Well-Defined, Model Long Chain Branched Polyethylene. 1. Synthesis and Characterization

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ABSTRACT: We describe the synthesis and characterization of a number of polymers with well-defined structures that serve as models for polyethylene with long chain branching. All of them have been made by using anionic polymerization techniques and controlled chlorosilane chemistry to give nearly monodisperse polybutadienes with precise control of the number, length, and placement of long ($\bar{M}_w$ > 1500 g/mol) branches on each chain. This was followed by hydrogenation to give saturated polymers with the same well-defined long chain branching and the local structure of a typical linear low-density polyethylene. That is, both the backbones and the long branches had 17−25 ethyl branches per 1000 total carbons. Among the structures made were some with no long branches ("linears"), some with a single long branch ("stars"), others with exactly two branch points (the α−ω type, "H's", "super-H's", and "pom-poms"), and some with several long branches randomly distributed along the backbone ("combs"). Essentially all types of branching from a linear backbone can be made by the techniques described herein. While linear and symmetrical star models of polyethylene have been made previously, the other structures are the first examples of polyethylene models with multiple branches and precise control of the molecular architecture. We use the results given here to discuss how long chain branching can be detected in polyethylene. We also show how the branching structure controls chain dimensions. The Zimm−Stockmayer model works well to describe the sizes of the lightly branched molecules, but its predictions are too small for those with many long branches. This is presumably due to crowding of the branches. The rheological properties of these polymers will be described in subsequent publications.

Introduction

The value of long chain branching (LCB) in polyethylene (PE) has long been known. The first form of PE to be produced was low-density PE (LDPE),[1] which is highly branched. Once linear versions of PE became available (high-density PE, or HDPE,[2] and linear low-density PE, or LLDPE[3]), it became clear that while most of the physical properties (e.g., toughness) of the linear polymers were superior, LDPE was much easier to process in many applications, for instance, film blowing.[4−6] Here ease of processing refers to the amount of energy or power needed to fabricate articles from the PE resins, which can be measured by such quantities as motor load in an extruder. Examples of the mechanical properties of interest are the tear and puncture resistance of films and the toughness and stiffness of molded articles. Thus, although many believed at the time of the introduction of LLDPE that because of its superior properties it would replace LDPE in film applications, LDPE still has a large share of the market due to its greater processability.

The rheological behavior that leads to the enhanced processability of LDPE is attributed to the presence of long branches.[5,7−9] What is meant by long chain branching, that is, how long a branch needs to be to be counted as "long"? The clearest definition of this is that to be long a branch needs to have a molecular weight at least greater than the entanglement molecular weight, M_e. This is defined in terms of the plateau modulus, G_N^0, which can be directly measured from the linear viscoelasticity of the polymer.[10] For polyethylene, M_e is around 1000 g/mol, so branches need to be at least this long to be counted as long.

One of the difficulties in making improvements on the currently available forms of LDPE is in determining the nature of the long chain branching.[8] LDPE is believed to have a highly branched structure. That is, it has a central backbone from which are appended many branches, which themselves have branches, and those branches also have branches, etc. The lengths of all of these branches are broadly distributed, and so it becomes very difficult to determine all of the branch lengths and spacings between them that define the structure of a single molecule. Several chemical mechanisms are thought to be responsible for this extensive branching, which also makes it difficult to understand.[8,11] Until recently, no other commercial means to synthesize highly branched PEs has been available. There is now some evidence that LCB can be produced by metallocene catalysts.[12,13]

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The characterization of LCB in polymers is in general quite difficult. Because long branches are defined as being at least as long as the entanglement molecular weight of the polymer, they need to be at least 70 methylene units long for polyethylene and generally longer. This means that the branch point will be difficult to detect by spectroscopic means. One needs to look for at most one bond in 100 and usually more like one in 1000. Such spectroscopy can be useful, but only in certain cases.[11,14] Another way to detect the presence of LCB is to study the dimensions of the polymer molecules.[15−17] A branched chain will be more compact than a linear of the same molecular weight, and its dimension will decrease as the degree of branching increases at constant molecular weight. However, the use of this technique requires the absolute determination of both molecular size and molecular weight, which can be challenging. In this paper we will discuss this approach in detail for the model polyethylenes we have made. While the predictions of several models for the dimensions of branched polymers are shown to work well at low levels of branching, we also show that knowledge of the chain dimensions alone does not allow one to determine the nature of the branching structure. The other method to characterize LCB is by melt and solution rheology. The flow of LCB polymers is both quantitatively and qualitatively different from that of linear polymers (which is of course why they are of practical interest), and so rheology can be used to detect the presence of LCB.[4−6,8,18−21] The difficulty here is the indirectness of these rheological methods. This leads to the need to have some standard polymers for which the nature of the LCB has been well determined by other means and from which the basic "rules of rheology" can be written. The rheological behavior of the model polymers will be discussed in subsequent publications.

All of the above shows the utility of producing model polyolefins with controlled LCB. In the work described herein we have taken advantage of the ability to produce saturated hydrocarbon polymers with precisely controlled branching structures through the saturation of anionically synthesized polydienes.[22] Much work has been done to develop living anionic polymerizations, which means that chains propagate without significant transfer or termination reactions.[23] The result is the ability to produce nearly monodisperse homopolymers as well as block copolymers.[24] Many branched structures such as stars[25,26] and combs[27,28] have been produced by anionic techniques as well. This synthetic scheme has been extensively used with monomers such as styrene and various dienes and can be used with several others as well, but it cannot be used for olefins. However, Graessley and co-workers have discovered catalysts that can be used to saturate various polydienes to give structures that are identical to those of polyolefins.[29] These techniques can completely saturate the polydiene without side reactions that might degrade or cross-link the molecules. The controlled molecular weight and structure are thus preserved. For example, a unit of butadiene that has been incorporated in a 1,4 manner into the polybutadiene chain will have the structure of two ethylenes (four methylenes) after saturation, and those that go in as 1,2 will be identical to one butene unit. So the saturated versions of polybutadienes of a range of microstructures will be the same as a series of ethylene−butene copolymers. Similarly saturated polyisoprenes resemble an alternating ethylene−propylene copolymer, and other polydienes can give the structures of atactic polypropylene and other polyolefins upon saturation.[30] A wide variety of saturated hydrocarbon polymers can be made in this way.

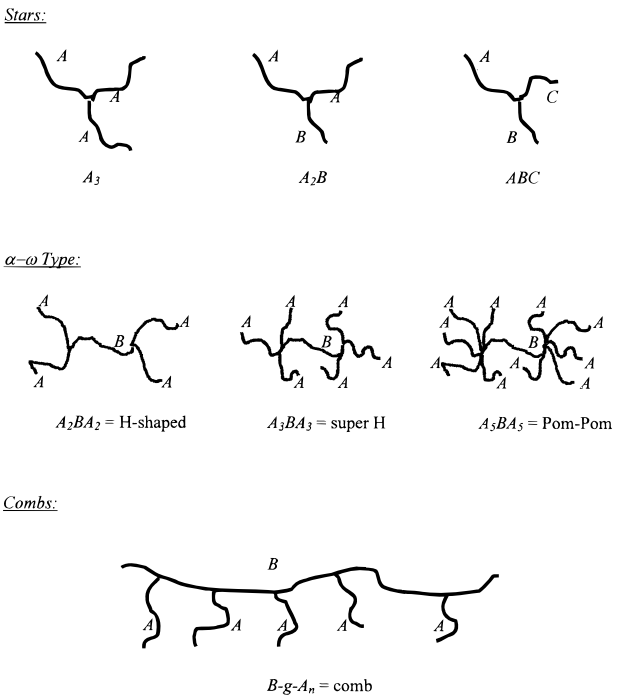

Figure 1. Schematic of LCB structures.

In this paper we describe the application of well-developed strategies for the synthesis of model nonlinear co- and terpolymers to prepare branched polybutadienes and by hydrogenation the corresponding polyethylenes. The range of structures is shown in Figure 1. For nearly all of the polymers described herein, we have attempted to keep a constant backbone molecular weight of 100 000 g/mol. It should be noticed here that the 1,2 content of the different polybutadienes, determined by NMR, varies from 7 to 11%, meaning that the polyethylenes will have 7 to 11 wt % butene monomeric units randomly distributed along the chain (corresponding to 18 to 28 ethyl branches per 1000 total carbons). While the linear and symmetric star polyethylenes have been synthesized and examined previously,[20] the combs, α−ω types, and asymmetric stars are new. The combined characterization results show these to be well-defined models for branched polyethylene.

Experimental Section

Synthesis. *Butadiene Polymerizations.* The purification of butadiene, benzene, and cyclohexane to the standards required for anionic polymerization has been described elsewhere.[23,31] The liquid linking agents methyltrichlorosilane and tetrachlorosilane were purified by fractional distillation on a vacuum line. The solid linking agent 1,2-bis(trichlorosilyl)ethane was purified by several crystallizations from *n*-hexane under vacuum. The T_m of the crystallized compound was 25 °C in agreement with the value reported in the literature.[32] The purified compounds were diluted in benzene and subdivided into tubes carrying break-seals. The silicon−chlorine bond concentration of the chlorosilanes was determined by acid−base titration. *n*-Butyllithium (*n*-BuLi, Aldrich) and *sec*-BuLi, prepared in vacuo from *sec*-butyl chloride and a lithium dispersion, were the initiators for the polymerizations leading to monofunctional living polybutadienes. The *n*-BuLi was used to prepare the linear polybutadienes, whereas the *sec*-BuLi was the initiator for the arms of the stars, combs, and α−ω

types and for the backbones of the combs. 1,3-Bis(1-phenyl-3-methyl-pentylidenelithium)benzene (DLI) was the initiator for α−ω difunctional living polybutadiene connectors. Details for the preparation of this benzene soluble initiator were given in a previous paper.[33]

The polymerizations were carried out in classic secondary reactors,[34,35] while the linking reactions were performed in main reactors similar to those described previously.[36] The main reactors were equipped with tubes for sample removal at any stage of the synthesis.

