Arborescent Graft Polybutadienes

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ABSTRACT: Cascade-branched, "graft on graft" polybutadienes, denoted arborescent graft polymers, were prepared by hydrosilylation of polybutadiene vinyl groups with chlorodimethylsilane, followed by grafting with living polybutadiene chains. Repeated hydrosilylation−anionic grafting cycles led to a treelike outward growth, yielding well-defined, spherically shaped macromolecules. The molecular weight of the materials increased dramatically with each grafting cycle, since polymer chains rather than small molecules were used as building blocks. The materials were characterized by means of gel permeation chromatography, static light scattering measurements, and viscosimetry.

Introduction

Highly branched polymers are of academic and industrial interest because of their peculiar rheological properties[1−3] and their potential application as impact modifiers.[4] Of the branched polymers, star polymers and cascade-branched polymers are of special interest because they are well-defined and enable studies on the basic structure−property relations but also because they can provide very peculiar properties, e.g., they have the ability to enclose small molecules.[5,6] Several approaches to cascade-branched polymers have been developed. Starting from a core molecule, suitably functionalized molecular building units can be added in repeated reaction sequences, such that each monomer unit links at least three more units of monomers in the next addition. This stepwise growth can be effected in a divergent[7] or in a convergent[8] manner and leads to the well-known synthesis of dendrimers.

Well-defined branched macromolecules can also be constructed by linking macromolecules instead of small molecules. By connecting several polymer chains to one multifunctional core, multiarm star polymers are obtained.[9] The grafting of polymer chains onto a linear macromolecule leads to a comb polymer, which can be converted to cascade-branched polymers by the development of new reactive sites along the side chains of the comb polymers, followed by grafting (Figure 1). The few cascade-branched polymers, which have been produced by this "graft on graft" strategy so far, are described in the literature as arborescent graft[10] or comb-burst[11] polymers. With a sufficiently high and constant grafting density f, a dramatic increase of the molecular weight with each generation can be achieved according to the following:

$$M_\mathrm{w} = M_\mathrm{bb} + fM_\mathrm{b} + ffM_\mathrm{b} + fffM_\mathrm{b} + ...$$

where the index bb denotes the backbone and b the grafts. A backbone and graft molecular weight $M_\mathrm{b} = M_\mathrm{bb} = 10\ 000$ and a grafting density of 10 grafts per primary chain, e.g., leads to $M_\mathrm{w} = 1.1 \times 10^7$ g/mol in three grafting steps. A peculiar aspect of the graft on graft strategy is that the architecture can be controlled by varying the grafting density or the length of the constituent macromolecules in each generation separately.

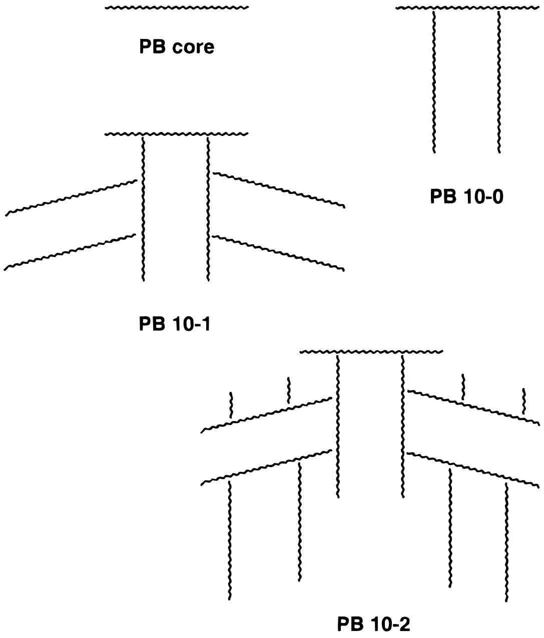

Figure 1. Formation of the cascade-branched polybutadienes. Each chain is grafted with about 10 side chains.

This work describes a rather simple synthesis of cascade-branched polybutadienes on the basis of the reaction of ω-polybutadienyllithium with chlorosilane groups which have been introduced into the parent polymer chain by hydrosilylation.

