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Structural Information Recoverable from ¹H NMR Integration of Polystyrene–Polybutadiene Block Copolymers

Proton Bookkeeping, Butadiene Microstructure, Styrene Sequence Distribution, and the Boundaries of the Method

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Abstract

The ¹H NMR spectrum of a polystyrene–polybutadiene block copolymer resolves into four integrable envelopes whose areas are related to molecular structure by a fixed and unambiguous proton stoichiometry. This paper sets out that relationship in full, establishes what it determines and what it does not, and quantifies the reliability of each result. Four repeat-unit types are present — styrene, cis-1,4-butadiene, trans-1,4-butadiene, and 1,2-butadiene — and their proton inventories generate three independent equations together with one redundant equation that can be used as an internal consistency check. Solving the system yields two structural quantities absolutely and without calibration: the styrene-to-butadiene ratio, reportable on either a molar or a mass basis, and the 1,2 (vinyl) fraction of the butadiene portion. The terminal vinylidene resonance between 4.80 and 5.15 ppm is the analytical keystone, being the only region populated by a single structural type, and the internal olefinic integral must be corrected for the methine proton that each 1,2 unit contributes to it — an omission that overstates the 1,4 content by fifty percent in a copolymer of fifty mole percent vinyl.

Two worked examples are carried through in both directions, a conventional linear triblock containing 30.00 mass percent styrene with 8.00 mole percent vinyl, and a high-vinyl copolymer containing 25.00 mass percent styrene with 50.00 mole percent vinyl. Error propagation shows that a one percent relative integration error displaces bound styrene by roughly two-tenths of a percentage point, while its effect on the vinyl figure grows with vinyl content from less than a tenth of a mole percent at 8 mole percent vinyl to nearly four-tenths at 50 mole percent, a consequence of the subtraction term. The redundant aliphatic integral is developed into a quantitative closure test, and a simulation of hydrocarbon extender oil shows that this test responds with residuals between forty-seven and ninety-two percent at commercially realistic oil loadings while the vinyl determination remains entirely unaffected and apparent bound styrene is inflated by up to eight percentage points absolute.

The limits of the method are treated at equal length. The cis-1,4 and trans-1,4 units are proton-degenerate and cannot be separated by any integration scheme; that determination requires ¹³C NMR, where the allylic carbons are separated by more than five parts per million, or infrared spectrometry, for which the international standard designates the proton method as the absolute reference. Chain architecture — diblock against triblock against radial star, and a true block copolymer against a physical blend of homopolymers — is not encoded in the integral at all, though styrene sequence distribution is partially accessible through the ring-current-shielded ortho proton shoulder between 6.20 and 6.85 ppm, from which a blockiness index can be calculated at field strengths above roughly 200 MHz. Composition and vinyl content, by contrast, remain accessible on 43 to 100 MHz benchtop instruments without calibration, a conclusion supported by published direct comparison against high-field determination. Acquisition and processing requirements, a recommended workflow, and a critical assessment of common reporting failures are given, and all calculations are reproduced with live formulas in an accompanying Excel workbook.

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1. Introduction and Scope

Styrene–butadiene block copolymers occupy a position in the polymer industry that is out of all proportion to the simplicity of their chemistry. Two monomers, joined by living anionic polymerization, yield a family of materials that spans thermoplastic elastomers for footwear and medical tubing, impact modifiers for polystyrene and polypropylene, pressure-sensitive and hot-melt adhesives, viscosity-index improvers for lubricating oil, asphalt modifiers for paving and roofing, and precursors to the hydrogenated styrene–ethylene/butylene–styrene grades that dominate soft-touch overmolding. In every one of those applications the end-use performance is governed not by the gross styrene-to-butadiene ratio alone but by a set of structural variables that are, to varying degrees, encoded in the ¹H NMR spectrum: the mass fraction of bound styrene, the partition of butadiene among 1,4 and 1,2 addition modes, the degree to which styrene units are clustered into blocks rather than distributed statistically, the extent of any post-polymerization modification, and the state of oxidative degradation of the diene phase.

This white paper addresses a narrow and practical question. Given a single quantitative ¹H spectrum of a polystyrene–polybutadiene block copolymer, what structural information can be extracted from the areas under the resolved regions of that spectrum, how is that information calculated, how reliable is it, and — of at least equal importance — what structural questions are not answerable from proton integration no matter how carefully the experiment is executed? The treatment is deliberately quantitative. Every relationship is written out as an explicit proton-bookkeeping equation, two fully worked numerical examples are carried through in both directions, an error-propagation analysis is presented, and the interferences that commercial formulations introduce are simulated rather than merely described.

The emphasis on limits is intentional. The ¹H spectrum of a styrene–butadiene copolymer is an unusually well-behaved one for a macromolecule: four regions are cleanly resolved at moderate field, the proton stoichiometry of each repeat unit is unambiguous, and no calibration standard is required because the method is absolute in the same sense that any single-pulse proton experiment is absolute. That very tractability invites overreach. It is common to encounter certificates of analysis and technical reports in which cis/trans ratios, block architectures, and block molecular weights are attributed to a proton spectrum that cannot, in principle, contain them. Distinguishing what the integral genuinely determines from what has been assumed, inferred from a supplier data sheet, or silently carried over from an orthogonal measurement is the central purpose of the discussion that follows.

Throughout, the spectral parameters and integration limits quoted correspond to dilute solution in deuterochloroform at ambient temperature, which remains the standard condition for this analysis and is the condition specified in the relevant international standard.[20] Where a statement depends on spectrometer frequency it is flagged explicitly, and Section 15 treats the benchtop case separately, since the 43–100 MHz permanent-magnet instruments now common in quality-control laboratories change several of the practical conclusions without altering the underlying algebra.

2. Molecular Architecture and the Origin of the Spectral Regions

2.1 Anionic synthesis and the variables it fixes

Commercial polystyrene–polybutadiene block copolymers are, with rare exceptions, made by sequential living anionic polymerization in a hydrocarbon solvent. An alkyllithium initiator — most often sec-butyllithium — is used to grow a first polystyrene block; butadiene is then charged and propagates from the living polystyryl anion; and the chain is either terminated, coupled through a difunctional or polyfunctional electrophile, or charged with a second aliquot of styrene to give a linear triblock. Because chain transfer and termination are effectively absent,

the molecular weight of each block is set by the monomer-to-initiator ratio and the dispersity is narrow, and because the crossover from polystyryl to polybutadienyl is rapid and essentially irreversible, the block boundaries are sharp unless they are deliberately tapered by co-feeding.[45]

Two consequences follow that matter directly for the interpretation of the spectrum. The first is that the butadiene block is not structurally homogeneous. Butadiene can add to a lithium-carbon bond in three ways, and the resulting proportions of cis-1,4, trans-1,4, and 1,2 (vinyl) units are set by the polarity of the medium and the nature of the counterion environment rather than by the monomer itself. In pure hydrocarbon solvent with an alkyllithium initiator, 1,4 addition predominates and the vinyl content typically falls between 8 and 12 mol % of the diene. Addition of a Lewis base — tetrahydrofuran, a glycol diether, ditetrahydrofurylpropane, or a tertiary diamine — solvates the lithium counterion, opens the coordination geometry at the chain end, and drives vinyl content upward in a controllable fashion, with values above 70 mol % accessible under strongly modified conditions.[26] The structure of the propagating chain end under these conditions has itself been examined by ^{13}C NMR, which established the allylic delocalization that underlies the change in regiochemistry.[14] The vinyl fraction is thus a deliberate process variable, and it is one of the two primary quantities that the proton integral returns.

The second consequence is that the sequence distribution of styrene along the chain is also under process control. In a strictly sequential synthesis the styrene is confined to the terminal blocks. In a randomized or controlled-distribution synthesis, styrene and butadiene are copolymerized together in the presence of a modifier that equalizes the reactivity ratios, producing a midblock in which styrene units are isolated or present in short runs. These two materials can share an identical bulk composition and an identical vinyl content while behaving very differently as elastomers, and the ^{1}H spectrum does distinguish them — but through the line shape of the aromatic envelope rather than through its total area, a point developed in Section 8.[28] The structure–property consequences of that distinction were mapped early, in work that compared random and three-sequence block copolymers of the same gross composition and found their mechanical behavior to be entirely different.[3]

2.2 The four repeat-unit types

Four structurally distinct repeat units are present in a hydrogenation-free styrene–butadiene copolymer. The styrene unit contributes a monosubstituted benzene ring and a backbone methylene–methine pair. The cis-1,4 and trans-1,4 butadiene units are constitutional isomers of one another, each contributing an internal disubstituted olefin flanked by two allylic methylene groups. The 1,2 unit carries the double bond as a pendant vinyl group on a backbone methine, so that its olefinic protons are split between an internal methine proton and a terminal methylidene pair, and only three aliphatic protons remain. It is worth stating explicitly that no 3,4 unit exists for butadiene; the 3,4 designation belongs to isoprene, where the additional methyl substituent makes 1,2 and 3,4 addition distinguishable, and its appearance in a butadiene context is a reliable indicator that a template has been applied without thought.

The proton inventory of these four units is the entire basis of the quantitative analysis and is set out in Table 1. Each row states how many protons that repeat unit places into each of the four integration windows, and it is the linear algebra implied by this table — four unknowns, three usable equations, and one redundant equation available as a consistency check — that determines both what can be calculated and what cannot.