All glassware was evacuated, washed with *n*-BuLi, and rinsed by distilling benzene from a reservoir. Benzene was finally distilled into the reaction vessel, and the reservoir with the residual *n*-BuLi and its undesirable products with the impurities was sealed off. Benzene or cyclohexane was the solvent for all polymerizations of butadiene in order to obtain high 1,4-polybutadiene (PB).

In the case of the branched PB, the final reaction product was separated from the unreacted precursors by adding the nonsolvent methanol to the polymer solution (0.5−1% w/v) in toluene. The above procedure was repeated until complete elimination of the precursors. The fractionation was monitored by size exclusion chromatography. The fractionated polymer was dried to constant weight and stored under vacuum or in a freezer.

Hydrogenation. The polybutadienes were saturated catalytically. Typically the polybutadiene was dissolved in cyclohexane and reacted with H_2 gas at 90 °C and 700 psi in the presence of a catalyst made by supporting Pd on $CaCO_3$. The mass of catalyst used was equal to that of the polymer. For some of the highly branched polybutadienes (especially the comb and α−ω types), the so-called Wilkinson's catalyst was used. In these cases 0.2 g of triphenyl phosphate and 0.0366 g of tris-(triphenylphosphine)rhodium(I) chloride were added to the reaction for every gram of polymer, in addition to some amount of the Pd catalyst. The reaction was allowed to proceed until the H_2 pressure stopped dropping, or generally about 24 h. The polymer solution was then filtered to remove the catalyst residues. The saturation of the polymer was seen to be greater than 99.5% by ^{1}H NMR. The result in each case was a model for polyethylene.

Nomenclature. In this paper, we use names for the polymers that indicate their architecture and molecular weight. We use PBLA for a linear polybutadiene with $\bar{M}_w$ = A × 10^3 g/mol (for example, PBL100 for one with $\bar{M}_w$ = 100 000 g/mol). Similarly for the stars we use $PBS(A)_2(B)$ for a star with two arms of A × 10^3 g/mol and one of B × 10^3 g/mol; a corresponding nomenclature is used for other types of stars. For the H's, super-H's, and pom-poms we have $PBH(A)_2(B)(A)_2$, $PBSH(A)_3(B)(A)_3$, and $PBPP(A)_5(B)(A)_5$, with a similar meaning for the molecular weight designations. Finally we use PBC(B)-*g*-$(A)_n$ for a comb with a backbone of $\bar{M}_w$ = B × 10^3 g/mol and *n* arms of $\bar{M}_w$ = A × 10^3 g/mol. The saturated versions of these polymers are models for polyethylene, and so we give them the corresponding names: PELA, $PES(A)_2(B)$, $PEH(A)_2(B)(A)_2$, $PESH(A)_3(B)(A)_3$, $PEPP(A)_5(B)(A)_5$, and PEC(B)-*g*-$(A)_n$.

Characterization. *^{1}H NMR Analysis.* The PBs produced by *n*-BuLi, *s*-BuLi, and DLI initiators were analyzed by ^{1}H NMR spectroscopy using a Varian Unity+ 500 mHz NMR or a Bruker AC200 in $CDCl_3$ at 25−30 °C. The region of the spectrum from 4.8 to 6.0 ppm was used to determine the amount of 1,2-polybutadiene in the samples. The values obtained for the 1,2 content were always between 7 and 11% (see Tables 1−6). Proton NMR was also used to determine the extent of hydrogenation of the polybutadienes. Dry, hydrogenated samples were dissolved in deuterated 1,2-dichlorobenzene, and the NMR was run at 90 °C. We again analyzed the 4.8−6.0 ppm shift region of the proton spectrum to determine whether there was any residual unsaturation remaining in the samples.

^{13}C and ^{1}H NMR Analysis for Branching. Because all the branch points have been introduced through the use of silicon chloride linking agents, it is possible to determine the level of LCB from NMR. In the ^{13}C NMR, the resonances used to determine branch content are those between −3.0 and −4.0 ppm and 19.0 and 19.5 ppm. On the basis of model compounds, chemical shift calculations, and ^{13}C NMR multiplicity data both signal regions are assigned to methyl groups. Those between −3.0 and −4.0 ppm are assigned to the methyls attached to the silicon linker. This chemical shift position suggests that these methyls were not in a chlorodimethylalkylsilane but in a structure having the silicon bonded to four alkyl groups. The resonance between 19.0 and 19.5 ppm was due to the methyl adjacent to the methine in a *sec*-butyl end group ($CH_3-CH-CH_2-CH_3$). It is assumed that this end group was the result of the initiator used in the polybutadiene synthesis. For the ^{1}H NMR, the $Si(CH_3)_2$ concentration was determined from the intensity between −0.2 and 0.2 ppm, while the number of *sec*-butyl groups was found from the resonance between 0.9 and 1.0 ppm. The ^{1}H NMR resonances are illustrated in Figure 2 for PBC(98)-*g*-$(5)_{27}$.

The concentrations of dimethylsilyl groups and *sec*-butyl end groups per 10 000 carbons were calculated by ratioing the signal intensity from these two methyl types to the total carbon intensity. Combining this information with molecular weights from SEC data allowed an estimation of the number of branches per molecule. These calculations were based on the assumptions that each polybutadiene molecule had one *sec*-butyl end group and that only the lower molecular weight branch contributed to the intensity in the end group spectral region. This method thus provides an independent way to check on the number of branches per chain.

SEC of Polybutadienes. Size exclusion chromatography (SEC) of the polybutadiene precursors was performed with the following instrumentation. A Waters model 510 differential pump was combined with a Waters model 470 differential refractometer. A set of three Phenomenex columns having a continuous porosity from 50 to 10^6 Å was also used. The solvent was THF, and the chromatography was performed at 30 °C.

LALLS of Polybutadienes. The weight-average molecular weight ($\bar{M}_w$) of the PB was measured with a Chromatix KMX-6 fixed low-angle laser light scattering (LALLS) equipped with a He−Ne laser operating at 633 nm. Cyclohexane, purified over CaH_2, was the solvent at 25 °C. The refractive index increment (dn/dc) in cyclohexane at 25 °C was determined for each PB with a Chromatix-16 refractometer, operating at 633 nm and calibrated with aqueous NaCl solutions. The dn/dc values obtained varied between 0.109 and 0.110 ± 0.002 mL/g. The $\bar{M}_w$ values were obtained from the $((Kc/\Delta R_\theta))^{1/2}$ vs c plots (where ΔR_θ is the excess Rayleigh ratio, K is a combination of known optical constants, and c is the polymer concentration) in order to minimize the curvature due to the third virial coefficient. In all cases the correlation coefficient was better than 0.98.

SEC-RALLS of Polybutadienes. The molecular weights ($\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_p$) were determined using TriSEC SEC 3.0 triple detector software from Viscotek. Data were acquired with an SEC setup consisting of a Waters Alliance 2690 solvent delivery system, seven Waters Styragel HR columns (HR 0.5 to HR 6), a Waters 410 refractive index detector, and a Viscotek T-60 dual detector (viscometer and right angle laser light scattering). The run conditions were 1.0 mL/min flow of tetrahydrofuran (THF) (EM Scientific; prefiltered to 0.2 μm) at 32 °C.

The standard used to calibrate the instrument for triple detector analysis is a polystyrene sample with a stated peak molecular weight of 105 000 g/mol and a polydispersity of 1.02 (American Polymer Standards Corp.). We used 0.185 for the dn/dc value and 0.481 dL/g as $[\eta]$ for this standard. Occasionally, low molecular weight (<10 000 g/mol) materials were analyzed by a universal calibration method. The method was created from a series of narrow PS standards from Polymer Labs and American Polymer Standards Corp., with molecular weights from 700 to 370 000 g/mol.

Osmometry of Polybutadienes. The number-average molecular weight ($\bar{M}_n$) for PB was determined with a Wescan model 230 membrane osmometer (MO) at 34 °C and in a few cases ($\bar{M}_n$ < 10 000) with a Wescan model 233 vapor pressure osmometer (VPO) at 50 °C. Toluene distilled over CaH_2 was the solvent. The $\bar{M}_n$ values from MO were obtained from the