Experimental Section

Materials. 1,3-Butadiene (99.5%) was obtained from Union Carbide. *n*-Hexane (99%) was purchased from Merck; chlorodimethylsilane (98%), dibutylmagnesium (1.0 M in heptane), and *n*-butyllithium (1.6 M in hexanes) were obtained from Aldrich; platinum−cyclovinylmethylsiloxane complex (3−3.5 wt % Pt) was obtained from ABCR (Karlsruhe), *sec*-butyllithium (1.4 M in cyclohexane/hexane) from Chemetall (Langelsheim), and Argon 5.0 from Hoek Loos (Schiedam).

Characterization. Gel permeation chromatography (GPC) was performed in cyclohexane using Waters microstyragel $10^5 + 10^4 + 10^3 + 10^6$ columns, a Waters 410 refractive index (RI) detector, and a Viscotec H102B viscosity detector. Molecular weights of the linear polybutadienes were calculated by

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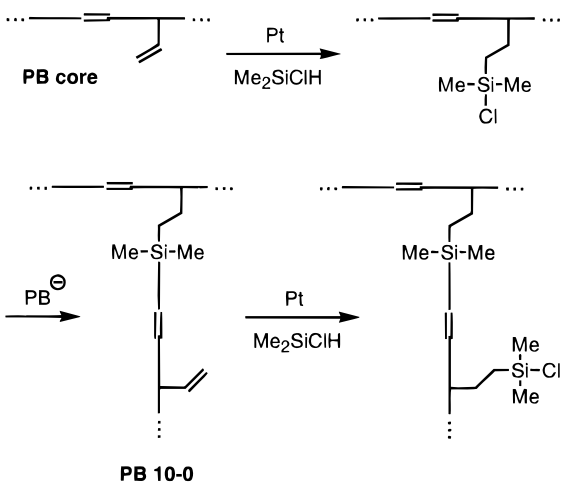
Scheme 1. Hydrosilylation and Anionic Grafting of Polybutadiene



comparison of the elution volumes with a calibration obtained for narrow polyisoprene samples (PSS, Mainz). Light-scattering measurements on the polybutadienes were carried out in THF. A wavelength of 632.8 nm was used, and scattered intensities in the angular range $28.1° \leq \theta \leq 140°$ were measured using a Wyatt DAWN DSP-F light-scattering detector (Wyatt Technology, Santa Barbara) that was connected to the GPC system. Polybutadiene (PB) d*n*/d*c* values in THF were calculated from the RI signal and the concentration of the polymer solutions. Values for linear PB obtained this way ($dn/dc = 0.130$ g/mL, 20 °C) agree well with literature.[12] PB 10-0, $dn/dc = 0.122 \pm 0.001$; PB 10-1, $dn/dc = 0.121 \pm 0.001$; PB 10-2, $dn/dc = 0.043 \pm 0.001$. Weight-average molecular weights $\langle M_w \rangle$ (g/mol) and root-mean-square radii of gyration $\langle R_g \rangle$ (nm) were calculated using the Debye equation.[13] Prior to light-scattering and viscosity measurements, sample solutions were filtered through 0.45 μm pore filters.

Intrinsic viscosities $[\eta]$ of the branched polybutadienes were determined in toluene at 25 °C in a Schott Ubbelohde Viscometer 531 01 (capillary diameter i.d. = 0.53 mm). A 531 03 type (i.d. = 0.46 mm) was used for the backbone PB 10 000. Flow times for the solvent and six polymer concentrations below the overlap concentration c^* were measured in a setup consisting of a Schott T100 titrator and a Schott AVS350 control unit and used to determine $[\eta]$.

^1H NMR spectra were recorded at 250.1 MHz in $CDCl_3$ on a Bruker-AC 250 instrument. All chemical shifts refer to tetramethylsilane (0 ppm).

Purification of Solvents and Monomer. *n*-Hexane was dried on *n*-butyllithium and distilled. 1,3-Butadiene (36 g, 0.665 mol) was dried *in vacuo* on dibutylmagnesium (5 mmol) at −30 °C and condensed into an ampoule of a known weight. The ampoule was sealed under vacuum and stored at −20 °C.

Polymerization. Anionic polymerization of butadiene was carried out by using standard high-vacuum techniques.[12] Polymerization vessels were dried under high vacuum (10^{-5} mbar). *sec*-Butyllithium (3.6 mmol) was added to degassed *n*-hexane (400 mL) in an argon-filled vessel connected to a vacuum line. The solution was then frozen in liquid nitrogen, the vessel was evacuated, and butadiene (36 g, 0.665 mol) was condensed into the reaction vessel. The frozen vessel was sealed, separated from the high-vacuum line, and immersed in a water bath (17 °C), and the mixture was stirred for 48 h.

