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PAPER

Low-Field ¹H-NMR Spectroscopy for Compositional Analysis of Multicomponent Polymer Systems

Sneha B. Chakrapani,[a,†] Michael J. Minkler Jr.[a,†] and Bryan S. Beckingham[a,*]

The accurate characterization of relative composition in multicomponent polymer systems such as statistical copolymers, block copolymers, and polymer blends is critical to understanding and predicting their behavior. Typically, polymer compositional analysis is performed using ¹H Nuclear Magnetic Resonance (NMR) Spectroscopy which provides quantitative chemical group concentrations without prior calibration. This utility has led ¹H NMR spectroscopy to become a routine method for the molecular characterization of polymers. Unfortunately, due to cost constraints, NMR spectroscopy is rarely used for routine materials verification such as quality control in industrial settings that commonly lack on-site advanced instrumentation facilities. Recently, low-field or so-called benchtop NMR spectrometers have been introduced commercially as a less expensive alternative to higher field, and costlier, NMR spectrometers. Here, we examine the capability of a low-field ¹H NMR spectrometer (60 MHz) for the compositional analysis of select block copolymers and polymer blends by direct comparison with results obtained using a 400 MHz NMR spectrometer. In the analysis of high 1,4-content polyisoprene we find quantitative agreement between the 400 and 60 MHz spectrometers. Furthermore, quantitative agreement is demonstrated for compositional analysis of commercially available poly(styrene-*b*-isoprene-*b*-styrene) (SIS) and poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymers and polymer blends of polystyrene/polyisoprene (PS/PI) and polystyrene/poly(methyl methacrylate) (PS/PMMA) that also serve as proxies for statistical and block copolymer analysis. Overall, we find low-field ¹H NMR spectroscopy to be an accessible, powerful and useful tool for polymer characterization.

INTRODUCTION

Polymeric materials are ubiquitous in our daily lives due to the breadth of material properties afforded by variation in molecular architecture, chemical microstructure and functionality. A classic and industrially important method for tuning material properties for target applications using polymeric materials is by mixing two chemically dissimilar polymers forming a polymer blend.[1-5] One such classic example is the polymerization of polystyrene or styrene-acrylonitrile copolymers in the presence of rubber to produce high impact polystyrene or ABS respectively which have greatly improved mechanical properties compared to any of the homopolymers or mechanically prepared blends.[6-8] Another example are blends of polystyrene and poly(phenylene ether), i.e. Noryl™, which possesses the high heat resistance, high dielectric strength, and hydrolytic stability attributed to PPO resin in combination with lower cost, lower Tg, and ease of processing due to the presence of polyisoprene in the blend.[9] In the analysis of multicomponent polymer systems, such as polymer blends and statistical copolymers, the composition of the polymer blend and individual polymer chains is crucial.

Typically, the composition of multicomponent polymer systems is characterized with ¹H Nuclear Magnetic Resonance (NMR) Spectroscopy.[10-12] ¹H NMR spectroscopy is particularly useful for polymer chemical structure and composition as nearly all polymers have abundant and distinct protons for analysis. Additionally, ¹H NMR spectroscopy yields quantitative chemical group concentrations without prior calibration. This has led ¹H NMR spectroscopy to become a routine method for the molecular characterization of polymers.

Over the last several decades NMR spectrometers have improved significantly, and current state-of-the-art spectrometers have increasingly high magnetic fields (i.e. Bruker Aeon 1 GHz Spectrometer).[13] It is currently common practice to refer to these high-field magnets by their corresponding magnetic field strength for hydrogen. Equations 1 and 2 show the relationship between gyromagnetic ratio (γ_n) and spectrometer field strength (B_0):

$$\frac{\gamma_n}{2\pi} = \frac{\mu_N g_n}{h} \qquad (1)$$

$$f = \frac{\gamma_n}{2\pi} B_0 \qquad (2)$$

where μ_N is the nuclear magneton, g_n is the g-factor for a nucleus, h is Planck's constant, f is frequency (MHz).[14] To determine the frequency of a particular NMR spectrometer, the user needs only multiply the field strength of the magnet (in

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Tesla) by $\gamma_n/2\pi$ or 42.577 MHz T^{-1} for hydrogen (i.e. 1 GHz spectrometer has a field strength of 23.5 T).[14] The increase in magnetic field strength has led to several orders of magnitude improvement in sensitivity.[13,15] This increase in sensitivity is typically characterized as a signal to noise ratio which is proportional to both field strength and the number of scans acquired (n); as shown in Equation 3.