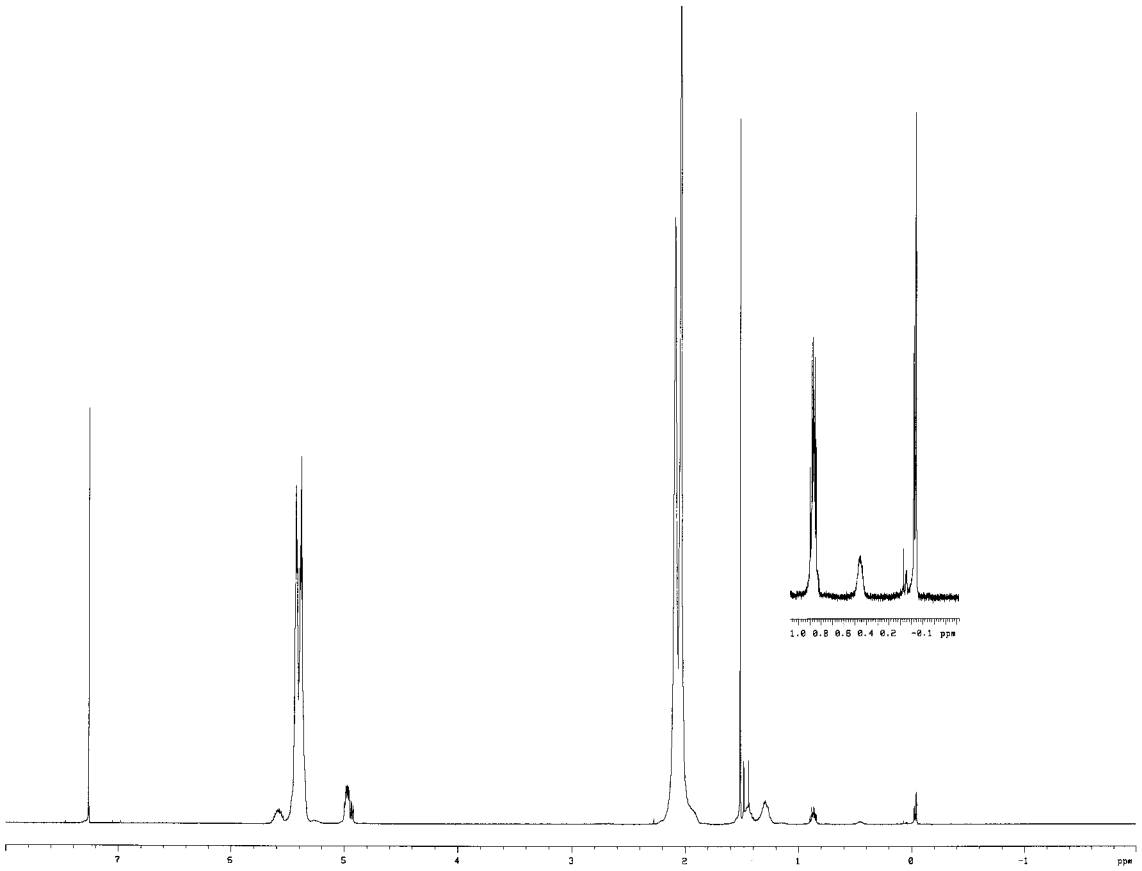

Figure 2. ^{1}H NMR trace for comb PBC(98)-*g*-(5)$_{27}$; *sec*-butyl resonance at 0.9−1.0 ppm, and Si(CH$_3$)$_2$ resonance at −0.2 to 0.2 ppm.

corresponding $((\pi/c))^{1/2}$ vs c plots, where π is the osmotic pressure. In the case of VPO the $\bar{M}_n$ values were obtained from the $(\Delta R/c)$ vs c plots (ΔR is the change in the resistance of the transistor), using the relation $((\Delta R/c))_{c\to 0} = ((K_v/\bar{M}_w)$, where K_v is the calibration constant. In all cases the correlation coefficient was better than 0.98.

SEC-MALLS and SEC-VIS of Polyethylenes. Two separate experimental setups were used to measure the radius of gyration and intrinsic viscosity. The setup used to measure the polymer molecular weight and radius of gyration was composed of a Wyatt Technology Dawn DSP multiangle laser light scattering (MALLS) detector connected to a Waters 150C size exclusion chromatography (SEC) instrument. The setup used to measure the polymer intrinsic viscosity was composed of a second Waters 150C instrument which contained an online Viscotek high-temperature viscometer and a Precision Detector two angle light scattering detector. The SEC run conditions for both setups were 0.5 mL/min flow of 1,2,4-trichlorobenzene (TCB) at 135 °C. The polymer concentrations varied with polymer type. The columns used were three Polymer Laboratory mixed B (10 μm) type columns. The injection volume was 300 μL.

The Wyatt Technology MALLS detector contained a 30 mW argon ion laser (488 nm) and an array of photodiodes. The instrument was calibrated using the Rayleigh ratio for TCB at 135 °C. The photodetectors were normalized with NBS1482, which is an NBS polyethylene standard with a stated weight-average molecular weight of 13 600 g/mol and polydispersity of ∼1.2. We used a value of −0.1074 for dn/dc. This value was based on the literature value of dn/dc = −0.109 for homopolyethylene at 488 nm[37] and the dependence of dn/dc on butene content as measured from the area response of a Waters differential refractometer for a series of ethylene−butene copolymers ranging from 0 to 18 wt % butene.

The differential viscometer was a four capillary type made by Viscotek. It was calibrated with a series of polymers of known intrinsic viscosities (a combination of NBS polyethylenes and narrow polystyrene standards). The viscometer was positioned behind the LS detector but before the differential refractometer (series configuration). The light scattering detector was from Precision Detector that used a 690 nm diode laser and had two detection angles (15° and 90°). It was calibrated by running a series of polymers of known molecular weights (same ones as for the viscometer). Only the 15° angle was used in data analysis. The data analysis was done with in-house-written software. We used a value of dn/dc = −0.1025. This value was determined in the manner described above, except that we used dn/dc = −0.104 for λ = 690 nm for the homopolyethylene case.[38]

Results and Discussion

Synthesis of Linear Polyethylene Models. A number of linear polyethylenes have been made by the saturation of linear polybutadienes, and these are listed in Table 1. They were all prepared by anionic synthesis on a vacuum line.[23] This was done in cyclohexane at ∼0 °C, with *n*-butyllithium as initiator. These were then saturated under H_2 pressure using a Pd/$CaCO_3$ catalyst.[29]

$$\text{butadiene} \xrightarrow[\text{cyclohexane}]{n\text{-BuLi}} \text{PBLi}$$

$$\text{PBLi} + CH_3OH \rightarrow \text{PB} + CH_3OLi$$

$$\text{PB} \xrightarrow[\text{Pd/CaCO}_3]{H_2} \text{linear polyethylene}$$

This technique was used to make polymers with molecular weights from 19 000 to 800 000 g/mol. The characteristics of these polymers are given in Table 1. (As the synthesis of linear polybutadienes is well-known,

Table 1. Molecular Characteristics of Linear Polyethylenes

sample	vinyl content of parent PB,[a] %	$\bar{M}_n$,[b] 10^3 g/mol	$\bar{M}_w$,[b] 10^3 g/mol	R_g,[b] nm	$[\eta]$,[c] dL/g
PEL19	8.6	18.3	18.7	3.3	0.52
PEL90	6.4	86.9	87.4	16.2	1.42
PEL123	7.8	123	124	21.3	1.84
PEL125	7.9	121	123	20.0	1.86
PEL147	7.5	143	144	21.8	2.10
PEL193	7.5	187	189	25.3	2.59
PEL243	8.1	236	247	30.4	3.08
PEL280	7.3	277	283	32.5	3.30
PEL685	7.3	669	771	62.0	7.24

[a] By ^{1}H NMR. [b] By SEC-MALLS. [c] By SEC-VIS; NM = not measured.

we present here only the characterization of the saturated polymers.) Herein we use these polymers to determine the dependence of R_g on $\bar{M}_w$; in subsequent papers we use them to establish quite precisely the rheological behavior of polymers of this type that have no long branches.

Synthesis of Three-Arm Star Polyethylenes. Three-arm star PE can be considered as the simplest branched PE carrying one single branch. We have followed the method of Zelinski and Wofford to prepare symmetric three-arm star PB[25] with all three arms of the same molecular weight (A_3). One may think of this structure as consisting of a single branch located exactly at the middle of the backbone, where the molecular weight of the branch is half of that of the backbone. Model PEs with a single long branch where the branch length and position varied were made by having unequal arm lengths. (We always take the shortest arm as the branch, with the backbone consisting of the other two.) The majority of these had two arms of one length and one of another (A_2B). If $M_A > M_B$, then again the branch is located at the middle of the backbone, but its molecular weight is less than half of the backbone. If $M_B > M_A$, then the branch is located away from the center of the backbone and has a molecular weight equal to its distance from the closer chain end. Asymmetric stars of the A_2B type were made using the reaction scheme of Pennisi and Fetters.[26] Finally, by using the approach of Iatrou and Hadjichristidis,[35] we have prepared one asymmetric star where all three arms are of different molecular weight (*ABC*), allowing one to put any length branch anywhere along the backbone.

The basic reactions are given below:

Symmetric Star Synthesis (A_3 Method)

$$\text{butadiene} \xrightarrow{s\text{-BuLi}} \text{PBLi} = A\text{Li, the } A \text{ arm}$$

$$3A\text{Li} + \text{excess } CH_3SiCl_3 \rightarrow CH_3SiA_3 + 3\text{LiCl}$$

The A_3 method is exemplified in the procedures used to make sample PBS(43)$_3$. Fifteen grams of butadiene was reacted with 0.300 mmol of *s*-BuLi in 350 mL of benzene, and a PB with $\bar{M}_n = 43\,000$ g/mol by SEC was obtained. One gram was removed before the linking reaction for characterization purposes. A 0.075 mmol sample of trichloromethylsilane was used as a linking agent in order to have a 20% excess of the arm to force the reaction to completion. The progress of the reaction was monitored by SEC and was left to proceed for 3−4 weeks. Fractionation to remove excess arms was accomplished with a toluene/methanol system. The SEC traces in Figure 3 show that essentially all of the unreacted arms were removed in this way. This polymer was hydrogenated using Pd on $CaCO_3$ as described above. The molecular weight characterization of this and the other symmetric polybutadiene stars is given in Table 2.

