such as CH_2OH or COOH, did not show any thermal profiles up to 400 °C. The fact that the T_g's are so dependent on the terminal group polarity indicates that they might be related to the translational motion of the polymers rather than the segmental chain motion.

Star-Branched Polymerization. Several strategies have been developed in the last few decades to make star-shaped polymers. Star polymers containing a microgel core can be made by either a "core first"[25] or "arm first"[26] method that employs bifunctional monomers to tie up reactive chain ends as a cross-linked core. These methods allow one to make star polymers with more than 100 arms. Better defined star polymers with fewer arms can be made by coupling reactive polymer chain ends,[27] such as those in a living polymer, with multifunctional linking agents or by initiating polymerization with multifunctional initiators.[28]

In principle, any hyperbranched polymer with suitable end groups could serve as a multifunctional initiator or linking agent for various types of polymerizations in the "core first" manner. The hyperbranched polymer of molecular weight 5000 would have about 60 terminal functional groups capable of forming the same number of star arms. We have prepared several star-shaped polymers to illustrate this idea. Since the arms of the star polymers we have prepared are mostly short, a large fraction of the polymer moiety is polyphenylene. These polymers have a very high core segmental density, and the short chain should be extended. Star polymers with short chains were found to deviate strongly from the normal behavior predicted by theory for the dynamic light scattering study on 12-arm polyisoprene star polymer.[29] Thus, polymers with $\bar{M}_w$ less than 150 000 showed an exceptionally large g' factor in good and Θ solvents. Therefore, characterization of our star polymers by conventional methods, such as the g' factor, would not be as meaningful as in the case of mostly star homopolymers. We employed polymer **3** ($\bar{M}_n \approx 3500$) made in xylene throughout the investigation below.

First, star-shaped polymers with arms analogous to oligomeric polyethylene were prepared by reaction of polymer **3A** with chlorosilanes having one long-chain alkyl group, to illustrate that the hyperbranched polymer is

Table IV
Effect of the Polymer Functional Group on the Thermal and Solution Properties of Polymer 3

polymer	functional group	T_g (°C)	solubility in THF	CH_2Cl_2	ether	water
3	Br	238	++	–	–	–
3B	COOLi		–	–	–	++
3G	H	127	++	+	–	–
3H	CH_3	179	++			
3I	$(CH_3)_3Si$	152	++	++	++	–
3J	COOH		++	–	–	–
3K	CH_2OH		++	++	–	–
3L	CH_2Cl		++	–	–	–
3O	*p*-methoxyphenyl		++	++	–	–
3P	*p*-hydroxyphenyl		+	–	–	–
3R	phenyl-α-vinyl	96	++	++	–	–
4	Cl		++	++	++	–

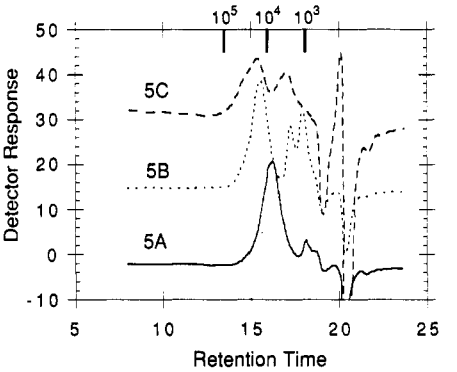


Figure 9. GPC of hyperbranched polymers coupled with a long alkyl chain containing chlorosilanes (**5A–C**).

Table V
Reaction of Alkyldimethylchlorosilane with Lithiated Polymer 3A

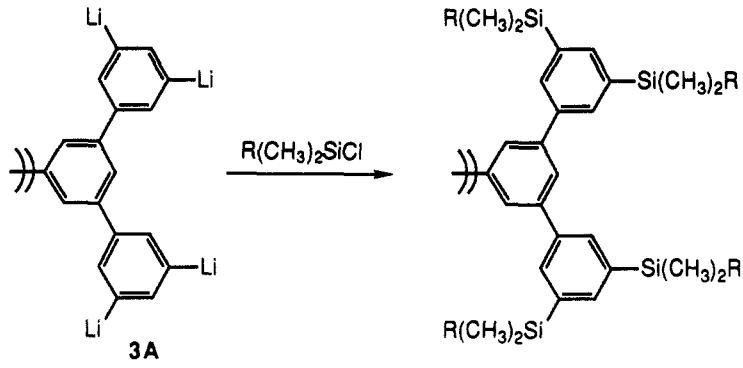
$R(CH_3)_2SiCl$	coupling yield (%)	GPC peak mol wt	physical appearance
$R = CH_3$	90		white solid
$R = C_8H$	85	6 700	oil
$R = C_{18}H$	55	13 000	wax
$R = C_{30}H$	<50	17 000	wax

capable of acting as a multifunctional linking agent. The coupling yield decreased as the alkyl group increased in length. The polymers prepared by reaction with silanes containing alkyl groups higher than octadecyl could not be purified by precipitation. In the case of triacontyldimethylchlorosilane coupling, about 40% of **3A** was found to have not reacted at all (Figure 9). This is another example where the partially reacted polymer is more reactive than the starting polymer. The unreacted silane was also difficult to remove. However, the peak molecular weights of the polymers by GPC showed a linear increase with the size of the arm (Table V). Similar to polymers with small functional groups, the alkylsilyl end groups control the physical properties of the polymers. Other hyperbranched polymers with active end groups, such as benzylic halides (**3L**), could be used as linking agents for nucleophilic polymer chain ends, but we have not pursued this route in detail.

