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Synthesis and Self-Assembly of 2nd Generation Dendritic Homopolymers and Copolymers of Polydienes with Different Isomeric Microstructures

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Summary: Synthesis of 2^{nd} generation dendritic polymeric materials via anionic polymerization procedures in combination with chlorosilane chemistry, consisting either from one polydienic segment (homopolymers) or from two chemically different polydienic components (copolymers), is described. The polydienes used were poly(butadiene) (PB) with ~90% 1,4-isomerism and poly(isoprene) (PI) with increased 3,4-isomerism (~60%). Molecular characterization of intermediate products and the final dendritic materials was made with Gel Permeation Chromatography (GPC), Membrane and Vapour Pressure Osmometry (MO and VPO respectively), Gas Chromatography –Mass Spectroscopy (GC-MS) and ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR) Spectroscopy, leading to the conclusion that they can be considered model polymers. Morphological studies solely with Transmission Electron Microscopy (TEM) have been conducted on two of the four synthesized copolymer samples exhibiting microphase separation between the two polydiene segments.

Keywords: anionic polymerization; gel permeation chromatography (GPC); macromonomers; morphology; TEM

Introduction

A dendritic structure is considered as an architecture including random hyper branched, dendrigrafts and dendrimers. It is of great importance to differentiate these polymeric materials according to their divergences in properties and behavior. Extreme differences in properties can be attributed to the generation; therefore a large dependence on the complexity of the studied macromolecule is being observed. The successful synthesis of dendritic homopolymers and copolymers of various generations has been thoroughly reviewed and reported in the literature.[1]

The polymers synthesized in this work are eight 2^{nd} generation dendritic samples consisting of poly(butadiene) (PB) (with ~90% 1,4 isomeric microstructure) and poly(isoprene) (PI) (with increased 3,4 isomeric microstructure, ~60%),: four homopolymers of the $[(PB)_2PB]_3$ - $[(PI)_2PI]_3$ types and four copolymers of the $[(PB)_2PI]_3$ - $[(PI)_2PB]_3$ types, exhibiting compositional and molecular homogeneity.

The low expected value of the Flory-Huggins interaction parameter χ for the case of PB and PI, suggests that the two diene blocks would be miscible for a wide variety of molecular weights and compositions. Moreover, the role of molecular architecture to increase the critical value of χN (N: degree of polymerization) for microphase separation would suggest that polydienic dendritic copolymers would likely be single phased materials. However, since polydienes exhibit a range of isomeric

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microstructures, one should carefully consider the type and relative amount of the particular block stereoisomers, since local structure influences the segment-segment interaction parameter. The possible segment isomerisms for PB are 1,4- cis, 1,4-trans and 1,2-. In a non-polar synthesis procedure the resultant isomeric microstructure of a PB segment is predominantly 1,4- (92 wt % 1,4- and 8 wt % 1,2-). For the PI case there are more isomerisms: cis or trans 1,4-, 3,4- and 1,2-. The morphological study of linear[2] and non linear[3] ABC terpolymers consisting of one styrenic component and two dienes (PB and PI with isomeric microstructures identical with those reported in this work) lead to very well microphase separated three-phase structures, never observed before in the literature for such materials. This observation indicated that the 1,4-PB/3,4-PI interaction parameter is larger from that expected for other PB/PI pairs. The morphological characterization is completed on two of the copolymer samples, those of the $[(PB)_2PI]_3$ type, using Transmission Electron Microscopy (TEM).

Experimental Part

The purification of all reagents (monomers, solvents, initiator, linking and termination reagents) was carried out following the standards required for anionic polymerization procedures. The molecular characterization instrumentation used (GPC, MO, VPO, GC-MS and ^{1}H-NMR) is described analytically elsewhere.[1]

The abbreviations used to identify the different samples are $[(PB)_2PB]_3$-A, $[(PI)_2PI]_3$-A, $[(PB)_2PI]_3$-A and $[(PI)_2PB]_3$-A respectively (Table 1). The letter next to the sample types corresponds to the approximate molecular weight of each arm. In all samples the molecular weight of the chains is approximately the same (10,000 g/mol or 20,000 g/mol), therefore for the copolymers the volume fraction of the minority component is ~0.33.