Table 1. Proton inventory per repeat unit, by spectral region.

Repeat unit	Repeat-unit mass (g mol^{-1})	Aromatic 6.20–7.30 ppm	Olefinic 5.15–5.80 ppm	Terminal vinylidene 4.80–5.15 ppm	Aliphatic 0.70–2.60 ppm	Total H
Styrene, –CH_2–$CH(C_6H_5)$–	104.149	5	0	0	3	8

Repeat unit	Repeat-unit mass (g mol⁻¹)	Aromatic 6.20–7.30 ppm	Olefinic 5.15–5.80 ppm	Terminal vinylidene 4.80–5.15 ppm	Aliphatic 0.70–2.60 ppm	Total H
cis-1,4-butadiene	54.090	0	2	0	4	6
trans-1,4-butadiene	54.090	0	2	0	4	6
1,2-butadiene (vinyl)	54.090	0	1	2	3	6

The cis-1,4 and trans-1,4 rows are identical in every column. This degeneracy is not an artifact of the chosen integration limits; the two isomers place the same number of protons into the same spectral regions, and no redefinition of the windows can separate them. Section 7 treats the consequences.

3. The ¹H Spectrum: Regions and Assignments

A dilute solution of an unmodified styrene–butadiene block copolymer in deuterochloroform gives a proton spectrum of four broad envelopes. Resolution within each envelope is limited by the superposition of configurational and compositional sequences rather than by field inhomogeneity, so the lines are broad at any field strength and the apparent multiplet structure visible in oligomeric model compounds is largely washed out in the polymer. The assignments are long settled and have been confirmed repeatedly by model-compound synthesis, selective deuteration, and two-dimensional correlation.[4,17,41,42,44]

The highest-frequency envelope, between roughly 6.20 and 7.30 ppm, contains the five aromatic protons of each styrene unit. This envelope is internally structured in a way that carries sequence information. In a run of three or more consecutive styrene units the phenyl rings of adjacent residues are held close enough for the ring current of one to shield the ortho protons of its neighbors, displacing those two protons upfield into a distinguishable shoulder between about 6.20 and 6.85 ppm while the meta and para protons remain near 7.05 ppm. Where a styrene unit is isolated between butadiene units this shielding is absent and all five protons resonate in the narrower high-frequency band. The effect was characterized quantitatively on styrene oligomers of defined length and remains the standard ¹H route to styrene blockiness.[4]

Between approximately 5.15 and 5.80 ppm lies the internal olefinic envelope. It contains two protons from every 1,4 unit, cis and trans indistinguishably superimposed, together with the single internal methine proton of every 1,2 unit, which resonates toward the high-frequency edge of the envelope near 5.5 ppm and is not cleanly resolved from the 1,4 signals in the polymer.[6] Below it, between roughly 4.80 and 5.15 ppm, is the pendant methylidene resonance of the 1,2 unit. This region is the analytical keystone of the whole determination: it is the only part of the spectrum populated by exactly one structural type, and every microstructure calculation is anchored to it.

The aliphatic envelope from about 0.70 to 2.60 ppm collects the allylic methylenes of the 1,4 units near 2.0 ppm, the backbone methylene and methine protons of the styrene units, and the saturated backbone protons of the 1,2 units. Within a homopolymer these can be partially assigned, but in a copolymer the overlap is severe and the region is of no use for composition. Its value is entirely as a redundancy check, and that check turns out to be one of the more informative quantities available, for reasons taken up in Section 12.

Table 2. ¹H and ¹³C chemical shift assignments for styrene–butadiene block copolymers in $CDCl_3$.

Nucleus	δ (ppm)	Assignment	Protons or note	Source
¹H	7.30–6.85	*meta* and *para* aromatic H of styrene	3 H per styrene unit	4, 41
¹H	6.85–6.20	*ortho* aromatic H of styrene flanked by styrene neighbors	2 H per blocky styrene unit	4

Nucleus	δ (ppm)	Assignment	Protons or note	Source
^{1}H	5.80–5.45	internal –CH= of the 1,2 unit; overlaps the 1,4 envelope	1 H per 1,2 unit	6, 20
^{1}H	5.55–5.25	–CH=CH– of *cis*- and *trans*-1,4 units, unresolved	2 H per 1,4 unit	1, 6
^{1}H	5.15–4.80	pendant $=CH_2$ of the 1,2 unit	2 H per 1,2 unit	6, 20
^{1}H	2.60–1.80	allylic CH_2 of 1,4 units, methine CH of 1,2 units, styrene methine	overlapping	42
^{1}H	1.80–0.70	backbone CH_2 of styrene and of 1,2 units	overlapping	42
^{1}H	2.90–2.55	oxirane CH of epoxidized *trans*- and *cis*-1,4 units	derivative only	30
^{1}H	0.85–0.40	pendant CH_3 from a hydrogenated 1,2 unit (SEBS)	3 H per unit	28
^{13}C	32.8–32.6	allylic CH_2 adjacent to a *trans*-1,4 double bond	—	9, 12
^{13}C	27.5–27.3	allylic CH_2 adjacent to a *cis*-1,4 double bond	—	9, 12
^{13}C	131.8–127.7	olefinic carbons of 1,4 units, *cis* and *trans* overlapping	—	15, 16
^{13}C	144.7–143.3	internal olefinic CH of the 1,2 unit	—	15
^{13}C	114.8–113.8	terminal $=CH_2$ of the 1,2 unit	—	15
^{13}C	146.5–145.0	*ipso* aromatic carbon of styrene, sequence sensitive	—	17

Reference numbers correspond to the numbered reference list at the end of this document. The ¹³C entries are included because they define the orthogonal measurement required for the information that ¹H integration cannot supply.

4. Proton Bookkeeping: The Algebra of the Integration

4.1 Definition of the integration regions

Five integrals are measured, of which four are used in the primary calculation and the fifth serves the blockiness determination. They are defined in Table 3. The limits quoted are conservative for a 300 MHz instrument and should be adjusted to the observed minima in the particular spectrum rather than applied dogmatically; what must not be adjusted is the assignment of protons to regions, since that is fixed by chemistry.

Table 3. Integration regions, their proton content, and the corresponding coefficient equations.

Symbol	Limits (ppm)	Protons contained	Coefficient equation	Practical note
A(ar)	6.20–7.30	5 H per styrene unit	$A(ar) = 5 \cdot n(S)$	Upper limit is set below the residual $CHCl_3$ line at 7.26 ppm, or the solvent peak is deconvoluted out.
A(ol)	5.15–5.80	2 H per 1,4 unit plus 1 H per 1,2 unit	$A(ol) = 2 \cdot n(1,4) + n(1,2)$	*cis* and *trans* contributions are inseparable within this window.
A(tv)	4.80–5.15	2 H per 1,2 unit	$A(tv) = 2 \cdot n(1,2)$	The only region unique to a single structural type; it anchors the entire calculation.
A(al)	0.70–2.60	3 H per styrene, 4 H per 1,4, 3 H per 1,2	$A(al) = 3 \cdot n(S) + 4 \cdot n(1,4) + 3 \cdot n(1,2)$	Used only as a closure check; corrupted by oils, plasticizers, antioxidants, and residual

Symbol	Limits (ppm)	Protons contained	Coefficient equation	Practical note
				solvent.
A(or)	6.20–6.85	2 H per styrene unit having two styrene neighbors	A(or) = 2·n(S,blocky)	Split at the local minimum of the aromatic envelope, typically between 6.80 and 6.88 ppm.

4.2 Solving for the molar amounts

The approach is the one introduced for these copolymers in the earliest proton work on the system, in which the aromatic and olefinic absorptions were shown to fix the composition without any calibration,[1] and extended shortly afterward into a general treatment of copolymer composition analysis by NMR.[2] The system is solved from the low-frequency end. Because the terminal vinylidene region is populated exclusively by 1,2 units and each such unit contributes exactly two protons there, the molar amount of 1,2 units follows directly. That amount is then subtracted from the internal olefinic integral to remove the single methine proton each 1,2 unit contributes to it, and what remains is divided by two to give the combined molar amount of 1,4 units. The styrene amount comes independently from the aromatic integral. In symbols, with all integrals in the same arbitrary units:

$$n(1,2) = A(tv) / 2$$

$$n(1,4) = [\ A(ol) - A(tv)/2\ ] / 2$$

$$n(S) = A(ar) / 5$$

$$n(B) = n(1,2) + n(1,4)$$

The order of operations is not arbitrary. Attempting to obtain n(1,4) from the olefinic integral alone overestimates it by half the vinyl content, an error that is negligible in a conventional low-vinyl SBS but reaches twenty-five percent of the reported 1,4 figure in a high-vinyl grade. The subtraction is mandatory, and its presence is the reason that the vinyl result carries a larger relative uncertainty than the composition result, a point quantified in Section 14.

4.3 Composition on molar and mass bases

Molar composition follows immediately from the four amounts. Conversion to a mass basis, which is how bound styrene is universally reported in the rubber and adhesive industries, requires the repeat-unit masses of 104.149 g mol^{-1} for styrene and 54.090 g mol^{-1} for butadiene:

$$\text{mol \% styrene} = 100 \cdot n(S) / [\ n(S) + n(B)\ ]$$

$$\text{mass \% styrene} = 100 \cdot 104.149 \cdot n(S) / [\ 104.149 \cdot n(S) + 54.090 \cdot n(B)\ ]$$

The discrepancy between the two bases is large and is a recurring source of confusion in specification disputes. A copolymer containing 30.00 mass % styrene contains only 18.21 mol % styrene, because the styrene repeat unit is nearly twice the mass of the butadiene repeat unit. Any specification, certificate, or expert report that quotes a styrene content without stating the basis is incomplete, and the difference is far larger than any plausible analytical uncertainty.

