Multiblock Inverse-Tapered Copolymers: Glass Transition Temperatures and Dynamic Heterogeneity as a Function of Chain Architecture

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Sample M_n calculation for ITB-20:

Each block (of total 6 blocks) has 200 grams of monomer, assuming no extra impurity and no termination reaction during the polymerization. The molecular weight of single block could be calculated as

$$M_n = \frac{weight\ of\ monomers}{moles\ of\ n-BuLi} = \frac{200\ g}{37g\ \times 2\%\ \div\ 64\ g/mol} = 20\ kg/mol$$

Thus the total molecular weight is 20 kg/mol x 6 = 120 kg/mol

Calculation of THF/Li ratio:

$$18\ ml\ x\ \frac{moles\ of\ THF}{moles\ of\ n-BuLi} = \frac{18\ ml\ \times 0.2\ g/ml\ \div 72\ g/mol}{37g\ \times 2\%\ \div\ 64\ g/mol} = 5$$
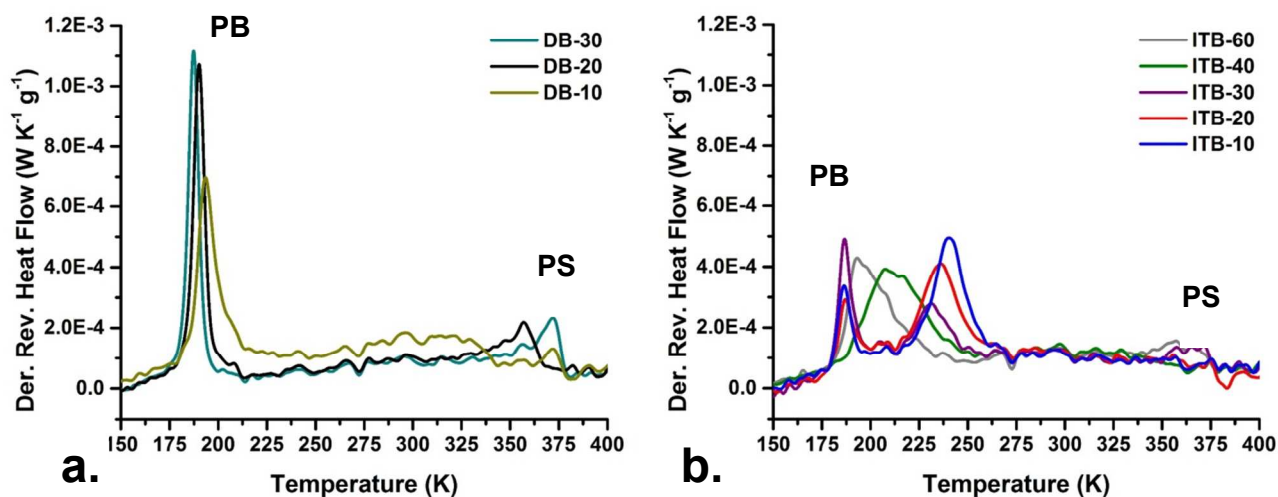
Figure S1. Overlay of the same modulated DSC thermograms shown previously in Figure 1 for the series of multiblock (a) discrete and (b) inverse-tapered copolymers, presented with the heat flow values on the y-axis.
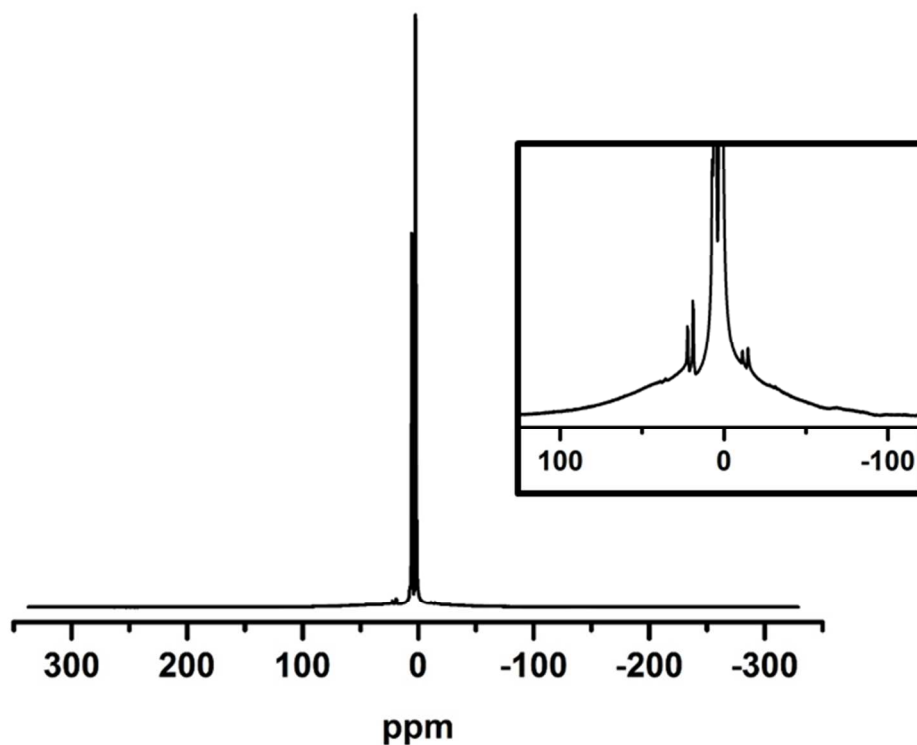