Synthesis of Dendritic Copolymer of the $[(PB)_2PI]_3$ -10K Type

The PB living chain was synthesized by polymerizing 10 g of butadiene (0.135 mol) with sec-BuLi (0.1 mmol), in 150 ml of benzene at room temperature for 24 hours. The molecular weight of the living chain was approximately 10,000 g/mol. It was divided in 2 ampoules (approximate concentration of living chain $PB^{(-)}Li^{(+)}$ 0.05 mmol in each case). The 1st quantity was added drop wise in the 4-(chlrodimethylsilyl)styrene (CDMSS) solution (0.05 mmol in 10 ml of benzene); synthesized from p-chlorostyrene and dichlorodimethylsilane through a Grignard reaction,

Table 1.
Molecular characterization of precursors, intermediate and final polymers

Sample	total $\overline{M}_w \times 10^{-3}$ a)	total $\overline{M}_n \times 10^{-3}$ b)	$\overline{M}_w/\overline{M}_n$ d)	φ_{PB} e)
PB-10K	10.5	10.1	1.04	–
PB-20K	19.1	18.5	1.03	–
PI-10K	9.6	9.3 c)	1.03	–
PI-20K	20.2	19.5	1.04	–
$[(PB)_2PB]_3$-10K	88.6	82.0	1.08	–
$[(PB)_2PB]_3$-20K	152.7	141.4	1.08	–
$[(PI)_2PI]_3$-10K	85.5	78.4	1.09	–
$[(PI)_2PI]_3$-20K	175.8	162.8	1.08	–
$[(PB)_2PI]_3$-10K	92.0	85.2	1.08	0.70
$[(PB)_2PI]_3$-20K	161.7	147.0	1.10	0.66
$[(PI)_2PB]_3$-10K	90.2	82.8	1.09	0.34
$[(PI)_2PB]_3$-20K	165.2	150.2	1.10	0.32

a) Calculated from the results from Osmometry and SEC.
b) MO in toluene at 35 °C.
c) VPO in toluene at 50 °C.
d) SEC in THF at 30 °C with PS standards.
e) Volume fractions of PB segments calculated from ^{1}H-NMR in $CDCl_3$.

under high vacuum techniques; leading to the formation of the macromonomer. 2–3 monomeric units if styrene were added at the macromonomer for end-capping reasons. The addition of the PB living chain was accomplished via titration and controlled through GPC by collecting aliquots during the reaction. The solution was then added in the 2nd ampoule containing the remaining living chain in order to link the two chains creating the macroinitiator. Polymerization of 7 g or 0.9 mol of isoprene is initiated by the macroinitiator and completed within 24 hours. Prior to the addition of the monomer a very small amount of polar solvent (THF) is added in order to alter the microstructure of the finally synthesized PI chain. After the completion of the polymerization, trichloromethylsilane (CH_3SiCl_3) (0.025 mmol) is added in the flask and the linking reaction is completed in 25 days. The synthesis reactions are given in Figure 1.

Transmission Electron Microscopy (TEM)

Approximately 0.7 mm thick films of the materials were cast from a dilute solution (~4 wt %) in toluene, which is a nearly nonselective solvent, over a period of 1 week at ambient conditions. In order to obtain near-equilibrium microstructures, the films were annealed above the T_g of both segments ($-80\,^{\circ}$C and $-25\,^{\circ}$C for the PB and the PI with increased 3,4-isomerism respectively) for 7 days (at $40\,^{\circ}$C) under vacuum. For the TEM investigations, 50 to 100 nm thick sections were ultra-cryomicrotomed at $-90\,^{\circ}$C (lower than the T_g of the PB segments) and the sections were picked up on 300 mesh copper grids. Selective staining was necessary, since the intrinsic difference in electron density of PB and PI blocks does not provide adequate mass thickness image contrast. The grids were placed in the vapors of a 4% w/w OsO_4 – water solution for selective staining of the two diene domains for a small period of time (30–45 minutes, depending on the quality of the stainer solution). TEM experiments were carried out on a JEOL 2010F equipped with a post-column Gatan Imaging Filter (GIF). The zero loss energy filtered images were taken with an energy window of 15 eV.

