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STAR-BRANCHED AND HYPERBRANCHED POLYISOBUTYLENES

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Abstract: The synthesis of branched (star-branched and hyperbranched) polyisobutylenes (PIBs) is described in this paper. Multiarm-star and brush-like structures were prepared by using a tert -hydroxy functionalized polystyrene macroinitiator (4-(1-hydroxy-1-methylethyl)styrene-**co**-styrene (HMESt-**co**-St). These polymers were characterized by SEC-light scattering. The first successful synthesis of gel-free high molecular weight hyperbranched PIBs was achieved by using HMESt as an *inimer (**ini**tiator-mono**mer**)* in conjunction of living isobutylene (IB) polymerization. Initial characterization of the structure of this polymer included SEC analysis and selective destruction of the HMESt-junctions.

INTRODUCTION

Branched polymers are of substantial commercial interest, due to their markedly lower solution and bulk viscosities and less shear sensitivity, than their linear counterparts. Commercially they are produced by living anionic polymerizations and are used as viscosity improvers in lubricating oils. Star-branched polymers can be made the "Arm first" and the

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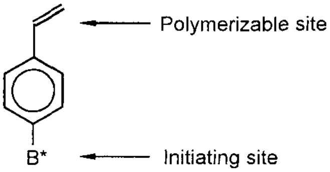
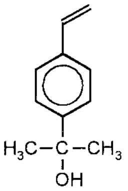
"Core first" method, which were first developed in anionic systems (Ref. 1). In carbocationic IB polymerization systems, the "Arms first" method was used successfully for the synthesis of star-branched polyisobutylenes (PIBs) with 6-70 arms (Ref. 2 - 6). In this process, the monofunctional living PIB chains are reacted with bifunctional monomers such as divinyl- or diisopropyl benzene to form the crosslinked core. Unfortunately, this method leads to "ill-defined" cores thus the number of the arms cannot be controlled precisely, and the reaction times are very long (10-100 hrs). The "Core first" method is based on the usage of multifunctional initiators from which the star arms are grown. This method was successfully used for the synthesis of three- and four-arm star PIBs in non-living systems (Ref. 7, 8) and three- and six-arm star PIBs in living systems (Ref. 9, 10, 11). Recently the elegant synthesis of an eight-arm star PIB using a calixarene-based multifunctional initiator was reported (Ref. 12). The present paper describes the synthesis of high molecular weight (MW) multiarm-star branched PIBs under living conditions using multifunctional polystyrene (PSt)-based macroinitiators, and the synthesis of novel, hyperbranched PIBs. The concept of self-condensing polymerization was introduced very recently by Frechet (Ref. 13). Monomers capable of self-condensation contain two functional groups; one for polymerization, and one for initiation:



This concept was extended to copolymerizations to produce random hyperbranched polyisoolefins (Ref. 14) and the term *inimer* was coined. Interestingly, the first hyperbranched PIB structure prepared by using 4-chloromethylstyrene as an *inimer* was reported by Nuyken's group (Ref. 15) well before the introduction of the self-condensation concept. In the present work HMESt was used as an *inimer*.



HMESt

EXPERIMENTAL

Materials

Methyl chloride (MeCl) and isobutylene were condensed from the gas phase. Methyl cyclohexane (MeCHx) (Phillips, polymerization grade) and Hexane (Caledon, 99%) were distilled off CaH_2. THF (Baker, HPLC grade) was distilled off $LiAlH_4$. Styrene (St) was purified by chromatography to remove the inhibitor followed by distillation. The synthesis of HMESt and HMESt-**co**-St have been described (Ref. 16 - 18). The composition of the copolymers was determined by ^1H NMR spectroscopy. Titanium tetrachloride ($TiCl_4$), boron trichloride (BCl_3), di-t-butylpyridine (DtBP), dimethyl acetamide (DMA), *p*-bromo-styrene, magnesium, trifluoroacetic acid (Aldrich), ethanol (Phillips, technical grade), methylene chloride ($MeCl_2$, HPLC grade), hydrogen peroxide (30 %), and acetone (anhydrous) (Baker) were used as received.

