

*Appendix A*SYNTHESIS AND CHARACTERIZATION OF SIDE-GROUP LIQUID
CRYSTAL POLYMERS

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A.1 Appendix

All reagents were purchased and used as received from Aldrich, unless otherwise noted.

A.1.1 Strategy for Synthesis of Side-Group Liquid Crystal Polymers

Polymer-analogous synthesis is used to attach liquid crystalline side-groups to existing polymer backbones. A library of polybutadiene (PB) homopolymers (Figure A.1-Figure A.3) and PB-containing block copolymers (Figure A.4-Figure A.12) was obtained from various sources. The PB portion of every polymer contains a high percentage (> 80 mol %) of 1,2-addition monomers. A cyanobiphenyl-based mesogen is synthesized separately and attached in one step to the pendant vinyl groups of 1,2-PB, yielding a side-group liquid crystal polymer (SGLCP).

A.1.2 Synthesis of Cyanobiphenyl-Based Mesogenic Side Groups

A cyanobiphenyl-based mesogen is synthesized by Mitsunobu reaction^[1, 2] between 4-cyano-4'-hydroxybiphenyl (CHB) and 3-buten-1-ol (4OH) (Scheme A.1). CHB (1.3 g, 6.2

mmol, purchased and used as received from TCI America) and 1.1 equivalents each of 4OH (0.60 mL, 6.8 mmol) and triphenylphosphine (TPP) (1.8 g, 6.8 mmol) are dissolved together in 50 mL anhydrous tetrahydrofuran (THF). The solution is chilled in an ice water bath followed by the dropwise addition of 1.1 equivalents of diisopropyl azodicarboxylate (DIAD) (1.3 mL, 6.8 mmol). The reaction flask is then removed from the ice water bath and the reaction proceeds at room temperature until thin-layer chromatography no longer reveals the presence of CHB (approximately 3-5 hours). Upon completion, the THF is evaporated and the product, 4-cyano-4'-(3-butenoxy)-biphenyl (CBV4), is dissolved in dichloromethane (DCM) and purified on a silica gel column using 5% ethyl acetate in hexane as the mobile phase. CBV4 is further purified by recrystallization from hexane, achieving 77% yield overall (1.2 g, 4.7 mmol).

The phenolic Mitsunobu reaction (Scheme A.1) is the preferred scheme for synthesizing CBV4 because relatively high yield is achieved in a single reaction. However, an alternate scheme is Williamson ether synthesis (Scheme A.2).^[3, 4] 4OH (10. mL, 120 mmol) is first converted to 3-butenyl-1-tosylate (4OTs) by reaction with two equivalents of *p*-toluenesulfonyl chloride (tosyl chloride, TsCl) (44 g, 230 mmol) in 150 mL DCM along with one equivalent of pyridine (9.4 mL, 120 mmol).^[5, 6] Reagents are mixed at 0 °C then the reaction flask is removed to room temperature and the reaction proceeds for approximately ten hours. The product, 4OTs, is purified by liquid-liquid extraction. After adding an excess of pyridine (100 mL), the DCM solution is washed with 400 mL of aqueous hydrochloric acid (5% HCl). 4OTs remaining in the aqueous layer is extracted with DCM then the combined organic layers are washed once more with 5% HCl. The organic layer is dried with anhydrous sodium sulfate and the DCM evaporated to recover the product (83% yield, 22 g, 96 mmol). Williamson ether synthesis yields the final product, CBV4. A seventy percent excess of 4OTs (22 g, 96 mmol) is added to a solution of CHB (11 g, 57 mmol) in 50 mL of *N,N*-dimethylformamide (DMF). A seventy percent excess of anhydrous potassium carbonate is added (13 g, 96 mmol) and the mixture heated at 90 °C for eight hours. Upon completion, the potassium tosylate byproduct is precipitated with an excess of DCM and removed by filtration. After evaporating the majority of the solvent the remaining CBV4 is purified on a silica gel column using ten percent ethyl

acetate in hexane, then recrystallized from hexane for an overall yield of 43% (6.1 g, 25 mmol).

A siloxane linking group is attached to the cyanobiphenyl mesogen, CBV4, by hydrosilylation (Scheme A.3). A tenfold excess of 1,1,3,3-tetramethyldisiloxane (TMDS) (18 mL, 99 mmol) is dissolved together with CBV4 (2.5 g, 9.9 mmol) in 20 mL anhydrous toluene. A drop of platinum catalyst (PC072 platinum divinyl complex in xylene, United Chemical Technologies, Bristol, PA) is added and the mixture is stirred at room temperature for 16 hours under inert gas. Upon completion, the solvent and excess TMDS are evaporated at 80 °C under vacuum and the product, 4-cyano-4'-(5-(1,1,3,3-tetramethyldisiloxane)butoxy)biphenyl (SiCB4), is purified by column chromatography. An anhydrous chromatography column is prepared in order to prevent the degradation of SiCB4 by reaction with water. The column is filled with silica gel dried in a 150 °C oven and then repeatedly flamed with a propane torch while dry, inert gas flows through the silica. The column is then filled with anhydrous hexane and mixed to create a slurry of silica gel in hexane. Once the silica gel settles, the SiCB4 is loaded onto the column and eluted with an anhydrous mixture of 10% ethyl acetate in hexane. Anhydrous column chromatography is sometimes repeated to recover a clear, liquid product (75% yield, 2.1 g, 7.4 mmol).

A.1.3 Attaching Side Groups to Polymer

The cyanobiphenyl-based mesogen with attached siloxane linking group (SiCB4) is suitable for attachment to the pendant vinyl groups of a 1,2-polybutadiene polymer by platinum-catalyzed hydrosilylation (Scheme A.4) in manner similar to the synthesis of SiCB4. 1,2-Polybutadiene (0.14 g, 2.5 mmol) is dissolved in 5 mL of anhydrous tetrahydrofuran (THF) in inert atmosphere. A threefold excess of freshly purified SiCB4 (2.1 g, 7.4 mmol) is added along with a drop of platinum catalyst (PC085 platinum cyclovinyl complex in vinylmehtylsiloxanes, United Chemical Technologies, Bristol, PA) and the mixture heated at 50 °C for between four and seven days. Reaction progress is monitored periodically by proton NMR. When the reaction is complete, as evidenced by

the disappearance of the 1,2-PB vinyl resonance peak at $\delta = 4.9$ ppm, it is quenched by heating at 50 °C overnight after addition of excess styrene (~2-5 mL).

After quenching with styrene the polymer is concentrated by evaporating approximately half the solvent under vacuum. Unreacted mesogen is removed by precipitating the polymer from solution using an excess of methanol. The precipitated polymer is then repeatedly dissolved in THF and precipitated with methanol. The methanol used for precipitation contains 10 ppm of a radical inhibitor (BHT) to improve stability during long-term storage. After the final precipitation the solid polymer is dried in vacuum. Polymer conversion is nearly quantitative; yield is greater than 95% of the theoretical value.

Cross-linking reactions are seemingly unavoidable; polymers almost always have a bimodal molecular weight distribution with a small fraction of high molecular weight, cross-linked polymers, which is removed by solvent fractionation. A solution of approximately ten percent polymer in THF is passed through a 0.45 μm syringe filter then diluted with toluene and THF for a final composition of 0.5% polymer dissolved in a mixture of 60% THF and 40% toluene. While stirring vigorously, methanol is added until the solution becomes cloudy (the amount of methanol required is typically almost equal to the volume of the solution). THF is then slowly added until the solution becomes clear; at this point it is very near its room-temperature cloud point. Next, a small amount of methanol is added, usually between 5 and 15 mL. The amount of methanol added determines the degree to which the polymer will fractionate: more methanol will result in more polymer dropping out of solution. The cloudy solution is heated to 70 °C and stirred until it becomes clear again. Finally, the clear, hot solution is poured into a hot separatory funnel wrapped in plenty of insulation. The insulated funnel is isolated from air currents and left to cool very slowly overnight. A viscous syrup composed largely of high molecular weight polymer separates into the bottom of the separatory funnel while low molecular weight polymer remains in the dilute solution above. The high molecular weight fraction is easily drained off, precipitated with methanol, and dried in vacuum. The low molecular weight fraction is recovered by evaporating the solvent and drying in vacuum.

A.1.4 Characterization of Polybutadiene-Containing Prepolymers

The molecular weight of the SGLCP precursor polymers is measured by the manufacturer using light scattering. Proton NMR is used to measure the percentage of 1,2-PB monomers and to verify the mass fraction of PB in block copolymers (Figure A.1-Figure A.12). A 300 MHz Varian NMR spectrometer is used to collect proton NMR spectra from solutions of polymers in deuterated chloroform (CDCl_3). Hydrogen atoms in the vinyl group of 1,2-butadiene contribute to the intensities of peaks at $\delta = 4.9$ ppm (two hydrogens) and $\delta = 5.4$ ppm (one hydrogen). The two hydrogen atoms attached to the double-bonded carbons of 1,4-butadiene contribute to the peak intensity at $\delta = 5.4$ ppm. The 1,2-butadiene content is calculated from these peak intensities: $x_{1,2} = I_{\delta=4.9\text{ppm}} / (I_{\delta=4.9\text{ppm}} + I_{\delta=5.4\text{ppm}} - \frac{1}{2} I_{\delta=4.9\text{ppm}})$. The mole fraction of PB in a PB-polystyrene (PS) block copolymer is computed by comparing the intensity per mole of hydrogen of PB peaks (both 1,4- and 1,2- addition) to that of aromatic peaks in the range of $\delta = 6.2 - 7.4$ ppm. The mole fraction is easily converted to the mass fraction using the monomers' molar masses.

The polymers' molecular weight distributions, characterized by the polydispersity index ($\text{PDI} = M_w / M_n$), is measured using gel permeation chromatography (GPC) (Figure A.1-Figure A.12). A dilute solution of the polymer in THF is eluted through four gel columns (Polymer Laboratories PLgel 10 μm analytical columns, 30 cm long) using THF flowing at a rate of 0.9 mL/min and is detected at the outlet by a Waters 410 differential refractometer. The chromatograph is calibrated with monodisperse PS standards and the PDI is calculated using the Millenium® software from Waters. The total time to traverse all four columns is approximately 45 minutes. In some cases (when the GPC trace only goes from zero to 30 minutes) only two columns were used.

Prepolymer properties are summarized in Table A.1-Table A.4. NMR and GPC data from prepolymers are presented in Figure A.1-Figure A.12.

A.1.5 Characterization of Side-Group Liquid Crystal Polymers

The degree of conversion (percentage of reacted 1,2-PB monomers) of SGLCPs is measured by proton NMR (Figure A.13-Figure A.25). Just as was the case in the

prepolymer, the mole fraction of unreacted 1,2-butadiene monomers is quantified by the intensity of the peak at $\delta = 4.9$ ppm. Using the peak at $\delta = 3.9$ ppm (two alkyl hydrogens adjacent to the cyanobiphenyl core) as a convenient measure of the mesogenic side groups, the degree of conversion is the ratio of this peak intensity to that of 1,2-PB: $x_{LC} = I_{\delta=3.9\text{ppm}} / (I_{\delta=4.9\text{ppm}} + I_{\delta=3.9\text{ppm}})$. The mole fraction of unreactive 1,4-PB and the molecular weight of the coil block(s) is assumed to be the same as in the prepolymer. The molecular weight of SGLCP block is calculated using the measured composition and the known molecular weight of polybutadiene in the prepolymer. Polydispersity of the SGLCPs is measured by GPC, just like the prepolymer (Figure A.13-Figure A.25).

SGLCP properties are summarized in Table A.5-Table A.8. NMR and GPC data from SGLCPs are presented in Figure A.13-Figure A.25.

A.2 Tables

Table A.1 Molecular weight, composition, and polydispersity of 1,2-polybutadiene prepolymers used to synthesize side-group liquid crystalline homopolymers in Table A.5. See Figure A.1-Figure A.3 for data used to calculate and composition of the PB block and polydispersity.

Name	M_n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB	PDI ^a
50H	47.5 ^b	0.89	0.11	1.06
60H	63 ^c	0.97	0.03	1.05
100H	104 ^b	0.96	0.04	1.05

^aPDI = Polydispersity Index (M_w/M_n)

^bInformation provided by the supplier, Polymer Source (Montreal, Quebec)

^cPolymer synthesized by Steven Smith (Proctor and Gamble, Inc.), M_n independently measured by Michael Kempe using multi-angle laser light scattering^[4]

Table A.2 Molecular weight, composition, and polydispersity of poly[styrene-*b*-1,2-butadiene] diblock prepolymers used to synthesize PS-SGLCP diblock copolymers in Table A.6. See Figure A.4-Figure A.10 for data used to calculate and composition of the PB block and polydispersity.

Name	PS Block	PB Block		PDI ^a	
	M _n [kg/mol]	M _n [kg/mol]	Mole Fraction 1,2 PB		Mole Fraction 1,4 PB
30(60)AB	33 ^b	63.5 ^b	0.85	0.15	1.12
100(70)AB	97 ^b	70 ^b	0.88	0.12	1.19
100(190)AB	97 ^b	191 ^b	0.77	0.23	1.42
60(40)AB	59 ^c	43 ^c	0.99	0.01	1.04
60(60)AB	57 ^c	59 ^c	0.97	0.03	1.08
60(80)AB	57 ^c	83 ^c	0.95	0.05	1.09
50(120)AB	50 ^c	121 ^c	0.99	0.01	1.06

^aPDI = Polydispersity Index (M_w/M_n)

^bInformation provided by the supplier, Polymer Source (Montreal, Quebec)

^cInformation provided by the supplier, David Uhrig (Center for Nanophase Materials Sciences, Oak Ridge National Laboratory)

Table A.3 Molecular weight, composition, and polydispersity of poly[styrene-*b*-1,2-butadiene-*b*-styrene] triblock prepolymer used to synthesize the PS-SGLCP-PS triblock copolymer in Table A.7. See Figure A.11 for data used to calculate and composition of the PB block and polydispersity.

