Light Scattering for the Masses™

Poly(styrene-block-1,2-butadiene) Block Copolymers Functionalized with Ferrocenylsilane Units

e aim to functionalize polystyrene-block-1,2-butadiene (PS-b-PB) prepared by anionic polymerization with HSiMe₂Fc ferrocenylsilanes under hydrosilylation conditions using the Karstedt catalyst. Ferrocene functionalized polymers can have very interesting properties for biosensoric applications.

The PS-b-PB polymer was characterized by SEC using polystyrene standards, online MALS, membrane osmosis and 1H-NMR-spectroscopy. As can be seen, the results from both absolute methods were almost identical. The polymer composition was calculated using the results for the molecular weight from the lightscattering and the molar ratio from 1H-NMR experiments.

The functionalized polymer was analyzed by the same methods except for membrane osmosis. The results for the molecular weight obtained by SEC using polystyrene standards were underestimated, indicating that the hydrodynamic radii did not change after the reaction. The results from 1H-NMR indicated a complete conversion, which could be proved using online light-scattering techniques.

The increased PDI and unexpected high molecular weight as determined by MALS can be explained by the cross linking of unreacted double bonds under the hydrosilylation conditions. The observed peak of double molecular weight indicates a dimerization as the main side reaction.

In conclusion, it was possible to demonstrate the successful and quantitative attachment of the HSiMe₂Fc units to the block copolymer. The next steps will be the functionalization of block copolymers with higher butadiene content and the evaluation of the functionalized polymers for biosensor applications.

This note graciously submitted by Francisco-Javier López-Villanueva, Institute of Organic Chemistry, Johannes Gutenberg-University of Mainz, D-55099 Mainz, Germany

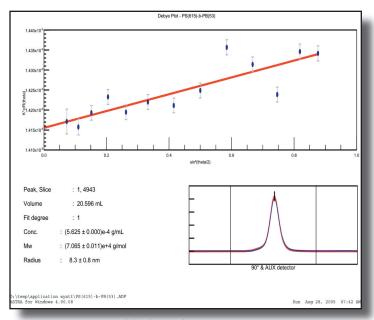


Figure 1. PS-b-PB blockcopolymer.

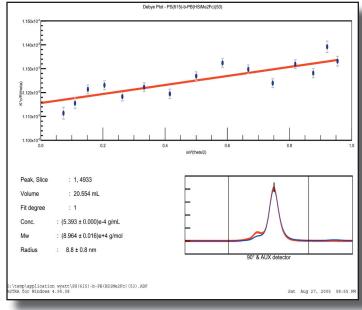


Figure 2. PS-b-PB blockcopolymer after hydrosilylation with ferrocenylsilane

	SEC ^a (THF, UV)		MALS (THF, online)			
Polymer	M_n	PDI	M_n	M_w	M_n^{b}	M_n^{c}
PS ₆₁₅ -PB ₅₃	57.900	1,06	66.930	68.070		63.100
PS ₆₁₅ -PB(HSiMe ₂ Fc) ₅₃	59.900	1,09	87.100	90.360	79.900	

Table 1. Polymer properties before and after hydrosilylation



^a Calculated using polystyrene standards b Calculated from 1H-NMR

^c Determined by membrane osmosis