$$\frac{Signal}{Noise} \; \alpha \; B_0^{\frac{3}{2}} \sqrt{n} \qquad (3)$$

Thus, spectrometers with higher field strengths require less sample and will produce spectra with significantly sharper peaks.[14] High-field—where here we denote high-field as > 5.8 T field strength (or alternatively > 250 MHz)—NMR spectrometers require cryogenic cooling due to their superconducting magnets and advanced probes as well as staffing by dedicated professionals due to the numerous, and at times very complex, NMR experiments that can be performed and the associated upkeep and maintenance requirements.[13] Unfortunately, due to the high capital and operating costs associated with high-field spectrometers, NMR spectroscopy is not commonly considered a low-cost analysis technique. This is especially true for routine materials verification such as quality control in industrial settings that commonly lack on-site advanced instrumentation facilities.

The recent development of commercially available low-field benchtop NMR spectrometers may provide a less expensive alternative to higher field, and costlier, NMR spectrometers once validated for desired analyzes.[16-18] These low-field NMR spectrometers or compact "benchtop" NMR spectrometers feature permanent magnets with typical magnetic field strengths of 20-80 MHz (0.46-1.88 T), a lower capital cost, little to no operating expense, and have a small physical footprint. As a consequence of the lower field strength these spectrometers have lower overall sensitivity and spectral dispersion.[13,15,19] For the analysis of polymers, where peaks are characteristically broader than small molecule analogs, the lower spectral dispersion exacerbates issues with resonance overlap.[19] This resonance overlap can impede quantitative analysis of polymer materials with closely situated peak signatures using 1D ^{1}H NMR spectra much more at low-field than at high-field. Figure 1a shows spectra acquired with a 60 MHz benchtop spectrometer, a 250 MHz spectrometer, and a 400 MHz spectrometer. The spectra are reasonably similar; however, the spectra produced by higher field strength spectrometers appear cleaner with less visible noise. It should be noted that all three spectra were produced with 16 scans, standard acquisition parameters, and the data produced were processed in the same manner using MNOVA. The difference in the data is due to the frequencies at which protons are detected in each of the spectrometers. These differences can also be visualized by plotting the data in frequency space as shown in Figure 1b. This illustrates how at the expanded frequency space at higher field strength leads to improved resolution upon transformation into the same range of ppm space; i.e. the weaker the magnet, the narrower the spectrum in frequency space.

The above mentioned issues with spectra quality notwithstanding, due to a recent surge in commercial availability of these instruments there has been increased interest in the application of low-field NMR spectroscopy and efforts have been made to benchmark and validate these instruments for applications both old and new.[19-23] For instance, low-field spectrometers have recently been applied to quality control aspects of agricultural products (beef authenticity, oil adulteration, alcohol content, etc.).[23-26] For characterizing synthetic polymer materials, low-field NMR spectrometers have been applied to a variety of applications including monitoring polymerization kinetics, crystallization kinetics and crystallite/amorphous morphology, nanocomposite miscibility and dynamics, network crosslink density and swelling, composition and glass transition.[17,19,20,26-31] Low-field ^{1}H NMR spectroscopy has also been coupled with gel permeation chromatography for chemical identity mapping with molecular weight distributions.[32-34] In the analysis of multicomponent polymer systems, Singh and Blümich recently investigated the ability of a 43 MHz (1 T) compact NMR spectrometer outfitted with both ^{1}H and ^{13}C probes for quality control of styrene-butadiene rubber (SBR) production.[35] By using 1D ^{1}H and ^{13}C spectra in combination with a partial least squares regression they found they could determine the S/B relative composition and the polybutadiene microstructure quantitatively.[35] Additionally, they were able to distinguish differences within lots and across production processes and suppliers as a proof of concept of this approach for quality control in industrial SBR production.[35] However, the total acquisition time for each sample was quite long—1 minute and 5.7 hours for ^{1}H and ^{13}C spectra acquisition respectively—and a multivariate calibration model which calibrates for the prediction of composition in unknown samples from known samples.[35] These complexities may hinder application such that a faster and model-free process would be desirable. For our primary purposes in the synthesis and characterization of various polymers, statistical copolymers and block copolymers, accurate characterization of copolymer composition and microstructure is paramount and so we set out to benchmark low-field ^{1}H NMR for composition and microstructural analysis.