Name	PS Blocks	PB Block		PDI ^a	
	M _n [kg/mol]	M _n [kg/mol]	Mole Fraction 1,2 PB		Mole Fraction 1,4 PB
(60)150(70)ABA	57, 67 ^b	146 ^b	0.86	0.14	1.43

^aPDI = Polydispersity Index (M_w/M_n)

^bPolymer purchased from Polymer Source (Montreal, Quebec), M_n independently measured by Michael Kempe using multi-angle laser light scattering^[4]

Table A.4 Molecular weight, composition, and polydispersity of poly[(methyl methacrylate)-*b*-1,2-butadiene] diblock prepolymer used to synthesize the PMMA-SGLCP diblock copolymer in Table A.8. See Figure A.12 for data used to calculate and composition of the PB block and polydispersity.

Name	PMMA Block	PB Block		PDI ^a	
	M _n [kg/mol]	M _n [kg/mol]	Mole Fraction 1,2 PB		Mole Fraction 1,4 PB
140(70)BdMMA	68 ^b	142 ^b	0.87	0.13	1.24

^aPDI = Polydispersity Index (M_w/M_n)

^bInformation provided by the supplier, Polymer Source (Montreal, Quebec)

Table A.5 Molecular weight, composition, and polydispersity of the side-group liquid crystal homopolymers synthesized from prepolymers in Table A.1. See Figure A.4-Figure A.10 and Figure A.17-Figure A.23 for data used to calculate composition, polydispersity, and the molecular weight of the SGLCP block.

Name	M_n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB	Mole Fraction LC	PDI ^a
350HSiCB4	347	0	0.11	0.89	1.27
d ₂ 350HSiCB4	348	0	0.11	0.89	1.27
490HSiCB4	489	0.01	0.03	0.96	1.48
760HSiCB4	762	0.06	0.04	0.90	1.11

^aPDI = Polydispersity Index (M_w/M_n)

Table A.6 Molecular weight, composition, and polydispersity of the side-group liquid crystal diblock copolymers with coil block composed of polystyrene (PS), synthesized from prepolymers in Table A.2 . See Figure A.4-Figure A.10 and Figure A.17-Figure A.23 for data used to calculate composition, polydispersity, and the molecular weight of the SGLCP block.

Name	PS Block M_n [kg/mol]	SGLCP Block			PDI ^a	
		M_n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB		Mole Fraction LC
210(60)ABSiCB4	63.5	205	0.13	0.15	0.72	1.22
700(70)ABSiCB4	70	700	0	0.11	0.89	1.50
580(190)ABSiCB4	191	577	0.09	0.23	0.68	1.56
470(40)ABSiCB4	43	472	0	0.01	0.99	1.19
390(60)ABSiCB4	59	388	0.15	0.03	0.85	1.11
420(80)ABSiCB4	83	422	0.05	0.05	0.90	1.07
320(120)ABSiCB4	121	323	0.22	0.01	0.77	1.05

^aPDI = Polydispersity Index (M_w/M_n)

Table A.7 Molecular weight, composition, and polydispersity of the side-group liquid crystal triblock copolymer with polystyrene endblocks, synthesized from the prepolymer in Table A.3. See Figure A.11 and Figure A.24 for data used to calculate composition, polydispersity, and the molecular weight of the SGLCP block.

Name	PS Blocks	SGLCP Block			PDI ^a	
	M _n [kg/mol]	M _n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB		Mole Fraction LC
1100ABASiCB4	57,67	1,012	0.02	0.14	0.84	1.16

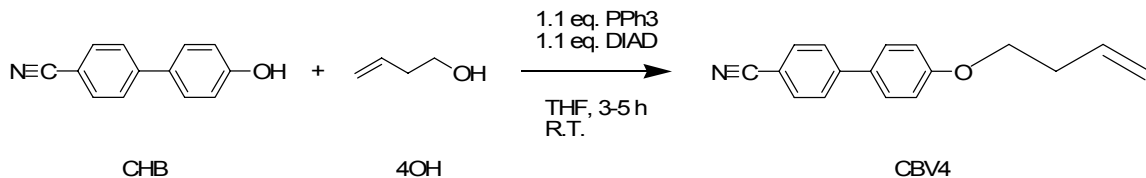
^aPDI = Polydispersity Index (M_w/M_n)

Table A.8 Molecular weight, composition, and polydispersity of the side-group liquid crystal diblock copolymer with coil block composed of poly(methyl methacrylate) (PMMA), synthesized from the prepolymer in Table A.4. See Figure A.12 and Figure A.25 for data used to calculate composition, polydispersity, and the molecular weight of the SGLCP block.

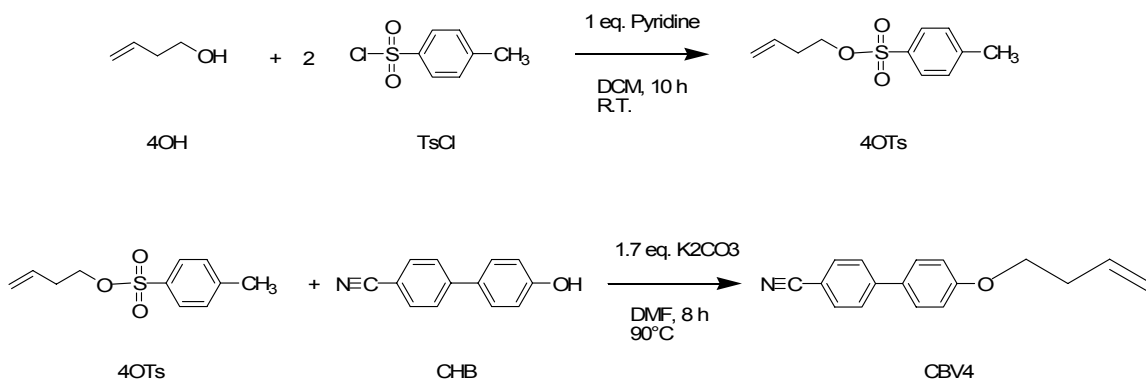
Name	PMMA Block	SGLCP Block			PDI ^a	
	M _n [kg/mol]	M _n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB		Mole Fraction LC
950(70)BdMMASiCB4	68	954	0.07	0.13	0.80	1.11

^aPDI = Polydispersity Index (M_w/M_n)

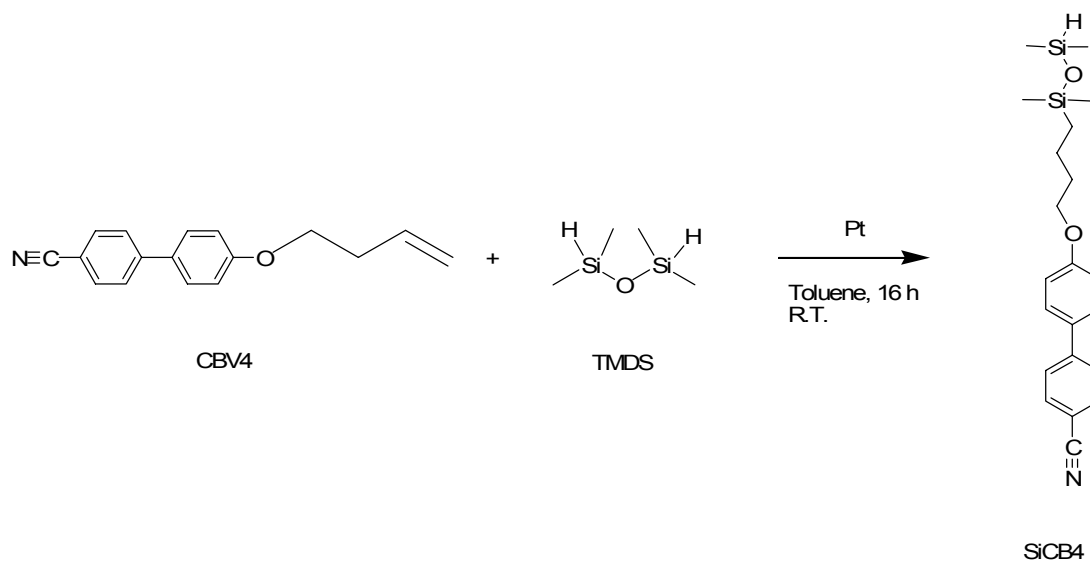
A.3 Schemes



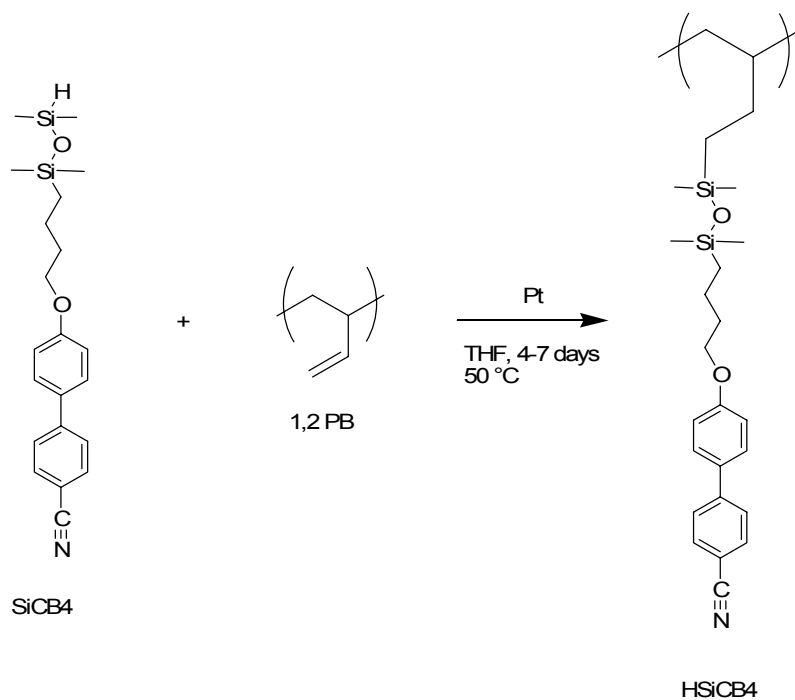
Scheme A.1 Synthesis of 4-cyano-4'-(3-butenoxy)-biphenyl (CBV4) by Mitsunobu reaction between 4-cyano-4'-hydroxybiphenyl (CHB) and 3-buten-1-ol (4OH) using diisopropyl azodicarboxylate (DIAD) and triphenylphosphine (TPP) in tetrahydrofuran (THF) at room temperature



Scheme A.2 Synthesis of 4-cyano-4'-(3-butenoxy)-biphenyl (CBV4) by Williamson ether synthesis. 3-buten-1-ol (4OH) is first converted to 3-butenyl-1-tosylate (4OTs) by reaction with p-toluenesulfonyl chloride (TsCl) and is subsequently reacted with 4-cyano-4'-hydroxybiphenyl (CHB) to yield the final product.



Scheme A.3 Synthesis of 4-cyano-4'-(5-(1,1,3,3,-tetramethyldisiloxane)butoxy)biphenyl (SiCB4) by platinum-catalyzed hydrosilylation



Scheme A.4 Attachment of SiCB4 to a 1,2-polybutadiene monomer by platinum-catalyzed hydrosilylation

A.4 Figures

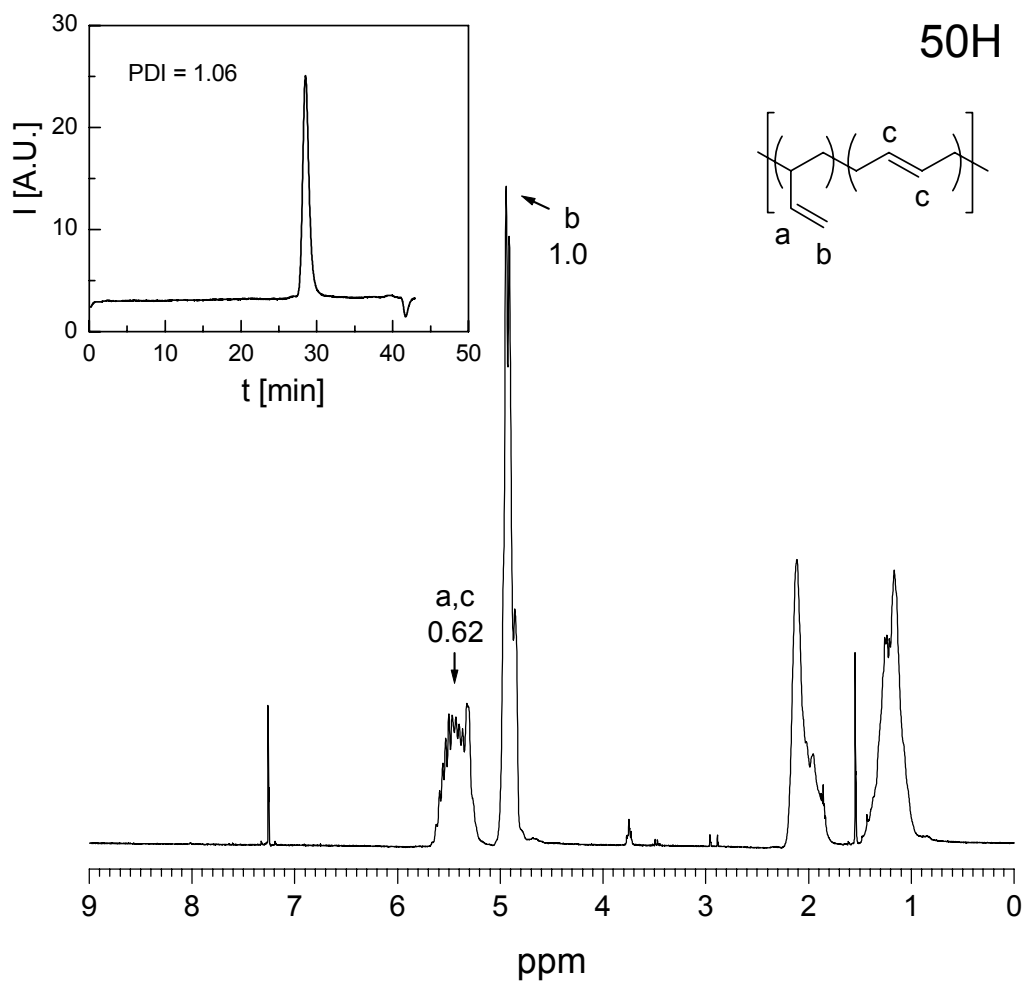


Figure A.1 300 MHz proton NMR spectrum of 50H, a 1,2-polybutadiene homopolymer with $M_n = 47.5$ kg/mol, in CDCl₃. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.1. The GPC chromatograph used to measure polydispersity is shown in the inset.