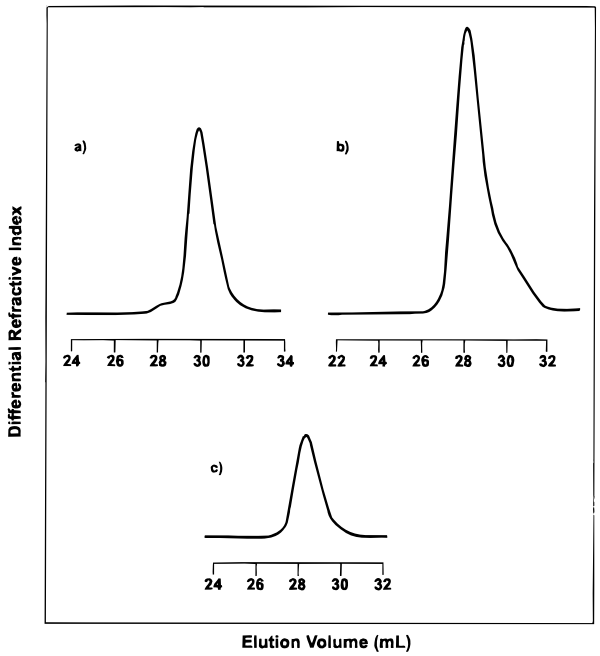

Figure 3. SEC analysis of symmetric star PBS(43)$_3$: (a) *A* arm; (b) unfractionated star; (c) fractionated star.

Asymmetric Star Synthesis (A_2B Method). We followed the same general approach and the ones we have already developed for asymmetric 3-arm star polyisoprenes[36] and 3-miktoarm star copolymers.[39] Two types of polybutadiene arms (*A*Li and *B*Li, $M_A \neq M_B$) were synthesized as described. In the first step of the A_2B synthesis we have to use an excess of chlorosilane (Si−Cl/C−Li: 100−500) in order to incorporate one only macromolecular chain onto the chlorosilane. The lower the molecular weight of the *B*Li, the easier the linking reaction (less steric hindrance) and consequently the higher the excess of chlorosilane that should be used in order to avoid the addition of two chains instead of one. The excess of the chlorosilane was removed in the vacuum line in order to avoid contamination of the A_2B by the B_3 star, which is generally very difficult to eliminate by fractionation.

$$B\text{Li} + \text{excess } CH_3SiCl_3 \rightarrow BCH_3SiCl_2 + \text{LiCl}$$

In the second step of the synthesis of A_2B, we have to use an excess of the living polymer in order to force the reaction for completion. This excess, after neutralization, is eliminated by fractionation.

$$BCH_3SiCl_2 + \text{excess } A\text{Li} \rightarrow A_2SiBCH_3 + 2\text{LiCl}$$

To make this more explicit, we now describe the detailed synthesis of sample PBS(50)$_2$(5). This was prepared by anionic polymerization using high-vacuum techniques in evacuated, *n*-BuLi washed and benzene rinsed glass reactors. Addition of the reagents was made through fragile glass membranes (break-seals) and removal of samples for characterization by heat sealing of the constrictions. *sec*-BuLi, prepared in a vacuum from *sec*-butyl chloride and a lithium dispersion, was

Table 2. Molecular Characteristics of Star Polybutadienes

	A-arm		B-arm		C-arm		star		
sample	vinyl,[a] %	$\bar{M}_n$,[b] 10^3 g/mol	vinyl,[a] %	$\bar{M}_n$,[b] 10^3 g/mol	vinyl,[a] %	$\bar{M}_n$,[b] 10^3 g/mol	$\bar{M}_n$,[c] 10^3	$\bar{M}_n$,[f] 10^3 g/mol	$\bar{M}_n^{pred}$, 10^3 g/mol
$PBS(27)_3$	7.9	27 (25.7[c])					76.7	73	81
$PBS(43)_3$	9.0	43					NM	NM	129
$PBS(45)_3$	7.3	45					112	100	135
$PBS(48)_3$	6.8	48					NM	NM	146
$PBS(50)_3$	8.7	50					NM	NM	150
$PBS(53)_3$	6.5	53					119	100	159
$PBS(49)_2(5)$	11	50 (49[c])	10	5.0 (5.3)[c]			98.8[e]	NM	105
$PBS(50)_2(5)$	8.9	50	8.9	5.0			102[d]	NM	105
$PBS(50)_2(15)$	7.9	50	7.9	15			NM	NM	115
$PBS(50)_2(25)$	7.5	50	7.5	25			120[d]	NM	125
$PBS(19)_2(83)$	7.7	19	7.7	83			NM	NM	121
$PBS(15)_2(85)$	9.9	15	9.9	85			NM	NM	115
$PBS(40)_2(60)$	9.0	40	9.0	60			NM	NM	140
PBS(40)(30)(20)	9.0	40	9.0	30	9.0	20	NM	NM	90

[a] By ^{1}H NMR. [b] By SEC (polystyrene standard, corrected for polybutadiene). [c] By MO. [d] Calculated from SEC and presumed structure. [e] By SEC-RALLS. [f] By ^{13}C NMR; NM = not measured. $\bar{M}_w/\bar{M}_n$ was less than 1.1 for all of the arms and fractionated stars.

the initiator and benzene the solvent for all the polymerizations. Trichloromethylsilane was the linking agent. For the synthesis of the *B* arms 2 g of butadiene was reacted with 0.400 mmol of *sec*-BuLi in 100 mL of benzene in order to obtain a polymer with $\bar{M}_n = 5000$ g/mol. A sample was removed (1 g) for characterization. The living polymer *B*Li was reacted with a large excess (500:1) of linking agent in order to avoid the formation of dimer or trimer so that only one of the three chlorine atoms of the linking agent would be substituted by the *B*Li arms. The solvent and the unreacted linking agent were removed under vacuum by heating at 45 °C for 1 week. The polymer was then redissolved in benzene and was ready to react with the two *A* arms. The synthesis of the *A* arms was done by reacting 25 g of monomer with 0.500 mmol of initiator in 350 mL of benzene in order to obtain a polymer with $\bar{M}_n = 50\,000$ g/mol. One gram of *A*Li was taken for characterization purposes. This was then added to the *B*CH_3SiCl_2 solution for the reaction to make the star. A 20% excess of *A*Li was used in order to be sure that all the *A*Li arms had reacted. The reaction was left to take place for 3−4 weeks. The progress of the reaction was monitored by removing samples and analyzing them by SEC. After no more progress was observed from the SEC chromatographs the living polymer was killed with a small amount of methanol, and the whole product was precipitated in methanol. The polymer was protected against oxidation by 2,6-di-*tert*-butyl-*p*-cresol and was fractionated in a toluene−methanol system. Fractionation was performed until no free arm was shown to be present by SEC, as shown in Figure 4. The polymer was finally precipitated in methanol containing antioxidant, dried, and stored under vacuum in the dark. Characterization carried out by SEC, MO, VPO, LALLS, and laser differential refractometry indicates the high degree of molecular and compositional homogeneity. The polymer was hydrogenated as described above. The characterization of this and of all of the model star PEs is given in Table 3.

For the preparation of the asymmetric 3-arm star PB with three different arms (*ABC*) the synthetic route of Iatrou and Hadjichristidis used for the synthesis of 3-miktoarm star terpolymers of styrene, isoprene, and butadiene was adopted.[35] The highest molecular weight PB was incorporated first and the lowest last for steric hindrance reasons. A schematic representation of the sequence of the reactions is shown below:

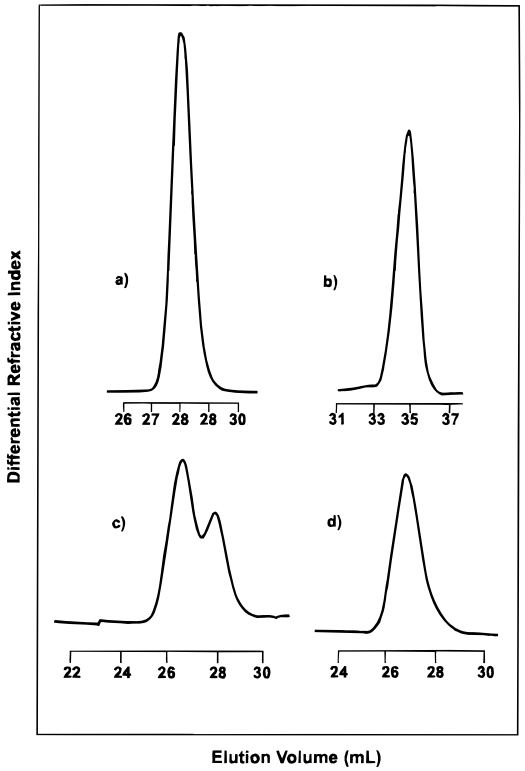

Figure 4. SEC analysis of asymmetric star $PBS(50)_2(5)$: (a) *A* arm; (b) *B* arm; (c) unfractionated star; (d) fractionated star.