Here, we investigate the utility of low-field 1D ^{1}H NMR spectroscopy as a stand-alone technique for quantitative molecular characterization of a set of polymer blends and block copolymers. In particular, we investigate (1) microstructure analysis of polyisoprene (2) compositional and polydiene microstructural analysis of commercially available poly(styrene-*b*-isoprene-*b*-styrene) (SIS) and poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymers, and (3) compositional analysis of a series of polystyrene/polyisoprene (PS/PI) and polystyrene/poly(methyl methacrylate) (PS/PMMA) polymer blends as proxies for statistical and block copolymer analysis. The ability to conduct routine analyses such as these of polymer blends and copolymers at comparatively low cost in-house has potential implications for polymer instrumentation in academic and industrial research laboratories as well as industrial implications in quality control scenarios.
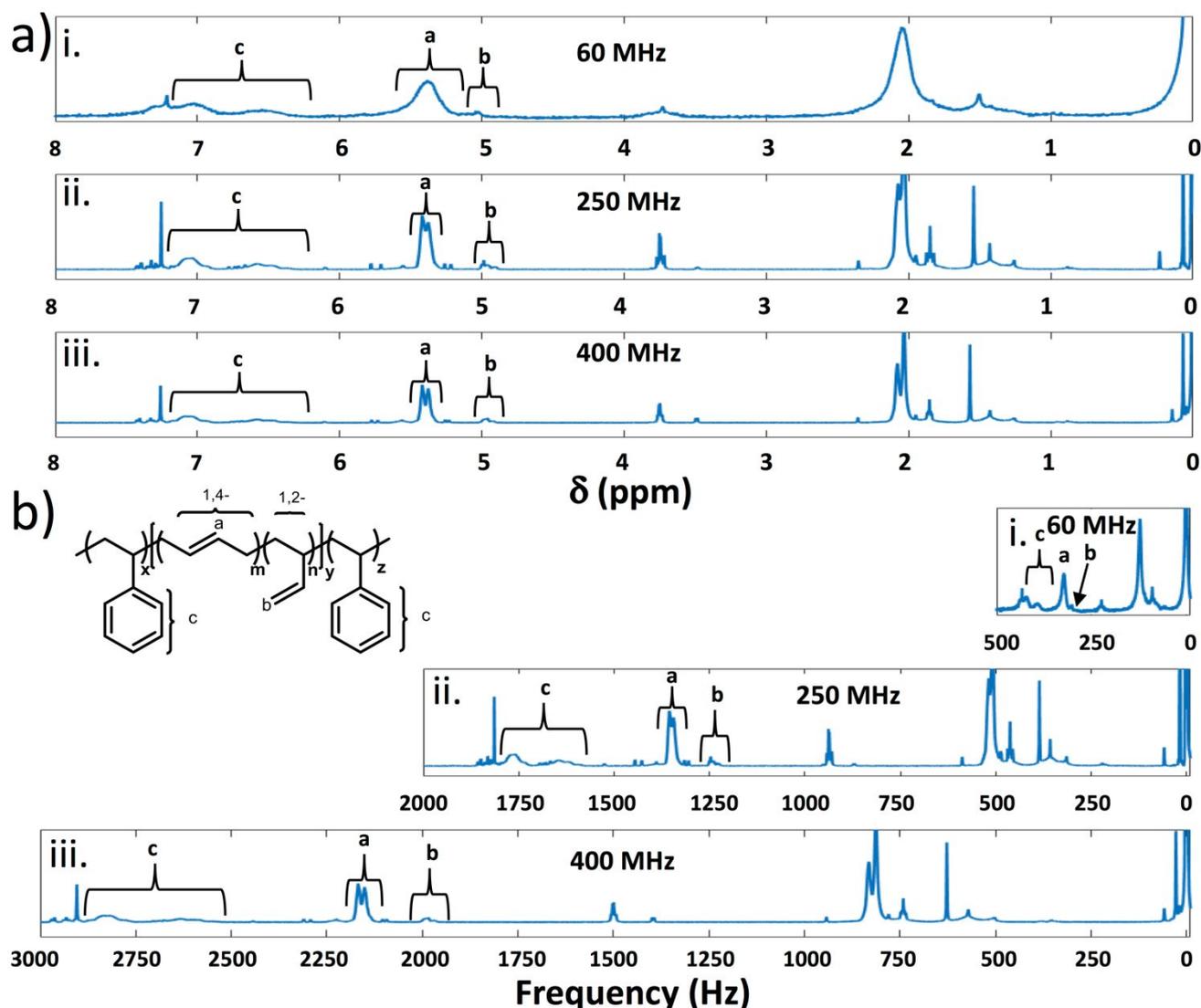
Figure 1. a) ^{1}H NMR spectra of SBS acquired with a i) 60 MHz spectrometer, ii) 250 MHz spectrometer, and iii) 400 MHz spectrometer. b) Frequency shift spectra of SBS acquired with a i) 60 MHz spectrometer, ii) 250 MHz spectrometer, and iii) 400 MHz spectrometer.