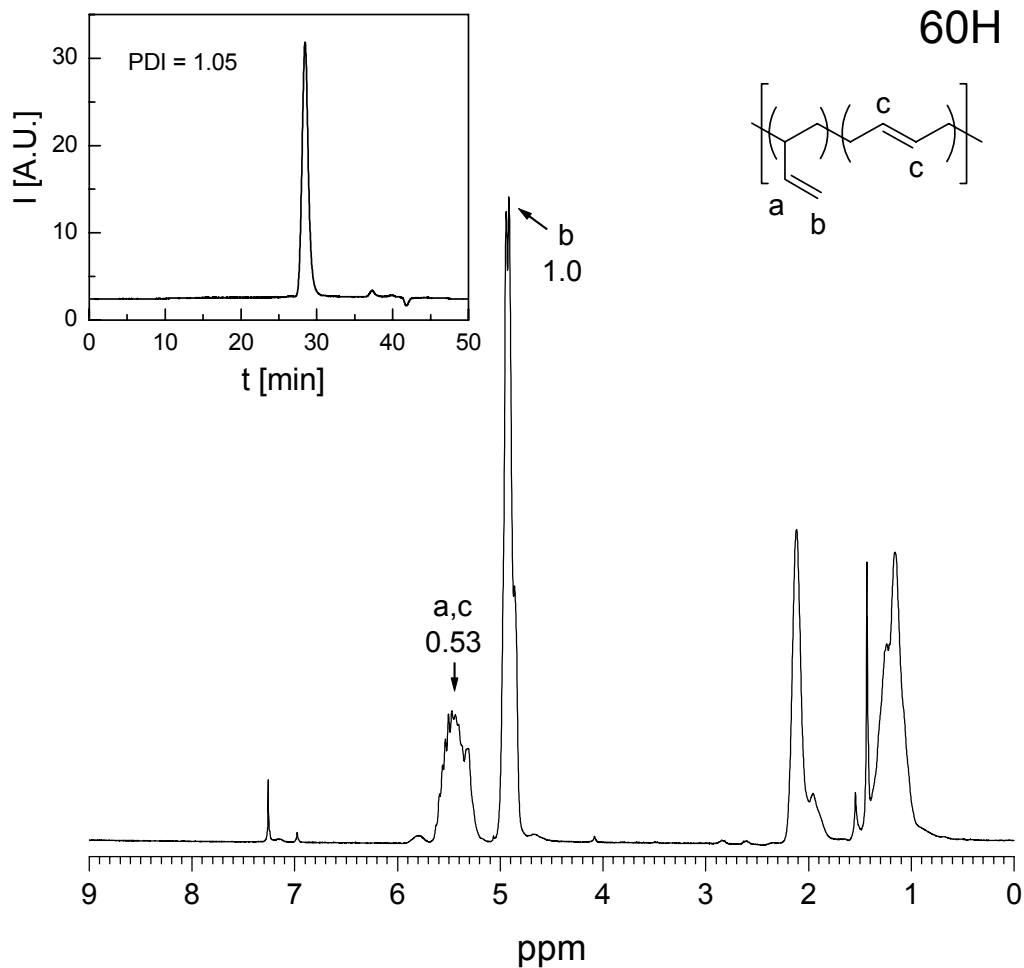


Figure A.2 300 MHz proton NMR spectrum of 60H, a 1,2-polybutadiene homopolymer with $M_n = 63$ kg/mol, in CDCl₃. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.1. The GPC chromatograph used to measure polydispersity is shown in the inset.

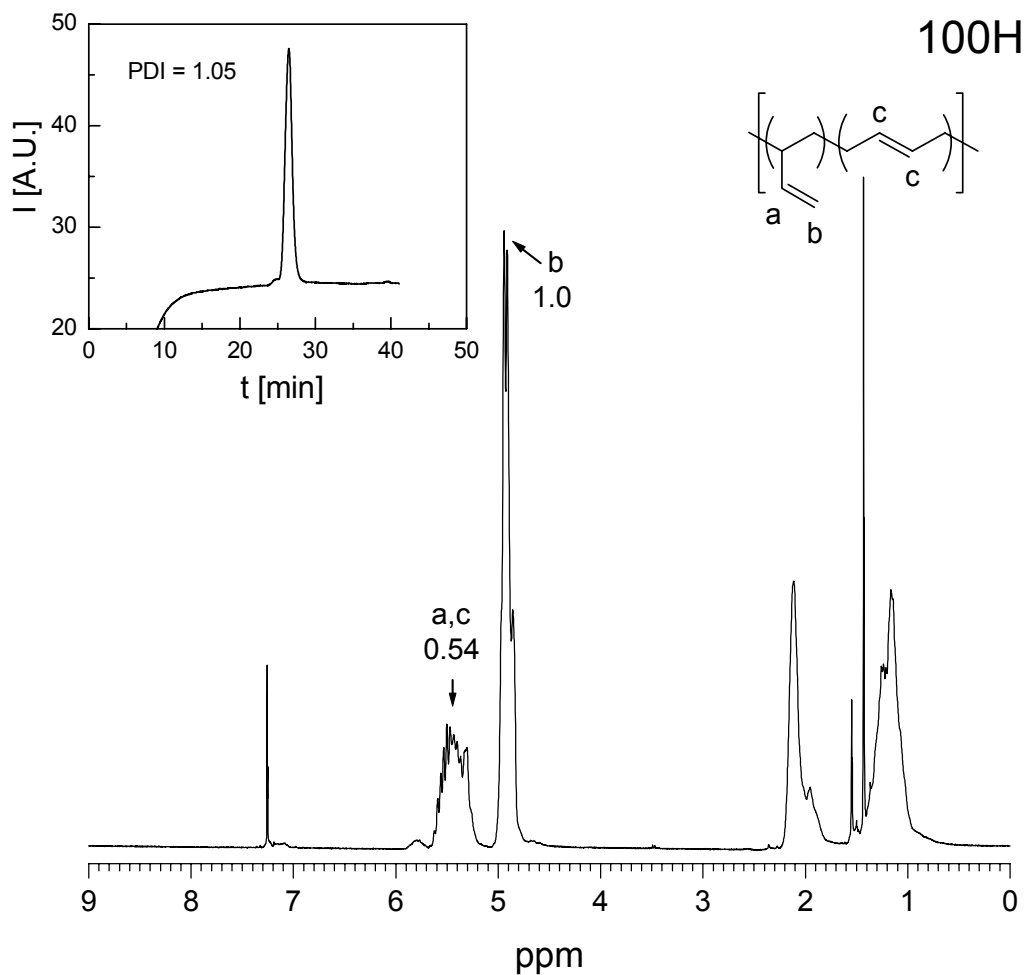


Figure A.3 300 MHz proton NMR spectrum of 100H, a 1,2-polybutadiene homopolymer with $M_n = 104$ kg/mol, in CDCl₃. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.1. The GPC chromatograph used to measure polydispersity is shown in the inset.

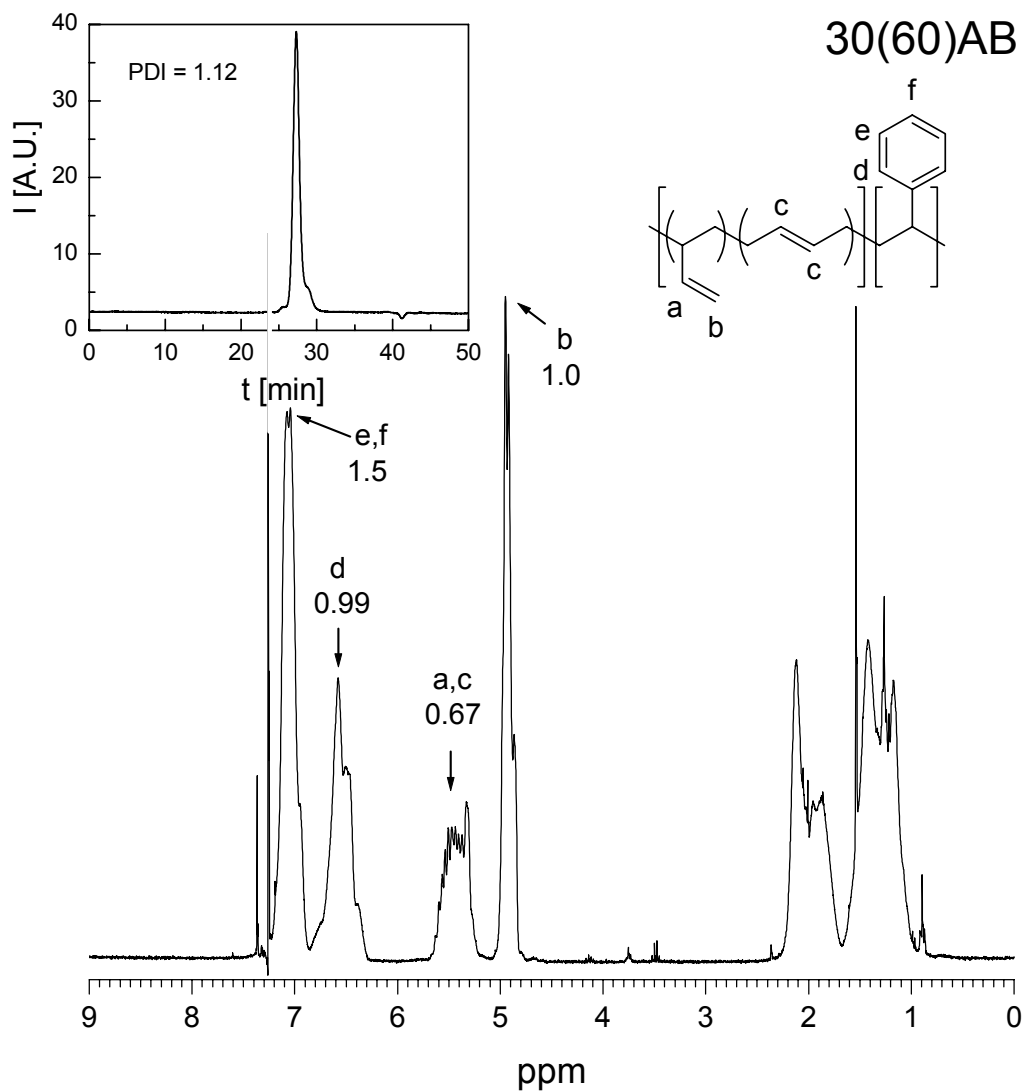


Figure A.4 300 MHz proton NMR spectrum of 30(60)AB, a poly[styrene-*b*-1,2-butadiene] block copolymer with $M_{PS} = 63.5$ kg/mol and $M_{PB} = 33$ kg/mol, in $CDCl_3$. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.2. The GPC chromatograph used to measure polydispersity is shown in the inset.

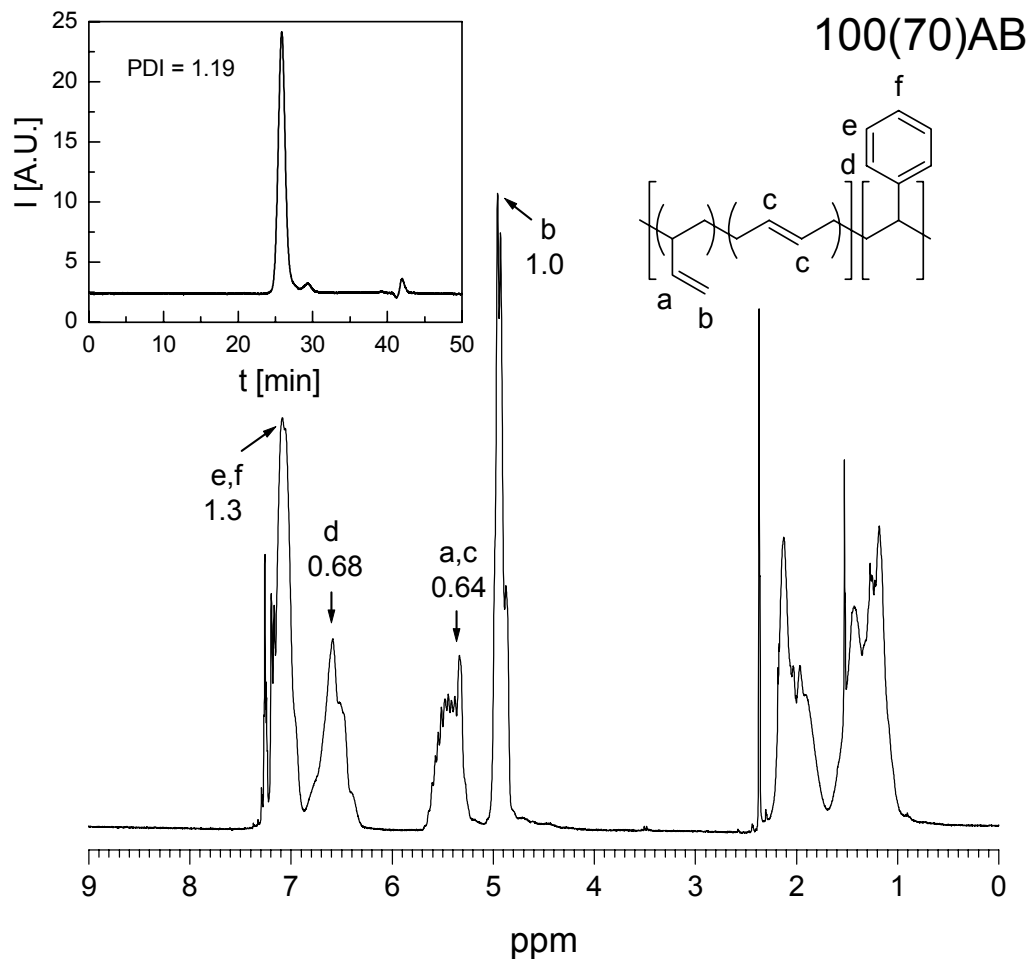


Figure A.5 300 MHz proton NMR spectrum of 100(70)AB, a poly[styrene-*b*-1,2-butadiene] block copolymer with $M_{PS} = 70$ kg/mol and $M_{PB} = 97$ kg/mol, in $CDCl_3$. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.2. The GPC chromatogram used to measure polydispersity is shown in the inset.