Procedures

Polymerizations were carried out in round-bottomed flasks equipped with an overhead stirrer and a thermocouple, in a dry box under a dry nitrogen atmosphere. Typical living polymerization recipes were used as described (Ref. 19, 20) at -80°C. Samples were taken at specified times into chilled culture tubes containing ethanol. Conversions were determined gravimetrically. Core destruction was performed as described (Ref. 21).

Molecular weights (MW) and molecular weight distributions (MWD) were determined by Size Exclusion Chromatography (SEC) using a Waters system equipped with 6 Ultrastyragel columns (100, 500, 10^3, 10^5 and 10^6 Å) thermostatted at 35 °C. The mobile phase was THF at 1 ml / min flow rate. The flow rate was monitored by the use of elemental sulfur as the internal marker. The instrument was calibrated with 14 narrow MWD PSt standards. MW and MWD values were calculated using the Universal Calibration Principle, which was demonstrated to give excellent agreement with narrow PIB calibration (Ref. 22). In case of the branched polymers, the SEC data measured by the above discussed instrument can be considered as orienting values only for comparison. Absolute molecular weights were measured on two samples by light scattering using a miniDAWN Laser Light Scattering detector; dn/dc values were measured by an Optilab 903 instrument (Wyatt Technology) using the mass method (measurement courtesy of I.Majoros, University of Akron). ^{1}H NMR spectra were run on a Bruker AC200 spectrometer.

RESULTS AND DISCUSSION

Synthesis of Multiarm-Star PIBs by Living Polymerization

Frechet described the synthesis of tert-ester functionalized PSt macroinitiators which he used to initiate IB polymerization, producing graft copolymers with very short PIB arms with poor efficiency (Ref. 16). We decided to use tert-hydroxy functionalized PSt as a macroinitiator, because tert-hydroxy compounds were shown to be effective initiators of living IB polymerizations (Ref. 9).

A series of St/HMESt copolymer macroinitiators were prepared by the radical copolymerization of HMESt and St as described. Copolymerization was found to be ideal with $r_1 \equiv r_2 \equiv 1$ (Ref. 18). Characteristic data of the macroinitiators used for the star-synthesis are given in Table 1.

Table 1. MWs and Average Number of Initiating Sites for Macroinitiators used in Star-PIB Synthesis

M_n 10^3 g/mol	Initiating sites mol% by NMR	Initiating sites Avg. #
15.2	11.8	16
8.2	35.2	23

These macroinitiators were found to have limited solubility in 40/60 mixtures of MeCl with MeCHx or Hexane. The solubility was improved by *in situ* chlorination of the active hydroxy sites. First the chlorination was done by dissolving the first macroinitiator with an average of 16 initiating sites per chain in MeCl, and adding BCl_3 to this mixture in the presence of a small amount of IB. The amount of IB was calculated so that about three units of IB would add to each initiating site. Then Hexane was added to the mixture to yield the desired 40/60 MeCl/Hexane composition, followed by the addition of IB and $TiCl_4$. A similar two-step process for living IB polymerization has been reported (Ref. 23). The MW increased with time, and the final conversion was 42 %. Figure 1 shows the SEC traces of the starting macroinitiator and the resulting PIBs. This latter shows a bimodal distribution with a lower molecular weight shoulder. The M_p values for the two peaks are $M_{p,1}$ = 105,000 and

$M_{p,2}$ = 16,000. The shoulder constitutes about 15 % of the total amount of PIB, and most probably represents leftover initiator and / or low molecular weight PIB. Assuming that all sites of the macroinitiator initiated, the PIB of the higher molecular weight fraction would have M_n = 7000 per arm. Thus this structure can rather be considered as a graft copolymer. It should be noted here that these MW values are for comparative and orienting purposes, as the SEC calibration is valid for linear polymers only.