Hydrosilylation and Anionic Grafting. A degassed mixture of dry *n*-hexane (25 mL), chlorodimethylsilane (1.6 mL, 14.4 mmol), comb polybutadiene PB 10-0 (3.58 g, 3 mmol of vinyl groups), and platinum−cyclovinylmethylsiloxane complex (1 drop) was stirred overnight under argon in a flask connected to a high-vacuum line. After 20 min, a light-yellow color, indicating the start of the hydrosilylation, was observed. Quantitative hydrosilylation of the vinyl groups required about 6 h (^1H NMR). Excess chlorodimethylsilane was removed *in vacuo*. Dry *n*-hexane (25 mL) was added to the hydrosilylated PB, and the flask was frozen in liquid nitrogen, evacuated, separated from the vacuum line, and molted onto a polymerization vessel. In this vessel, living polybutadiene 10 000 was prepared as described above. Then, when the breakseal was opened, the hydrosilylated PB 10-0 was added to the polybutadienyl anions (20% excess to chlorosilane groups) and the mixture was stirred overnight at 25 °C. The vessel was opened, degassed MeOH was added, and the 20% excess PB 10 000 was removed by means of fractionation in 2-propanol/toluene mixtures. The product, PB 10-1, was precipitated in MeOH containing 0.02% of 2,6-di-*tert*-butyl-4-methylphenol and stored at −20 °C. Yield was 30 g. Higher generations were prepared using the same conditions and reaction times.

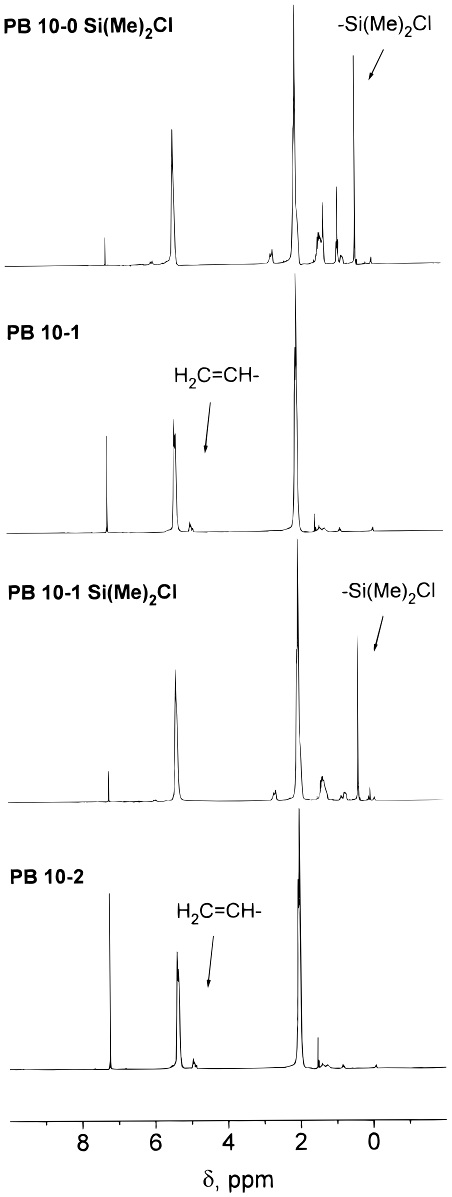


Figure 2. ^1H NMR spectra of the arborescent graft polybutadienes after hydrosilylation (PB 10-0 $Si(Me)_2Cl$ and PB 10-1 $Si(Me)_2Cl$) and anionic grafting (PB 10-1 and PB 10-2), evidencing the complete conversions achieved in both reactions.