EXPERIMENTAL

Materials.

Styrene, cyclohexane, deuterated chloroform and tetramethylsilane (TMS) were purchased from EMD Millipore Corporation. Isoprene was obtained from Acros Organics. Tetramethylethylenediamine, polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) symmetric triblock copolymer (catalog # 432415), polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) (catalog # 43249-0), *sec*-Butyllithium and 2,2'-azobis(2-methylpropionitrile) were used as received from Sigma Aldrich. 1,1 diphenylethylene, *n*-butyllithium and inhibitor removal column resin (catalog # 42489) were procured from Alfa Aesar. Methanol and Chloroform were obtained from VWR International and *tert*-Butyllithium was received from TCI America. Cyclohexane was stirred over diphenylhexyllithium (adduct of *sec*-butyllithium and 1,1-diphenylethylene), degassed via freeze-pump-thaw (FPT) cycles, and vacuum transferred prior to use. Isoprene was stirred over *n*-butyllithium, degassed via FPT, and vacuum transferred prior to

use. *Caution! sec-butyllithium and n-butyllithium are pyrophoric and moisture-sensitive materials and should be handled with appropriate care.* Styrene and methyl methacrylate were passed through the inhibitor removal column and degassed by FPT cycles prior to use. Methanol, for terminating the anionic polymerization of isoprene, was degassed via FPT cycles prior to use.

Polymer Synthesis.

All reactors were flamed out under vacuum. *tert*-butyllithium initiated anionic polymerization of isoprene was performed at 60 °C. *Caution! tert-butyllithium is a pyrophoric and moisture-sensitive material and should be handled with appropriate care.* Cyclohexane, isoprene and *tert*-butyllithium were charged to a reactor in a nitrogen-filled glovebox prior to removal and heating to 60 °C by submersion in a temperature-controlled water bath. Upon completion the polymerization was terminated with degassed methanol. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) were synthesized by free radical polymerization at 70 °C, neat, using 2,2'-azobis(2-

methylpropionitrile) (AIBN) as the initiator. AIBN and monomer were charged to a reactor in a nitrogen-filled glovebox prior to removal and heating to 60 °C by submersion in a temperature-controlled water bath. Upon completion the polymerizations were removed from the water bath, precipitated in methanol and the product collected and dried in vacuo.

Instrumentation.

Two NMR spectrometers were primarily used in this study to obtain ^{1}H NMR spectra. Spectra at 400 MHz (9.4 T) were collected on a Bruker Avance 400 spectrometer and spectra at 60 MHz (1.4 T) were collected on an Oxford Instruments Pulsar 60 MHz spectrometer. The spectrum at 250 MHz shown in Figure 1 was collected on a Bruker Avance II 250 MHz spectrometer.

Polymer Blend Preparation and Characterization.

PS/PI and PS/PMMA polymer mixtures of varied relative composition were prepared gravimetrically, dissolved in deuterated chloroform to 10-50 mg/mL (maintaining the minority constituent concentration at 5 mg/mL) and doped with 1-2 drops of TMS for analysis. At 400 MHz, 16 scans were collected at room temperature in 1.32 minutes using standard sample parameters unless otherwise noted. At 60 MHz, 128 scans were collected in 19.82 minutes using a relaxation delay of 2 seconds between scans, unless otherwise noted. The 60 MHz spectrometer internal temperature was 37 °C and the 400 MHz spectrometer internal temperature was 19 °C. Free induction decays (FIDs) were Fourier-transformed, manually phase-corrected and the chemical shift calibrated relative to the TMS peak prior to peak integration using MNOVA.

RESULTS AND DISCUSSION

In order to assess the utility of low-field benchtop spectrometers for routine applications in polymer characterization, we examined three common operations. First, we examined the characterization of polyisoprene (PI) microstructure using PI synthesized via alkyllithium-initiated anionic polymerization in cyclohexane. Next, we examined the compositional analysis and polydiene microstructural analysis of two commercially available triblock block copolymers, polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) and polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS). Lastly, we synthesized polystyrene and poly(methyl methacrylate) via free-radical polymerization and examined the composition of prepared polymer blends based on these three common polymers (PS/PI and PS/PMMA) at a range of relative compositions. In each of the above cases, we characterized the samples with ^{1}H NMR spectroscopy using both a 60 MHz and a 400 MHz spectrometer. Importantly, to prevent sample preparation, metering or other experimental errors, each prepared sample was characterized using both spectrometers in order to directly compare the results.