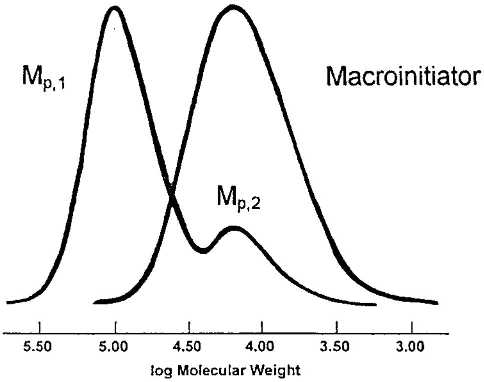


Fig. 1. SEC traces of branched PIBs made with a 16-functional macroinitiator (see Table 1) using BCl_3 followed by $TiCl_4$

In the next experiment the macroinitiator with an average of 23 initiating sites was used (see Table 1). In this case the chlorination was done in MeCHx using $TiCl_4$. A fraction of the initiator precipitated as an insoluble gel. It has been reported that under similar conditions the resulting tert-chloro compounds may eliminate HCl and crosslink (Ref. 24). The soluble portion of the initiating system, which was a bright yellow colour, produced a living system with a monomodal GPC trace growing linearly with time. Figure 2 shows the SEC traces of the samples. 66% conversion was reached within 60 minutes, producing a high MW polymer with narrow MWD and no detectable side products. The MW increased linearly with time, indicating living conditions. The final sample was analyzed by SEC-LLS. With the dn/dc measured as 0.09, the miniDAWN gave M_n = 375,000 and MWD = 1.1. The slope of the radius of gyration - MW plot constructed for this peak was 0.5, indicating the formation of a branched polymer, but this value is higher than the 0.3 expected for a compact star-branched polymer. Assuming that all sites initiated, the PIB arms would have M_n = 16,000 emanating from a PSt-based core of M_n = 8,200; this structure rather resembles a dense 'brush'. Most probably the initiator efficiency was less than 100% and not all of the sites initiated, so the exact number of arms and arm lengths cannot be calculated. "Core destruction" of this polymer yielded PIB arms with M_n = 10,000 and MWD = 2.

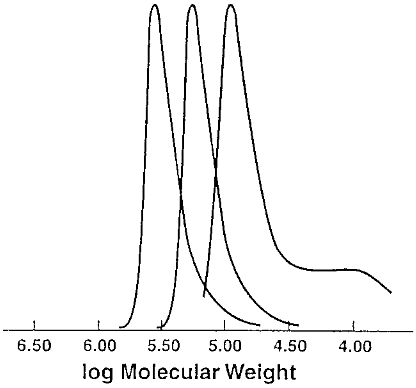


Fig. 2. SEC trace of a branched PIBs made with a 23-functional macroinititor (see Table 1) using $TiCl_4$ in MeCHx

In the next experiment the macroinitiator with an average of 16 initiating sites was added to the 40/60 MeCl/MeCHx mixture and $TiCl_4$ was used for the chloride exchange. The final conversion was 93.2% in 16 minutes. Similarly to that shown in Figure 1, the MW of the polymer grew with time, and a low MW shoulder developed in the final product. The final bimodal sample showed $M_{p,1}$ = 400,000 (80 wt%) and $M_{p,2}$ = 80,000 (20 wt%). As in the prior experiment, the results demonstrate multiple initiation but less than optimal conditions. The final sample was analyzed by SEC-LLS. With the dn/dc measured as 0.09, the miniDAWN gave M_n = 200,000 and MWD = 1.1 for the lower MW peak, and M_n = 750,000 and MWD = 1.3 for the high MW peak.