Asymmetric Star Synthesis (*ABC* Method). First synthesize *A*Li, *B*Li, and *C*Li as the three PB arms.

$$A\text{Li} + \text{excess } CH_3SiCl_3 \rightarrow ACH_3SiCl_2 + \text{LiCl}$$

$$B\text{Li} + ACH_3SiCl_2 \xrightarrow{\text{titration}} ABCH_3SiCl + \text{LiCl}$$

$$ABCH_3SiCl + \text{excess } C\text{Li} \rightarrow ABCSiCH_3 + \text{LiCl}$$

($M_A > M_B > M_C$). To further exemplify this method, we describe here the details of the synthesis of PBS(40)-(30)(20). Ten grams of butadiene was reacted with 0.250 mmol of initiator, and a PB with $\bar{M}_n = 40\,000$ g/mol (*A*Li) was obtained. The molecular weight was high enough in order to be sure that only one of the chlorine atoms of the linking agent would be substituted by the polymer. The other two arms were synthesized in a

Table 3. Molecular Characteristics of Star Polyethylenes

sample	$\bar{M}_n$,[a] 10^3 g/mol	$\bar{M}_w$,[a] 10^3 g/mol	R_g,[a] nm	$[\eta]$,[b] dL/g
$PES(27)_3$	87.9	92.3	14.6	NM
$PES(43)_3$	118	133	18.0	1.61
$PES(45)_3$	135	141	17.8	NM
$PES(48)_3$	150	133	18.2	1.66
$PES(50)_3$	190	194	22.5	2.06
$PES(53)_3$	143	162	20.2	NM
$PES(49)_2(5)$	101	105	17.1	1.49
$PES(50)_2(5)$	126	130	19.7	1.77
$PES(50)_2(15)$	133	138	19.7	1.76
$PES(50)_2(25)$	123	131	18.1	1.61
$PES(19)_2(83)$	117	120	18.5	1.66
$PES(15)_2(85)$	110	129	19.3	1.74
$PES(40)_2(60)$	129	132	18.8	1.55

[a] By SEC-MALLS. [b] By SEC-VIS; NM = not measured.

similar manner: 8.4 g of monomer with 0.280 mmol of initiator to make *B*Li ($\bar{M}_n$ = 30 000 g/mol) and 6.4 g of butadiene with 0.320 mmol of initiator to form *C*Li ($\bar{M}_n$ = 20 000 g/mol). One gram of each of these arms was use for its characterization. In the first linking step, a large excess of CH_3SiCl_3 (500:1) to *A*Li was used in order to ensure that only one *A* arm was attached to any of the linking agent. To add the second arm (*B*Li), an apparatus with 7−8 samplers was used. An excess of 10% of *B*Li to ACH_3SiCl_2 was used to be sure that the second chlorine atom was substituted by the polymer. The progress of the reaction was monitored by removing samplers and analyzing them by SEC. The addition of the *B*Li was stopped when a small amount of AB_2 was observed in the SEC chromatograms. After this, the *C*Li arm was added. A 40% excess of the arm was used to ensure complete reaction. The reaction was left to proceed for 3−4 weeks, and SEC was used to monitor its progress. Fractionation was performed as for $PBS(50)_2(5)$. This polymer was not hydrogenated.

That the purported structures for these stars were indeed made is attested to by the several pieces of characterization data given in Table 2. The molecular weights of these stars were measured in a few cases, and here the values predicted from the sum of the three arms that constitute them are in good agreement. (For $PBS(50)_2(5)$ and $PBS(50)_2(25)$, we have taken the shown value of $\bar{M}_n$ from SEC, corrected for the presumed star structure.) For three symmetric stars, we have used ^{13}C NMR (see above) to determine $\bar{M}_n$ from the number of Si linking groups, and these numbers agree well with the MO results as can be seen in Table 2. These are confirmed by the molecular weights of the hydrogenated model PBs (Table 3).

Further confirmation comes from the measurement of the R_g of the PBs and the model PEs. These polymers are all smaller than their linear counterparts of the same molecular weight. The same is true for the intrinsic viscosity as seen in Tables 2 and 3. A more complete discussion of this is given in the final section that compares these values to theoretical predictions.

Synthesis of α−ω Branched Polyethylenes. The general method of the α−ω polybutadiene synthesis is to use a difunctional initiator (1,3-bis(1-phenyl-3-methyl-pentylidenelithium)benzene, "DLI") to produce a central "connector" molecule. This is reacted with silicon chloride moieties and some PB arms to give a structure of several arms at each end of the connector. We call this general class "α-ω branched" polymers. If two arms are added at the end of each connector, the result is an H-shaped polymer. When three arms are added to each end, the product is called "super-H". For more than three arms per end, the branched end product is termed a "pom-pom". For the synthesis of the α−ω branched PB we have adopted two general methods, which we call here "divergent" (the arms are attached one by one to the ends of the connector) and "convergent" (the arms are first reacted into a bunch, which is then put onto the connector). The divergent method was introduced by Roovers for the case of H-shaped polymers,[40] which we have extended to the super-H[41,42] and pom-pom molecules.[43] The convergent method is similar to the synthesis of the stars we have described above, but applied on both ends of the connector molecule. The general scheme of the synthesis is given below:

α−ω Branched Polyethylene Synthesis (x = 2: H-shaped; x = 3: super H; x > 3: pom-pom):

$$\text{butadiene} \xrightarrow[n\text{-BuLi}]{} \text{PBLi} \qquad \text{arm PB, } A\text{Li}$$

$$\text{butadiene} \xrightarrow[\text{DLI}]{} \text{LiPBLi} \qquad \text{connector PB, Li}B\text{Li}$$

Divergent Method

$$\text{Li}B\text{Li} + \text{excess } SiCl_{x+1} \rightarrow Cl_xSiBSiCl_x + 2\text{LiCl}$$

$$Cl_xSiBSiCl_x + \text{excess } A\text{Li} \rightarrow A_xSiBSiA_x + 2x\text{LiCl}$$

Convergent Method

$$xA\text{Li} + SiCl_{x+1} \rightarrow SiA_xCl + x\text{LiCl}$$

$$\text{excess } SiA_xCl + \text{Li}B\text{Li} \rightarrow A_xSiBSiA_x + 2\text{LiCl}$$

$SiCl_{x+1}$ is $(CH_3)SiCl_3$ for H-shaped polymers, $SiCl_4$ for super-H, and $Cl_3SiCH_2CH_2SiCl_3$ for the pom-poms with five arms on each end that we have made for this work. The divergent method was used for $PBH(10)_2(95)(10)_2$, $PBH(50)_2(25)(50)_2$, and $PBSH(10)_3(107)(10)_3$ and the convergent method for $PBH(6)_2(27)(6)_2$, $PBH(12)_2(27)(12)_2$, $PBH(24)_2(27)(24)_2$, and $PBPP(10)_5(92)(10)_5$.

The divergent method is illustrated more clearly with the details of the synthesis of $PBH(50)_2(25)(50)_2$:

Preparation of the Connector. The difunctional initiator 1,3-bis(1-phenyl-3-methylpentyllithium)benzene (DLI) was prepared by reacting *sec*-BuLi with 1,3-bis(1-phenylethenyl)benzene. A 1.2×10^{-4} mol sample of the DLI along with 4×10^{-4} mol of *sec*-BuOLi was added in a solution of 4.10 mL of butadiene-1,3 (3 g) dissolved in 100 mL of benzene (*B*Li, stoichometric $\bar{M}_n$ = 25 000 g/mol). A 1 g (4×10^{-5} mol) sample of the connector was removed and terminated with degassed methanol for characterization. The living connector was transferred into a reactor and reacted with 10 mL of $MeSiCl_3$ (8×10^2 mol) for 1 h. The reactor was connected to a vacuum line, and the excess of trichloromethylsilane along with the solvent (benzene) was distilled in a flask followed by pumping off the polymer to dryness. The formed what is essentially a tetrafunctional macromolecular linking agent, $Cl_2SiBSiCl_2$. This was redissolved in benzene and pumped to dryness three more times.

Preparation of Arms and Linking Reaction. A 28.5 mL (21 g) aliquot of butadiene (ρ = 0.73 g/cm^3; −78 °C) was polymerized by using 4×10^{-4} mol of *sec*-BuLi in benzene. The polymerization was left for 24 h for completion. One gram of polybutadiene (*A*Li, stoichometric $\bar{M}_n$ = 50 000 g/mol) was removed for characterization. The rest was added to the $Cl_2SiBSiCl_2$. After 3

Table 4. Molecular Characteristics of α−ω-Type Polybutadienes

	arm			connector			α−ω type			
sample	vinyl,[a] %	$\bar{M}_n$,[c] 10^3 g/mol	$\bar{M}_w$,[c] 10^3 g/mol	vinyl,[a] %	$\bar{M}_n$,[c] 10^3 g/mol	$\bar{M}_w$,[c] 10^3 g/mol	$\bar{M}_n$,[c] 10^3 g/mol	$\bar{M}_w$,[c] 10^3 g/mol	$\bar{M}_w^{pred}$, 10^3 g/mol	n_{bp}[f]
$PBH(6)_2(27)(6)_2$	10	5.5[b]	6.2	10	27.1[b]	24.9[e]	NM	50.0[e]	49.7	2.0
$PBH(12)_2(27)(12)_2$	10	11.6[b]	10.8	10	27.1[b]	24.9[e]	NM	67.0[e]	68.1	2.3
$PBH(10)_2(95)(10)_2$	10	10.1	10.3	10	95.4	112	146	155	153	NM
$PBH(50)_2(25)(50)_2$	NM	49.7[d]	NM	NM	24.5[d]	NM	230[d]	206	223	NM
$PBSH(10)_3(107)(10)_3$	10	10.1	10.3	10	107	127	173	183	189	NM
$PBPP(10)_5(92)(10)_5$	9	10.4	10.5	10	91.9	109	210	228	214	NM

[a] By ^{1}H NMR. [b] By SEC. [c] By SEC-RALLS. [d] By MO. [e] By LALLS. [f] Number of branch points as calculated from ^{13}C NMR; NM = not measured. $\bar{M}_w/\bar{M}_n$ was less than 1.1 for all of the arms, connectors, and fractionated α−ω polymers.