Derivatives **3B**, **3D**, **3R**, and **3L** can be used as initiators in various types of living polymerization to generate star polymers (Scheme IV). Since ring-opening living polymerization of β-propiolactone by aromatic carboxylate anion initiators is well-known,[30] the possibility of using carboxy-containing polymers, **3B** and **3J**, for polymerization of 2-methyl-2-propyl-3-propiolactone was investigated. Attempts to complex the Li salt with 12-crown-4 and dissolve it in THF or toluene were unsuccessful. Initiators prepared

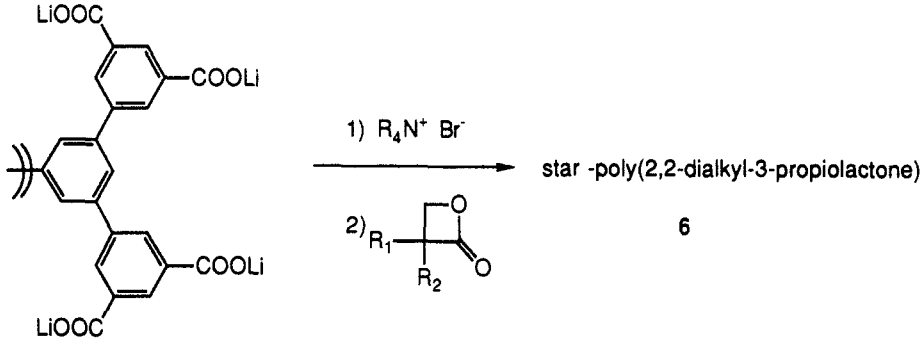
Scheme IV

MODEL STAR-SHAPED POLYMER

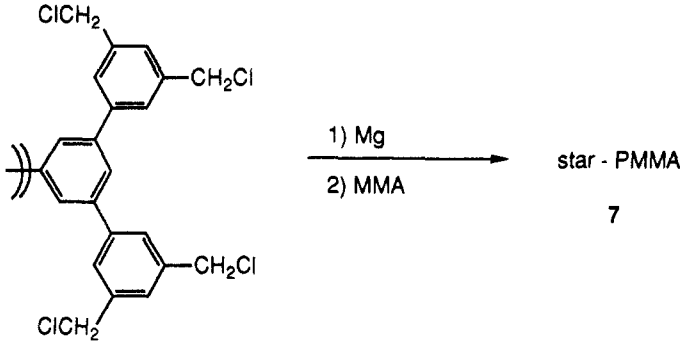


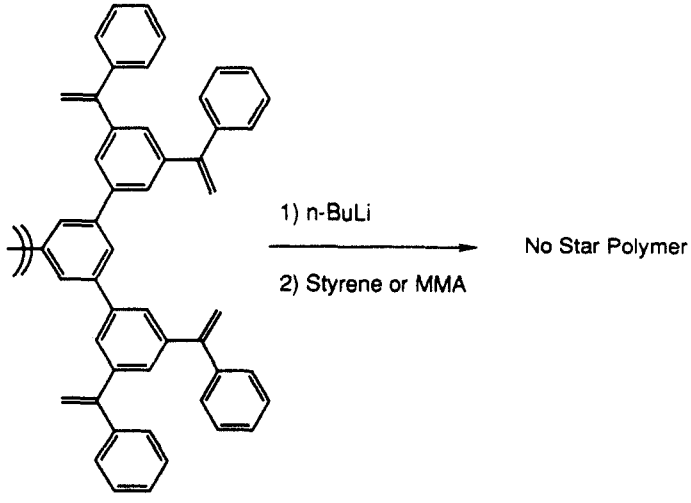
3I	$R=CH_3$
5A	$R=C_8H_{17}$
5B	$R=C_{18}H_{17}$
5C	$R=C_{30}H_{61}$

RING OPENING POLYMERIZATION



ANIONIC POLYMERIZATION





by treating polymer **3J** with tetrabutylammonium hydroxide followed by azeotropic distillation of water with toluene, or with $KHCO_3$ and dicyclohexyl-18-crown-6, gave polymers with a bimodal molecular weight (Figure 10). The best result was obtained by using an initiator from equilibration of **3B** with tetraheptylammonium bromide in toluene. The hyperbranched polymer slowly dissolves while LiBr is left in suspension. The propiolactone was

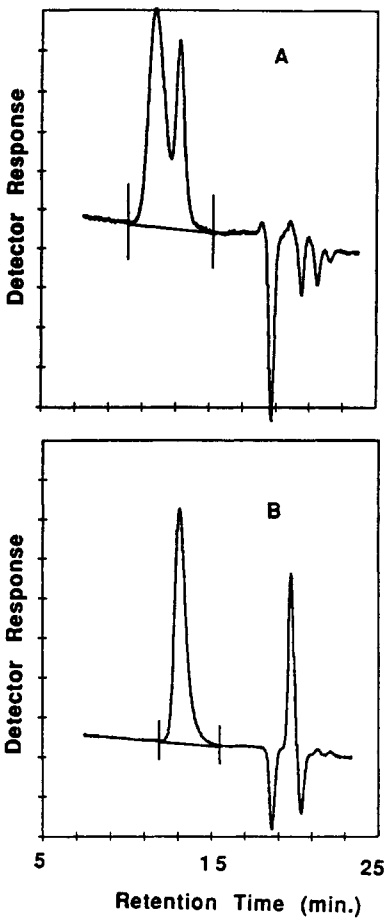


Figure 10. GPC of star-shaped polypropiolactone polymerized using the hyperbranched polymer as an initiator: (A) Initiated by **3J** treated with $KHCO_3$ and dicyclohexyl-18-crown-6. (B) Initiated by **3B** equilibrated with tetraheptylammonium bromide in toluene.