4.4 Butadiene microstructure

Microstructure is conventionally expressed as a mole percentage of the butadiene portion rather than of the whole polymer, and the international standard follows that convention.[19] Both forms are useful and they are not interchangeable:

$$\text{vinyl (mol \% of butadiene)} = 100 \cdot n(1,2) / n(B)$$

$$\text{1,4 total (mol \% of butadiene)} = 100 \cdot n(1,4) / n(B) = 100 - \text{vinyl}$$

$$\text{vinyl (mol \% of all repeat units)} = 100 \cdot n(1,2) / [\, n(S) + n(B) \,]$$

4.5 The aliphatic closure test

The three equations of Section 4.2 use only three of the four measured integrals. The aliphatic integral is therefore redundant, and that redundancy can be converted into a quantitative diagnostic. Its expected value is calculable from the three molar amounts already determined, and the residual between the observed and predicted values is a direct measure of whatever aliphatic material is present in the sample but not accounted for by the copolymer itself:

$$A(\text{al, predicted}) = 3 \cdot n(S) + 4 \cdot n(1,4) + 3 \cdot n(1,2)$$

$$\text{closure residual (\%)} = 100 \cdot [\, A(\text{al, observed}) - A(\text{al, predicted}) \,] / A(\text{al, predicted})$$

For a clean raw polymer with a properly phased and baseline-corrected spectrum the residual should fall within roughly ±2 %, and in the two worked examples of Section 5 it is zero by construction. A large positive residual indicates extraneous aliphatic protons, of which extender oil is by far the most common source in commercial samples; the magnitude of that effect is simulated in Section 12. A negative residual generally points to a processing fault — a baseline dragged low across the broad aliphatic envelope, or an integration limit set too tightly — rather than to a compositional anomaly. The test costs nothing, requires no additional measurement, and in the writer's experience catches more reporting errors than any other single check available in this analysis.

4.6 Derived quantities

Several further quantities of practical interest follow arithmetically from the same three amounts and require no additional measurement. Residual unsaturation, which governs susceptibility to oxidative and ozonolytic attack and sets the stoichiometry for any intended hydrogenation, epoxidation, or hydrosilylation, is simply the molar amount of butadiene units per unit mass. The theoretical iodine value follows from the same quantity and provides a bridge to the wet-chemical specifications still current in some supply agreements. The elemental carbon and hydrogen fractions are obtained by the same bookkeeping and offer an orthogonal cross-check against combustion analysis when one is available:

$$\text{unsaturation (mmol C=C g}^{-1}) = 1000 \cdot n(B) / [\, 104.149 \cdot n(S) + 54.090 \cdot n(B) \,]$$

$$\text{iodine value (g I}_2 \text{ per 100 g)} = 100 \cdot 253.81 \cdot n(B) / [\, 104.149 \cdot n(S) + 54.090 \cdot n(B) \,]$$

For the 30 mass % styrene copolymer of Worked Example A these expressions return 12.94 mmol C=C g⁻¹ and a theoretical iodine value of 328.5 g I_2 per 100 g. The corresponding figures for the high-vinyl material of Worked Example B are 13.87 mmol g⁻¹ and 351.9, the increase arising solely from the lower styrene content, since the number of double bonds per butadiene unit is invariant with respect to addition mode.

5. Worked Examples

Two examples are carried through in full, in both directions, so that the arithmetic can be audited rather than taken on trust. Both are generated by a forward calculation from a stated structure to a set of normalized integrals, followed by an independent reverse calculation from those integrals back to the structure. Agreement between the input and the recovered values confirms that the bookkeeping is internally consistent; it does not, of course,

validate the chemistry, which rests on the assignments of Table 2. Every figure quoted here is reproduced with live formulas in the companion workbook that accompanies this document.

5.1 Example A — conventional linear SBS

The first example represents a typical commercial linear styrene–butadiene–styrene triblock of the kind used in adhesives and asphalt modification: 30.00 mass % bound styrene, with the butadiene block containing 8.00 mol % 1,2 units and the balance 1,4. On a 100 g basis this corresponds to 0.28806 mol of styrene units and 1.29414 mol of butadiene units, of which 0.10353 mol are 1,2 and 1.19061 mol are 1,4. Applying the coefficients of Table 1 and normalizing the total proton count to 100.000 gives the integral set in Table 4.

Table 4. Worked Example A — forward and reverse calculation for a linear SBS containing 30.00 mass % styrene and 8.00 mol % vinyl.

Region	Coefficient equation	Raw proton moles per 100 g	Normalized integral (total = 100.000)
A(ar) 6.20–7.30	5·n(S)	1.44024	14.3035
A(ol) 5.15–5.80	2·n(1,4) + n(1,2)	2.48473	24.6766
A(tv) 4.80–5.15	2·n(1,2)	0.20706	2.0564
A(al) 0.70–2.60	3·n(S) + 4·n(1,4) + 3·n(1,2)	5.93714	58.9635
Total	—	10.06917	100.0000

Reversing the calculation from the normalized integrals alone, the vinyl amount is 2.0564/2 = 1.0282, the 1,4 amount is (24.6766 − 1.0282)/2 = 11.8242, and the styrene amount is 14.3035/5 = 2.8607. These give 18.206 mol % styrene, 30.000 mass % styrene, and 8.000 mol % vinyl on the butadiene portion, recovering the input exactly. The predicted aliphatic integral is 3(2.8607) + 4(11.8242) + 3(1.0282) = 58.9635, identical to the tabulated value, so the closure residual is zero as it must be for a synthetic dataset. Residual unsaturation is 12.94 mmol C=C g^{-1}.

5.2 Example B — high-vinyl styrene–butadiene copolymer

The second example is chosen to stress the algebra where it is weakest. A high-vinyl material containing 25.00 mass % styrene with 50.00 mol % of the butadiene present as 1,2 units is representative of the solution-polymerized grades used in tread compounds and of the high-vinyl midblocks used where a raised midblock glass transition is wanted. The vinyl content is now high enough that the correction term in the 1,4 equation is no longer a minor adjustment.

Table 5. Worked Example B — forward and reverse calculation for a copolymer containing 25.00 mass % styrene and 50.00 mol % vinyl.

Region	Normalized integral	Quantity recovered from that region	Value
A(ar) 6.20–7.30	11.7210	n(S) = A(ar)/5	2.34421
A(tv) 4.80–5.15	13.5411	n(1,2) = A(tv)/2	6.77053
A(ol) 5.15–5.80	20.3116	n(1,4) = [A(ol) − A(tv)/2]/2	6.77053
A(al) 0.70–2.60	54.4263	A(al) predicted = 3·n(S) + 4·n(1,4) + 3·n(1,2)	54.4263
Total	100.0000	closure residual (%)	0.000
—	—	styrene recovered (mass %)	25.000
—	—	vinyl recovered (mol % of butadiene)	50.000

Here the uncorrected olefinic integral would have implied 10.156 units of 1,4 material against a true value of 6.771, an overstatement of exactly 50 %. The magnitude of that error scales linearly with vinyl content and is the single most common arithmetic mistake made in this analysis. It is worth noting also that the terminal vinylidene integral has grown from 2.06 to 13.54 on the same normalized scale, so that the precision of the vinyl determination improves markedly as vinyl content rises even though the propagated error in the 1,4 figure worsens.

6. Butadiene Microstructure and What the Vinyl Content Signifies

Of the two primary results the proton integral delivers, the vinyl content is the one more often underused. Composition is usually known approximately from the grade designation before the sample reaches the laboratory; microstructure frequently is not, and it exerts control over properties that composition alone cannot explain.

The mechanical consequence arises from chain stiffness. A 1,4 unit places the double bond in the backbone and contributes four freely rotating skeletal bonds per monomer; a 1,2 unit places the double bond on a pendant substituent and leaves a shorter, more hindered backbone segment. Increasing the 1,2 fraction therefore raises the glass transition temperature of the diene phase monotonically, from roughly −95 °C for a low-vinyl polybutadiene toward values several tens of degrees higher as vinyl content approaches the upper end of the accessible range. In a thermoplastic elastomer this shifts the lower service limit and the damping maximum; in a tread compound it is the primary lever for wet-grip and rolling-resistance balance. Since the DSC transition and the ¹H vinyl content are measuring the same underlying structural variable, disagreement between them in a routine control setting is generally a signal that something else has changed — plasticizer content, phase mixing, or a second polymer in the blend — rather than that either measurement is wrong.

The chemical consequences are equally direct. Pendant vinyl groups are considerably more reactive than internal backbone olefins toward radical addition, hydrosilylation, and thermal crosslinking, so a high-vinyl grade is more susceptible to gel formation during compounding and more responsive to peroxide cure. Under hydrogenation, by contrast, 1,4 units become ethylene-like sequences while 1,2 units become pendant ethyl groups; the original vinyl content therefore determines the ethylene-to-butylene ratio of the resulting saturated midblock and thus whether that midblock is amorphous or partially crystalline.[28] A vinyl content measured on the unsaturated precursor is, in that sense, a prediction about a material that does not yet exist.