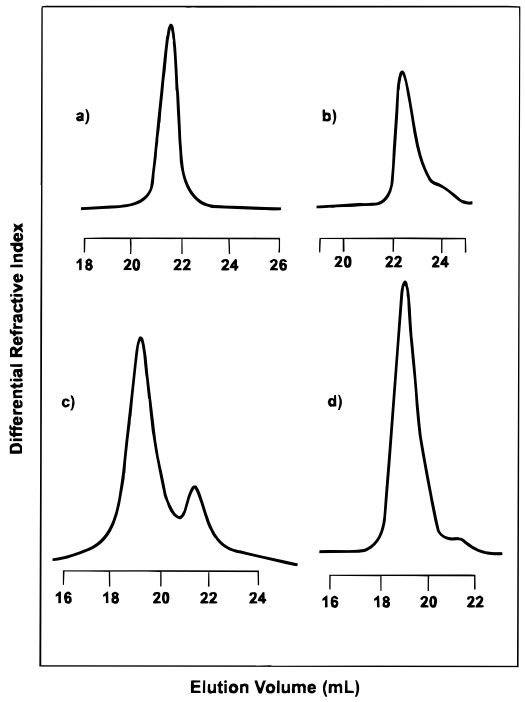

Figure 5. SEC analysis of $PBH(50)_2(25)(50)_2$: (a) *A* arm; (b) *B* connector; (c) unfractionated H; (d) fractionated H.

weeks the linking reaction was complete, and the excess of the living arm was terminated with degassed CH_3OH.

Fractionation. The solution of the raw product (about 300 mL) was diluted with 1.2 L of toluene. About 400 mL of CH_3OH was added, and the solution was stirred at room temperature until it became slightly cloudy. After that, an extra 20 mL of CH_3OH was added and the solution was heated until it became clear. It was then poured into a warm separatory funnel and left to cool slowly. The lower fraction was carefully removed and precipitated in methanol. Then another 25 mL of CH_3OH was added to the upper phase, and the procedure was repeated until most of the $PBH(50)_2(25)(50)_2$ was separated from the raw product. The success of this fractionation can be seen in Figure 5. This polymer was dried in a vacuum.

Saturation. The $PBH(50)_2(25)(50)_2$ was saturated in the same manner as the samples described above, except that 0.2 g of triphenyl phosphate and 0.0366 g of tris(triphenylphosphine)rhodium(I) chloride were added to the reaction for every gram of polymer. Essentially complete saturation was achieved to form $PEH(50)_2(25)(50)_2$. The molecular characterization of this polymer is given in Table 5.

The convergent method is illustrated by the synthesis of $PBPP(10)_5(109)(10)_5$:

Table 5. Molecular Characteristics of α−ω-Type Polyethylenes

sample	$\bar{M}_n$,[a] 10^3 g/mol	$\bar{M}_w$,[a] 10^3 g/mol	R_g,[a] nm	$[\eta]$,[b] dL/g
$PEH(6)_2(27)(6)_2$	45.1	45.7	10.6	NM
$PEH(12)_2(27)(12)_2$	62.1	63.6	12.6	NM
$PEH(10)_2(95)(10)_2$	154	162	23.2	2.15
$PESH(10)_3(107)(10)_3$	175	190	24.9	2.16
$PEPP(10)_5(92)(10)_5$	233	247	25.9	2.19

[a] By SEC-MALLS. [b] By SEC-VIS; NM = not measured.

Preparation of Arms and Cluster. A 9.97 g sample of 1,3-butadiene was diluted in 145 mL of benzene. To this solution was added 9.97×10^{-4} mol of *sec*-BuLi. The product polybutadiene (*A*Li) had an $\bar{M}_n$ of 10 000 g/mol by SEC. A 20 mL aliquot of the polymer solution was removed for characterization, and the rest of *A*Li was reacted with 9.36×10^{-4} mol of 1,2 di(trichlorosililo)ethane (a 30% molar excess of *A*Li) to create A_5SiCl.

Preparation of Connector. Seven grams of butadiene was polymerized with 1.4×10^{-4} mol of DLi, in the presence of 15.4×10^{-4} mol of *sec*-BuOLi in a reactor with 195 mL of benzene. This resulted in a living polybutadiene (Li*B*Li) with $\bar{M}_n = 120\,000$ g/mol by SEC. 33 mL of the polymer solution was removed for characterization.

Formation of $PBPP(10)_5(109)(10)_5$. A_5SiCl (8.97 g) and Li*B*Li (6 g) were mixed (40% molar excess of A_5SiCl). To the solution was added 0.3 mL of THF. After 7 days at room temperature the formation of the PP5-1 was complete. Excess Cl was deactivated with CH_3OH.

Fractionation. The procedure followed was the same as for $PBH(50)_2(25)(50)_2$. The removal of excess arm is clear from Figure 6. Hydrogenation was also done as for $PBH(50)_2(25)(50)_2$. The characterization results are given in Tables 4 and 5.

The data shown in those tables provide good proof that these syntheses were successful in providing the anticipated structures. The first piece of evidence is the narrowness of the SEC traces of the final, fractionated product. Examples for the H, pom-pom, and super-H types are shown in Figures 5−7. It is clear that after the unreacted arms are removed a nearly monodisperse product is left. A comparison of the molecular weights of the arms and connectors with those of the final products also shows that the desired structures have been made. The predicted molecular weights, based on the sum of the connector molecular weight plus those of the expected number of arms, are seen to be in good agreement with the measured values of the final product (Table 4). This is confirmed by the measured molecular weights of the hydrogenated versions of these polymers as well. Finally, the ^{13}C NMR measures of the number of branch points were also in very good agreement with the α−ω structure for the two polymers for which this

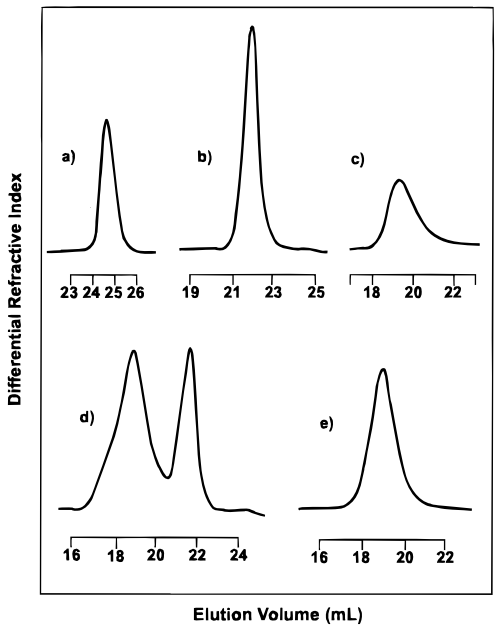

Figure 6. SEC analysis of PBPP$(10)_5(92)(10)_5$: (a) *A* arm; (b) A_5SiCl cluster; (c) *B* connector; (d) unfractionated pom-pom; (e) fractionated pom-pom.

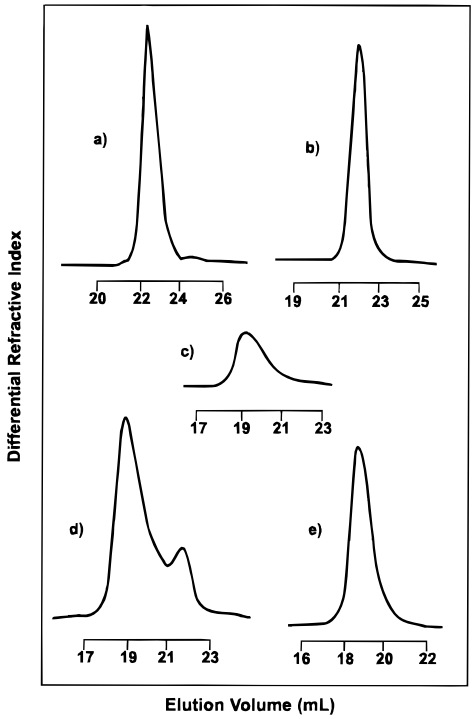

Figure 7. SEC analysis of PBSH$(10)_3(107)(10)_3$: (a) *A* arm; (b) A_3SiCl cluster; (c) *B* connector; (d) unfractionated super-H; (e) fractionated super-H.

was measured. Thus, by careful characterization we have shown that these polymers do indeed have the structures of a single connector bridge with 2, 3, or 5 arms at each end.

The hydrogenated $\alpha-\omega$ polybutadienes are good models for polyethylenes with exactly two branch points. H-shaped PE can be considered as having exactly two long branches, both of the same length and both as far from the closer end of the backbone as they are long. The super-H-shaped can be considered as PE with two tetrafunctional branch points and the pom-pom as PE with two hexafunctional branch points. Again the data on R_g, $[\eta]$, and $\bar{M}_w$ for these polymers show that the branched chains are smaller than their linear analogues, confirming the presence of long branches.

Synthesis of Comb Polyethylenes. Comb polybutadienes were prepared by coupling hydrosilylated PB with PBLi. The hydrosilylation reaction was performed in THF using platinum divinyltetramethyldisiloxane complex in xylene (Petrarch PC072) as catalyst in a round-bottom flask equipped with condenser, communicating with the atmosphere through a $CaCl_2$ filled tube. The solution was dried overnight with trimethylchlorosilane to destroy any impurity that could react with the chlorosilane, followed by the addition of dimethychlorosilane. The temperature was slowly raised to the boiling point of THF (67 °C). The change of the color indicated the starting of the reaction that was allowed to proceed, under refluxing, for 24 h. All further manipulations were performed under vacuum. The hydrosilylated product was dried for several days. THF and the unreacted silanes were eliminated. The dried polymer was dissolved in benzene and sealed off. Living polybutadiene was prepared in a secondary reactor and, in about a 30% excess, added to the main reactor containing the hydrosilylated PB. The coupling reaction, monitored by SEC, was allowed to proceed for 2 weeks. The excess of the living branch, after neutralization with methanol, was eliminated by fractionation. More details are given in a recent paper[44] and below.