polymerized under reflux in about 2 h. Relatively low dispersity ($D < 13$) polypropiolactone was obtained. The theoretical arm length was calculated assuming the hyperbranched polymer is fully carboxylated, so that there will be a star branch on every repeating phenyl ring. The ^1H NMR spectrum of a polymer containing arms of theoretical DP = 10 ($\bar{M}_n$ = 10 400 GPC) did not explicitly show peaks due to hyperbranched polymer. Since the polypropiolactone itself showed substantial amounts of absorption in a UV detector at 254 and 280 nm, the comparison of RI and UV detector traces of GPC curves did not give additional information on the efficiency of the initiation. However, while the RI trace shows a single peak for this polymer, the UV trace shows bimodal peaks and both are of higher molecular weight than the correspondng hyperbranched polymer (Figure 11). The thermal properties of these polymers are quite similar to those of linear polymers, i.e., a T_m at 81.6 °C in the first DSC run and a T_g at −5.3 °C in the second run. Polymers having arms of DP less than 100 showed poor mechanical properties. When the polypropionate was precipitated in a nonprotonic solvent, the polymer chain end is still able to do ring-opening polymerization of propiolactone. Thus, a higher molecular weight polymer was prepared by using the oligomeric star polymers as the initiator. Figure 12 shows the molecular weights of polypropiolactones based on the added monomer. These were compared to the theoretical molecular weights of the linear polymers which were calculated as if the bromide had been the initiator. The molecular weights of the star polymers are about 3 times larger than those expected for linear polymers. However, the polymers exhibit much lower molecular

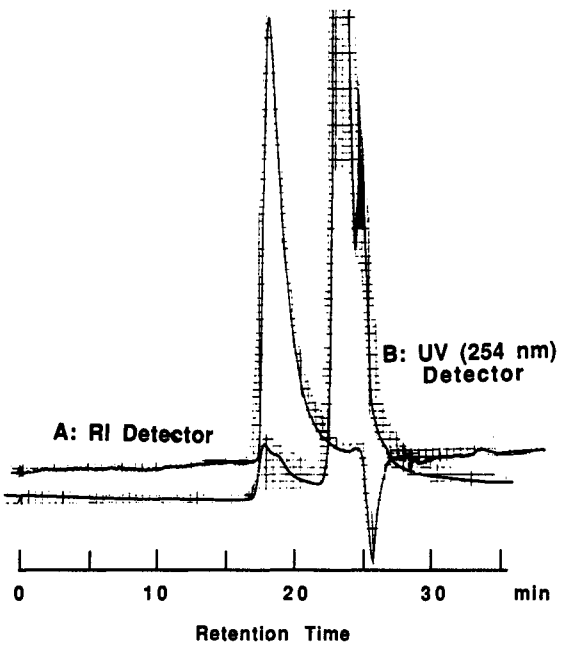


Figure 11. UV and RI detector traces of GPC of star-shaped polypropiolactone (theoretical arm DP = 10) polymerized using the hyperbranched polymer **3B** as an initiator which was equilibrated with tetraheptylammonium bromide.

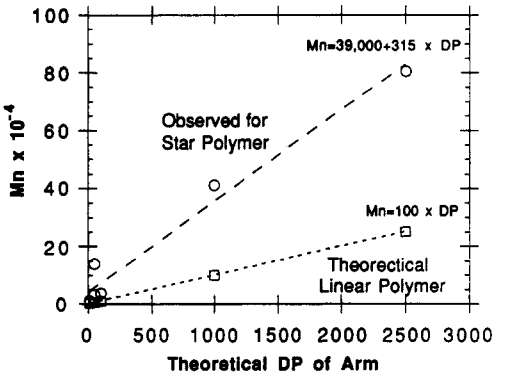


Figure 12. Molecular weight increase of polypropiolactone with incremental addition of monomer.

weights than expected. It seems that the efficiency of initiation of star polymerization by these multifunctional initiators is rather poor. This observation is in accordance with a report that even three-arm star polymers could not be prepared efficiently if multifunctional initiators were used.[28] We have attempted several other approaches to prepare star polymers using derivatives of **3** as initiators with mixed results.

In spite of the structural similarity between polymer **3R** and MDDPE, anionic polymerization of styrene or methyl methacrylate (MMA) using it as an initiator was unsuccessful (Scheme IV). **3R** was passed through a silica gel column with CH_2Cl_2 and dried under vacuum at 100 °C; above the temperature this polymer shows an endotherm. Addition of *n*-BuLi to polymer gave an intense red color, indicating formation of the anion. However, this anion seems to be quite unstable in THF, even at −78 °C. Some polymer with a high molecular weight dispersity can be obtained if the monomer is added before the color fades. This polymer contains about 20–30 mol % of unreacted bromide functional groups which would be also reacting with *n*-BuLi, but it is not obvious that this bromide functionality would cause instability. It might be that the proximity of a large amount of anions causes instability of the polyanion.[31] We also attempted anionic polymerization of MMA using **3A** as an initiator but without

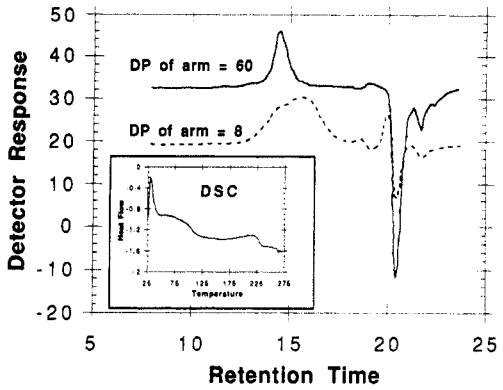


Figure 13. GPC and DSC of star PMMA 7.

success, even though phenyllithium is known to initiate polymerization of MMA. The Grignard reagent, prepared from polymer **3L**, initiated polymerization of MMA. The Grignard reagent was prepared by using $MgBr_2$ etherate and lithium metal in the presence of equivalent amounts of anthracene. The PMMA segment was found to be essentially syndiotactic based on IR and ^{13}C NMR[32] spectra. For a polymer with very short arms (DP = 7.8, calcd), the DP based on the ^1H NMR intensity ratio between the PMMA segment and polymer **3L** was found to be 5.4. For a polymer with long arms (DP = 65, calcd), a DP of 36 was estimated from ^{13}C NMR. The polymer with short arms had a very broad molecular weight dispersity and two T_gs (Figure 13), and the one with longer arms showed a narrow molecular weight distribution (D = 1.3) and a single T_g at 107 °C.