The results obtained from analysis of the spectra acquired at 400 MHz are taken as the "true" values and used to benchmark the performance of the 60 MHz spectrometer. In all the samples examined deuterated solvent was included in order to obtain a lock when acquiring spectra with the 400 MHz spectrometer. However, the 60 MHz spectrometer does not require a locking signal such that spectra can be obtained using standard non-deuterated chloroform or other non-deuterated solvents; a definitive cost and ease of use advantage for the 60 MHz spectrometer. However, in order to properly reference the spectra obtained at 60 MHz, TMS was included to provide for consistent spectral shift in ppm during the spectra analysis with MNOVA.

Polyisoprene Microstructural Characterization.

Polymers such as polyisoprene (PI) and polybutadiene (PB) are essentially copolymer structures due to the different modes of addition during polymerization; 1,4-, 1,2-, and 3,4-polyisoprene and 1,2- and 1,4-polybutadiene (see Supporting Information Figure S1 for polymer structures). We synthesized polyisoprene in cyclohexane using anionic polymerization to yield a high 1,4-content polyisoprene analogous to that typically present in commercially available SIS triblock copolymers. The polyisoprene product was dissolved in deuterated chloroform, doped with TMS and analyzed using ^{1}H NMR spectroscopy at both 400 MHz and 60 MHz (Figure 2).

Comparing the spectra in Figure 2, clearly distinguishable peaks are observed in both with the 60 MHz spectra peaks appearing broader, less defined, with slight overlap. As mentioned above, the sharpness and contrast of the peaks is directly dependent on both field strength and the number of scans. By increasing the number of scans and thereby improving the signal-to-noise ratio (Equation 3), the spectra quality improves visually as shown in Figure 3a. Of interest for polyisoprene microstructural characterization are the peaks at 4.7 ppm, 5.1 ppm, and 5.7 ppm corresponding to 3,4-, 1,4- & 1,2-, and 1,2-addition respectively. Based on these peak areas, the microstructure can be determined. In both the 400 MHz and 60 MHz spectra no 1,2-PI content is observed, i.e. no peak at 5.7 ppm, as expected for the synthetic route chosen.
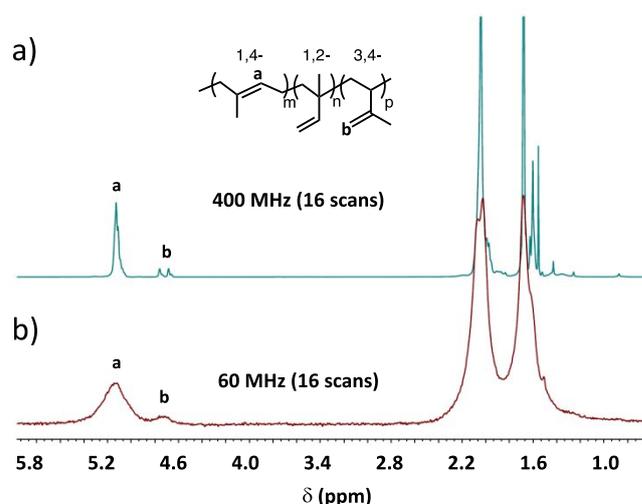

