NMReady-60 Benchtop NMR Spectrometer for Block Copolymer Characterization

Copolymers have become increasingly commercially relevant due to the development of polymers with engineered properties. For example, acrylonitrile butadiene (ABS) for thermoplastics or styrene-butadiene (PS-PB) for car tires.

NMR Spectrsocopy is a proven analytical technique for the characterization of fundamental polymer parameters because, in a single experiment you can:

1) Observe reaction completion & uniformity. Unreacted monomers are easily observable due to well-defined and resolved lines among the broad polymeric resonances.

2) Quantify the relative composition through pre-defined integral regions.

3) Quantify the relative percentages of structural isomers (*e.g.,* branched *vs.* linear).

4) Observe tacticity and stereoisomers

5) Determine molecular weight, molecular number and polydispersity index (PDI)

Polymer characterization has been performed on traditional NMR systems for years, but now this technique is also available directly the benchtop. The affordable, lightweight and intuitive NMReady-60 is perfectly suited to improve analytical workflow. This high-resolution 60 MHz spectrometer generates results that are comparable and statistically equivalent to a high field super-conducting spectrometer. Unlike traditional spectrometers, however, the NMReady-60 is low maintenance, robust and easy-to-use.

Specifications:

Frequency: ^{1}H 60 MHz, ^{31}P 24 MHz
Magnet: permanent, cryogen-free
Stray field: confined within enclosure
Uses Stanard 5 mm NMR Tubes
Spectral resolution:
LW at 50%: 1.5 Hz
LW at 1%: <25 Hz
Power: 100-240 VAC, 50-60 Hz
Weight: 50lbs
Dimensions: 9.5 x 11 x 17"
User Interface: Built-in Touchscreen
Connectivity: USB, Ethernet

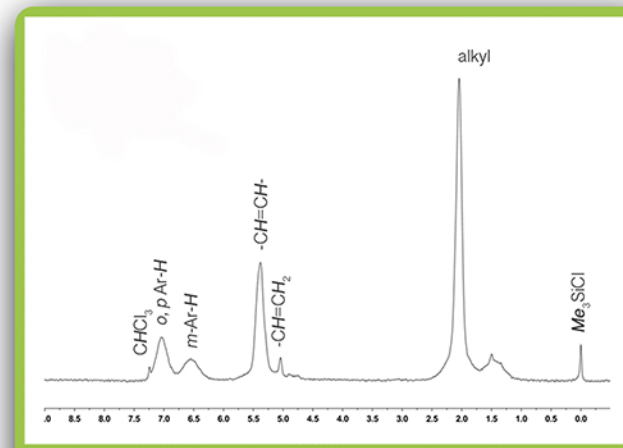
www.nanalysis.com

Example #1: Polystyrene-polybutadiene (PS-PB)

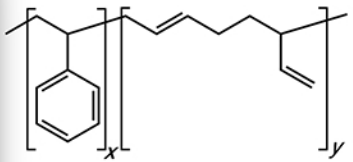
Around the world millions of tonnes of copolymers are produced annually. By varying the polymerization process (*e.g.*, the order and/or quantity of monomers added, the monomer ratios etc.), the polymer's properties are fine-tuned. On the NMReady, reaction completeness, relative composition, and the ratio of structural isomers can be characterized within minutes. These capabilities are illustrated here for PS-PB and polystyrene-polyisoprene (PS-PI).

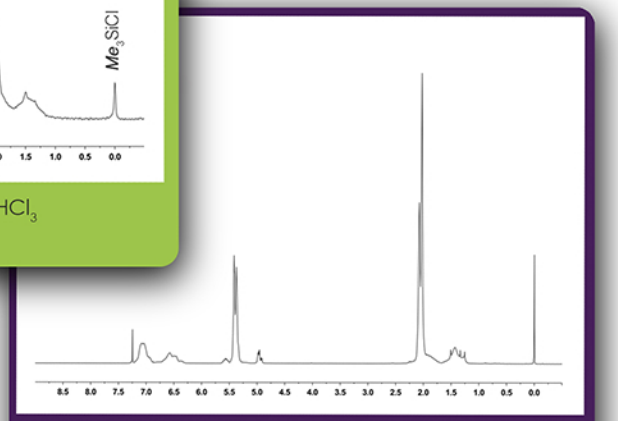
At a glance, it is clear that the reaction is complete and that there is no monomeric material remaining. The relative composition of the copolymer can then be reliably determined by: *(i)* normalizing; and *(ii)* correlating the integrals of the aromatic region (*i.e.*, the styrene component) and the olefin region (*i.e.*, the butadiene or isoprene component).