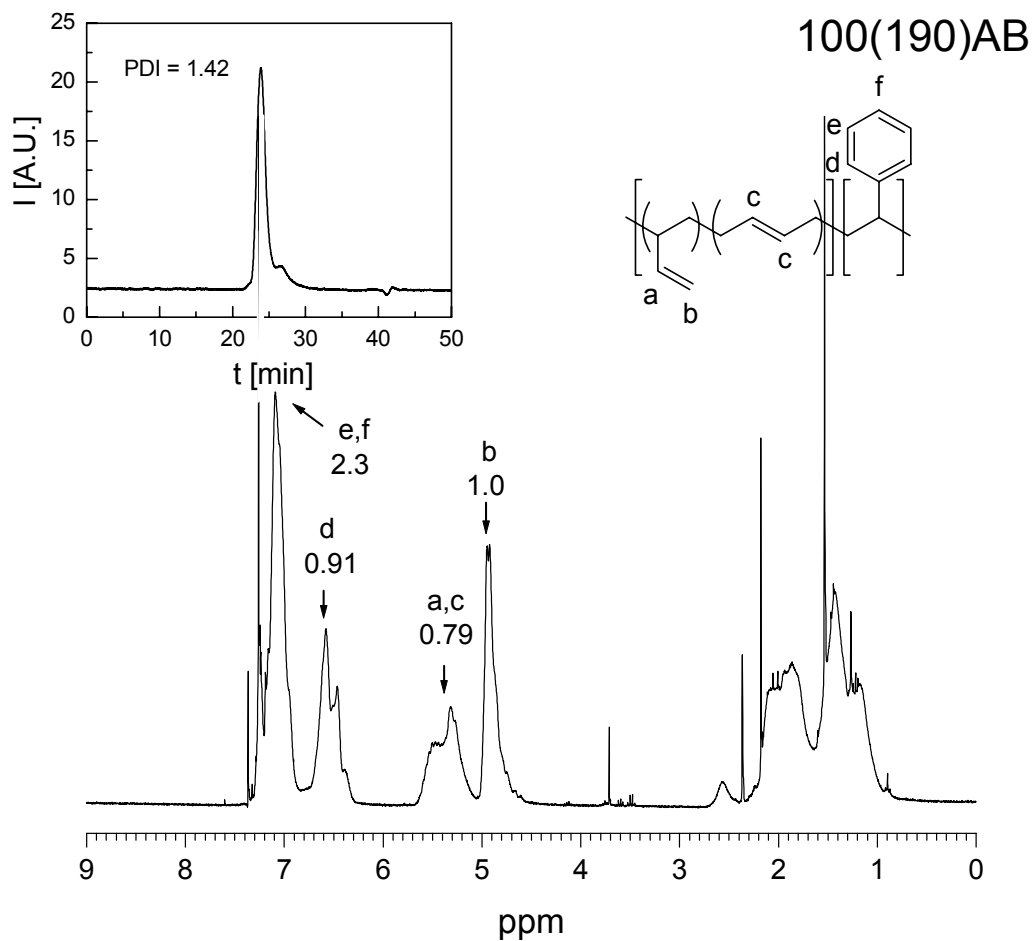


Figure A.6 300 MHz proton NMR spectrum of 100(190)AB, a poly[styrene-*b*-1,2-butadiene] block copolymer with $M_{PS} = 191$ kg/mol and $M_{PB} = 97$ kg/mol, in CDCl₃. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.2. The GPC chromatogram used to measure polydispersity is shown in the inset.

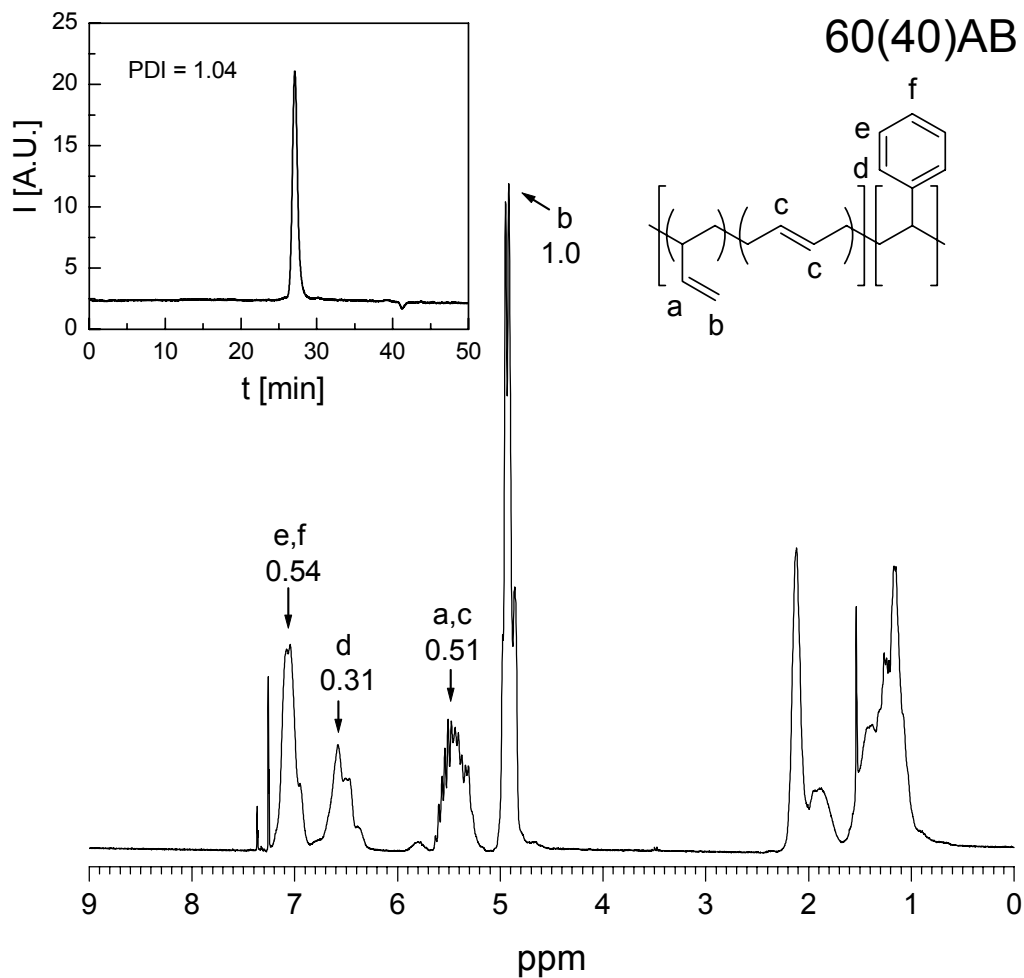


Figure A.7 300 MHz proton NMR spectrum of 60(40)AB, a poly[styrene-*b*-1,2-butadiene] block copolymer with $M_{PS} = 43$ kg/mol and $M_{PB} = 59$ kg/mol, in $CDCl_3$. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.2. The GPC chromatograph used to measure polydispersity is shown in the inset.

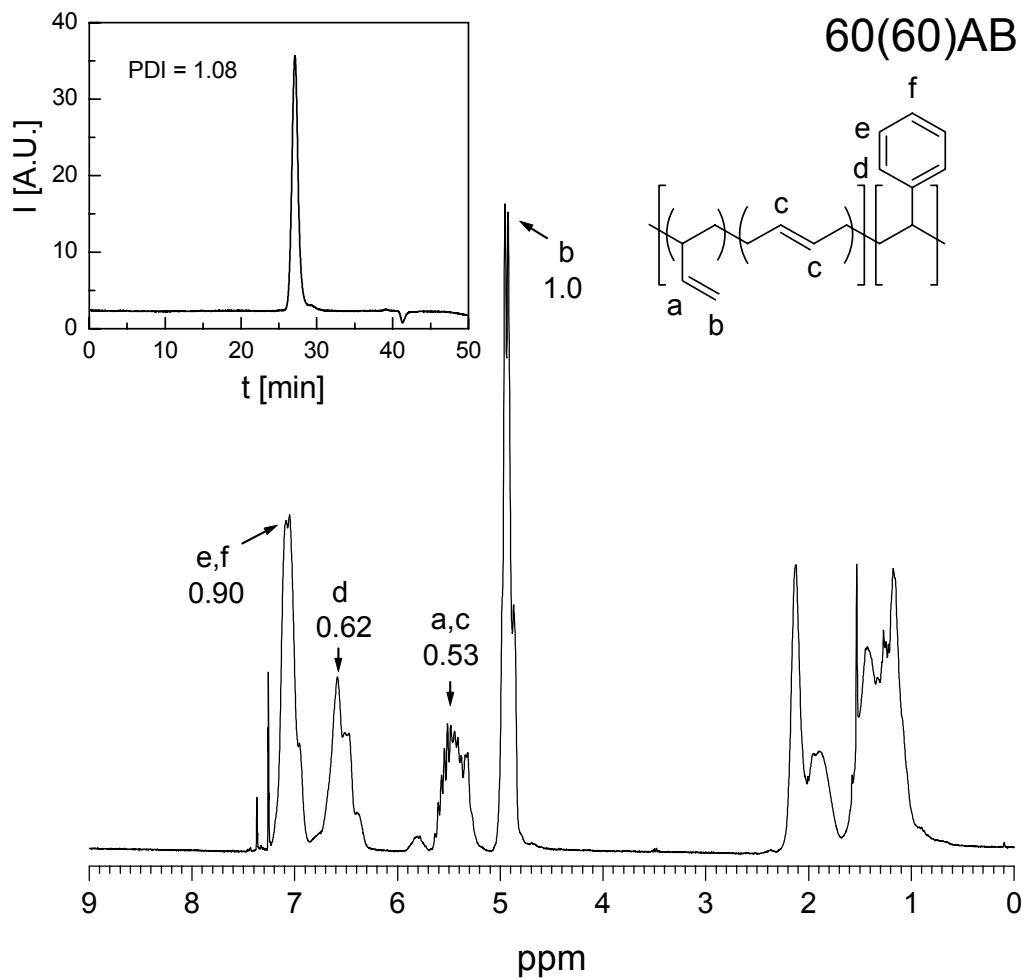


Figure A.8 300 MHz proton NMR spectrum of 60(60)AB, a poly[styrene-*b*-1,2-butadiene] block copolymer with $M_{PS} = 59$ kg/mol and $M_{PB} = 57$ kg/mol, in CDCl₃. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.2. The GPC chromatograph used to measure polydispersity is shown in the inset.