Reactivity toward oxidation deserves a separate remark, because the direction is not always the one expected. In thermo-oxidative aging of styrene–butadiene copolymers the internal 1,4 unsaturation is consumed preferentially, so that the apparent vinyl fraction of an aged sample rises even though no 1,2 units have been created.[29] A vinyl content reported for a service-aged or reclaimed material therefore should not be compared directly against a specification written for virgin polymer, and the distinction is one that opposing technical review will find if the report does not make it first.

Table 6. Typical butadiene microstructures encountered in commercial styrene–butadiene materials.

Material class	Typical vinyl (mol % of butadiene)	Typical bound styrene (mass %)	Comment
Linear SBS, hydrocarbon-solvent anionic	8 – 12	28 – 33	Unmodified alkyllithium polymerization; the reference case.
Radial (S–B)$_n$ SBS	8 – 15	28 – 40	Coupled architecture; ¹H integration cannot distinguish it from linear.
Medium-vinyl solution SBR	25 – 45	15 – 30	Polar modifier used to raise vinyl; often oil extended.

Material class	Typical vinyl (mol % of butadiene)	Typical bound styrene (mass %)	Comment
High-vinyl solution SBR	50 – 70	20 – 35	Strongly modified conditions; the subtraction correction is critical.
Emulsion SBR	15 – 20	23 – 25	Free-radical mechanism; microstructure set by temperature, not by modifier.
Precursor for SEBS	8 – 45	13 – 33	Vinyl content sets the ethylene/butylene ratio after hydrogenation.

Ranges are indicative of the classes named and are given to orient an analyst confronting an unidentified sample; they are not specifications and should not be used as acceptance criteria.

7. The *cis*/*trans* Degeneracy: What Proton Integration Cannot Deliver

The most consequential limitation of the method is stated plainly in Table 1. The cis-1,4 and trans-1,4 repeat units place the same number of protons into the same spectral windows, and their olefinic resonances are superimposed within a few hundredths of a part per million. No integration scheme, no choice of solvent, and no increase in field strength separates them in a routine proton spectrum of a polymer. Any report that presents a cis/trans split alongside a proton-only method has obtained that split from somewhere else, and the provenance should be stated.

A qualification is owed. The allylic methylene protons adjacent to cis and trans double bonds do differ slightly in shift, appearing near 2.05 and 2.02 ppm respectively, and at high field on a polybutadiene homopolymer of narrow configurational distribution a partial separation can sometimes be discerned. In a styrene-containing copolymer that separation is destroyed by the overlapping styrene backbone resonances, and even in the homopolymer case the quantitative reliability of such a deconvolution has been examined critically and found wanting. A careful 600 MHz study concluded that significant limitations attend the quantitative characterization of polybutadiene configurational isomers by NMR generally, and specifically that ¹H-based cis/trans assignments do not survive scrutiny.[6] That assessment should be regarded as the governing one.

Two orthogonal methods supply the missing information reliably. Carbon-13 NMR resolves the allylic carbons cleanly, with the methylene carbon adjacent to a cis double bond near 27.4 ppm and its trans counterpart near 32.7 ppm, a separation of more than five parts per million that is unambiguous at any field.[9,12,16] The assignment has been established through model compounds, through equibinary polymers of known composition, and through the diad and triad analysis that also yields sequence information inaccessible to proton work.[10,11,13,15] The practical cost is sensitivity: quantitative ¹³C acquisition on a polymer solution requires inverse-gated decoupling to suppress the nuclear Overhauser enhancement, a relaxation delay long enough to accommodate the olefinic carbons, and acquisition times measured in hours rather than minutes.

Infrared spectrometry supplies the same information far more rapidly and remains the routine industrial method. The out-of-plane bending vibrations of the three unsaturation types fall at approximately 967 cm^{-1} for trans-1,4, 911 cm^{-1} for the 1,2 vinyl group, and near 730–740 cm^{-1} for cis-1,4, with the monosubstituted phenyl ring of styrene contributing at 699 and 757 cm^{-1}. The quantitative treatment of these bands was worked out in the 1950s and has changed remarkably little since.[18,19] The method is relative rather than absolute: the absorptivities depend on the surrounding microstructure and must be calibrated against polymers of known composition, and the international standard accordingly designates the ¹H NMR determination as the absolute method and the infrared determination as the relative one calibrated against it.[20,21]

The correct framing, therefore, is that proton NMR and infrared spectrometry are complementary rather than competing. The proton experiment fixes bound styrene and vinyl content absolutely and without calibration; the

infrared measurement partitions the 1,4 fraction into its geometric isomers using absorptivities traceable to proton-characterized standards. A laboratory offering microstructure determination on styrene–butadiene materials needs both, and a report presenting only one should say which quantities it is and is not able to support.

Table 7. Structural questions and the measurement that answers them.

Structural question	Answered by ¹H integration?	Method of choice	Basis
Bound styrene, mass or mole basis	Yes, absolutely	¹H NMR	A(ar)/5 against the diene integrals
1,2 (vinyl) content of the butadiene	Yes, absolutely	¹H NMR	A(tv)/2, the one unique region
Total 1,4 content	Yes, absolutely	¹H NMR	A(ol) corrected for the 1,2 methine
cis-1,4 versus *trans*-1,4 split	No	¹³C NMR or FTIR	27.4 vs 32.7 ppm; 730 vs 967 cm^{-1}
Styrene blockiness (three or more in a run)	Yes, semi-quantitatively	¹H NMR at ≥ 200 MHz	*ortho* ring-current shoulder, 6.20–6.85 ppm
Mean styrene sequence length	Partially	¹³C NMR	Aromatic *ipso* carbon sequence sensitivity
Diblock versus triblock versus radial	No	SEC, osmometry, TEM, SAXS	Molar mass and chain-end count
Block molecular weights	No, not alone	¹H composition combined with SEC Mn	Composition partitions a measured Mn
Total molecular weight	Only for low Mn	SEC-MALS; ¹H end-group analysis	Initiator residue near 0.8 ppm
Tacticity of the styrene block	No	¹³C NMR	*ipso* carbon configurational sensitivity
Microphase morphology	No	SAXS, TEM, AFM	Domain spacing and geometry
Degree of hydrogenation	Yes	¹H NMR	Loss of olefinic area against aromatic
Degree of epoxidation	Yes	¹H NMR	Oxirane CH at 2.55–2.90 ppm
Extender oil present	Indicated	¹H closure residual; then extraction	Aliphatic excess over prediction

8. Sequence Distribution and Styrene Blockiness

The total aromatic integral is blind to sequence. A triblock copolymer with 30 mass % styrene confined to two terminal blocks and a statistical copolymer with 30 mass % styrene distributed at random produce aromatic integrals of identical area. What differs is the distribution of that area within the envelope, and the physical origin of the difference is the ring-current anisotropy of the phenyl group.

When a styrene unit is flanked by other styrene units, the local conformation of the chain brings neighboring phenyl rings into positions where their induced ring currents shield the ortho protons of the central ring. Those two protons are displaced upfield, emerging as a resolved shoulder between roughly 6.20 and 6.85 ppm, while the meta and para protons are much less affected and remain near 7.05 ppm. The magnitude of the displacement was mapped systematically on styrene oligomers of increasing degree of polymerization, where the ortho proton shift was shown to move progressively upfield as the run length grew, and the fraction of styrene in sequences longer than six units was shown to be estimable from the relative intensity of the upfield ortho signal.[4] In an isolated

styrene unit surrounded by butadiene the shielding neighbors are absent and all five aromatic protons resonate in the high-frequency band.

The industrial practice that has grown from this observation defines a blockiness index as the proportion of styrene units possessing two styrene nearest neighbors. Two integrals are required: the total aromatic envelope divided by five, giving the total styrene count, and the upfield ortho sub-integral divided by two, giving the count of blocky styrene units. The index is their ratio:

$$B = 100 \cdot [\, A(or) / 2 \,] / [\, A(ar) / 5 \,]$$

The split between the two sub-regions is made at the local minimum of the aromatic envelope, which in practice falls between about 6.80 and 6.88 ppm and should be located on the spectrum at hand rather than assumed. Applied to Worked Example A with 92 % of the styrene resident in true blocks, the ortho sub-integral is 5.2637 against a total aromatic integral of 14.3035, and the index returns 92.0 %, as Table 8 records across a range of hypothetical sequence distributions.

Table 8. Blockiness index across sequence distributions, computed on the Example A aromatic integral of 14.3035.

Sequence scenario	Blocky styrene fraction	A(or), 6.20–6.85 ppm	Blockiness index B (%)
Sharp block boundaries, no taper	1.00	5.7214	100.00
Commercial SBS with a short taper	0.92	5.2637	92.00
Controlled-distribution midblock	0.50	2.8607	50.00
Randomized solution SBR	0.10	0.5721	10.00
Statistical emulsion SBR, low styrene	0.02	0.1144	2.00

Three cautions attach to this index and all three are material. The first is that it saturates. Any genuinely blocky architecture returns a value near 100 %, so the index separates block from statistical copolymers decisively but discriminates poorly among block copolymers of differing block length; a polystyrene block of degree of polymerization 40 and one of degree of polymerization 400 both return essentially the same number. The second is that the shielding effect requires a run of at least three, and more reliably more than three, consecutive styrene units, so short runs of two are counted inconsistently and the index should not be read as a sequence-length distribution. The third is instrumental: the ortho and meta-para sub-envelopes are separated by about 0.50 ppm, which is 150 Hz at 300 MHz but only 30 Hz at 60 MHz, and against polymer linewidths of five to twenty-five hertz the split ceases to be reliably integrable below roughly 200 MHz. Blockiness is therefore a high-field determination even though composition and vinyl content are not.