Similarly, the internal/terminal isomerism of the olefin component can be quantified by looking at the relative ratios in the 5-6 ppm range for all three polymeric samples shown here.



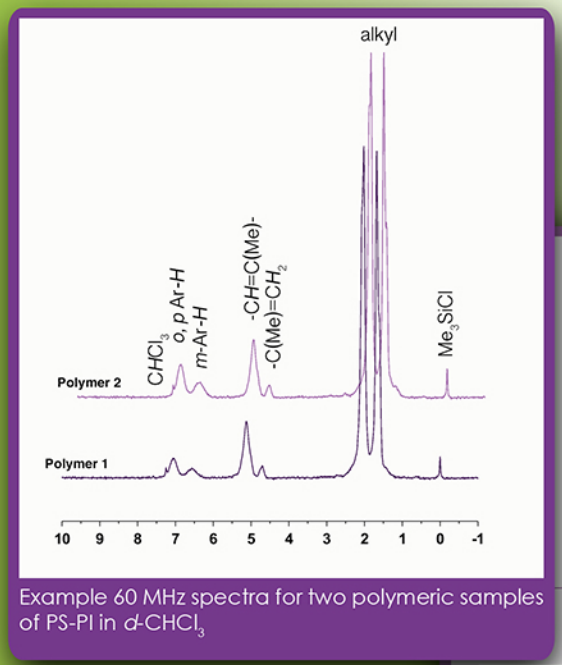
Example 60 MHz spectrum for PS-PB in *d*-$CHCl_3$



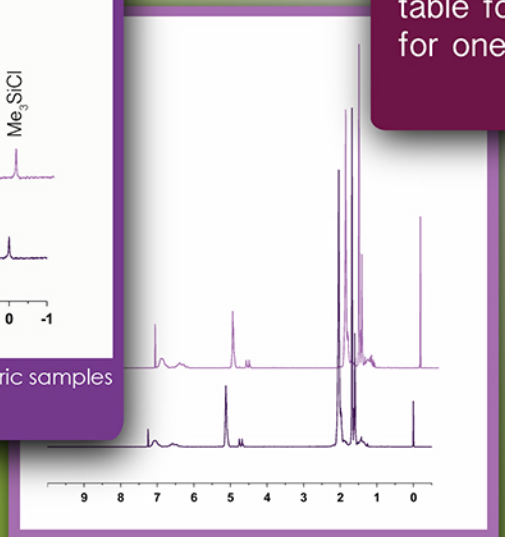


Example 400 MHz spectrum for PS-PB in *d*-$CHCl_3$

Through numerous trials, the results acquired on the 60 MHz NMReady are consistent with those obtained on a 400 MHz spectrometer. See the adjacent table for sample results obtained for one PS-PB, and two different PS-PI samples.

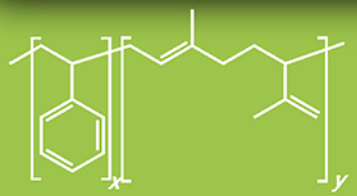


Example 60 MHz spectra for two polymeric samples of PS-PI in *d*-$CHCl_3$



Example 400 MHz spectra for two polymeric samples of PS-PI in *d*-$CHCl_3$

		60 MHz	400 MHz	% Difference
PS-PB	$\int_{Ar\text{-}H}$ Total	17.6	16.7	5.21 %
	$\int_{olefin}$ Total	25.6	24.4	5.00 %
	%PS	27.4	27.4	0.20 %
	$\%Olefin_{internal}$	92.0	91.3	1.09 %
PS-PI Polymer 1	$\int_{Ar\text{-}H}$ Total	6.5	6.3	1.6 %
	$\int_{olefin}$ Total	12.0	11.6	1.6 %
	%PS	10.9	10.9	0.01 %
	$\%Olefin_{internal}$	93.6	93.0	0.33 %
PS-PI Polymer 2	$\int_{Ar\text{-}H}$ Total	10.1	9.8	1.7 %
	$\int_{olefin}$ Total	11.2	10.9	1.8 %
	%PS	18.0	18.0	0.06 %
	$\%Olefin_{internal}$	93.5	92.8	0.33 %



The characterization of polymers is only one potential application for the NMReady-60. For more information on this, or for other ideas of how to include a benchtop NMR spectrometer into your daily workflow, please visit or contact us directly.

www.nanalysis.com/apps.html

Example #2: Polystyrene-polyisoprene (PS-PI)