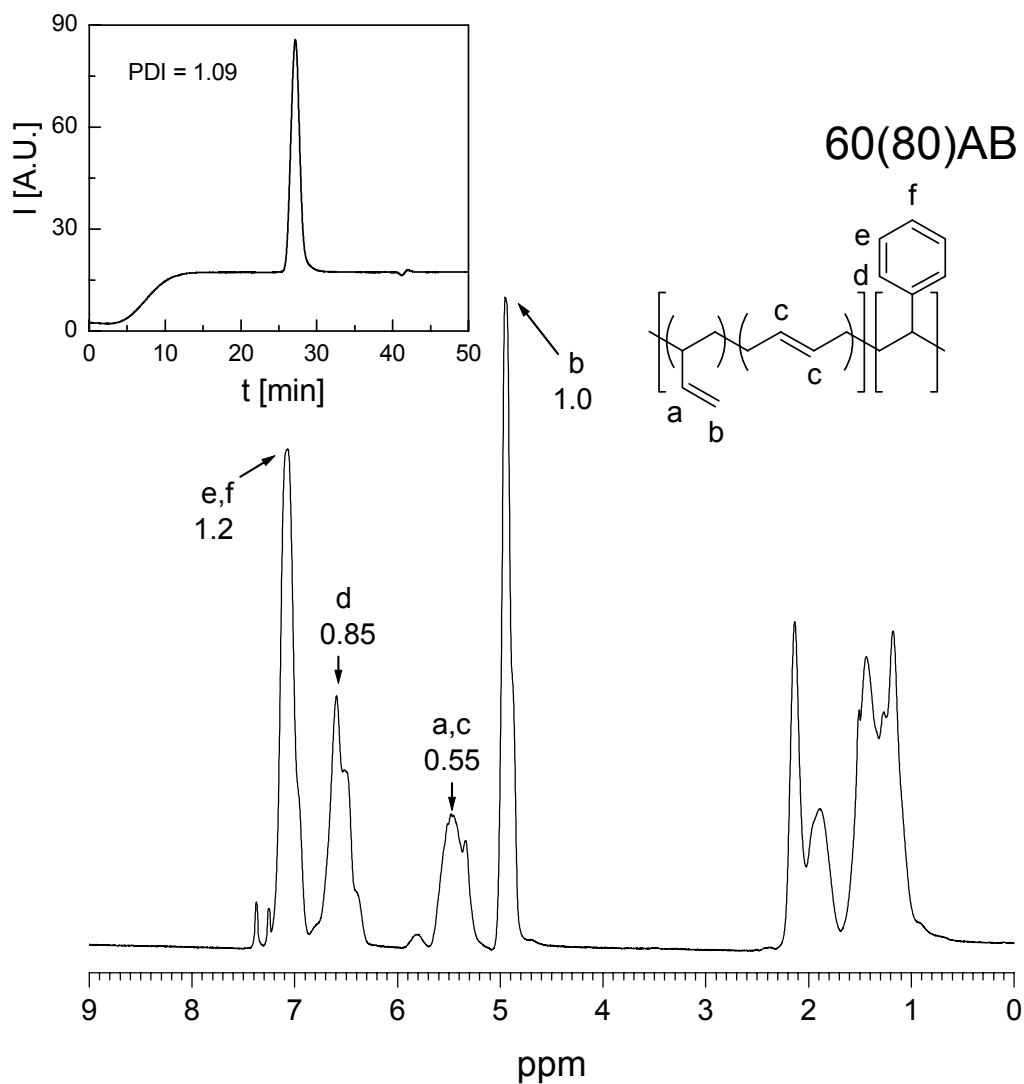


Figure A.9 300 MHz proton NMR spectrum of 60(80)AB, a poly[styrene-*b*-1,2-butadiene] block copolymer with $M_{PS} = 83$ kg/mol and $M_{PB} = 57$ kg/mol, in $CDCl_3$. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.2. The GPC chromatograph used to measure polydispersity is shown in the inset.

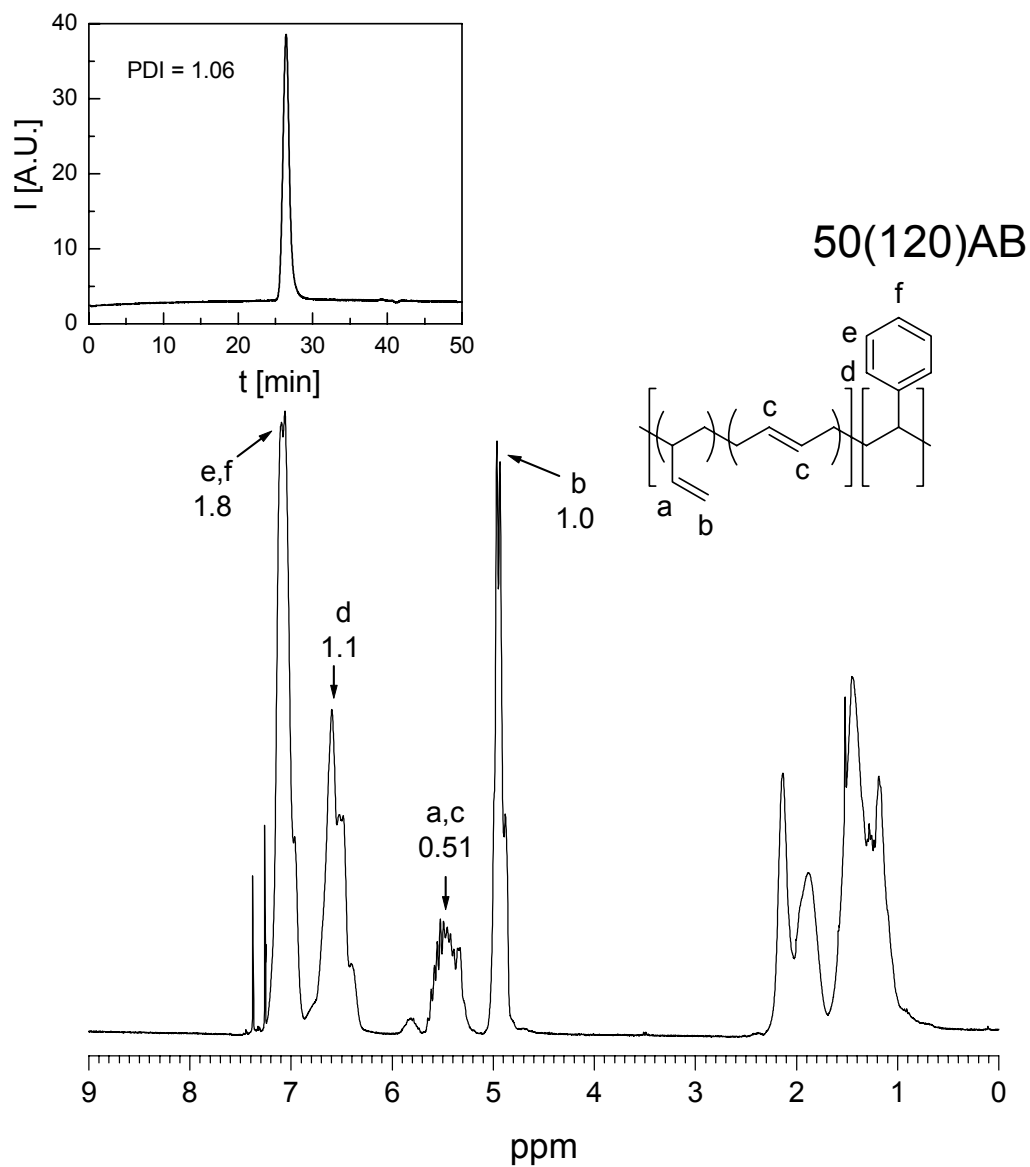


Figure A.10 300 MHz proton NMR spectrum of 50(120)AB, a poly[styrene-*b*-1,2-butadiene] block copolymer with $M_{PS} = 121$ kg/mol and $M_{PB} = 50$ kg/mol, in CDCl₃. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.2. The GPC chromatogram used to measure polydispersity is shown in the inset.

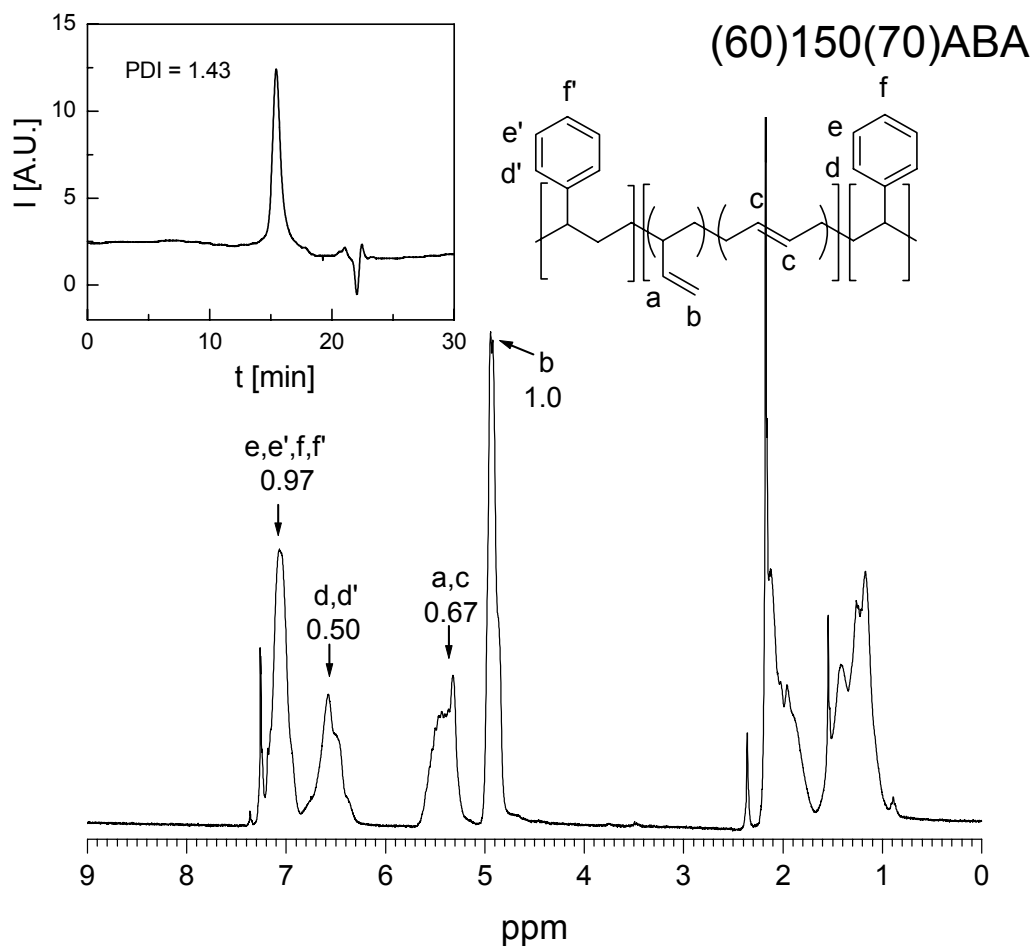


Figure A.11 300 MHz proton NMR spectrum of (60)150(70)ABA, a poly[styrene-*b*-1,2-butadiene-*b*-styrene] triblock copolymer with $M_{PS} = 57$ and 67 kg/mol and $M_{PB} = 146$ kg/mol, in $CDCl_3$. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.3. The GPC chromatogram used to measure polydispersity is shown in the inset.

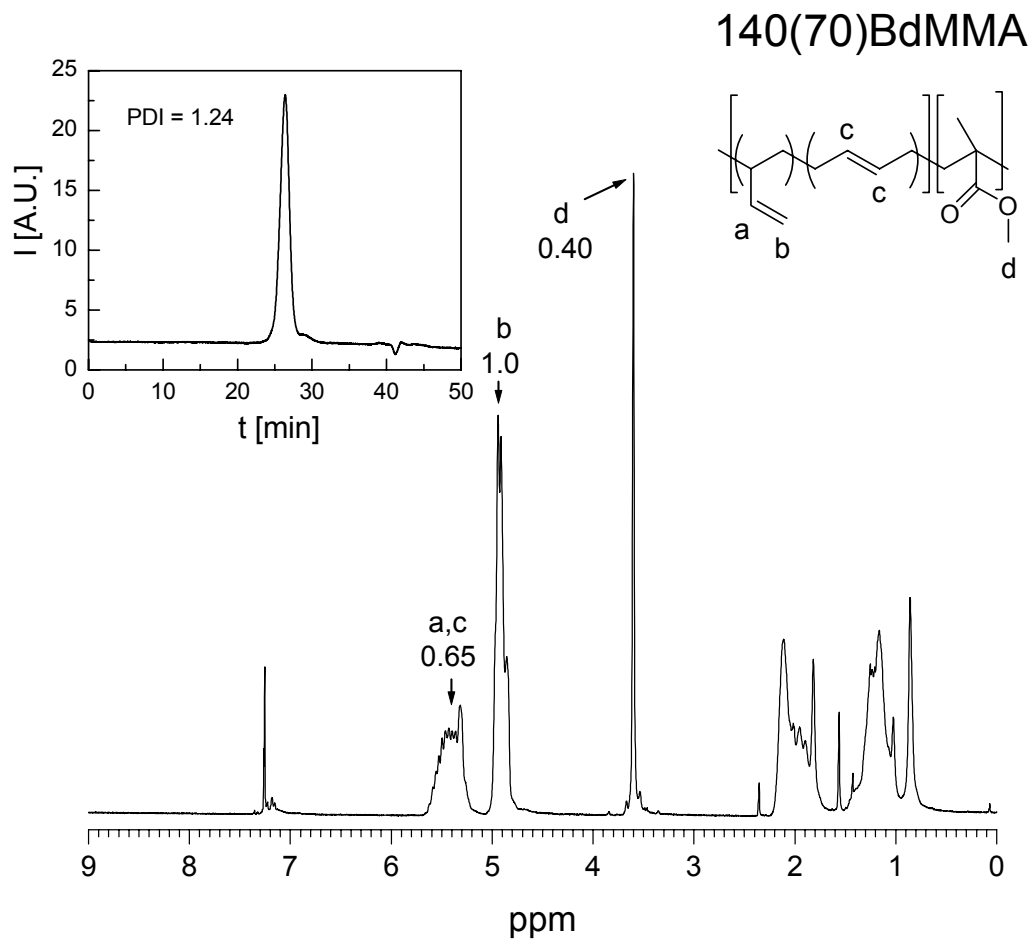


Figure A.12 300 MHz proton NMR spectrum of 140(70)BdMMA, a poly[(methyl methacrylate)-*b*-1,2-butadiene] block copolymer with $M_{P_{MMA}} = 68$ kg/mol and $M_{P_B} = 142$ kg/mol, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition reported in Table A.4. The GPC chromatogram used to measure polydispersity is shown in the inset.