The basic reactions are given in Scheme 1.

To illustrate more clearly how this was done, we give here the detailed procedure[44] used for PBC(101)-*g*-$(5)_{12}$. The polybutadiene that was used as backbone (*B*) for the hydrosilylation reaction was prepared by anionic polymerization using high-vacuum techniques in the manner described above, with *sec*-BuLi in benzene at room temperature. 2.5 g of *B* was dissolved in 60 mL of tetrahydrofuran (THF) in a 1 L round-bottom flask equipped with a good condenser, to which 3 drops of platinum divinyltetramethyldisiloxane complex in xylene (Petrarch PC072) were added. The solution was dried overnight with 0.5 mL of trimethylchlorosilane, followed by the addition of 0.1 mmol of dimethylchlorosilane. The mixture's temperature was raised slowly to 70 °C. Changing of the color, vigorous boiling, and refluxing indicated the start of the reaction which was continued for 24 h at 70 °C. THF and chlorosilane compounds were removed in the vacuum line by heating the polymer at 45 °C for 5 days. The polymer was dissolved in benzene and sealed under vacuum. Living PBLi (*A*Li) used for the coupling reaction was prepared in the same manner as *B*Li. The synthesis of *A*Li was accomplished by reacting 10.7 g of monomer with 2.020 mmol of initiator. Prior to the coupling reaction 1 g of *A*Li was removed, terminated with methanol, and used for characterization. Twenty percent excess of *A*Li was used for the coupling reaction, which was monitored by SEC and allowed to proceed for 2 weeks. Excess *A*Li was terminated with methanol. The comb polymer was protected against oxidation by 2,6-di-*tert*-butyl-*p*-cresol and was fractionated in a toluene−methanol system. Fractionation was performed until no arm or undesirable products were shown to be present by SEC; the success of the fractionation can be seen in Figure 8. The comb was finally precipitated in methanol containing antioxidant, dried, and stored under vacuum in the dark. Characterization, which was carried out by SEC, MO, VPO, LALLS, and laser differential refractometry,

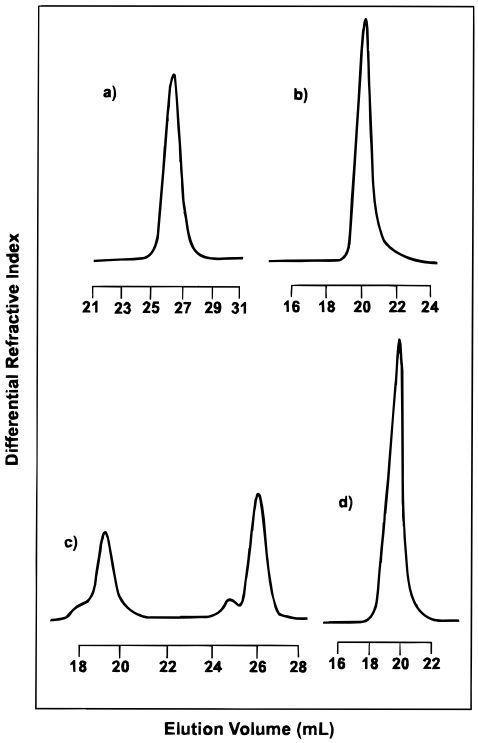

Figure 8. SEC analysis of comb PBC(101)-*g*-$(5)_{12}$: (a) *A* arm; (b) *B* backbone; (c) unfractionated comb; (d) fractionated comb.

Scheme 1

Butadiene → (*sec*-BuLi) PBLi — arm PB, *A*Li

Butadiene → (*sec*-BuLi) PBLi — backbone PB, *B*Li

*B*Li → (CH_3OH) *B* + CH_3OLi

$(CH_2CH{=}CHCH_2)_a(CH_2CH)_b$ (CH, CH_2) + c $HSi(CH_3)_2Cl$ → (Pt catalyst)

"*B*"

$(CH_2CH{=}CHCH_2)_a(CH_2CH)_{b-c}(CH_2CH)_c$ (CH, CH_2; CH_2, CH_2; $(CH_3)Si(CH_3)$; Cl) = "*B*-Si_c"

B-Si_c + excess *A*Li → *B*-*g*-A_c + c LiCl

indicated the high degree of molecular and compositional homogeneity.

The success of these polymerizations was shown by evidence (Tables 6 and 7) similar to that for the stars and α−ω polymers. We cannot make a prediction of the comb molecular weight, since we determine the number of arms attached to the backbone from the measured $\bar{M}_w$. However, we have an independent confirmation of the number of arms from ^{13}C NMR, which agrees well with that derived from molecular weight measurements. Moreover, the molecular weights of the hydrogenated PBs are in good agreement as well.

Chain Dimensions. One aim of this work is to show how chain dimensions vary with the nature of long chain branching for polyethylene. (We can neglect the effects of the short ethyl branches since the frequency of these is the same in all cases.[45]) This is commonly expressed in terms of the Zimm−Stockmayer model,[15−17,45] which characterizes the radius of gyration of a branched molecule in terms of that of a linear one of equal total molecular weight:

$$g = \frac{\langle R_g^2 \rangle_{branched}}{\langle R_g^2 \rangle_{linear}} \quad (1)$$

From the chain dimensions and molecular weight data in Table 1 we can derive an expression for how R_g depends on $\bar{M}_w$ for linear polyethylene:

$$R_g = 0.0194 \bar{M}_w^{0.590} \quad (2)$$

where R_g is in nm and $\bar{M}_w$ in g/mol. In deriving eq 2, we have only used the data for polymers with $\bar{M}_w >$ 100 000 g/mol, so that there is no screening of the excluded volume. This is in very good agreement with other relations for PE in good solvents.[5,7] Equation 2 allows us to estimate the R_g for a linear polyethylene that can be used to calculate the Zimm−Stockmayer *g* for a branched polymer using eq 1.

The basic assumption in the Zimm−Stockmayer calculation is that each linear chain section (i.e., arm, backbone, connector) has its random-walk dimensions. For an A_2B star the predicted value of *g* is[15,17]

$$g^{pred} = 1 - \frac{6s}{(s+2)^3} \quad [A_2B \text{ star}] \quad (3)$$

where $s = M_A/M_B$ is the ratio of molecular weight of the *A* arm to that of the *B* arm. The Zimm−Stockmayer prediction for H polymers was first made by Berry and Orofino.[17] The more general expression for all α−ω polymers is[46]

$$g^{pred} = \kappa^3 + 3\kappa^2(1-\kappa) + \frac{3}{2}\left(\frac{f+1}{f}\right)\kappa(1-\kappa)^2 + \frac{3f-1}{2f^2}(1-\kappa)^3 \quad [\alpha{-}\omega] \quad (4)$$

where κ is the fraction of the polymer in the connector and *f* is the functionality of the end branch points. The Berry and Orofino expression for combs is

$$g^{pred} = \lambda^3 + \frac{2p+1}{p+1}\lambda^2(1-\lambda) + \frac{p+2}{p}\lambda(1-\lambda)^2 + \frac{3p-2}{p^2}(1-\lambda)^3 \quad [\text{comb}] \quad (5)$$

where λ is the fraction of the molecule in the backbone and *p* is the number of arms per comb.

Another common measure of LCB comes from a comparison of the intrinsic viscosity of a polymer with that of a linear chain of the same molecular weight. This ratio is called *g*′:

$$g' = \frac{[\eta]_{branched}}{[\eta]_{linear}} \quad (6)$$

Table 6. Molecular Characteristics of Comb Polybutadienes

	arm			backbone			comb			
sample	vinyl,[a] %	$\bar{M}_n$,[f] 10^3 g/mol	$\bar{M}_w$,[c] 10^3 g/mol	vinyl,[a] %	$\bar{M}_n$,[e] 10^3 g/mol	$\bar{M}_w$,[d] 10^3 g/mol	$\bar{M}_n$,[e] 10^3 g/mol	$\bar{M}_w$,[d] 10^3 g/mol	n_{arm}[g]	n_{arm}[h]
PBC(79)-*g*-$(3)_3$	NM	3.1[b]	NM	NM	78.5[b]	NM	104[b]	NM	3	8
PBC(98)-*g*-$(5)_{27}$	9	5.1	NM	9	98	99	260	290	27	32
PBC(101)-*g*-$(7)_{30}$	9	6.5	NM	9	101	103	274	286	30	27
PBC(101)-*g*-$(5)_{12}$	NM	5.4	NM	NM	101	103	165	NM	11	12
PBC(87)-*g*-$(5)_3$	10	4.5	NM	10	87.0	90.0	106	107	3	4
PBC(97)-*g*-$(23)_{26}$	10	NM	23.5	11	NM	97	NM	612	26	22[i]
PBC(100)-*g*-$(5)_2$	9	5.2[c]	5.3	10	96.8[c]	99.7[c]	109[c]	111[c]	0	2
PBC(100)-*g*-$(5)_{12}$	10	5.2[c]	5.3	10	96.8[c]	99.7[c]	173[c]	178[c]	12	15
PBC(108)-*g*-$(6)_{12}$	9	5.7[c]	5.8	10	108[c]	109[c]	170[c]	178[c]	12	11

[a] By ^{1}H NMR. [b] By SEC. [c] By SEC-RALLS. [d] By LALLS. [e] By MO. [f] By VPO. [g] By ^{13}C NMR. [h] Calculated from $\bar{M}_n$ of each component. [i] Calculated from $\bar{M}_w$ of each component; NM = not measured. $\bar{M}_w/\bar{M}_n$ was less than 1.1 for all of the arms, backbones, and fractionated combs.