The radius of gyration - MW plot constructed for this peak gave a slope of 0.3, demonstrating the formation of a star-branched polymer (Ref. 25, 26). Assuming that all sites initiated, the PIB arms would have M_n = 46,000 emanating from a PSt-based core of M_n = 15,200. The molecular weight of the high MW peak indicates that the initiating efficiency was less than 100% and/or not all of the sites initiated, thus the arm MW is most probably higher than M_n = 46,000. The arms thus are considerably longer than the macroinitiator core, which explains the compact star behaviour.

Synthesis of Hyperbranched PIBs by Living Polymerization

In the course of our investigations it occurred to us that hyperbranched PIBs could be prepared using HMESt as an *inimer* in our living polymerization. While the tert-hydroxy functionalities would serve as initiating sites, the *inimer* would incorporate into the PIB chain via its double bond. The HMESt thus incorporated could then form branches by initiating a new chain, producing the following hypothetical structure (Refs.14,15):

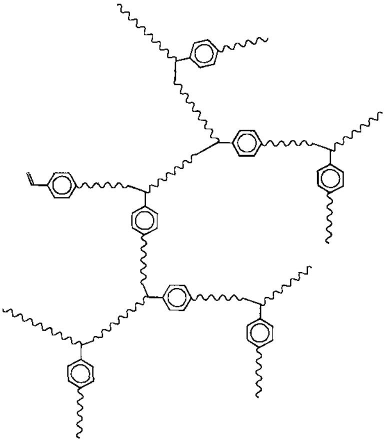


Fig.3. Hypothetical structure of a hyperbranched PIB

Figure 4 shows the SEC traces of a hyperbranched PIB made by monomer/*inimer* ratio of 150. The IB conversion was 86% in 60 minutes. The SEC trace is multimodal, with three distinct peaks at $M_{p,1}$ = 200,000, $M_{p,2}$ = 500,000 and $M_{p,3}$ = 1,300,000. The overall MW was calculated to be M_n = 155,000 with an MWD of 2.5. It should be noted here again that the MW values are for comparative and orienting purposes only. This polymer was subjected to the "core destruction" procedure that selectively destroys the aromatic rings but leaves the PIB chains intact . The SEC trace of the resulting PIB is shown as an insert in Figure 4; it is monomodal with an M_n = 19,000 and MWD = 2. These results indicate that the structure of the branched PIB is most probably similar to that shown in Figure 3, with the junctions being HMESt units. Further characterization of this and similar PIB structures is needed to prove the hyperbranched structure.

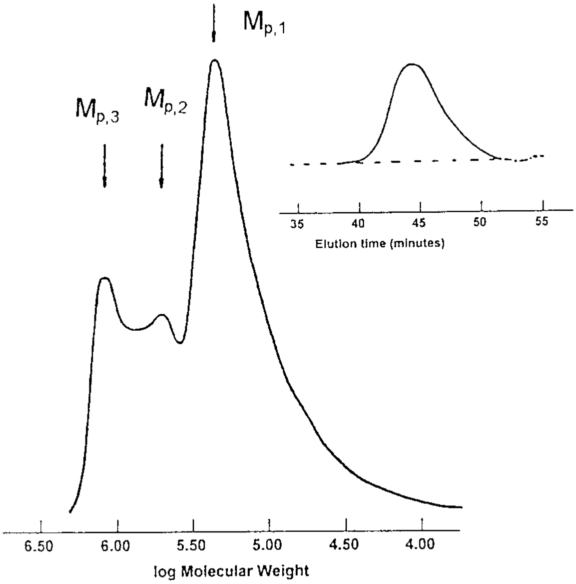


Figure 4. SEC traces of a hyperbranched PIB before and after (inset) "core destruction"

In sum, the successful synthesis of multiarm-star branched and hyperbranched PIBs by living polymerization was achieved. Initial characterization of a multiarm-sample with no detectable side products (BRUSH-1), and a hyperbranched sample indicated that they had the desired branched architecture. Optimization of the syntheses and further characterization of the branched polymers are in progress.

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