Experimental Section

General Procedures. All reactions were performed under a nitrogen atmosphere unless otherwise specified. THF and diethyl ether were distilled from a sodium diphenyl ketyl solution just prior to use. Xylenes, toluene, ODCB, 1-methylnaphthalene, 1,1,2,2-tetrachloroethane, and nitrobenzene were reagent grade and used without further purification. 1,3,5-Tribromobenzene (from Eastman Kodak) was distilled under vacuum. Trimethyl borate, $MgBr_2$ etherate, 1,3,5-trichlorobenzene, and polystyrene were obtain from Aldrich and used as received. Methyl methacrylate was purified by a literature method,[33] and 2-methyl-2-propyl-3-propiolactone was a gift from Dr. R. Blume of Du Pont CR&D. Chlorosilanes were purchased from Petrarch. Peak intensities in ^1H NMR spectra, expressed as the number of corresponding protons, were normalized by taking the intensity at the aromatic region peaks to be three protons. GPC was performed either in THF at ambient temperature or in ODCB at 135 °C using a polystyrene gel column which was calibrated with polystyrene standards. The results obtained from these two conditions were identical within experimental error. GPC polydispersity was given as D which is $\bar{M}_n/\bar{M}_w$. Thermal analysis was done on a Du Pont 9001 thermal analyzer with a 20 °C/min heating rate. Melt viscosity and mechanical properties were measured on an Instron capillary rheometer and mechanical tester model 2001, respectively. The theoretical compositions given for elemental analyses were calculated for an ideal polymer which has one functional group per repeat unit. The observed composition was used to estimate the conversion percentage.

(3,5-Dibromophenyl)boronic Acid (1). To 9.44 g (30 mmol) of 1,3,5-tribromobenzene in 200 mL of diethyl ether was added 19.4 mL (30 mmol) of 1.55 M *n*-BuLi in hexane at −78 °C under an inert atmosphere. The suspension was stirred for 30 min and then added to 30 mL (264 mmol) of trimethyl borate in 300 mL of diethyl ether at −78 °C. The mixture was stirred 30 min and then allowed to warm to room temperature. The solution was treated with 50 mL of 1 N HCl for 2 h. The boronic acid was extracted from the ether layer with a 2 N NaOH solution (5 × 100 mL). The combined aqueous solution was washed with 50 mL of ether and then acidified with 6 N HCl to pH 2 at 0 °C. A total of 8.49 g of a white powder was obtained after air drying. Mp: >300 °C. ^1H NMR (ppm, CD_3OD): 7.73 (1 H), 7.82 (2 H). Anal. Calcd for $C_{18}H_9O_3B_3Br_6$ as the tricyclic anhydride: C, 27.54; H, 1.16; Br, 61.06. Obsd: C, 26.47; H, 1.18; Br, 60.29.

Hyperbranched Polymer 3. To a mixture of 50 mL of xylene, 20 mL of a 1 M K_2CO_3 solution, and 30.8 mg of $Pd(PPh_3)_4$ was added 2.98 g of 1 in 5 mL of ethanol. The mixture was refluxed for 6 h and then cooled to room temperature. The polymer was precipitated by adding 100 mL of hexane, filtered, and washed with methanol, water, and methanol (50 mL each). After drying at 70 °C/100 mmHg, 0.86 g of the hyperbranched polymer **3** was obtained. ^1H NMR (ppm, THF-d_8): a set of broad peaks at 7.0–8.5. IR (cm^{-1}): 1580 (s), 1560 (s), 1450 (vs), 847 (s), 740 (s). GPC: $\bar{M}_n$ = 3820, $\bar{M}_w$ = 5750. Anal. Calcd for C_6H_3Br: C, 46.49; H, 1.95; Br, 51.55. Obsd: C, 48.00; H, 2.27; Br, 49.67.

Polymerization of 1,3,5-Tribromobenzene to Polymer 3 via a Grignard Route. To 6.30 g (20.0 mmol) of tribromobenzene in 30 mL of ether was added 12.9 mL (20.0 mmol) of *n*-BuLi at −78 °C. The mixture was stirred for 10 min. To the lithiate was added 6.06 g (25 mmol) of $MgBr_2$ etherate at −78 °C. The solution was warmed to room temperature and was added to a 500-mL THF solution of $Ni(acac)_2$ (642 mg, 2.5 mmol). The mixture was refluxed for 24 h, and then 5 mL of water was added carefully at room temperature. The solution was concentrated under reduced pressure, and the polymer was precipitated from petroleum ether. After washing with methanol, water, and a dilute HCl solution and drying, 1.82 g (59%) of a white powder was obtained. GPC: $\bar{M}_n$ = 3900, $\bar{M}_w$ = 7080.

Polymerization of 1,3,5-Trichlorobenzene to Polymer 4. Activated Mg was prepared by mixing 8.89 g (93 mmol) of $MgCl_2$ and 5 g of a K/Na (5:95) alloy in 200 mL of THF at room temperature for 2 h and then heating under reflux for 2 h. After the solution was cooled to ambient temperature, 13.64 g (75 mmol) of 1,3,5-trichlorobenzene in 50 mL of THF was added from a dropping funnel. The solution was stirred for 10 h and then 105 mg of $Ni(PPh_3)_4Cl_2$ was added. The polymerization was carried out for 24 h under reflux and was then quenched with water. THF was concentrated, and the polymer was precipitated into methanol. A total of 7.70 g (93% yield) of the polymer was obtained. ^1H NMR (ppm, $CDCl_3$): three sets of broad peaks at 7.0–8.5. IR ($cm^{-}11$): 1586 (vs), 1565 (vs), 857 (s), 802 (s), 700 (s). GPC: $\bar{M}_n$ = 7590, D = 2.3; T_g = 236 °C. Anal. Calcd for C_6H_3Cl: C, 65.19; H, 2.74; Cl, 32.07. Obsd: C, 69.72; H, 3.36; Cl, 26.65.