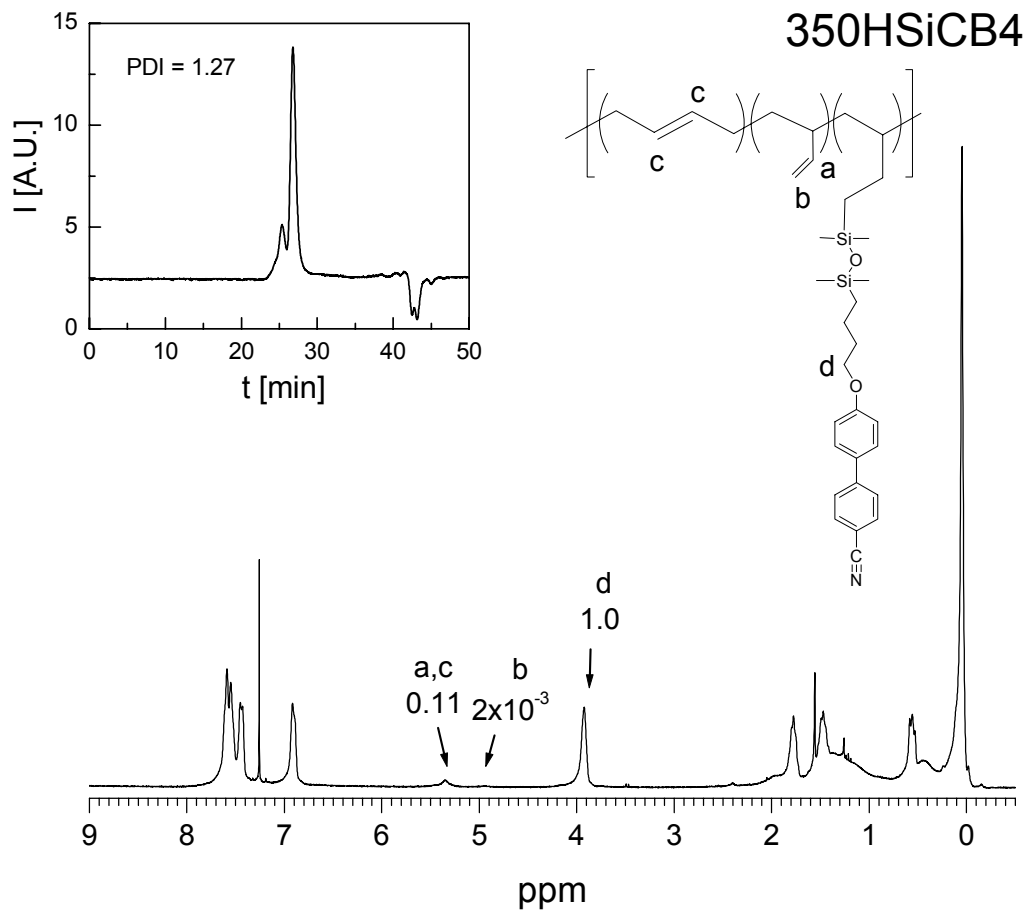


Figure A.13 300 MHz proton NMR spectrum of 350HSiCB4, an SGLCP homopolymer synthesized from 50H, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight reported in Table A.5. The GPC chromatograph used to measure polydispersity is shown in the inset.

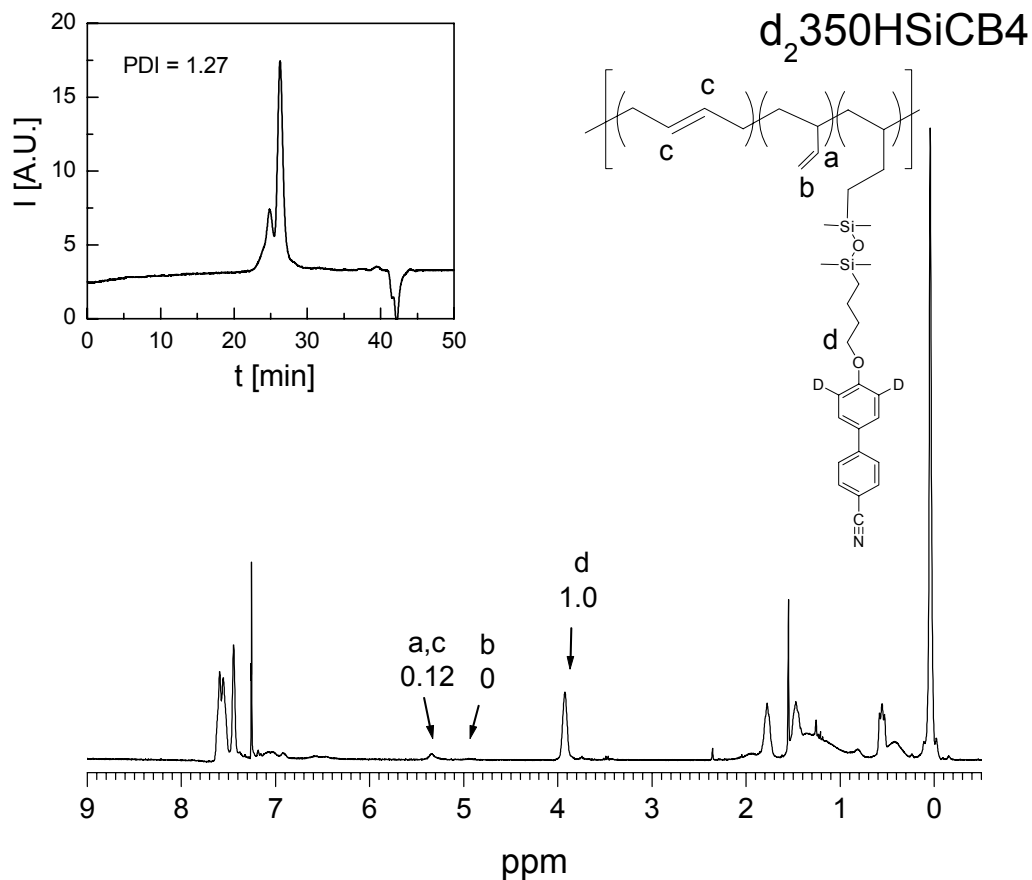


Figure A.14 300 MHz proton NMR spectrum of d_2 350HSiCB4, a deuterium-labeled SGLCP homopolymer synthesized from 50H, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight reported in Table A.5. The GPC chromatogram used to measure polydispersity is shown in the inset.

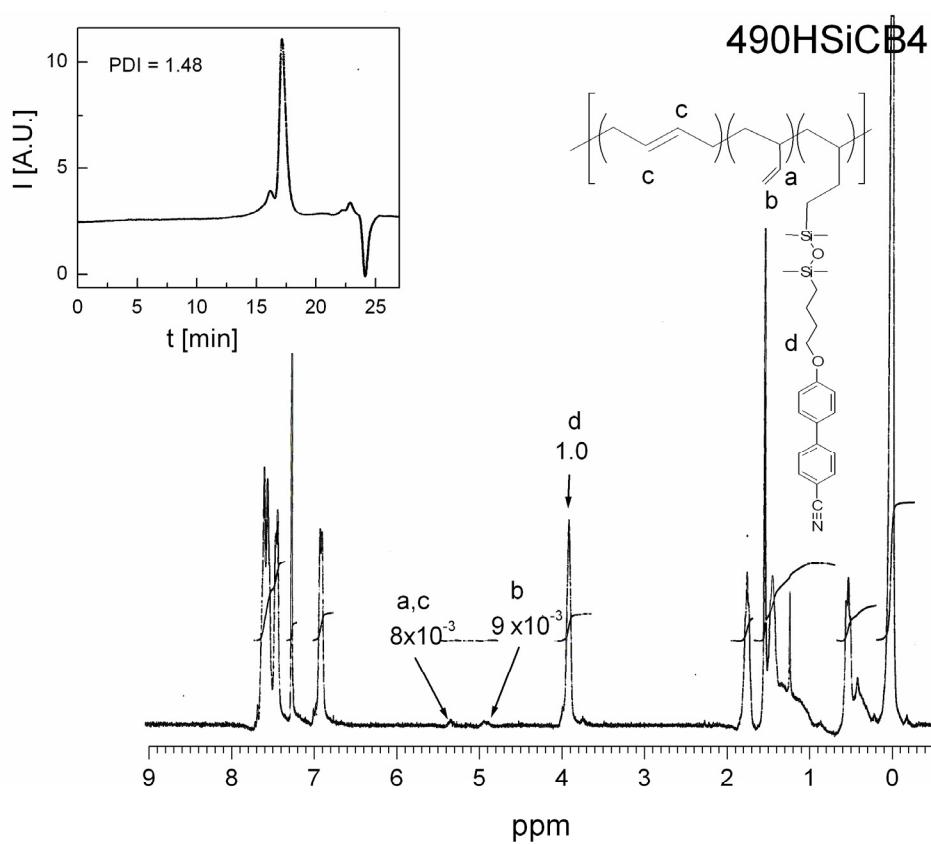


Figure A.15 300 MHz proton NMR spectrum of 490HSiCB4, an SGLCP homopolymer synthesized from 60H, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight reported in Table A.5. The GPC chromatograph used to measure polydispersity is shown in the inset. The relative intensity of peak **d** may be anomalously high due to incomplete removal of unreacted mesogen in this particular sample.

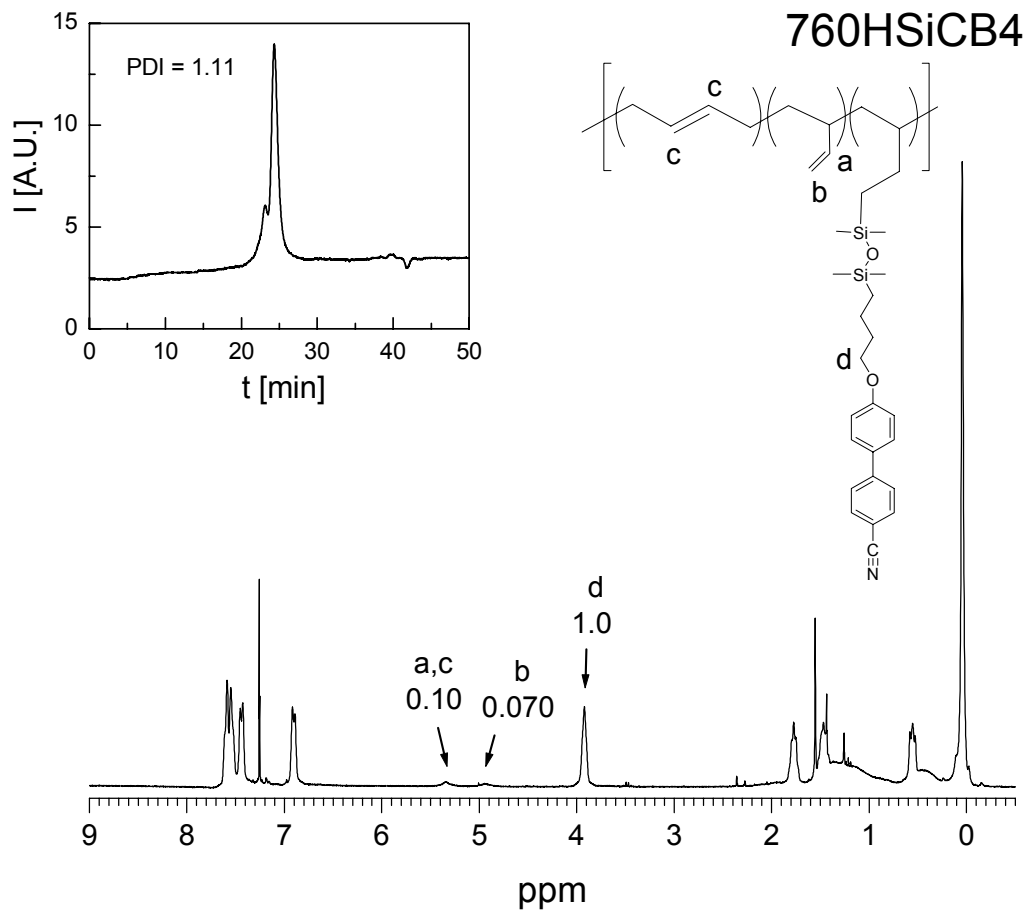


Figure A.16 300 MHz proton NMR spectrum of 760HSiCB4, an SGLCP homopolymer synthesized from 100H, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight reported in Table A.5. The GPC chromatograph used to measure polydispersity is shown in the inset.

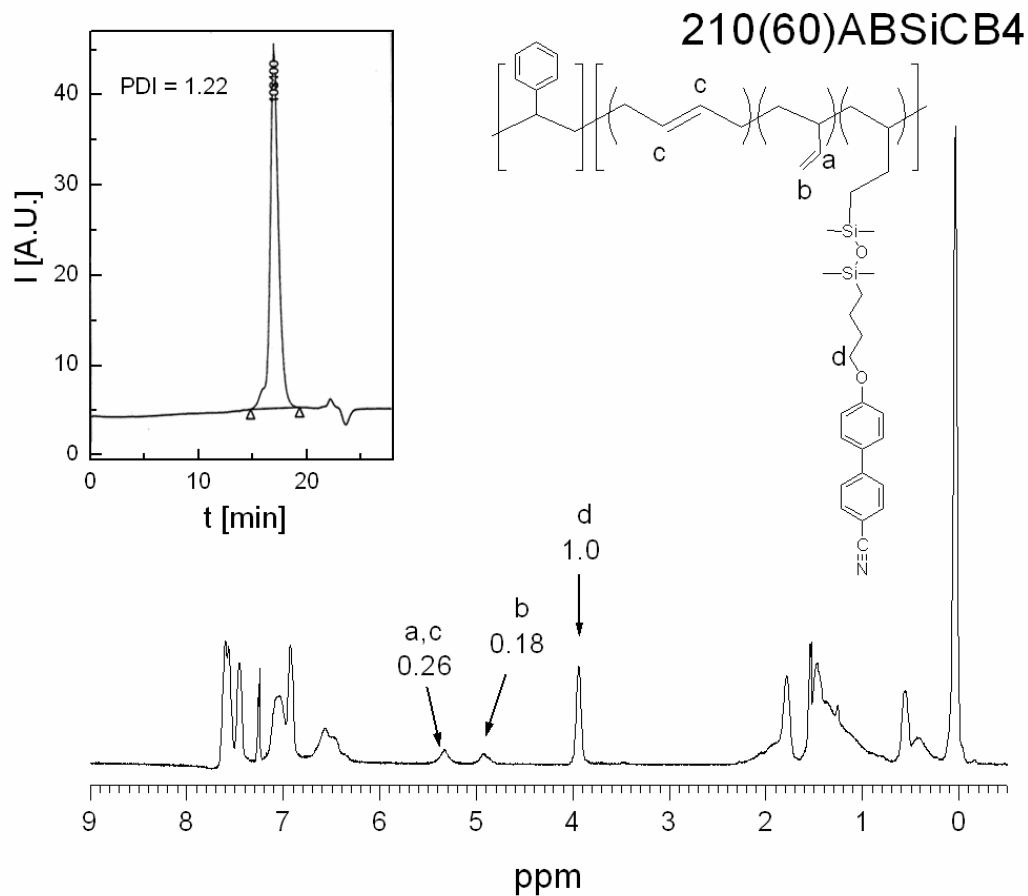


Figure A.17 300 MHz proton NMR spectrum of 210(60)ABSiCB4, a PS-SGLCP diblock copolymer synthesized from 30(60)AB, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.6. The GPC chromatograph used to measure polydispersity is shown in the inset.