Where a genuine sequence-length distribution is required, carbon-13 is the appropriate nucleus. The ipso aromatic carbon and the allylic carbons of the diene units are sensitive to diad and triad composition, and complete diad analyses of styrene–butadiene copolymers have been reported from which mean run lengths for each unit type can be extracted.[5,13,17] The classic finding of that work — that styrene shows the strongest tendency of any of the four unit types to block, and that cis and trans 1,4 units preferentially neighbor one another — remains the framework within which sequence data on these materials are interpreted.[13] Chemical degradation followed by chromatography provides a third and quite independent route, in which ozonolysis cleaves the diene unsaturation and the surviving styrene oligomers are sized by liquid chromatography to give a direct sequence-length distribution.

9. Architecture: The Information That Is Not in the Integral

It should be stated without hedging that a proton spectrum contains no information about chain architecture. A diblock, a linear triblock, a coupled radial star, and a physical blend of polystyrene with polybutadiene of matching composition all produce the same four integrals. In the blend case even the blockiness index fails to discriminate, since the polystyrene homopolymer contributes a fully shielded ortho population indistinguishable from that of a bound block. This is not a subtle limitation and it is not one that improved acquisition addresses; the integral counts repeat units and has no access to their connectivity.

Nor is the limitation confined to architecture in the topological sense. The number of blocks per chain, the presence of residual uncoupled diblock in a coupled product — routinely between ten and twenty-five percent in commercial radial grades and a significant determinant of melt viscosity and adhesive tack — the distribution of block lengths, and the microphase morphology all lie outside the reach of proton integration. Each requires an orthogonal measurement: size-exclusion chromatography with light-scattering detection for the molar mass distribution and coupling efficiency, small-angle X-ray scattering or transmission electron microscopy for domain geometry and spacing,[22] differential scanning calorimetry or dynamic mechanical analysis for the number and position of glass transitions, and diffusion-ordered NMR for distinguishing a true block copolymer from a blend of homopolymers in solution.[24] Proton relaxation behavior has also been used to probe the physical network formed by the polybutadiene midblock between glassy polystyrene domains, which is a property of the assembled architecture rather than of the chain composition.[23]

The diffusion experiment deserves particular mention because it is the one case where an NMR measurement does resolve the blend-versus-copolymer question directly. In a covalently joined block copolymer all resonances belong to a single diffusing species and therefore share a common translational diffusion coefficient; in a blend the polystyrene and polybutadiene resonances diffuse at rates set by their separate hydrodynamic sizes. A DOSY experiment consequently separates the two cases cleanly, and the approach has been applied successfully to amphiphilic block copolymer characterization.[24] It is, however, a different experiment from the one this paper is concerned with, and it returns a qualitative verdict rather than a composition.

The proper use of the proton result in this context is as a partitioning tool. Once the total number-average molecular weight has been established by an independent method, the ¹H composition divides it between the blocks. The architecture must still be supplied as an assumption, and the same spectrum is consistent with every row of Table 9, which is precisely the point.

Table 9. Block molecular weights obtained by partitioning an externally measured Mn of 100 000 g mol⁻¹ using the Example A composition of 30.00 mass % styrene.

Assumed architecture	PS blocks per chain	PS total (g mol⁻¹)	PS per block (g mol⁻¹)	DP per PS block	PB block (g mol⁻¹)	DP of PB block
S–B diblock	1	30 000	30 000	288	70 000	1 294
S–B–S linear triblock	2	30 000	15 000	144	70 000	1 294
$(S–B)_3$ radial star	3	30 000	10 000	96	70 000	1 294
$(S–B)_4$ radial star	4	30 000	7 500	72	70 000	1 294

10. Chain Ends, Molecular Weight, and the Limits of End-Group Analysis

Proton NMR can in principle deliver a number-average molecular weight directly, by counting the initiator residue against the repeat units. In an alkyllithium-initiated polymerization each chain carries a sec-butyl group at the initiating terminus, whose methyl protons resonate between roughly 0.7 and 0.9 ppm, and the ratio of that

resonance to the repeat-unit resonances gives the degree of polymerization without recourse to any calibration or column.[25]

The practical difficulty is arithmetic rather than conceptual. The sec-butyl residue contributes nine protons per chain against roughly six to eight protons per repeat unit, so in a chain of degree of polymerization 1 400 the end-group resonance represents on the order of 0.1 % of the total proton intensity, and it sits beneath the upfield edge of the polymer aliphatic envelope rather than in clear spectral space. For the hundred-thousand-molecular-weight materials that dominate the thermoplastic-elastomer market, end-group analysis is not a viable route to Mn. It becomes useful below roughly twenty to thirty thousand, which covers telechelic and liquid-rubber grades and the low-molecular-weight oligomers used in adhesive tackifier systems, and there it can be genuinely valuable because it is an absolute method independent of the column calibration that dogs size-exclusion chromatography of copolymers.

A more consequential subtlety attends the size-exclusion route itself. Chromatographic molecular weights for a copolymer calibrated against polystyrene standards are not true molecular weights, because the hydrodynamic volume of a styrene–butadiene chain differs from that of a polystyrene chain of the same mass, and the discrepancy varies with composition. A partitioning exercise of the kind shown in Table 9 therefore inherits whatever bias the chromatographic determination carries, and the bias is composition-dependent in exactly the way that makes it hard to detect. Where block molecular weights are to be reported as a deliverable, the Mn should come from a light-scattering or membrane-osmometry determination, and the report should say so.

Functionally terminated grades change the picture usefully. Hydroxyl-, carboxyl-, amine-, and silane-terminated styrene–butadiene copolymers carry end groups whose resonances fall in otherwise empty regions of the spectrum, and for those materials the end-group count is both more sensitive and more specific than the alkyl-residue count.[27] Functionality — the average number of reactive groups per chain — is itself a specification parameter for these products and is obtained from the same integral, which makes proton NMR the natural primary method rather than a fallback.

11. Chemically Modified and Derived Copolymers

11.1 Hydrogenation to SEBS and the fate of the microstructure

Selective hydrogenation of the diene block, leaving the aromatic rings intact, converts a styrene–butadiene–styrene triblock into the saturated styrene–ethylene/butylene–styrene family. Proton NMR follows this transformation with unusual clarity, because the reaction empties two whole spectral regions. The degree of hydrogenation is obtained directly from the residual olefinic and terminal vinylidene intensity measured against the invariant aromatic integral, and because the aromatic protons are untouched they serve as a built-in internal standard, removing any dependence on sample weight or concentration:

$$\text{degree of hydrogenation (\%)} = 100 \cdot \{\, 1 - [\, A(\text{ol}) + A(\text{tv}) \,]_{a} f_{t_{er}} \,/\, [\, A(\text{ol}) + A(\text{tv}) \,]_{\beta e} f_{ore} \cdot A(\text{ar})_{\beta e} f_{ore} \,/\, A(\text{ar})_{a} f_{t_{er}} \,\}$$

Residual unsaturation at the levels that matter commercially — typically below two percent of the original double bonds — is measurable by this route provided the acquisition is arranged with adequate signal-to-noise in an otherwise empty region, which is a far easier requirement than resolving a minor component beneath a major one.

The microstructural bookkeeping carries through the reaction. A hydrogenated 1,4 unit becomes a sequence of four methylene groups, indistinguishable from an ethylene diad; a hydrogenated 1,2 unit becomes a backbone methine bearing a pendant ethyl group, and the terminal methyl of that ethyl group resonates in a distinctive window between roughly 0.4 and 0.8 ppm where nothing else in the saturated polymer appears. The ethylene-to-

butylene ratio of the product is therefore recoverable from the saturated material, and it is fixed by the vinyl content of the precursor. Comprehensive NMR characterization of this family, including the controlled-distribution grades in which styrene is deliberately placed within the midblock, has shown that while ¹H integration gives composition reliably, the sequence-level detail requires ¹³C together with DEPT and two-dimensional heteronuclear correlation to assign triads and tetrads unambiguously.[28] That division of labor is the same one that governs the unsaturated parent.

11.2 Epoxidation

Peracid epoxidation of the diene block is used to introduce polarity, to raise the glass transition of the midblock, and to provide crosslinking sites. The reaction is strongly selective for internal 1,4 unsaturation over the pendant vinyl group, and proton NMR reports both the extent and the selectivity in a single spectrum. Oxirane methine protons appear between roughly 2.55 and 2.90 ppm, with the trans-derived and cis-derived signals resolved from one another near 2.8 and 2.7 ppm respectively, while the corresponding olefinic intensity is lost from the 5.15–5.80 ppm envelope. Studies on styrene–butadiene star block copolymers epoxidized over a range from 38 to 82 mol % have confirmed that the 1,2 unit signals remain unaltered throughout, so that the terminal vinylidene integral survives as an internal reference against which conversion can be normalized.[30] The degree of epoxidation is calculated as the oxirane intensity over the sum of oxirane and surviving 1,4 olefinic intensity, and an interesting secondary consequence follows: the epoxidized material offers a cis/trans discrimination in the proton spectrum that the parent polymer does not, because the derivatization resolves what the parent leaves degenerate.