Carboxy Polymers 3B and 3J. To 5.56 g (36 mmol) of polymer **3** in 350 mL of THF was added 28 mL (32 mmol) of 1.55 M *n*-BuLi, and the mixture was stirred for 20 min at this temperature. At the same time, anhydrous CO_2 gas was bubbled into 250 mL of THF in a separate flask for 5 min. The lithiated solution was then cannulated into the CO_2 solution, and additional CO_2 was bubbled in for 10 min. The solution was concentrated under reduced pressure, and ether was added to give **3B** as a white powder, yield 5.56 g. ^1H NMR (ppm, D_2O): a broad peak at 7.0–8.5. IR (cm^{-1}): 1700, 1580, 1420, 1370, 1210, 860, 770.

The acid form, **3J**, was prepared by treating 5.0 g of **3B** in 200 mL of water with 0.1 N HCl until a pH of 2.5 was reached. The white gelatinous substance was filtered, resuspended in a 1:1 water and MeOH mixture, and then filtered again. After vacuum drying, 3.33 g of product was obtained. ^1H NMR (ppm, THF-d_8): broad multiplets at 7.0–8.5. IR (cm^{-1}): 1700, 1590, 1440, 1370, 1220, 860, 770.

Hydroxymethyl Polymer 3K. To 24.09 g of **3J** in 600 mL of THF was added 85 mL of borane methylsulfide complex. The mixture was stirred for 1 h at room temperature and then was slowly warmed to gentle reflux for 20 h. After cooling to room temperature, 20 mL of water was carefully added in 1-mL portions, followed by 100 mL more of water. To this was added 100 mL of a saturated $NaHCO_3$ solution. THF was removed under reduced pressure, and the precipitate was filtered, washed with water, and then dried under high vacuum, yield 18.50 g. ^1H NMR (ppm, THF-d_8): 4.2–4.8 (2.2 H), 7.3–8.3 (3 H). Anal. Calcd for C_7H_6O: C, 79.23; H, 5.70. Obsd: C, 70.23; H, 5.74.

Chloromethyl Polymer 3L. To the phosphonium salt adduct prepared from 10.5 of (40 mmol) of triphenylphosphine and 6.00 g (45 mmol) of *N*-chlorosuccinimide in 200 mL of THF was added 3.72 g of **3K** at 0 °C, and the slurry mixture was stirred for 24 h at room temperature. At the end of the reaction, 5 mL of MeOH was added to consume the excess phosphonium salt. THF

was concentrated under reduced pressure, and the polymer was precipitated into methanol. ^{1}H NMR (ppm, THF-d_8): 4.68, 4.77 (br d, 1.3 H), 7.4–8.2 (m, 3 H). Anal. Calcd for C_7H_5Cl: C, 67.49; H, 4.05; Cl, 28.46. Obsd: C, 72.60; H, 4.75; Cl, 22.87.

Methoxymethyl Polymer 3C. To 15.50 g (0.10 mmol) of polymer **3** in 500 mL of THF was added 70 mL (0.11 mol) of 1.6 M *n*-BuLi from a dropping funnel at −78 °C over a period of 1 h, and then the mixture was stirred for 30 min. To the slurry was added 10.0 mL (0.12 mol) of bromomethyl methyl ether in 50 mL of THF. It was then allowed to warm slowly to room temperature, treated with 50 mL of concentrated NH_4OH, and concentrated under reduced pressure. The product was filtered after addition of methanol to form the homogeneous solvent. ^{1}H NMR (ppm, THF-d_8): 3.6 (2.1 H), 4.6, 4.7 (br d, 1.3 H), 7.3–8.3 (3 H). Anal. Calcd for C_8H_8O: C, 79.97; H, 6.71; O, 18.57. Obsd: C, 71.54; H, 5.64.

Formyl Polymer 3E. To 5.56 g (36 mmol) of polymer **3** were added 28 mL (32 mmol) of 1.55 M *n*-BuLi and 10 mL (1.145 mmol) of DMF at −78 °C. The product was precipitated into methanol. ^{1}H NMR (ppm, THF-d_8): 7.0–8.1 (br, 3 H), 9.4–9.8 (br, 0.3 H). IR (cm^{-1}): 1700 (vs), 1590 (s), 1565 (s), 860 (s), 700 (s).

α-Vinylbenzene Polymer 3R via 3F. To the lithiate prepared from 1.55 g (10 mmol) of **3** and 8.0 mL (12.8 mmol) of 1.6 M *n*-BuLi in 50 mL of THF was added 1.56 g (13 mmol) of acetophenone in 10 mL of THF at −78 °C. To this was then added 30 mL of a 30% aqueous NH_4Cl solution at room temperature. THF was removed to give a white precipitate, **3F**. ^{1}H NMR (ppm, $CDCl_3$): 1.95 (br, 2.5 H), 7.0–7.8 (br, 8 H).

Crude **3F** was dissolved in 25 mL of toluene and refluxed with 50 mL of a 30 vol % sulfuric acid solution in water for 20 h. The aqueous layer was discarded, and the polymer was precipitated from the toluene layer into methanol. A total of 500 mg of this crude polymer was passed through a short silica gel column with CH_2Cl_2 as the eluent to give 375 mg of a slightly yellow product, **3R**. ^{1}H NMR (ppm, $CDCl_3$): 5.6 (br, 1.4 H), 7.0–7.8 (br, 8 H). T_g: 96 °C.

Methyl Polymer 3H. To **3A** prepared from 0.21 g (1.4 mmol) of polymer **3** and 1.05 mL (1.6 mmol) of 1.55 M *n*-BuLi in 50 mL of THF was added 0.5 mL of dimethyl sulfate at −78 °C. ^{1}H NMR (ppm, THF-d_8): 1.9–2.1 (2.2 H), 6.9–7.6 (3 H). IR (cm^{-1}): 1580 (vs), 1565 (s), 1380 (s), 850 (vs), 710 (s), 695 (s).

Trimethylsilyl Polymer 3I. To **3A** prepared from 0.21 g (1.4 mmol) of polymer **3** and 1.05 mL (1.6 mmol) of 1.55 M *n*-BuLi in 50 mL of THF was added 0.5 mL of chlorotrimethylsilane at −78 °C. ^{1}H NMR (ppm, THF-d_8): −0.1 to 0.0 (7.8 H), 7.2–7.7 (3 H). IR (cm^{-1}): 2960 (s), 1580 (s), 1360 (s), 1250 (vs), 1140 (s), 860 (s), 840 (vs), 750 (s), 690 (s), 620 (s).