Results and Discussion

The synthesis of the 2nd generation dendritic homopolymers has been described in

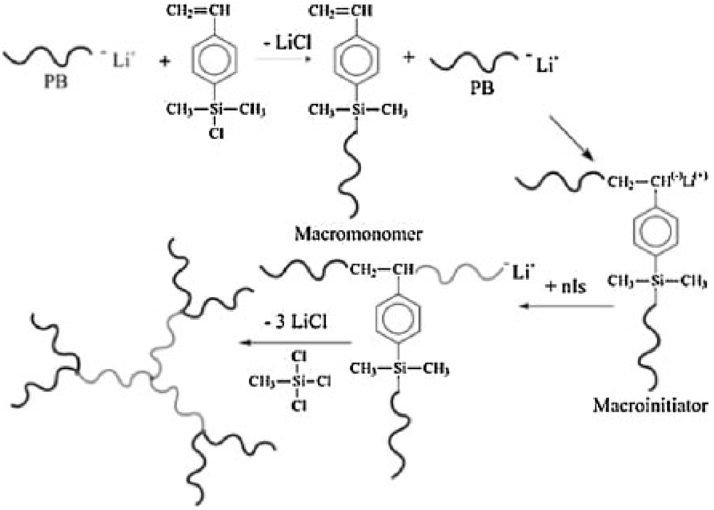

Figure 1.
Synthesis of the macromonomer, the macroinitiator, the 1st generation dendritic copolymer and the final 2nd generation dendritic copolymer of the $[(PB)_2PI]_3$ type from the 1st generation copolymer via linking reaction with CH_3SiCl_3.

details elsewhere.[1] When the living chain is synthesized a small number of styrenic monomeric units (2–3) are inserted in order to alter the reactivity of the living ends (end capping). Due to the minor steric hindrance of the polydiene living ends ($PI_{3,4}{}^{(-)}Li^{(+)}$ or $PB^{(-)}Li^{(+)}$), the insertion of specific amount of styrene (St) monomeric units at the end of the second living chain is adopted prior to the reaction of the intermediate product to the linking agent. This route is used in order to better control the addition of the dienic monomer at the vinyl bond, since the restricted movement of the new living chain (increased steric hindrance with St) leads to easier control during the addition to the CDMSS solution in order to substitute the para-positioned chlorine atom. This approach is different from the synthesis procedures reported by the Hadjichristidis' group[4,5] and has been used for both dendritic homopolymers and copolymers reported in this work. The molecular characterization results are exhibited in Table 1. Better control of the synthesis and less termination phenomena were observed with the aforementioned approach as can be noticed in Figure 2, where the GPC chromatographs of initial, intermediate and final products are exhibited. Finally the coupling of the monofunctional 1st generation copolymer with CH_3SiCl_3 gives the equivalent 2nd generation copolymer. Initially, in both homopolymer and copolymer samples when the capping reaction was not employed the first addition to the macromonomer was slightly successful but the 2nd addition to the vinyl bond of the macroinitiator was not possible.

The morphological studies on the copolymers have proven that the two dienic segments exhibit microphase separation. Until recently it was believed that all polydiene blocks stain identically.[2] However, OsO_4 staining depends on the detailed microstructure of a particular polydiene block. For example, with high 3,4 content (~55–60%) the PI block can stain less than the PB component with approximately 92% of 1,4-microstructure, probably due to steric hindrance, as observed via TEM and has already been reported in the literature.[2]

The morphology that was observed after TEM studies, for both $[(PB)_2PI]_3$-10K and $[(PB)_2PI]_3$-20K samples, is hexagonally close packed cylinders of PI (white regions) in the PB matrix (black regions). This result is quite consistent for PI minority samples with inner blocks of 30 vol. % and 34 vol. %. The cylinders consist of the inner PI chains and the matrix of the outer PB segments (majority component), as expected and are exhibited in Figure 3. $[(PB)_2PI]_3$-20K