Figure 2. ^{1}H NMR spectrum of PI acquired at a) 400 MHz and b) 60 MHz.
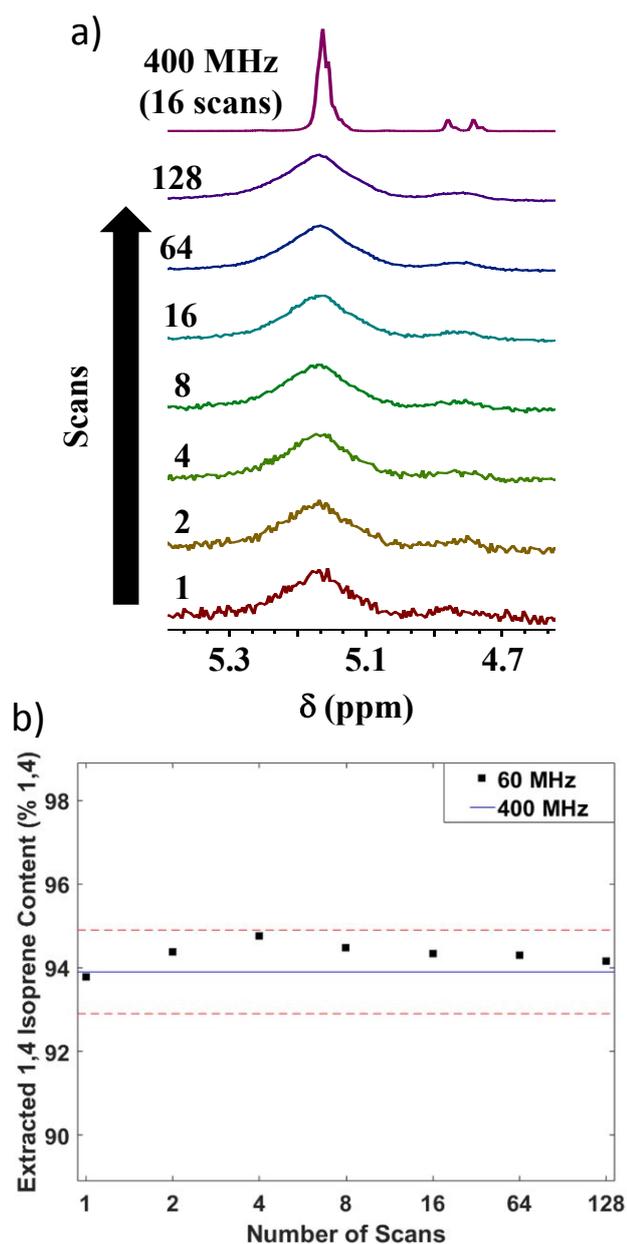
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Figure 3. a) Polyisoprene high-field ^{1}H NMR spectrum acquired at 400 MHz (top) compared to 60 MHz spectra of varied number of scans. b) Polyisoprene microstructure (% 1,4-addition) obtained from 60 MHz spectra at varied number of scans. The solid horizontal line indicates the % 1,4-addition obtained from the 400 MHz spectrum with dotted horizontal lines indicating +/- 1 % around the 400 MHz value.

In the absence of 1,2-PI, the 1,4- and 3,4-content can be calculated directly from the peaks at 4.7 ppm and 5.1 ppm according to Equations 4 and 5, where I_i is the area of the peak at i ppm, yielding the results shown in Figure 3b.[10]

$$\%1,4\,(=CH-) = 100 * \frac{I_{5.1}}{I_{5.1} + \frac{I_{4.7}}{2}} \quad (4)$$

$$\%3,4\,(=CH_2) = 100 * \frac{\frac{I_{4.7}}{2}}{I_{5.1} + \frac{I_{4.7}}{2}} \quad (5)$$

As shown in Figure 3b, excellent agreement is obtained, within 1 %, between the 60 MHz and 400 MHz spectra. For instance, at the same number of scans as a typical high-field experiment (16 scans), we find excellent agreement between the 60 MHz (94.3 % 1,4-PI) and 400 MHz (93.9 % 1,4-PI) results. As relative polymer compositions are typically rounded to the nearest percent, 94 % 1,4-polyisoprene is extracted from both spectra. Notably, even at a single scan excellent agreement is achieved even though the spectrum is considerably noisier. Overall, we find the 60 MHz spectrometer capable of performing this characterization quantitatively as desired.

Symmetric Triblock Compositional Analysis.

The block copolymers SBS and SIS are commercially available thermoplastic elastomers and utilized in a wide variety of applications from footwear to asphalt modification. Here, SBS and SIS triblock copolymers are purchased from Sigma Aldrich, dissolved in deuterated chloroform, and doped with TMS and ^{1}H NMR spectra were obtained at both 400 MHz and 60 MHz. Both ^{1}H NMR spectra are shown in Figure 4 for SIS while SBS is shown in Figure 1 for SBS (see Supporting Information S2 for expanded SBS spectra analogous to Figure 4).