Hydro Polymer 3G. The lithiate **3A** prepared from 6.20 g (40 mmol) of polymer **3** and 28.8 mL (46 mmol) of *n*-BuLi was reacted with 10 mL of methanol in THF at −78 °C. ^{1}H NMR (ppm, THF-d_8): broad multiplets at 6.8–7.6. IR (cm^{-1}): 1590 (vs), 1560 (s), 1470 (s), 867 (s), 779 (vs), 766 (vs), 70 (vs).

***p*-Methoxyphenyl Polymer 3O.** To 1.50 g (61.7 mmol) of Mg in 10 mL of ether was added 11.70 g (50 mmol) of *p*-iodoanisole in 100 mL of ether, and then the mixture was refluxed for 2 h. This solution was cannulated into a THF solution containing 2.78 g (17.9 mmol) of polymer **3** and 50 mg of $Ni(PPh_3)_2Cl_2$. The mixture was refluxed overnight, and then 30 mL of water was added carefully. The polymer was precipitated by concentrating the solution to about 50 mL and then adding 150 mL of methanol. The precipitate was filtered and washed with 3 N HCl, water, methanol, and ether, yield 2.52 g. ^{1}H NMR ($CDCl_3$, ppm): 3.7 (1.5 H), 6.9 (1.1 H), 7.5–8.2 (3 H). IR (cm^{-1}): 1610, 1585, 1512 (vs), 1290, 1250, 1180, 1030 (ether), 828, 710, 575.

***p*-Hydroxyphenyl Polymer 3P.** To 1.0 g of polymer **3O** in 20 mL of CH_2Cl_2 was added 0.5 mL of BBr_3 at −78 °C. A dark brown precipitate was found as BBr_3 was added. The solution was warmed to room temperature. The mixture was stirred for 24 h, and then an aqueous $NaHCO_3$ solution was added, which removed the coloration. The white precipitate was collected and washed with water. This polymer is insoluble in chlorinated solvents but soluble in polar solvents such as DMF. ^{1}H NMR (DMF-d_7, ppm): 6.9 (1.1 H), 7.5–8.2 (3 H). IR (cm^{-1}): 1610, 1585, 1512 (vs), 1260, 1170, 830, 705, 575.

3-Hydroxy-3-methylbutynyl Polymer 3Q. To 15.50 g (0.1 mol) of polymer **3** in 500 mL of degassed THF were added 10.7 mL (0.11 mol) of 2-methyl-3-butyn-2-ol, 244 mg (1.34 mmol) of copper(II) acetate, 1.83 g (6.98 mmol) of triphenylphosphine, 108 mg (0.61 mmol) of $PdCl_2$, and 41.8 mL (300 mmol) of triethylamine. The mixture was then refluxed for 24 h, during which a small amount of precipitate formed. After cooling, the precipitate was filtered off, and the filtrate was concentrated to about 50 mL. The product was precipitated into methanol. ^{1}H NMR (ppm, THF-d_8): 1.5 (1.9 H), 2.4 (0.3 H), 7.3–8.2 (3 H).

Ethynyl Polymer 3N. To a solution of 5.46 g (3.5 mmol) of **3Q** in 150 mL of THF was added 4.0 g of powdered KOH. The mixture was then refluxed for 1 h, after which the solvent was distilled off to leave about 20 mL, and an additional 150 mL of THF was added. This process was repeated two more times. Finally the solution was concentrated to 20 mL, and the insoluble material was filtered off. The polymer was precipitated into 100 mL of MeOH to give 3.57 g of product. ^{1}H NMR (ppm, THF-d_8): 3.26 (0.4 H), 7.5–8.5 (3 H). IR (cm^{-1}): 3300 (w), 1585 (vs), 1560 (s), 1375 (s), 860 (vs), 700 (s), 625 (s).

Alkylsilylated Polymers. Typically 1.03 g (6.7 mmol) of polymer **3** was treated with 5.5 mL (8.8 mmol) of 1.6 M *n*-BuLi followed by 10 mmol of chlorosilane in 20 mL of THF at −78 °C. See Table V for percent substitution as determined by ^{1}H NMR.

Octyldimethylsilyl Polymer 5A. ^{1}H NMR (ppm, THF-d_8): 0.29, 0.33 (5.2 H), 0.83 (4.3 H), 1.15–1.5 (8.6 H), 7.3–8.2 (3 H). IR (cm^{-1}): 1590, 1480 (CH_2), 1290 (CH_2), 840, 800, 740.

Octadecyldimethylsilyl Polymer 5B. ^{1}H NMR (ppm, THF-d_8): 0.3, 0.35 (3.3 H), 0.5–0.6 (2.7 H), 0.85–0.95 (7.1 H), 7.4–8.2 (3 H). IR (cm^{-1}): 1590, 1480 (CH_2), 1290 (CH_2), 840, 800, 740.

Triacontyldimethylsilyl Polymer 5C. ^{1}H NMR (ppm, THF-d_8): 0.2–0.4, 0.5–0.6, 0.8–0.95, 7.4–8.2 (overlapping of peaks with excess chlorosilane made the estimate of the integration impossible). IR (cm^{-1}): 1590, 1480 (CH_2), 1290 (CH_2), 840, 800, 740.

Polymerization of Propiolactone. To 63.0 mg (0.5 mmol of carboxylate) of polymer **3B** in 200 mL of toluene was added 245.1 mg (0.5 mmol) of tetraheptylammonium bromide. The mixture was stirred for 1 h at room temperature to give a cloudy solution. To this was added 6.41 g (50 mmol) of 2-methyl-2-propyl 3-propiolactone via a syringe at room temperature. This mixture was heated to reflux for 2 h. The solvent was removed to dryness, and 6.90 g of a waxy polymer was obtained. GPC: $\bar{M}_n$ = 36 300, D = 1.2.