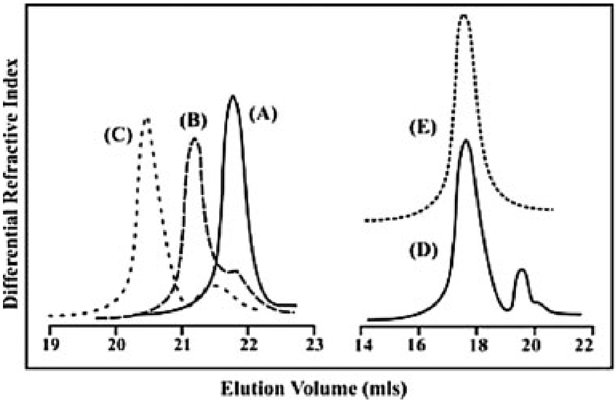

Figure 2.

SEC chromatographs of: (A) PB homopolymer with approximate number average molecular weight ($\overline{M}_n$) 10,000 g/mol, (B) $(PB)_2$-macroinitiator, (C) Living $(PB)_2PI^{(-)}Li^{(+)}$ 1st Generation Copolymer prior to linking with CH_3SiCl_3, (D) Unfractionated 2nd Generation Dendritic Copolymer of the $[(PB)_2PI]_3$ type and (E) Fractionated 2nd Generation Dendritic Copolymer of the $[(PB)_2PI]_3$ type.

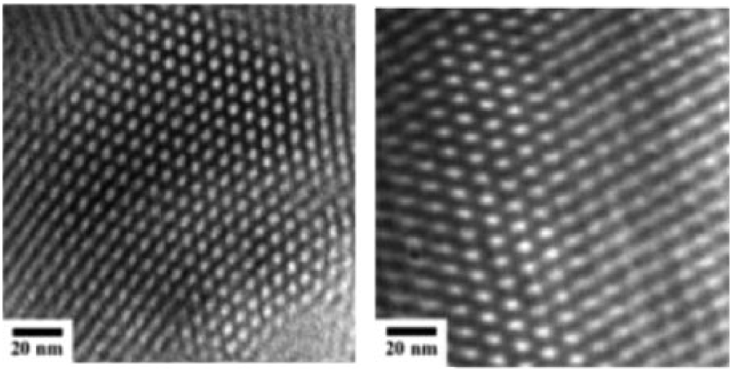

Figure 3.
TEM micrographs of the $[(PB)_2PI]_3$ 2nd generation dendritic copolymers. Left image corresponds to the $[(PB)_2PI]_3$-10K sample and right image to the $[(PB)_2PI]_3$-20K sample. Both cases exhibit hexagonally close packed cylinders of PI (lighter domains) in the matrix of PB segments (dark domains).

exhibited approximately twice the molecular weight of the $[(PB)_2PI]_3$-10K sample. Since the volume fractions of the minority component PI are quite identical (0.30 and 0.34 respectively) the morphology expected would be similar and the only difference is confined in the cylinder diameter and the inter-cylinder spacing leading to an increase in cylinder domains for the higher molecular weight up to ~60%. Raw calculations from the TEM images lead to the result that the cylinder – cylinder spacing is ~48 Å for the $[(PB)_2PI]_3$-10K sample and ~82 Å for the $[(PB)_2PI]_3$-20K sample. Since the mass densities of PB and PI are considered equivalent (0.900 and 0.903 g/mol, respectively); their electron density is approximately the same. Small-Angle X-Ray Scattering (SAXS) cannot be employed to verify the observed morphology.

Conclusion

The synthesis of 2nd generation dendritic homopolymers and copolymers consisting of poly(butadiene) (PB) ~90% of 1,4- and poly(isoprene) (PI) of increased 3,4 isomeric microstructures, via anionic polymerization techniques in combination with chlorosilane chemistry is accomplished. The molecular characterization leads to the conclusion that they can be considered model polymers, since they exhibit increased molecular and compositional homogeneity. Morphological characterization via TEM leads to microphase separation for the samples containing PI as the minority component and in both cases hexagonally close packed cylinders (hcp) of PI in PB matrix (majority component) were observed.

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