

Investigation of Branched Polydienes with GPC/MALS

Our work focuses on the synthesis of branched (functionalized) polydienes via a facile two-step synthesis. Despite the numerous strategies developed for the preparation of branched polymers in recent years, there is still a limited number of simple synthetic strategies based on common vinyl monomers.

Linear polyisoprene and polybutadiene AB_n-type macromonomers were prepared by living anionic polymerization in THF (to ensure 1,2-addition) and terminated with chlordimethylsilane to get a terminal silane as the A-functionality of the macromonomer and the pendant vinyl groups of the polymer backbone as the B-functionalities. The macromonomers were reacted in a hydrosilylation polyaddition using Karstedt's catalyst to give branched polymers (Fig. 1). We measured the macromonomers as well as the branched polymers using MALS. Even for the smallest macromonomer ($M_n=1000$) light scattering gives a reasonable result compared with NMR.

It is well-known that branched polymers elute later in a GPC-experiment than their linear analogues with same molecular weight, due to their compact architecture. So GPC alone can only give a rough estimation of the molar mass (because of polystyrene calibration). This becomes even more important when the double bonds are functionalized with small silanes, e.g. phenyldimethylsilane, which do not change the hydrodynamic radius of the polymer—and so show the same elution time as unfuntionalized polymers; the molecular weights are therefore drastically underestimated.

Using light scattering during the GPC experiment to determine the molar mass of the branched structures is an effective and rapid way to get quantitative information for the rate of functionalization and the molar mass (Fig. 2). For the linear polymers, the molar mass can be determined, and for the branched structures, light scattering is the only way to get to real mass.

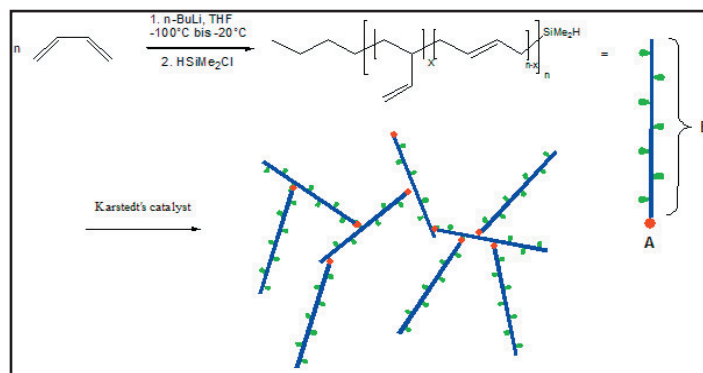


Figure 1. Synthesis of branched polybutadienes

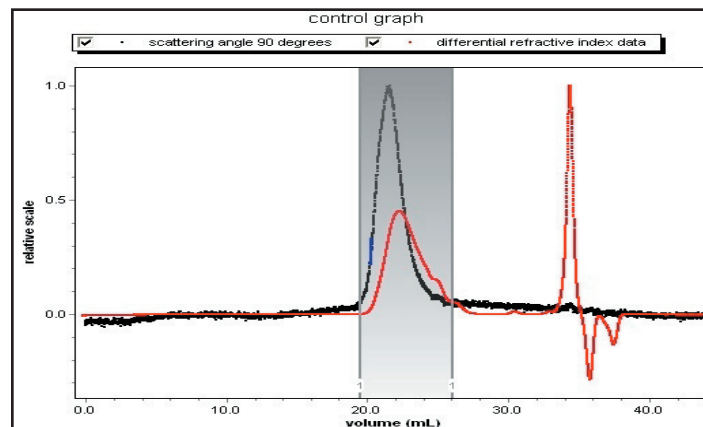


Figure 2. Chromatogram of a branched polybutadiene made from a macromonomer with $M_n=1000$ g/mol (MALS)

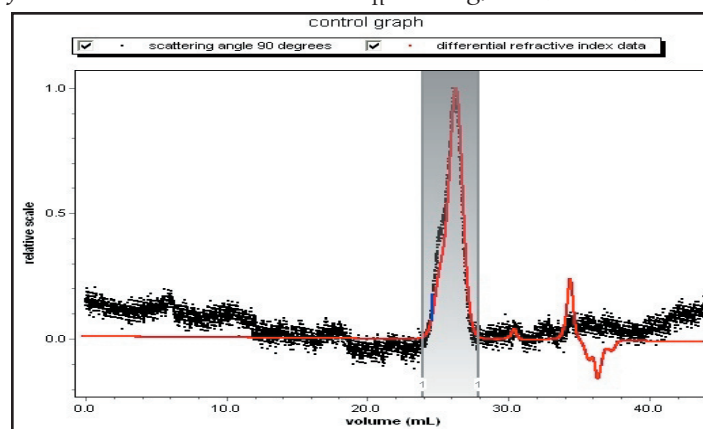


Figure 3. Chromatogram of the linear macromonomer PB 1K

Table 1. Molar Mass Comparisons

	M_n via NMR ^a	M_n via GPC ^a	M_n via MALS
PB-SiMe ₂ H	1600	1300	1300
Branched PB	---	8100	9100

^adetermined using endgroup analysis and integration of the Si(CH₃)₂-protons

^bGPC experiments using polystyrene standards as calibrant.