11.3 Anhydride grafting, silane functionalization, and telechelic grades

Maleic anhydride grafting, whether by radical initiation or by the thermal ene reaction, attaches succinic anhydride residues to the diene block and is used to compatibilize styrene–butadiene copolymers with polar polymers and with polar fillers. Grafting degrees are low — commonly one to three percent by mass — which places the diagnostic resonances near the detection limit of a routine proton experiment, and the methine and methylene protons of the grafted anhydride ring fall between roughly 2.6 and 3.2 ppm where they overlap the tail of the polymer aliphatic envelope.[31,32] Proton integration can quantify grafting at these levels only with careful baseline treatment and a long accumulation, and the result should be corroborated by titration or by infrared measurement of the anhydride carbonyl bands. This is a case where the proton method is workable but is not the method of choice, and saying so in a report is more useful than presenting a number of uncertain provenance.

Hydroxyl-terminated and hydroxyl-functionalized grades are more tractable, since the carbinol protons resonate in the 3.4 to 3.8 ppm window well clear of both the olefinic and aliphatic envelopes. Synthetic work on hydroxyl-terminated styrene–butadiene–styrene triblocks has used exactly this integral to establish functionality alongside the microstructure determination.[27]

11.4 Oxidative aging and service-life assessment

The diene block is the point of attack in essentially every degradation pathway these materials experience. Thermo-oxidative and photo-oxidative aging proceed through allylic hydrogen abstraction and hydroperoxide formation, followed by chain scission and by crosslinking, and the proton spectrum records the process as a progressive loss of olefinic intensity accompanied by the appearance of resonances associated with hydroxyl, carbonyl, and epoxide functionality. Comparative degradation studies of the saturated SEBS analogue against unsaturated parents have established the chemistry of these pathways and the role of the stabilizer package in retarding them.[29]

Two practical points follow for the analyst. The first, already raised in Section 6, is that the loss of unsaturation is not uniform across microstructure types; internal 1,4 unsaturation is consumed preferentially, so the vinyl fraction of an aged sample rises artifactually and must not be compared with a virgin specification. The second is that crosslinking progressively removes polymer from solution. As gel forms, the soluble fraction that the NMR tube actually samples becomes unrepresentative of the bulk, and the measured composition drifts toward whatever fraction remains soluble. A gel-content determination should therefore accompany any compositional analysis of an aged or thermally processed sample, and the report should state the soluble fraction on which the result was obtained. This is an issue that surfaces regularly in failure-analysis and litigation contexts, where the sample provided is by definition a degraded one.

12. Interferences in Commercial Samples

Everything in Sections 4 through 6 assumes that the only protons in the tube belong to the copolymer. Raw polymer as delivered by the reactor approximates that condition; almost nothing else that reaches an analytical laboratory does. The interferences fall into three groups according to where they deposit intensity, and their diagnosis is one of the more valuable uses of the closure test.

The first and most serious group deposits intensity in the aliphatic region alone. Extender oils — naphthenic, paraffinic, treated distillate aromatic extract, or mild extraction solvate types — are present in oil-extended grades at loadings between roughly twenty and forty parts per hundred rubber, and they are essentially pure aliphatic and naphthenic hydrocarbon with a modest aromatic proton content. Process oils, paraffin waxes, and polymeric plasticizers behave similarly. None of these contributes to the olefinic or terminal vinylidene regions, so the vinyl determination survives intact; what fails is the closure test, and it fails loudly. Table 10 simulates the effect quantitatively for the Example A polymer.

Table 10. Simulated effect of hydrocarbon extender oil on the Example A integrals. The oil is modeled as containing 12.5 mass % hydrogen, with the stated fraction of that hydrogen aromatic.

Case	Oil (mass % of sample)	Aromatic H fraction of oil	Apparent styrene (mass %)	Reported vinyl (mol % of BD)	Closure residual (%)
No oil, reference	0.0	0.00	30.00	8.00	0.00
Naphthenic oil	20.0	0.05	32.19	8.00	+47.30
Naphthenic oil	25.0	0.05	32.89	8.00	+62.74
Aromatic (DAE) oil	25.0	0.15	38.01	8.00	+49.79
Naphthenic oil	33.0	0.05	34.19	8.00	+91.81

Three conclusions follow from the simulation and each is worth stating. Apparent styrene content is inflated in every oil-containing case, because the oil's aromatic protons are counted as styrene; for a highly aromatic extract oil at twenty-five percent loading the error reaches eight percentage points absolute, which is far outside any acceptable tolerance for a bound-styrene specification. The vinyl determination is completely unaffected, because no interferent contributes to the two olefinic windows, which makes microstructure the more robust of the two primary results in real samples. And the closure residual rises to between forty-seven and ninety-two percent, a signal so large that it cannot be mistaken for a baseline artifact. The test does not identify the oil, but it establishes beyond argument that the specimen is not what the calculation assumes, and it does so from data already in hand.

The second group deposits intensity in the aromatic region and is correspondingly more insidious. Aromatic extender oils have already been noted. Hindered-phenol antioxidants of the butylated hydroxytoluene and

Irganox families contribute sharp aromatic singlets together with tert-butyl resonances near 1.4 ppm; phosphite co-stabilizers contribute aromatic intensity as well. At the loadings normally used, a few tenths of a percent, the error introduced into bound styrene is small but not always negligible, and the resonances are sharp against a broad polymer envelope and therefore easy to recognize and, if necessary, to exclude by deconvolution; compilations of additive spectra are available and are worth consulting before an unexplained line is dismissed.[43] Polystyrene homopolymer present as a blend component or as an impurity is the pathological case, because it is spectroscopically indistinguishable from bound styrene by any proton criterion whatever, including the blockiness index. The mirror-image problem — determining polybutadiene content and microstructure in a matrix that is predominantly polystyrene — arises in high-impact polystyrene and has been addressed by combining the proton determination with quantitative ^{13}C, which resolves what the proton spectrum cannot.[33]

The third group consists of small molecules with sharp lines: residual monomer, residual polymerization solvent such as cyclohexane or ethylbenzene, water, the protonated residue of the deuterated solvent, and adventitious contaminants introduced during sample handling. Their sharpness makes them easy to spot and to exclude, but two require particular attention. Residual chloroform in $CDCl_3$ resonates at 7.26 ppm, directly on the high-frequency edge of the aromatic envelope, and at the concentrations used for polymer work its integral can be comparable with the styrene signal of a low-styrene grade; the upper integration limit must be set below it, or the peak must be fitted and subtracted. A procedure has been published in which the contribution of the residual solvent protons is calculated from the ^{13}C satellites of the solvent signal and subtracted analytically, which removes the need to compromise the integration limit at all.[7] Residual ethylbenzene, a common polymerization solvent, contributes both aromatic and aliphatic intensity and will be counted as styrene by the naive calculation.

Table 11. Common interferents, their spectral positions, and their effect on the reported result.

Interferent	Where it deposits intensity	Effect on the result	Detection and remedy
Naphthenic or paraffinic extender oil	0.7–2.0 ppm, minor aromatic	Inflates styrene; large positive closure residual	Closure test; solvent extraction before analysis, with the extract weighed
Treated distillate aromatic extract oil	0.7–2.0 and 6.5–7.5 ppm	Severely inflates styrene	Closure test plus an aromatic line shape that does not match polystyrene
Polystyrene homopolymer in a blend	Identical to bound styrene	Indistinguishable by any ^{1}H criterion	DOSY, SEC, DSC, or selective extraction
Hindered-phenol antioxidant	Sharp aromatic singlet; 1.4 ppm *tert*-butyl	Small positive bias on styrene	Sharp lines on a broad envelope; deconvolute or exclude
Residual $CHCl_3$ in $CDCl_3$	7.26 ppm	Directly inflates the aromatic integral	Set the upper limit below 7.26 ppm, or fit and subtract
Residual ethylbenzene or toluene solvent	Aromatic and aliphatic	Inflates styrene and breaks closure	Sharp lines; devolatilize the sample before dissolution
Water	1.5–1.6 ppm in $CDCl_3$	Breaks closure; no effect on composition	Dry the solvent; recognize the singlet
Silica, carbon black, or other filler	None directly	Removes polymer from solution; biases toward the soluble fraction	Centrifuge or filter; report the soluble fraction
Crosslinked gel from aging or processing	None directly	Soluble fraction is unrepresentative of the bulk	Determine gel content alongside; state the basis

13. Acquisition and Processing for Quantitative Work

The proton experiment is quantitative only if it is arranged to be. Three requirements govern, and none is onerous.

The first is complete relaxation between transients. Proton spin–lattice relaxation times in dissolved polymers are shorter than in small molecules because of restricted segmental motion, generally falling between about 0.3 and 1.5 s, but they are not uniform across the spectrum: aromatic and olefinic protons on relatively mobile segments relax more slowly than backbone methylenes, and the ratio between the regions being compared is precisely what a too-short recycle delay distorts. General quantitative NMR practice requires a repetition time of at least five times the longest relevant T_1, and the discipline built up in the pharmaceutical qNMR literature is directly transferable here.[38,39] Where an absolute concentration rather than a composition ratio is wanted, external calibration schemes now provide an alternative to adding an internal standard that would itself have to be inert toward the polymer.[40] For this analysis a measured inversion-recovery determination on a representative sample is worth the half hour it costs; in its absence, a ninety-degree pulse with a ten-second relaxation delay is a defensible default that covers the range encountered in practice. Where throughput matters, a reduced flip angle with a correspondingly shortened delay can be used, but only after the equivalence of the two conditions has been demonstrated on the material in question.