Table 7. Molecular Characteristics of Comb Polyethylenes

sample	$\bar{M}_n$,[a] 10^3 g/mol	$\bar{M}_w$,[a] 10^3 g/mol	R_g,[a] nm	$[\eta]$,[b] dL/g
PEC(101)-*g*-$(7)_{30}$	400	426	25.6	1.75
PEC(97)-*g*-$(23)_{26}$	660	735	29.4	2.05
PEC(100)-*g*-$(5)_2$	105	105	18.5	1.62
PEC(100)-*g*-$(5)_{12}$	166	171	20.1	1.62
PEC(108)-*g*-$(6)_{12}$	163	170	20.1	1.67

[a] By SEC-MALLS. [b] By SEC-VIS.

From the data on the linear polyethylene models (Table 1), we can write an expression for how the intrinsic viscosity varies with molecular weight:

$$[\eta] = 0.000538\bar{M}_w^{0.695} \tag{7}$$

where $[\eta]$ is in dL/g and $\bar{M}_w$ in g/mol. From eqs 6 and 7 we can find g'.

There has been much less theoretical work to calculate values for g' than for g. For lightly branched polymers, it is expected that g' will be the square root of g.[16] We can express the relation between these two quantities in terms of an exponent, ϵ:

$$g' = g^{\epsilon} \tag{8}$$

For stars and some combs, it has been found that $\epsilon \approx 0.6$. For more complicated structures there is no prediction for ϵ.

Before discussing the comparison between theory and experiment, we wish to point out that the data in Table 8 show that measurements of the chain dimensions and molecular weight alone can only provide information on the degree of branching and not on the type of branching architecture. The pom-pom example (PEPP$(10)_5(92)$-$(10)_5$) and two of the combs (PEC(100)-*g*-$(5)_{12}$ and PEC-(108)-*g*-$(6)_{12}$) have g and g' values that are nearly equal to those of the symmetric stars such as PES$(45)_3$, but these four polymers have radically different architectures. In subsequent papers we will show that this leads to great differences in rheological performance as well. A proper analysis of the nature of LCB in polymers thus requires the combination of characterization data of the molecular weight and chain dimensions with rheology.

These predictions are compared with the experimental results for the model polyethylenes in Table 8. The predictions for the stars (eq 3) work quite well. This is somewhat surprising, given that the predictions apply to ideal, Θ conditions and the experimental results are for polymers in good solvent (TCB at 135 °C). The effect of the length of the arm can be seen in Figure 9, which

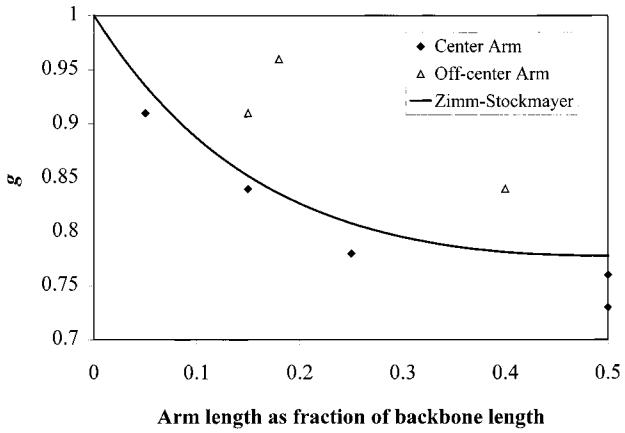

Figure 9. g vs ratio of length of arm to that of backbone for three-arm stars.

Table 8. Branched Polyethylene Chain Dimensions

sample	g^{pred}	g^{meas}	g'	ϵ
PES$(27)_3$	0.78	0.78		
PES$(43)_3$	0.78	0.73	0.080	0.73
PES$(45)_3$	0.78	0.70		
PES$(48)_3$	0.78	0.76	0.83	0.68
PES$(50)_3$	0.78	0.76	0.80	0.81
PES$(53)_3$	0.78	0.77		
PES$(49)_2(5)$	0.93	0.91	0.89	1.19
PES$(50)_2(5)$	0.94	0.91	0.90	1.17
PES$(50)_2(15)$	0.85	0.84	0.85	0.93
PES$(50)_2(25)$	0.81	0.78	0.82	0.78
PES$(19)_2(83)$	0.92	0.96	0.94	1.76
PES$(15)_2(85)$	0.92	0.91	0.90	1.12
PES$(40)_2(60)$	0.92	0.84	0.79	1.37
PEH$(6)_2(27)(6)_2$	0.95	0.94		
PEH$(12)_2(27)(12)_2$	0.95	0.90		
PEH$(10)_2(95)(10)_2$	0.95	0.97	0.93	2.62
PESH$(10)_3(107)(10)_3$	0.91	0.93	0.84	2.54
PEPP$(10)_5(92)(10)_5$	0.74	0.80	0.75	1.34
PEC(101)-*g*-$(7)_{30}$	0.31	0.46	0.43	1.07
PEC(97)-*g*-$(23)_{26}$	0.25	0.32	0.35	0.92
PEC(100)-*g*-$(5)_2$	0.88	1.00	0.94	
PEC(100)-*g*-$(5)_{12}$	0.58	0.70	0.68	1.05
PEC(108)-*g*-$(6)_{12}$	0.63	0.75	0.74	1.06

compares the predicted and measured values for the stars with a centrally located branch ($s \leq 1$). Also plotted in this figure are the values for stars where the branch is not at the center of the backbone ($s > 1$). Although Zimm−Stockmayer still predicts g well for the stars with off-center branches (see Table 8), it is clear from the figure that the greatest effect on chain dimensions occurs when the branch is located near the center of the backbone. Note also that the values of ϵ for the sym-

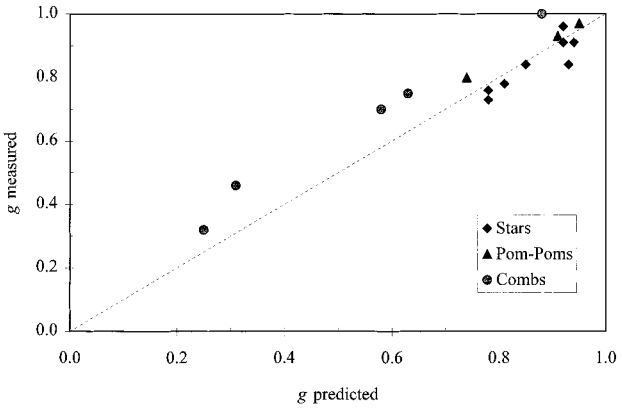

Figure 10. g^{meas} vs g^{pred} for branched model polyethylene. The dotted line is that for equality of the predicted and measured values.

metric stars are between 0.6 and 0.8. For those with shorter branches ϵ varies more widely, but since both g and g' are close to one this may not be significant.

The data in Table 8 show that the prediction of eq 4 is fairly good for the H ($f = 2$), super-H ($f = 3$), and pom-pom ($f = 5$) polymers, but in each case the value predicted is somewhat too small. For example, the $PEPP(10)_5(92)(10)_5$ polymer is somewhat larger than what would been expected if the arms and connector had their random-walk dimensions (although it is still smaller than the corresponding linear chain). This can be understood qualitatively in terms of the crowding of the arms that occurs for such high functionality molecules. This is similar to the result for symmetric stars.[47] The Zimm−Stockmayer prediction works well for three- and four-arm symmetric stars but is too small when the functionality is greater than four. The values of ϵ for these polymers are all greater than one ($g > g'$); we do not know the significance of this.

A similar result holds for the combs. The predictions from eq 5 underestimate g for all of the combs here, and the discrepancy tends to be larger as the number and length of the arms increase. As with the $\alpha-\omega$ polymers, this is likely due to crowding of the arms. Similar behavior has been seen for polystyrene combs by Roovers.[27] The values of ϵ for the combs are all approximately one. For all of the branched polymers discussed herein, the degree to which the Zimm−Stockmayer model fails to predict the true chain dimensions can be seen in Figure 10. Here we have plotted the measured g vs its predicted value. In general, the predictions work fairly well but tend to fail by underpredicting the chain dimensions. It appears that the greater the amount of polymer that is in the branches, the larger the discrepancy seen from assuming random-walk statistics for each chain section. A better theory of the dimensions of such highly branched chains would be useful.

Conclusions

Well-defined, branched polybutadienes have been synthesized by the use of several silicon chloride coupling reactions on nearly monodisperse, anionically prepared polybutadienes. Hydrogenation of these materials gave the corresponding model branched polyethylenes. The combined characterization results on the prepared polybutadiene and polyethylene indicated that these branched species have well-defined structures and narrow molecular weight distribution. By the methods outlined here, a wide variety of model polyethylenes with long branches have been produced. This only represents a small fraction of the structures that are possible, but even on this list the various parameters that control the properties of these polymers, particularly their flow behavior, are varied over an enormous range. These include the lengths of the main backbone of the polymer and of the branches attached to it, the number of those branches, and the manner of the placement of those branches along the backbone. Thus, these anionic techniques can be used to produce an extremely wide variety of branched polyethylenes. Several of these model branched polyethylenes (e.g., combs and pom-poms) have been reported for the first time. The relation of the details of long chain branching structure to chain dimensions has also been demonstrated. Predictions from ideal dimensions (Zimm−Stockmayer) agree well with the measured g values for the polymers with a small number of branches, but they underestimate g when there are many long branches. The rheological behavior of these polymers, both in shear and in extension, will be addressed in subsequent papers.

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