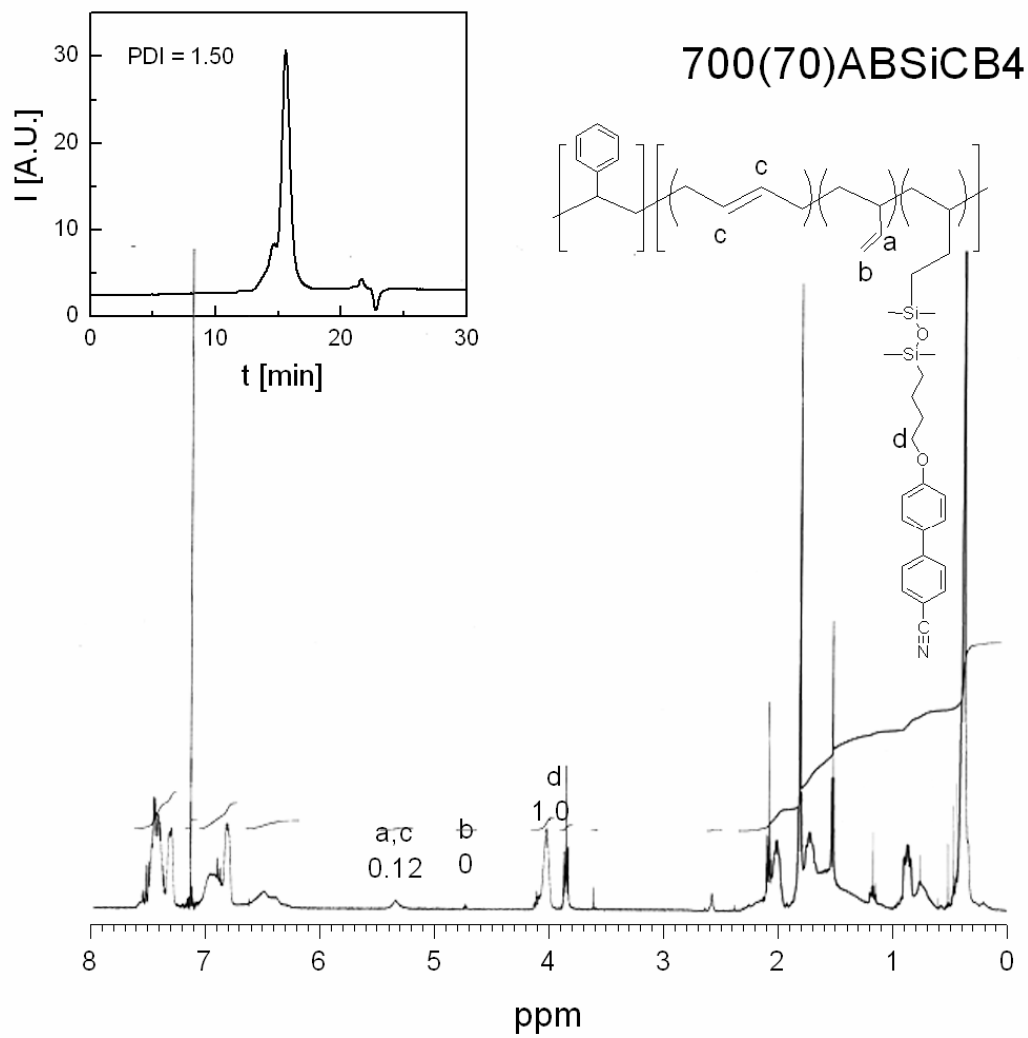


Figure A.18 300 MHz proton NMR spectrum of 700(70)ABSiCB4, a PS-SGLCP diblock copolymer synthesized from 100(70)AB, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.6. The GPC chromatogram used to measure polydispersity is shown in the inset. The relative intensity of peak *d* may be anomalously high and the presence of a peak at $\delta = 3.85$ ppm may be due to incomplete removal of unreacted mesogen in this particular sample.

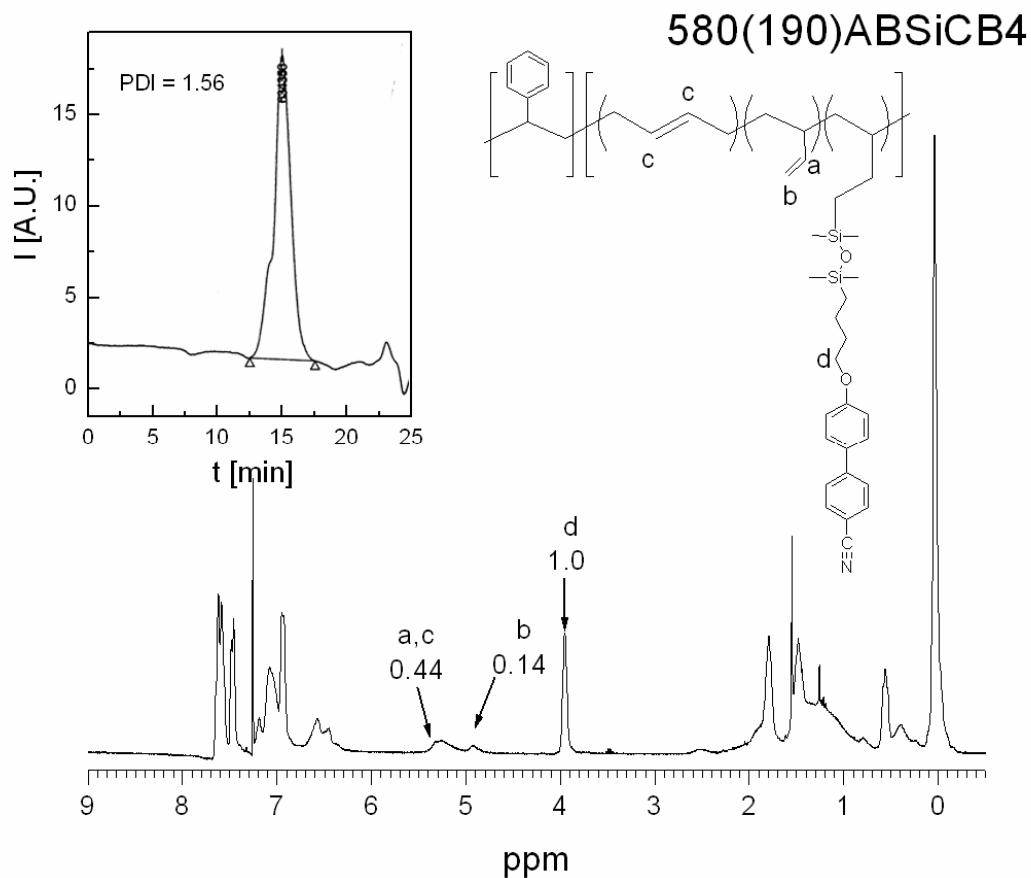


Figure A.19 300 MHz proton NMR spectrum of 580(190)ABSiCB4, a PS-SGLCP diblock copolymer synthesized from 100(190)AB, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.6. The GPC chromatograph used to measure polydispersity is shown in the inset.

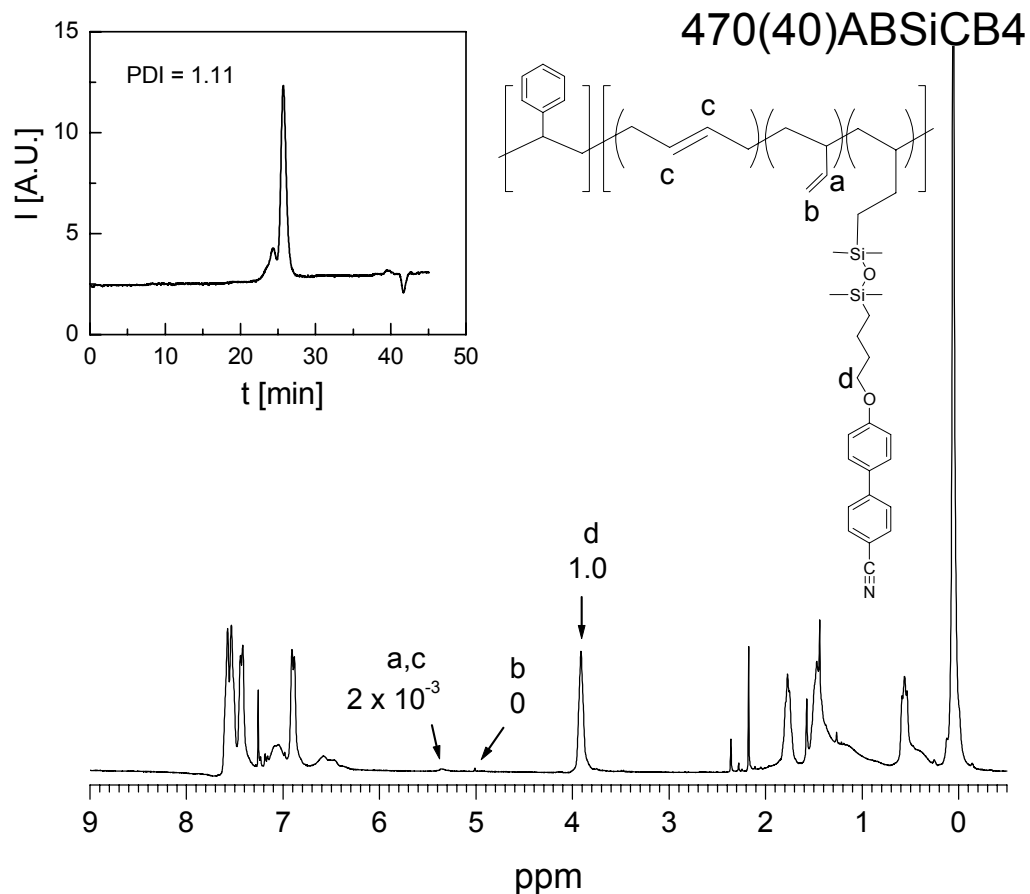


Figure A.20 300 MHz proton NMR spectrum of 470(40)ABSiCB4, a PS-SGLCP diblock copolymer synthesized from 60(40)AB, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.6. The GPC chromatograph used to measure polydispersity is shown in the inset.

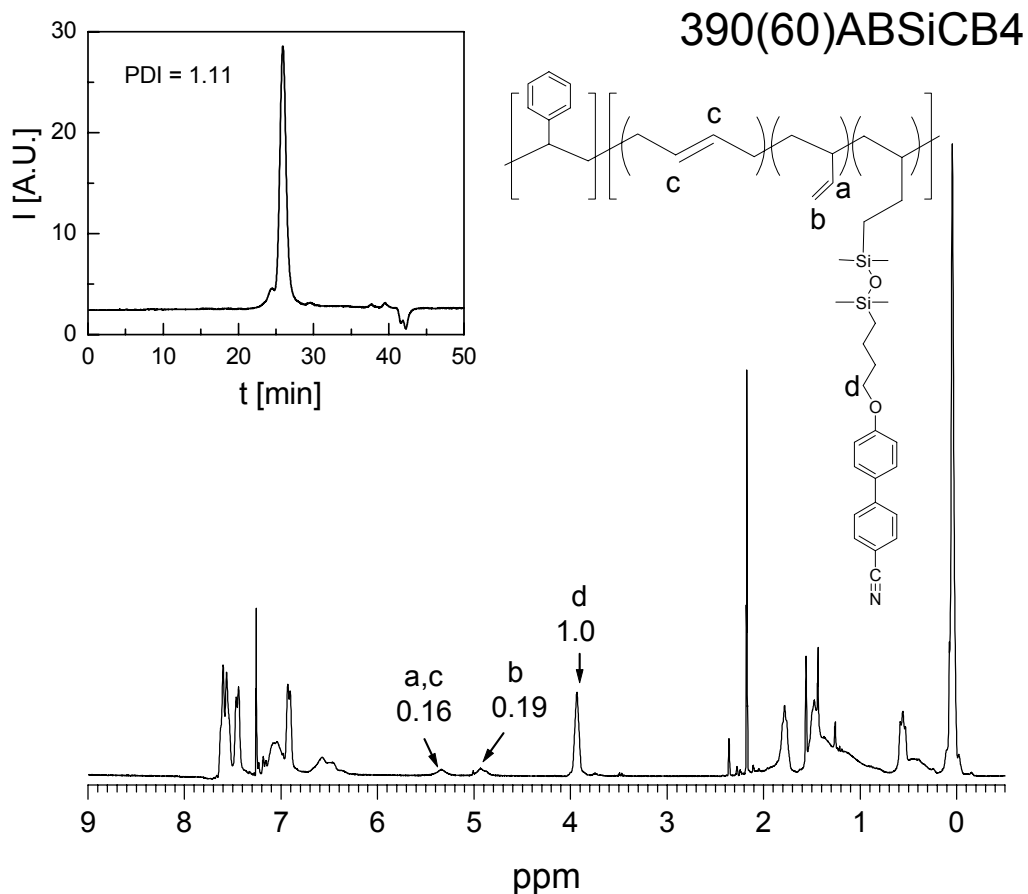


Figure A.21 300 MHz proton NMR spectrum of 390(60)ABSiCB4, a PS-SGLCP diblock copolymer synthesized from 60(60)AB, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.6. The GPC chromatograph used to measure polydispersity is shown in the inset.