The second requirement is that the sample be dilute enough to give narrow lines. Polymer solutions above roughly five percent by mass become viscous, and the resulting increase in correlation time broadens every resonance and degrades the resolution of the aromatic sub-envelopes on which blockiness depends. Between one and three percent by mass in deuterochloroform is the working range; below one percent the accumulation time needed to reach adequate signal-to-noise in the terminal vinylidene region becomes the limiting factor, particularly for low-vinyl grades where that region carries only two percent of the total intensity. Complete dissolution should be verified visually before the spectrum is acquired, since partial dissolution biases the result toward whichever component dissolves first.

The third requirement concerns processing, and it is where most of the avoidable error enters. Broad polymer resonances sit on baselines that are themselves broad, and an inadequate baseline correction shifts area between adjacent regions in a way that no amount of acquisition time repairs. Phase correction must be optimized across the whole spectral width rather than on the aromatic region alone, since a residual first-order phase error that is invisible at 7 ppm can be substantial at 1 ppm. A polynomial or spline baseline fitted to genuinely signal-free regions, with the fitting points chosen manually rather than by an automatic routine, is the appropriate treatment. Integration limits should be set at observed minima and recorded, and the same limits should be applied across a sample set so that comparisons are not corrupted by inconsistent boundary placement.

Table 12. Recommended acquisition and processing conditions for quantitative analysis of styrene–butadiene block copolymers.

Parameter	Recommendation	Rationale
Solvent	$CDCl_3$, dried, with the residual $CHCl_3$ line noted	Good solvation of both blocks; well-characterized reference shift at 7.26 ppm
Concentration	1–3 % by mass	Balances line width against acquisition time; avoids viscosity broadening
Temperature	298 K, regulated	Shift positions and line widths are temperature dependent; regulation makes limits transferable
Pulse angle	90°, calibrated on the sample	Maximum sensitivity; removes flip-angle dependence from the intensity ratios
Relaxation delay	≥ 10 s, or $5 \cdot T_1$(max) if measured	Polymer ¹H T_1 values are typically 0.3–1.5 s but are not uniform across regions
Acquisition time	≥ 3 s	Avoids truncation of the broad envelopes and the associated line shape distortion
Transients	64–256, more for low-vinyl grades	The terminal vinylidene region may carry only 2 % of total

Parameter	Recommendation	Rationale
		intensity
Spectral width	≥ 16 ppm, centered near 5 ppm	Ensures a flat region beyond the signal for baseline anchoring
Apodization	Minimal; ≤ 0.3 Hz exponential	Polymer lines are already broad; further broadening merges the aromatic sub-envelopes
Phasing	Manual, optimized across the full width	First-order error invisible at 7 ppm can be severe at 1 ppm
Baseline	Polynomial or spline on manually chosen signal-free points	Automatic routines mistake broad polymer signal for baseline
Integration	Limits at observed minima, recorded and applied consistently	Boundary placement is the dominant operator-dependent error
Reporting	Quote all five integrals, the closure residual, and the limits used	Allows an independent reviewer to reproduce the calculation

14. Uncertainty and Error Propagation

The error budget for this analysis is dominated by a single term. Instrumental contributions — receiver linearity, digitization, signal-to-noise at the levels used — are small compared with the operator-dependent placement of integration boundaries and the associated baseline treatment. A realistic estimate for the relative uncertainty on an individual region integral in careful routine work is one to two percent, and it is instructive to see how that propagates.

Table 13 presents the result of perturbing each region by one percent relative, in turn, while holding the others at the Example A values. The aromatic integral propagates almost entirely into composition and not at all into microstructure, which is expected since it enters neither microstructure equation. The olefinic and terminal vinylidene integrals propagate into the vinyl figure with opposite sign and nearly equal magnitude, a direct consequence of the subtraction in the 1,4 equation, and they also perturb composition through the denominator.

Table 13. Propagation of a ±1.0 % relative error in each integration region, computed on the Example A base case (30.00 mass % styrene, 8.00 mol % vinyl).

Perturbation	Styrene (mass %)	Δ styrene (mass %)	Vinyl (mol % of BD)	Δ vinyl (mol %)
Base case	30.000	—	8.000	—
A(ar) high by 1 %	30.209	+0.209	8.000	0.000
A(ar) low by 1 %	29.789	−0.211	8.000	0.000
A(ol) high by 1 %	29.800	−0.200	7.924	−0.076
A(ol) low by 1 %	30.203	+0.203	8.078	+0.078
A(tv) high by 1 %	29.992	−0.008	8.077	+0.077
A(tv) low by 1 %	30.008	+0.008	7.923	−0.077

The practical reading is reassuring for composition and requires attention for microstructure. A one percent integration error translates into roughly two-tenths of a percentage point on bound styrene, so that a routine determination can reasonably be reported to the nearest half percent and a careful one to the nearest tenth. The vinyl figure at eight mol percent moves by less than a tenth of a mole percent for the same perturbation, which appears excellent — but the relative error is about one percent of the reported value, and it grows. Repeating the exercise on the high-vinyl Example B, where vinyl is fifty mol percent, gives shifts of ±0.37 mol percent for the same one percent perturbation, roughly five times larger in absolute terms. The subtraction term is responsible: as

the vinyl correction becomes a larger share of the olefinic integral, the difference between two comparable numbers carries a proportionally larger error.

Two further sources deserve mention because they are systematic rather than random and therefore do not average out. Incomplete relaxation biases the ratio between regions in a direction set by the T_1 differences, and since the aromatic and olefinic protons generally relax more slowly than the aliphatic ones, a short recycle delay suppresses the numerator of the composition calculation and understates bound styrene. Baseline distortion beneath the broad aliphatic envelope, which is much wider than the others, biases the closure test specifically and can manufacture an apparent interference where none exists. Both are avoidable by the measures of Section 13, and both are invisible in the reported numbers unless the acquisition parameters are stated alongside them.

15. Field-Strength Dependence and the Benchtop Question

The four primary integration regions are separated by substantial chemical shift differences, and this is what makes the analysis unusually portable across field strengths. Table 14 converts those separations into hertz at frequencies from 43 to 500 MHz.

Table 14. Separation of the integration boundaries in hertz as a function of spectrometer ¹H frequency.

Boundary pair	Δδ (ppm)	43 MHz	60 MHz	80 MHz	100 MHz	300 MHz	400 MHz	500 MHz
Terminal vinylidene 4.95 ↔ olefinic 5.40	0.45	19	27	36	45	135	180	225
Olefinic 5.80 ↔ aromatic 6.20	0.40	17	24	32	40	120	160	200
ortho 6.55 ↔ *meta*/*para* 7.05	0.50	22	30	40	50	150	200	250
Aliphatic 2.60 ↔ terminal vinylidene 4.80	2.20	95	132	176	220	660	880	1100
Styrene aromatic 7.05 ↔ $CHCl_3$ 7.26	0.21	9	13	17	21	63	84	105

A dissolved polymer resonance is typically five to twenty-five hertz wide, and the broadening arises from two sources with different field dependence: unresolved chemical shift dispersion across configurational and compositional sequences, which scales with field in hertz, and restricted segmental motion, which does not. The net effect is that lines narrow somewhat in hertz as the field is reduced but not in proportion to the reduction in separation, so resolution degrades overall — but from a comfortable starting point.

The practical consequences are clear from the table. The separation between the terminal vinylidene and internal olefinic envelopes remains twenty-seven hertz at 60 MHz, which is integrable against typical line widths, and the separation between the aliphatic and olefinic regions remains very large at every frequency considered. Composition and vinyl content are therefore obtainable on a benchtop instrument, and this has been demonstrated directly: a 60 MHz determination on a commercial polystyrene-block-polybutadiene-block-polystyrene gave 12.2 % styrene with 98.7 % 1,4 content against 400 MHz values of 12.6 % styrene with 95.4 % 1,4, agreement close enough for quality-control purposes on both parameters.[36] The broader benchtop literature has been reviewed, and polymer characterization emerges as one of the more successful application areas for these instruments.[37]

Two things do not survive the descent in field. The first is the ortho sub-envelope split on which blockiness depends, separated by only thirty hertz at 60 MHz and effectively unresolvable against polymer line widths; blockiness is a high-field determination. The second is the separation between the styrene aromatic signal and the

residual chloroform line, thirteen hertz at 60 MHz, which means the solvent peak must be handled by fitting rather than by integration limits, or a different solvent used.

Where the full four-component microstructure is wanted from a low-field instrument, the answer has been to abandon direct integration in favor of multivariate calibration. A program of work on one hundred and eight styrene–butadiene samples at 1 T established partial least-squares models against 9.4 T reference values, achieving prediction errors between 0.15 and 0.29 percentage points for styrene, 1,2-butadiene, total 1,4, and trans-1,4 with coefficients of determination between 0.92 and 0.95, and demonstrating discrimination between manufacturing lots and between solution and emulsion products.[34,35] That work is the reference point for anyone contemplating benchtop deployment on these materials. It should be read with its dependence in mind: the models are only as good as the high-field reference set they were trained against, they require ¹³C acquisition as well as ¹H to reach the cis/trans split, and they inherit the transferability limits of any chemometric calibration when the sample population drifts. A benchtop instrument used for direct proton integration of composition and vinyl content requires no calibration at all and is on entirely firmer ground.