At 400 MHz clear distinct peaks are obtained, whereas at 60 MHz peaks appear broader and less defined. Both the polydiene microstructure and the relative composition of styrene and diene are extracted from the spectra. For SIS, the peak regions for the polystyrene aromatic protons (6.3-7.2 ppm) and the polyisoprene allylic protons (4.7 ppm, and 5.1 ppm) are integrated and the microstructure and composition determined for SIS using Equations 4-6. Analogous equations for SBS characterization are given in the Supporting Information (Equation S1-S3).

$$\%S\,(in\,SIS) = 100 * \frac{\frac{I_7}{5}}{I_{5.1} + \frac{I_{4.7}}{2} + \frac{I_7}{5}} \quad (6)$$

The spectrum acquired at 60 MHz again clearly possesses adequate capability to detect polystyrene peaks at 6.2-7.3 ppm, as well as both 1,4- and 3,4- polyisoprene configurations and no 1,2- content (5.7 ppm) is visible in either spectrum.
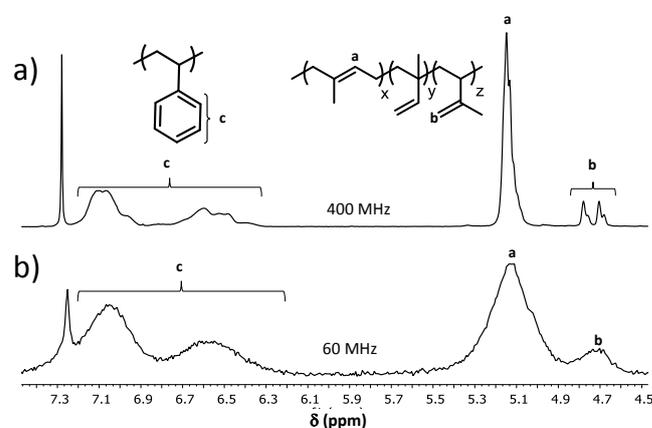

Figure 4. ^{1}H NMR spectra of SIS triblock copolymer at a) 400 MHz and b) 60 MHz.

Using the polydiene microstructures and polystyrene content obtained at 400 MHz as the "true" value, we find excellent agreement. Both SBS and SIS are high in 1,4-content as expected for these commercial triblock copolymers, which are typically synthesized via anionic polymerization in hydrocarbon solvents. For SBS, we find a composition of 10.1 % polystyrene with 95.4 % 1,4-polybutadiene using the 400 MHz spectra, while the 60 MHz spectra yields 12.2 % styrene with 98.7 % 1,4-polybutadiene. At 400 MHz we determine the SIS to be 16.4 % polystyrene with 94.3 % 1,4-polyisoprene compared to 15.5 % polystyrene with 92.9 % 1,4-polyisoprene at 60 MHz. This is excellent agreement as, generally, the confidence in compositional analysis performed using high-field NMR spectrometers in this manner for polymers is +/- 1 %. Here, the 60 MHz results fall within this typical experimental confidence for SIS while SBS is just outside with a 2 % difference in composition.

Overall, the 60 MHz results are quantitatively the same for SIS with slight deviation for SBS. This level of accuracy at lower cost and increased accessibility could find use for quality control, research characterization and other applications and is acceptable for validating the use of these low-field instruments for this analysis.

Polymer Blend Compositional Analysis.

To assess the utility of low-field ^{1}H NMR spectroscopy for the compositional analysis of polymer blends and other block copolymer systems, polystyrene and poly(methyl methacrylate) (PMMA) were synthesized using AIBN-initiated free-radical polymerization to complement the previously discussed PI. PS/PI and PS/PMMA mixtures were prepared gravimetrically at varied relative compositions, dissolved in deuterated chloroform to a concentration of 10-50 mg/ml as described in the Experimental section and their ^{1}H NMR spectra obtained at both 400 MHz and 60 MHz (see Supporting Information Figure S3 and S4 for spectra). The overall polymer composition for each blend was determined analogous to the triblock

copolymers using the PMMA methyl protons on the acrylate side chain (3.6 ppm) and the aforementioned polystyrene aromatic and polyisoprene allylic peaks (see Supporting Information Equation S4 for PS/PMMA).[36]

Compositions determined using the spectra obtained with the 60 MHz spectrometer are plotted against those obtained from the 400 MHz spectrometer for both PS/PS and PS/PMMA; Figure 5a and 5b respectively (see Supporting Information Table S1 for the composition values used to construct Figure 5). We find excellent agreement between the 400 MHz and 60 MHz results for both PS/PI and PS/PMMA blends as nearly all points in Figure 5 lie along the identity line. For five of the nine PS/PI blends the compositions obtained using the 60 MHz spectra are equivalent to those from the 400 MHz spectra, after rounding to the nearest percent, with the remaining 4 differing by only 1 %. Similarly, for PS/PMMA blends equivalent results are found for four of the nine blends, four differ by 1 % and one differs by 2 %. Overall, the average difference between the extracted compositions at 60 MHz and 400 MHz is 0.48 % for PS/PI blends and 0.66 % percent for PS/PMMA blends. These findings demonstrate the utility of low-field spectrometers for the quantitative determination of relative composition in these polymer blends.