Results and Discussion

A polybutadiene backbone with a narrow molecular weight distribution ($\langle M_w \rangle = 10\,000$, $\langle M_w \rangle / \langle M_n \rangle = 1.1$) was prepared by means of anionic polymerization techniques, using *s*-BuLi as the initiator and *n*-hexane as the solvent. ^1H NMR measurements indicated that polybutadiene chains with 6% 1,2-units[2,14] were produced. The pendant vinyl groups could readily be con-

Table 1. Characteristics of the Core and Outer Grafts of PB 10-0, PB 10-1, and PB 10-2

	$\langle M_n\rangle^a$ (g/mol)	$\langle M_n\rangle^b$ (g/mol)	$\langle M_w\rangle^b$ (g/mol)	$\langle M_w\rangle/\langle M_n\rangle^b$	vinyl groups^c per chain
PB core	10×10^3	8.7×10^3	9.6×10^3	1.1	9.7
PB 10-0	10×10^3	9.8×10^3	10.8×10^3	1.1	10.9
PB 10-1	10×10^3	10.0×10^3	11.0×10^3	1.1	11.1
PB 10-2	10×10^3	9.6×10^3	10.5×10^3	1.1	10.7

[a] Calculated from $[M]/[I]$. [b] GPC in cyclohexane. [c] Number of vinyl groups per chain, from $\langle M_n\rangle$ of the last generation of grafts and the ^{1}H NMR fraction (6% 1,2-units).

Table 2. Characteristics of the Cascade-Branched Polybutadienes

	$\langle M_n\rangle^a$ (g/mol)	no. of outer arms^a	$\langle M_w\rangle/\langle M_n\rangle^b$	$\langle M_w\rangle^c$ (g/mol)	$\langle R_g\rangle_z{}^c$ (nm)	$\langle R_h\rangle^d$ (nm)	$\langle R_g\rangle_z/\langle R_h\rangle^e$	$[\eta]^f$ (mL/g)
PB core	9.6×10^3		1.1					22
PB 10-0	1.03×10^5	10	1.2	1.9×10^5	14.5	10.5	1.4	71
PB 10-1	1.06×10^6	105	1.3	4.5×10^6	35.2	24.8	1.4	91
PB 10-2	1.27×10^7	1160	1.3	7.1×10^7	46.8	57.0	0.8	92

[a] Calculated from known graft molar mass $\langle M_n\rangle$ and 6 mol % vinyl groups in the polybutadiene chains (i.e., grafting density). [b] GPC in cyclohexane. [c] Light scattering (THF, $\lambda = 632.8$ nm). [d] Calculated from the Stokes−Einstein equation using $\langle M_n\rangle$. [e] $\rho = \langle R_h{}^{-1}\rangle_z \langle R_g\rangle_z$ (ref 21). [f] Viscosimetry (toluene, 25 °C).

verted into reactive grafting sites by hydrosilylation with chlorodimethylsilane in hexane, using a platinum−cyclovinylmethylsiloxane catalyst (Scheme 1). Very high-grafting efficiencies are essential for obtaining well-defined branched polymers. In general, it is known that hydrosilylation reactions,[15] as well as end-capping reactions of polystyryl-, polyisoprenyl-, and polybutadienyllithium with chlorosilanes[9,16] can proceed in quantitative yields.

Complete hydrosilylation of the vinyl groups was achieved in 6 h at 25 °C as evidenced from ^{1}H NMR spectrometry. The vinyl signal at $\delta = 4.9{-}5.1$ ppm disappeared, and a sharp signal at $\delta = 0.3$ ppm, belonging to $-\mathrm{Si(Me)_2Cl}$ appeared (Figure 2). The signal of the 1,4-units, at $\delta = 5.3{-}5.6$ ppm, was not affected, indicating that the internal double bonds of the polymer chains were left intact.

Living polybutadiene 10 000 was readily grafted onto the hydrosilylated core, and a comb polymer, PB 10-0, was obtained (Scheme 1). The grafting reaction was performed with a 20% excess of living polybutadiene, which could be removed by means of fractionation in 2-propanol/toluene mixtures and analyzed, in order to establish the molecular weight of the grafts. The high efficiency of the anionic grafting reaction was monitored by ^{1}H NMR spectrometry. After grafting overnight, the above-mentioned signal at 0.3 ppm had disappeared completely and a new signal at $\delta = 0.0$ ppm, typical of a tetraalkylsilane group, was observed.

Because of the complete conversion of the vinyl groups of the backbone (PB core), subsequent branching by hydrosilylation−anionic grafting therefore occurs exclusively on the side chains of the comb polymer PB 10-0, yielding PB 10-1. Branching of PB 10-1 led to the highest generation cascade-branched polybutadiene PB 10-2 discussed in this paper (Figure 1).

Table 1 summarizes the molecular weight data of the anionic polybutadienes which were employed in the different grafting steps. The molecular weight of the grafts was determined for each grafting generation and used to calculate the number average molecular weights $\langle M_n\rangle$ of the branched polybutadienes on the basis of the grafting density according to 6% 1,2-units (Table 2).