Polymerization of Propiolactone. To 667 mg (0.05 mmol of carboxylate) of the above polymer in 150 mL of THF was added 5.77 g (45 mmol) of 2-methyl-2-propyl-3-propiolactone, then the mixture was refluxed for 2 h. The polymer was precipitated into methanol to give 6.30 g of product. GPC of this polymer showed there was about 20% unreacted polymer of $\bar{M}_n$ = 48 100. The majority of the polymer has $\bar{M}_n$ = 411 000 and D = 1.2 by DPC.

Reaction of Polymer 3R with *sec*-BuLi. To 25.5 mg (0.1 mmol) of **3R**, which was passed through a silica gel column with CH_2Cl_2 and dried at 100 °C under high vacuum, in 40 mL of THF was added *sec*-BuLi at −30 °C, with a burgundy color forming as each drop was added but immediately disappearing. A total of 434 mL (0.7 mmol) of *sec*-BuLi was added to obtain a sustaining burgundy color. To this was added 1.07 mL (10 mmol) of methyl methacrylate, with color fading to a hazy yellow. This solution was chilled immediately to −78 °C and stirred for 2 h, and then methanol was added. After distilling the solvent and drying under high vacuum, 0.25 g of brittle PMMA was obtained. GPC: $\bar{M}_n$ = 118 000, D = 16.

Polymerization of MMA. Activated Mg was prepared by stirring 1.03 g of $MgBr_2$ etherate (4.0 mmol), 69.4 mg of Li ribbon (10 mmol), and 1.782 g of anthracene (10 mmol) in 50 mL of THF at room temperature for 2 h. To this was added 623 mg (5 mmol) of polymer **3L**. The mixture was stirred overnight. This solution was chilled to −78 °C, and 3.0 mL of methacrylate (28 mmol) was added in two portions. After 2.5 h, the reaction was terminated by addition of 3 mL of methanol. Polymer was precipitated by addition of hexane. It was dissolved in THF and reprecipitated into methanol. GPC: $\bar{M}_n$ = 6760, D = 4.5.

Thermolysis of Polymer 3. A total of 1.002 g of polymer 3 was heated at 600 °C in a borosilicate pyrolysis tube purged with a stream of nitrogen (ca. 1 cm^3/min). The other end of the tube was connected to Teflon tubing, which in turn was immersed into 10 mL of 1 N NaOH solution to trap the evolving HBr. The pyrolysis was continued for 4 h. The amount of liberated HBr was calculated by back-titration of excess NaOH with 0.1 N HCl. A total of 94% of theoretical HBr was trapped, and 467 mg of carbon (100%) was recovered.

Solution Blending of Polymer 3 with Polystyrene. Typically 2.50 g of polymer 3 and 47.50 g of uninhibited polystyrene were dissolved in 200 mL of uninhibited THF at 75 °C. The solution was poured on aluminum pans and air-dried. Turbid polymers were crushed and then dried under high vacuum at 70 °C.

Melt Blending of Polymer 2 with Polystyrene. To 40.0 g of molten polystyrene at 150 °C in a Brabender mixer fitted with a twin screw mixer (C. W. Brabender Instruments, Inc., South Hackensack, NJ) was added 2.00 g of polymer 3 as a powder under nitrogen atmosphere.

Acknowledgment. Assistance in the laboratory by S. Orescan and S. Bair is greatly appreciated.

References and Notes

(1) Raff, R. A. V. In *Ethylene and Its Industrial Derivatives*; Miller, S. A., Ed.; Ernest Benn Limited: London, 1969; Chapter 9.1.

(2) See, for example: (a) Zubay, G. *Biochemistry*; Addison-Wesley Publishing Company: Reading, MA, 1983; Chapters 1 and 12. (b) Clark, A. H.; Ross-Murphy, S. B. *Adv. Polym. Sci.* **1987**, *83*, 57.

(3) See: (a) Jacobson, R. A. *J. Am. Chem. Soc.* **1932**, *54*, 1513. (b) Hunter, W. H.; Woollett, G. H. *J. Am. Chem. Soc.* **1921**, *43*, 135.

(4) (a) Newkome, G. R.; Baker, G. R.; Saunders, M. J.; Russo, P. S.; Gupta, V.; Yao, Z.; Miller, J. E.; Bouillion, K. *J. Chem. Soc., Chem. Commun.* **1986**, 752. (b) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849.

(5) (a) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592. (b) Tomalia, D. A.; Berry, W.; Hall, M.; Hedstrand, D. M. *Macromolecules* **1987**, *20*, 1164.

(6) (a) Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155. (b) Mendenhall, G. D.; Liang, S. X.; Chen, E. H. T. *J. Org. Chem.* **1990**, *55*, 3697.

(7) (a) Newkome, G. R.; Baker, G. R.; Arai, S.; Saunders, M. J.; Russo, P. S.; Theriot, K. J.; Moorefield, C. N.; Rogers, L. E.; Miller, J. E.; Lieux, T. R.; Murray, M. E.; Phillips, B.; Pascal, L. *J. Am. Chem. Soc.* **1990**, *112*, 8458. (b) Newkome, G. R.; Lin, X. *Macromolecules* **1991**, *24*, 1443. (c) Newkome, G. R.; Nayak, A.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. *J. Org. Chem.* **1992**, *57*, 358.

(8) (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138 and references therein. (b) Kolc, J.; Lukasavage, W. J. U.S. Patent 4,289,872, 1981. (c) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J. (Tokyo)* **1985**, *17*, 117. (d) Tomalia, D. A.; Dewald, J. R. U.S. Patent 4,507,466, 1985. (e) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466. (f) Tomalia, D. A.; Dewald, J. R. U.S. Patent 4,587,329, 1986. (g) Padias, A. B.; Hall, H. K., Jr.; Tomalia, D. A.; McConnell, J. R. *J. Org. Chem.* **1987**, *52*, 5305. (h) Tamalia, D. A.; Berry, V.; Hall, M.; Hedstrand, D. M. *Macromolecules* **1987**, *20*, 1164. (i) Tomalia, D. A.; Hall, M.; Hedstrand, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 1601. (j) Naylor, A. M.; Goddard, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339. (k) Tomalia, D. A.; Hedstrand, D. M.; Ferrito, M. S. *Macromolecules* **1991**, *24*, 1435. (l) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043. (m) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077. (n) Imai, Y. *J. Macromol. Sci., Chem.* **1991**, *A28*, 1115. (o) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1991**, *24*, 3469. (p) Gauthier, M.; Möller, M. *Macromolecules* **1991**, *24*, 4548. (q) Rengan, K.; Engel, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1084. (r) Rengan, K.; Engel, R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 987.