CONCLUSIONS

^{1}H NMR spectroscopy is a powerful tool for the characterization of polymer structures and the relative compositions of repeat unit structures within multicomponent polymer systems. In this work we assessed the potential of a low-field spectrometer (60 MHz) to perform routine polymer characterizations; polydiene microstructure, triblock copolymer composition and polymer blend compositional analysis. While the 60 MHz spectrometer is less sensitive, with broader peaks due to the narrower frequency of acquisition, the acquired spectra possess distinct peaks containing the requisite relative concentration information for performing the desired compositional analysis.
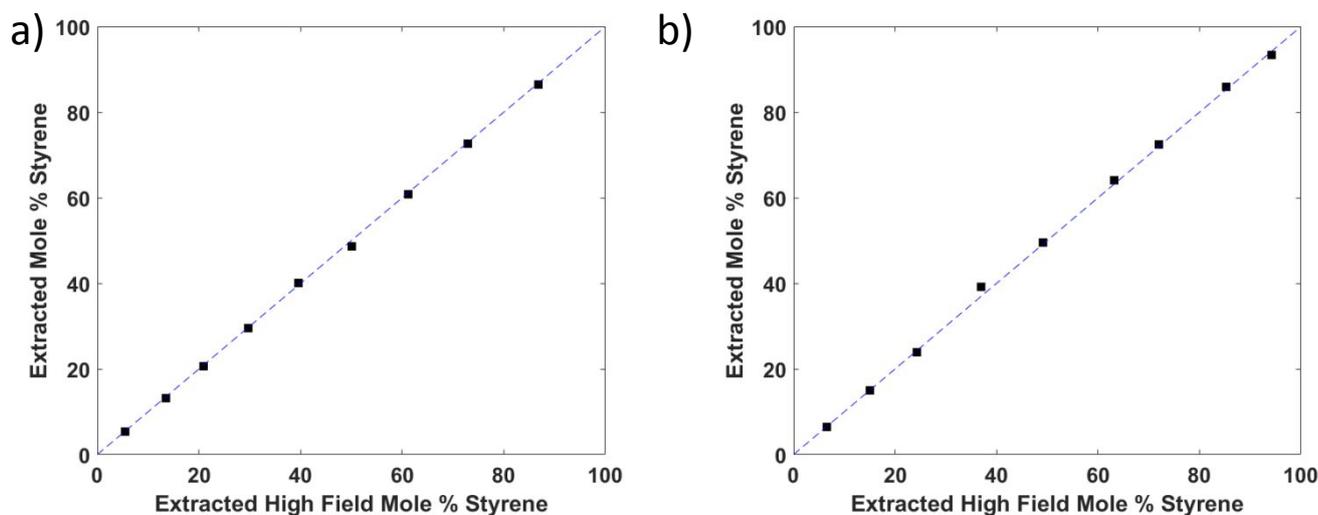

Figure 5. Extracted composition values from 60 MHz spectra plotted against values extracted from 400 MHz spectra for polymer blends of a) polystyrene and polyisoprene and b) polystyrene and poly(methyl methacrylate). Dashed line represents the identity line; y = x.

Five different polymer systems were analyzed and the results obtained using a 60 MHz spectrometer and a 400 MHz spectrometer were compared. A majority of results obtained for each sample using both spectrometers are within the typical experimental error anticipated for high-field spectrometers (+/- 1 %). Extracted compositions are within 3 % in all cases with a majority (26/31 or 84%) within 1 %. These results validate the use of 60 MHz ^{1}H NMR spectrometers for the polymer systems analyzed here. However, we note that additional systems of interest should be similarly validated before application of these instruments for quantitative analyses. Overall, ^{1}H NMR spectroscopy at low-field strength is a promising tool for the routine characterization of multicomponent polymer systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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COMPOSITIONAL ANALYSIS BY 1H NMR SPECTROSCOPY
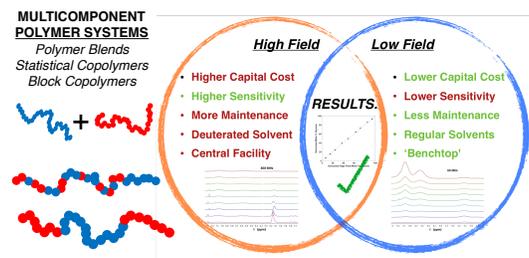
A low-field, 60 MHz, 1H NMR spectrometer yields quantitatively comparable results to 400 MHz spectrometers for the compositional analysis of multicomponent polymer systems.