16. Standardized Methods and Regulatory Context

The determination described in this paper is standardized. ISO 21561-1 specifies the quantitative determination of butadiene microstructure and styrene content in solution-polymerized styrene–butadiene rubber, designating ¹H NMR as the absolute method and infrared spectrometry with a cast-film preparation as a relative method calibrated against it. Styrene content is expressed as a mass percentage of the whole polymer; trans, cis, and vinyl contents are expressed as mole percentages of the butadiene portion — the conventions adopted throughout this paper. The standard applies to raw rubber only, a restriction that follows directly from the interference analysis of Section 12.[20] ISO 21561-2, revised in 2024, covers the attenuated total reflection infrared route and carries an informative annex on the NMR determination.[21] National equivalents exist in the Japanese and Chinese standards systems.

Two features of the standardized framework deserve comment. The designation of NMR as absolute and infrared as relative is not a statement of relative accuracy but of metrological structure: the proton experiment counts nuclei against a known stoichiometry and needs no calibrant, whereas the infrared absorptivities are empirical and must be transferred from characterized standards. A laboratory offering the infrared method therefore depends, directly or at one remove, on the proton method. The second is the restriction to raw rubber, which excludes oil-extended, compounded, and vulcanized materials. That exclusion is well founded — the interferences of Table 11 are severe — but it leaves a real analytical need unmet, since most samples submitted in a failure-analysis or forensic context are compounded. Work on sulfur-cured solution styrene–butadiene rubbers has shown that the microstructure determined on a vulcanizate differs from that of the raw polymer because of pendent groups introduced by the cure accelerator and because of cis-trans isomerization during cure, so that back-calculation to the original polymer is not straightforward.[8] An analysis performed on a compounded sample should be reported as such, with the extraction and cleanup steps documented.

17. Critical Assessment

Several conclusions from the preceding sections deserve restatement in a form that can be applied directly to the review of a report, whether one's own or another party's.

The proton integral determines exactly two structural quantities absolutely: the styrene-to-butadiene ratio and the 1,2 fraction of the butadiene. Everything else presented in a typical certificate of analysis is either derived from these by arithmetic, obtained from an orthogonal measurement, or assumed. A cis/trans split accompanying a

proton-only method has an undisclosed source. A block molecular weight has an undisclosed molar mass determination behind it, whose method and calibration basis matter. An architecture designation is a claim about the synthesis, not a measurement.

The closure test is underused and should be mandatory. It costs one additional integral, it is the only internal consistency check the experiment affords, and it detects the single most common real-world interference — hydrocarbon extension — with a signal-to-noise ratio that leaves no room for argument. A report that does not present it is asserting the absence of interference rather than demonstrating it.

Composition and microstructure differ in their robustness, and in a direction that is not intuitive. Bound styrene is the more precisely determined of the two in a clean sample and the more vulnerable of the two in a real one, because every common aromatic-region interferent inflates it. Vinyl content is the less precise in a clean sample, particularly at high vinyl levels where the subtraction amplifies error, and the more robust in a real one, because nothing normally present in a formulation contributes to the two olefinic windows. A laboratory reporting both should weight its confidence accordingly.

Field strength divides the deliverables. Composition and vinyl content are benchtop-accessible without calibration and the agreement with high-field determination is demonstrated in the literature. Blockiness, sequence-length distribution, tacticity, and cis/trans discrimination are not, and the chemometric route to some of these at low field carries the transferability burden that all calibrated methods carry. A quality-control deployment at 60 or 80 MHz is on sound ground for the first pair and is making a different kind of claim for the second.

Finally, the sample is more often the problem than the spectrum. Partial dissolution, gel from processing or aging, filler that removes polymer from solution, and extender oil that was not disclosed each corrupt the result in ways that are invisible in the numbers but visible in the closure residual, the line widths, or the appearance of the tube. Documenting the dissolution, the soluble fraction, and any cleanup performed is not administrative overhead; it is the part of the record that determines whether the analysis can be defended.

18. Recommended Workflow

The following sequence is the one applied at Process NMR Associates to styrene–butadiene block copolymers submitted for structural characterization. It is arranged so that the cheapest diagnostics are performed first and so that the decision to escalate to ^{13}C acquisition is made on evidence rather than by default.

Table 15. Recommended analytical workflow.

Stage	Action	Decision point
1	Record the sample as received: form, color, odor, any visible filler or bloom.	Compounded or filled material triggers a documented cleanup before dissolution.
2	Dissolve 1–3 % by mass in dried $CDCl_3$; verify complete dissolution visually.	Incomplete dissolution or visible gel requires a gel-content determination and a stated soluble-fraction basis.
3	Acquire a quantitative ^1H spectrum per Table 12; phase and baseline manually.	Sharp extraneous lines are identified before integration.
4	Integrate the five regions of Table 3, recording the limits used.	Limits are fixed for the sample set and not re-optimized per sample.
5	Calculate composition and microstructure per Sections 4.2 to 4.4.	—
6	Apply the closure test of Section 4.5.	A residual beyond ±2 % halts reporting of bound

Stage	Action	Decision point
		styrene pending investigation.
7	Calculate the blockiness index where field strength permits and sequence is in question.	Below about 200 MHz the index is not reported.
8	Escalate to quantitative ¹³C with inverse-gated decoupling where *cis*/*trans* or sequence data are required.	Escalation is triggered by the specification, not performed routinely.
9	Cross-check against FTIR for *cis*/*trans* where a rapid answer is acceptable and calibration standards exist.	—
10	Report all five integrals, the limits, the acquisition parameters, the closure residual, and an explicit statement of which quantities were measured and which were assumed.	—

The final stage is the one most often abbreviated and is the one that determines whether the work survives review. A result reported without its integrals, its limits, and its acquisition parameters cannot be reproduced by a third party, and a result that does not distinguish measured quantities from assumed ones invites exactly the challenge it should have preempted.

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All forty-five entries below were checked against the CrossRef REST API or the issuing body's catalog on 14 September 2026. For every entry carrying a DOI, the author list, title, journal, year, volume, issue, and pagination returned by the registry were compared against the citation as written and found to agree. No reference is cited in the text that was not verified in this way.

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Summary

The proton spectrum of a styrene–butadiene block copolymer is an unusually generous one, and the generosity invites a corresponding discipline about what it is generous with. Four envelopes are resolved at any practical field strength; four repeat-unit types populate them according to a stoichiometry that admits no ambiguity; and three equations with one redundancy follow. From those three equations the bound styrene content and the vinyl fraction of the butadiene emerge absolutely, without calibration, without a reference material, and without any assumption beyond the correctness of assignments settled more than forty years ago. That is a strong analytical position, and it is worth defending by being precise about its edges.

The edges are these. The cis and trans isomers of the 1,4 unit are proton-degenerate; their separation belongs to carbon-13 or to the infrared, and an infrared determination is itself calibrated against proton-characterized standards, which is why the international standard designates the proton method as absolute and the infrared method as relative. Chain architecture is absent from the integral entirely, so that a diblock, a triblock, a radial star, and a physical blend of the two homopolymers are indistinguishable on composition alone; the blend case

defeats even the blockiness index. Block molecular weights are a partition of an externally measured number-average molar mass, and they inherit whatever bias that measurement carries — a bias which, for size-exclusion chromatography calibrated against polystyrene standards, is composition-dependent in precisely the manner that makes it difficult to detect.

Sequence distribution occupies the middle ground. The ring-current shielding that displaces the ortho protons of styrene units flanked by styrene neighbors is a real and quantifiable effect, and the index built from it separates block from statistical copolymers decisively. It saturates near one hundred percent for any true block architecture, however, so it is a classifier rather than a measure of block length, and the thirty-hertz separation it depends on at 60 MHz places it beyond the reach of benchtop instrumentation. Composition and microstructure are not so constrained, and the published agreement between 60 and 400 MHz determinations on commercial styrene–butadiene triblocks is close enough that a quality-control laboratory has no reason to send those two parameters out.

Two practical conclusions carry more weight than their simplicity suggests. The first is that the redundant aliphatic integral should always be used. It costs one additional integration, it is the only internal consistency check the experiment offers, and against the most common real-world interference — undisclosed hydrocarbon extension — it responds with a residual so large that no baseline argument can accommodate it. A report that omits the closure test asserts the absence of interference rather than demonstrating it. The second is that composition and microstructure differ in robustness in a direction opposite to their precision: bound styrene is the better determined in a clean sample and the more easily corrupted in a real one, because every aromatic interferent inflates it, while vinyl content is the less precise and the more dependable, because nothing normally present in a formulation contributes to the olefinic windows.

Version 1.1 of this document is reserved for measured data. Sections 5 and 14 will be extended with spectra acquired on the Process NMR Associates Varian Mercury-MVX 300 and on the laboratory's 60 MHz benchtop systems, on a set of commercial styrene–butadiene block copolymers of independently established composition, so that the error budget presented here as a propagation exercise can be replaced by a measured reproducibility and an interlaboratory comparison against the standardized method.

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