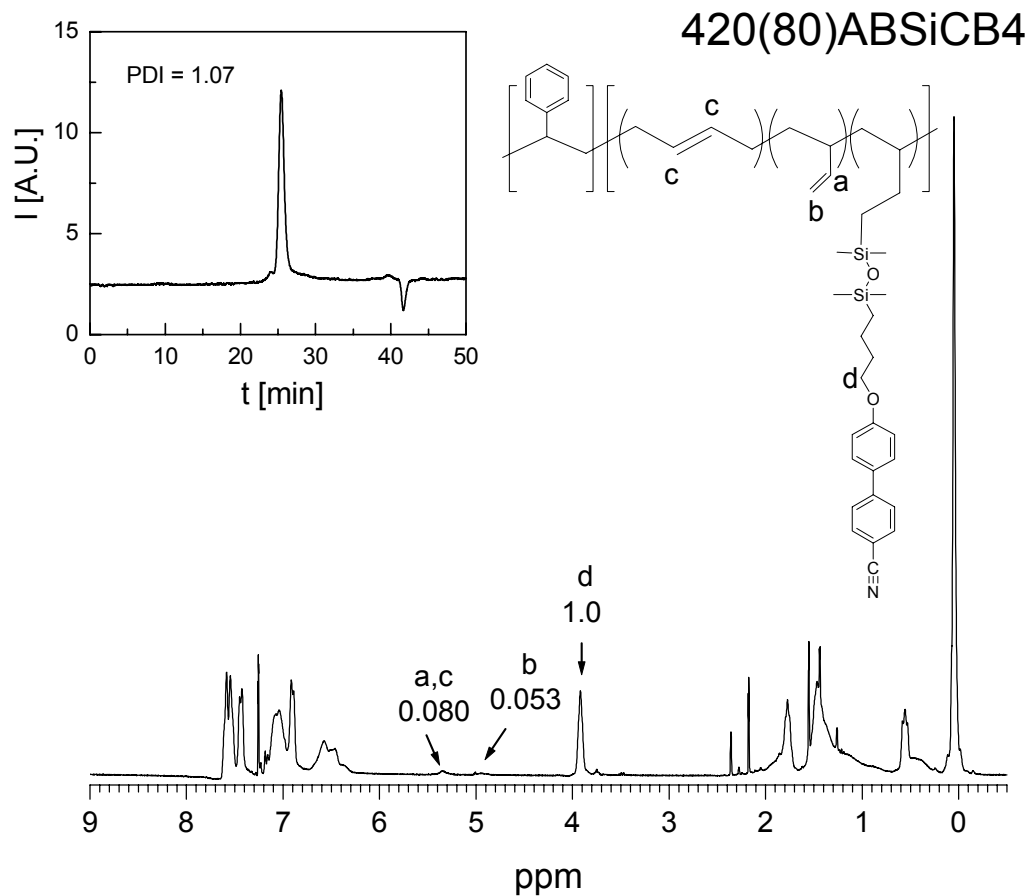


Figure A.22 300 MHz proton NMR spectrum of 420(80)ABSiCB4, a PS-SGLCP diblock copolymer synthesized from 60(80)AB, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.6. The GPC chromatograph used to measure polydispersity is shown in the inset.

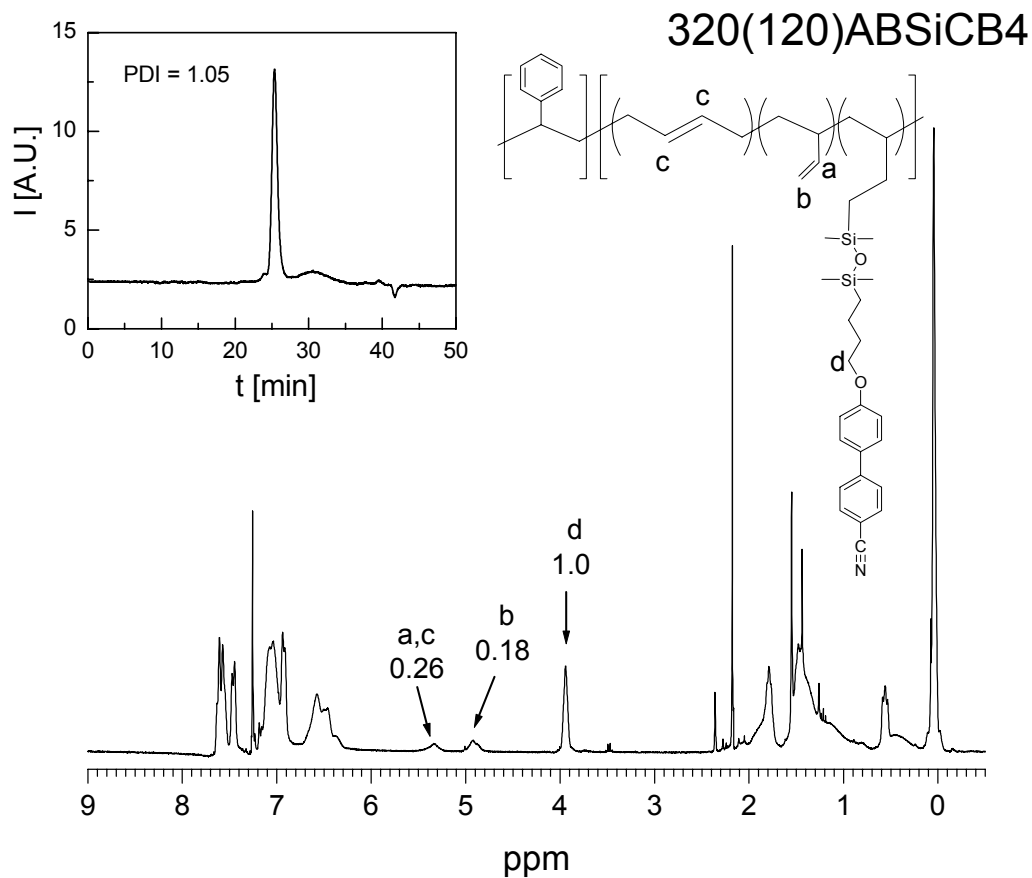


Figure A.23 300 MHz proton NMR spectrum of 320(120)ABSiCB4, a PS-SGLCP diblock copolymer synthesized from 50(120)AB, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.6. The GPC chromatograph used to measure polydispersity is shown in the inset.

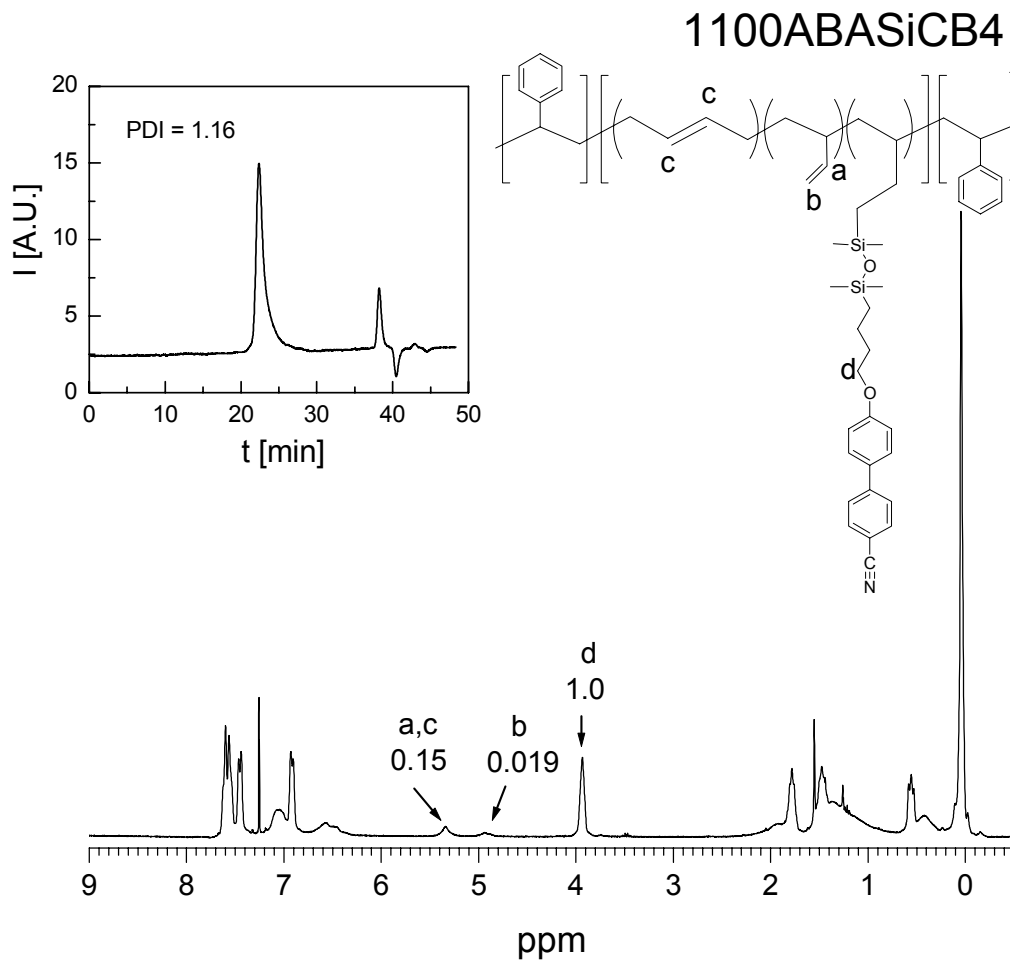


Figure A.24 300 MHz proton NMR spectrum of 1100ABASiCB4, a PS-SGLCP-PS triblock copolymer synthesized from (60)150(70)ABA, in CDCl₃. Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.7. The GPC chromatograph used to measure polydispersity is shown in the inset.

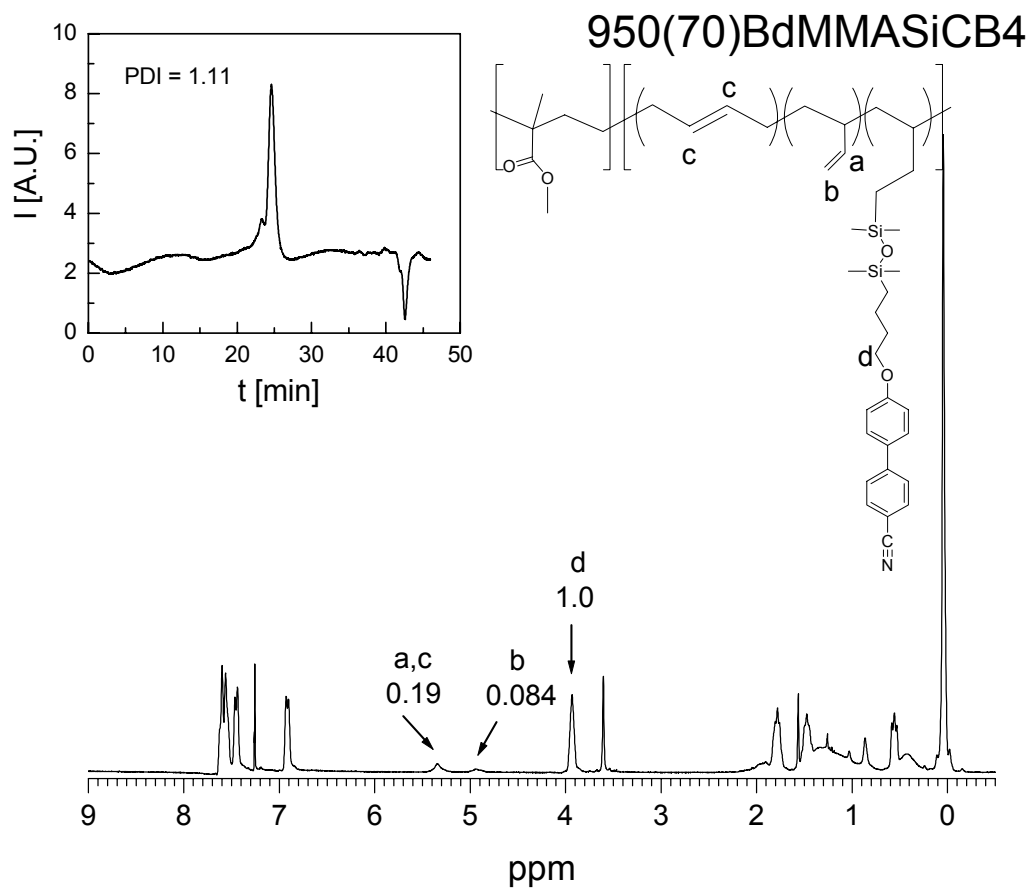


Figure A.25 300 MHz proton NMR spectrum of 950(70)BdMMASiCB4, a PMMA-SGLCP diblock copolymer synthesized from 140(70)BdMMA, in CDCl_3 . Peak labels include the relative intensity (integrated area) and their assignments. This data was used to calculate the polymer composition and molecular weight of the SGLCP block reported in Table A.8. The GPC chromatograph used to measure polydispersity is shown in the inset.

A.5 References

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