(9) (a) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (c) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. (d) Hawker, C. J.; Fréchet, J. M. J. *Macromolecules* **1990**, *23*, 4726. (e) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1059. (f) Miller, T. M.; Neeman, T. X. *Chem. Mater.* **1990**, *2*, 346. (g) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.

(10) (a) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718. (b) Flory, P. J. *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, NY, 1953; Chapter 9.

(11) (a) Baker, A. S.; John, D. U.S. Patent 3,669,939, 1972. (b) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.

(12) Kircheldorf, H. R.; Zang, Q.-Z.; Schwarz, G. *Polymer* **1982**, *23*, 1821.

(13) (a) Maciejewski, M. *J. Macromol. Sci., Chem.* **1982**, *A17*, 689–703. (b) Klein, D. J. *J. Chem. Phys.* **1981**, *75*, 5186. (c) de Gennes, P.-G.; Hervet, H. *J. Phys. (Paris)* **1983**, *44*, L351. (d) Naylor, A. M.; Goddard, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339. (e) Aharoni, S. M.; Crosby, C. R.; III; Walsh, E. K. *macromolecules* **1982**, *15*, 1093. (f) Farin, D.; Avnir, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *10*, 1379. (g) Lescanec, R. L.; Muthukumar, M. *Macromolecules* **1990**, *23*, 2280.

(14) This work has been presented previously in several conferences. See: (a) Kim, Y. H.; Webster, O. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 310. (b) Kim, Y. H. U.S. Patent 4,857,630, 1989. (c) Kim, Y. H.; Webster, O. W. *Pacific Polym. Prepr.* **1989**, *1*, 335.

(15) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

(16) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091.

(17) For example, see: Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551.

(18) Chen. G. J.; Tamborski, C. *J. Organomet. Chem.* **1982**, *251*, 149.

(19) Wrobel, D.; Wannagat, U. *J. Organomet. Chem.* **1982**, *225*, 203.

(20) (a) Lai, Y.-H. *Synthesis* **1981**, 585. (b) Bönnemann, H.; Bogsanovic, B.; Brinkmann, R.; He, D.-W. *Angew. Chem., Int. Ed. Engl.* **1983**, *11*, 307.

(21) Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237.

(22) Mantell, C. L. In *Carbon and Graphite Handbook*; Interscience Publishers: New York, 1968; Chapter 2.

(23) Wallace, J. S.; Arnold, F. E.; Feld, W. A. In *Reactive Oligomers*; Harris, F. W., Spinelli, H. J., Eds.; American Chemical Society: Washington, DC, 1985; p 17.

(24) (a) Tung, L. H.; Lo, G. Y.-S.; Rakshy, J. W.; Beyer, E. U.S. Patent 4,200,718, U.S. Patent 4,201,729, U.S. Patent 4,205,016, 1980. (b) Quirk, R. P.; Chen, W. C. *Macromol. Chem.* **1982**, *183*, 2071. (c) Broske, A. D.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (1), 241.

(25) (a) Eschwey, H.; Hallensleben, M.; Burchard, W. *Makromol. Chem.* **1973**, *173*, 235. (b) Lutz, P.; Rempp, P. *Makromol. Chem.* **1988**, *189*, 1051.

(26) (a) Worsfold, D. J.; Zilliox, J.-G.; Rempp, P. *Can. J. Chem.* **1969**, *47*, 3379. (b) Rempp, P.; Franta, E. *Pure Appl. Chem.* **1972**, *30*, 229. (c) Spinelli, H. J. In *Progress in Pacific Polymer Science Proceedings of the Pacific Polymer Conference*; Anderson, B. C., Imanishi, Y., Eds.; Springer: Berlin, 1991; p 249.

(27) (a) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11*, 668. (b) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1980**, *13*, 191. (c) Quirk, R. P.; Lee, B.; Schock, L. E. *Makromol. Chem., Macromol. Symp.* **1992**, *53*, 201.

(28) Fujimoto, T.; Tani, S.; Takano, K.; Ogata, M.; Nagasawa, M. *Macromolecules* **1978**, *11*, 673.

(29) Huber, K.; Burchard, W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 541.

(30) (a) Johns, D. B.; Lenz, R. W. In *Ring Opening Polymerization*; Ivin, K. J.; Saegusa, T., Eds.; Elsevier: Essex, U.K., 1984; Chapter 7. (b) Cornibert, J.; Marchessault, R. H.; Allegrezza, A. E.; Lenz, R. W. *Macromolecules* **1973**, *6*, 676. (c) D'hondt, C. G.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 261.

(31) For a stable polyanion of a highly branched compound, see: Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5889.

(32) Ferguson, R. C.; Ovenall, D. W. *Macromolecules* **1987**, *20*, 1245.

(33) Dicker, I.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034.

Registry No. **1a**, 117695-55-3; **1a** (homopolymer), 117695-56-4; **1b** (homopolymer), 143172-68-3; **2** (homopolymer), 125128-37-2; PMMA, 9011-14-7; PS, 9003-53-6; Me_3B, 121-43-7; Mg, 7439-95-4; tetraheptylammonium, 4368-51-8; 2-methyl-2-propyl-3-propiolactone (homopolymer), 29716-97-0; 2-methyl-2-propyl-3-propiolactone (SRU), 25265-42-3; 1,3,5-tribromobenzene, 626-39-1.