Independent information on the molecular weight of the higher generation cascade-branched polybutadienes PB 10-1 and PB 10-2 was obtained by light-scattering measurements on polymer solutions in THF. The molecular weights found by light scattering exceeded the calculated molecular weights $\langle M_n\rangle$ of PB 10-0, PB 10-1, and PB 10-2. Since arm molecular weights are accurately known and the branched molecules are assembled in a controlled manner, this might be attributed to a higher fraction of 1,2-units in the polybutadiene chains than that determined by ^{1}H NMR, i.e. 6%.

The intrinsic viscosity of the cascade-branched polybutadienes increased with the first branching step and leveled off to a constant value of about 90 mL/g, irrespective of the tremendous increase in molecular weight upon conversion of PB 10-1 to PB 10-2 (Table 2).

As could be anticipated from viscosity measurements on cascade-branched polystyrenes,[9] the measured intrinsic viscosities of the branched polybutadienes are much smaller than those calculated for linear polybutadienes of similar molecular weights using the Mark−Houwink relation $[\eta] = (30.5 \times 10^{-3}) \times M^{0.725}$ (mL/g).[17]

Studies on several classes of dendrimers have revealed a similar characteristic relation between the molecular weight and the intrinsic viscosity of these highly branched macromolecules. The intrinsic viscosity of poly(propylenimine) dendrimers[18] first increases with increasing generations but decreases after the fourth generation. This behavior was also observed with the poly(amido amine) dendrimers and was explained by the formation of a dense outer shell in the dendrimers.[19] Even though dendrimers have a much more perfect architecture than the cascade-branched polybutadienes, the higher generation cascade-branched polymers can also be regarded as spherical macromolecules.[10,20] From the trend in the intrinsic viscosities, it can be concluded that the transition from a flexible-branched macromolecule to a sphere, caused by steric crowding of the grafts, takes place upon developing PB 10-1 to PB 10-2.

The intrinsic viscosity of the branched polybutadienes PB 10-1 and PB 10-2 can be used to estimate the hydrodynamic radii $\langle R_h\rangle$ of these molecules by means of the Stokes−Einstein equation

$$V_h = \mathrm{M}[\eta]/2.5N_A$$

where N_A is Avogadro's number. The ratio of the z-average radius of gyration and the hydrodynamic radius,

$$\rho = \langle R_h{}^{-1}\rangle_z \langle R_g\rangle_z$$

varies for linear polymers, branched polymers, and spheres and can therefore provide information on the molecular geometry.[21−23] For monodisperse linear polymers, a theoretical value of $\rho = 1.48-1.50$ is predicted, while $\rho = 1.27$ is found experimentally. For hard spheres, the theoretical value $\rho = 0.774$ agrees quite well with the experimental value $\rho = 0.775$.[21−23]

In the case of the branched polybutadienes PB 10-0 and PB 10-1 (Table 2), the ratio of the hydrodynamic and gyration radii resulted to $\rho = 1.4$, indicating a coil type structure. For the highest generation of cascade-branched polybutadienes PB 10-2, a ρ value of 0.8 was found, which is close to that expected for a globular particle. This result supports the idea that cascade-branching ultimately leads to rigid, globular macromolecules.

In summary, it has been shown that the hydrosilylation−anionic grafting sequence can be successfully applied to prepare arborescent polybutadienes approaching a globular structure. As an outlook, it can be stated that the concept of arborescent graft copolymers provides, yet little explored, possibilities for controlling the architecture and the composition of the branched macromolecules.[20,24] The overall shape of the molecules can be influenced by changing the arm lengths or the grafting density.[25] The former can readily be controlled by varying the ratio of monomer to initiator. The latter depends on the vinyl content of the butadiene chains, which can be increased by preparing the grafts in solvents of appropriate polarity.[2,14] The graft on graft approach will also allow preparation of core-shell particles of well-controlled size by performing the last hydrosilylation−anionic grafting reaction on a cascade-branched polybutadiene with, for instance, living polystyrene or by functionalizing the outer vinyl groups, for instance by means of hydroboration−oxidation. Finally, hydrogenation of cascade-branched polybutadienes leads to interesting, well-defined highly branched polyethylenes. These aspects are currently under investigation.

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