Figure S2. Representative room-temperature ^{1}H MAS NMR spectra of a styrene-butadiene discrete block copolymer in the solid state, showing the entire 200-kHz spectral acquisition window. The broad 100-ppm fwhm signal from rigid components is seen more easily in the inset.
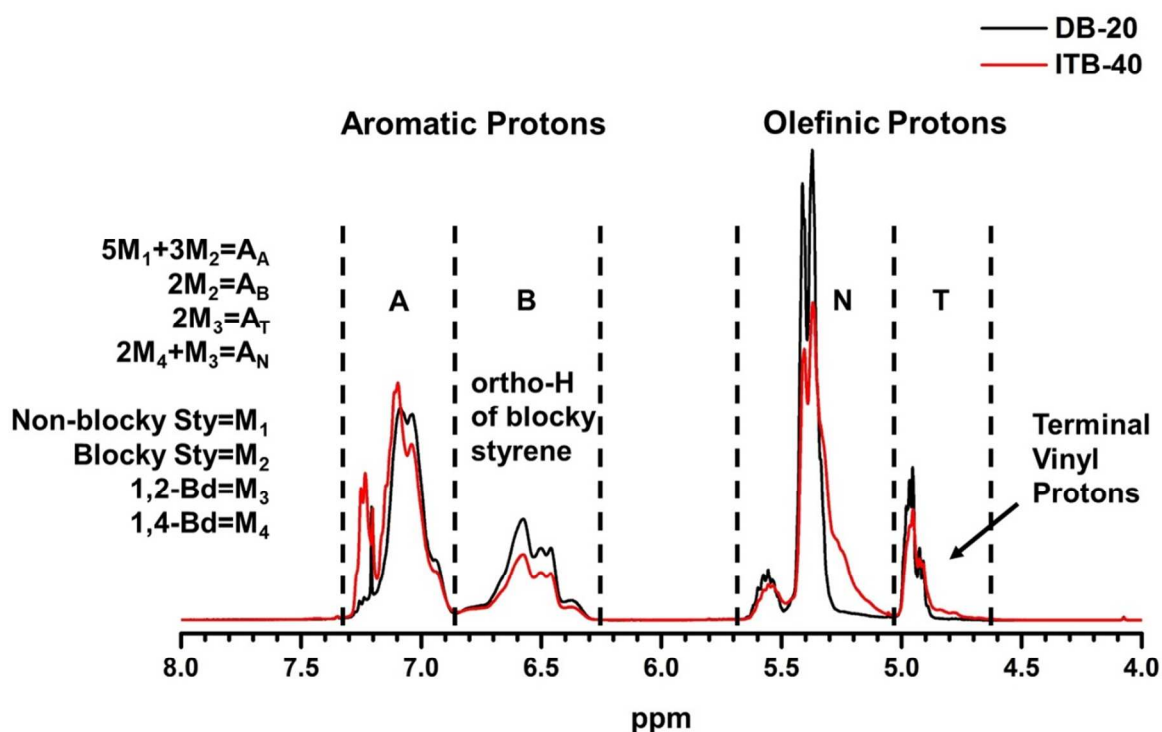
Figure S3. Representative ^{1}H solution NMR spectrum illustrating method for calculating % non-blocky styrene as reported in Table 1 of the manuscript, using the method and notation of Sardelis.[37] Some spectra were collected in THF to eliminate the chloroform peak at 7.3 ppm. Note the reduction of the blocky styrene signal in region B for the ITB copolymers.
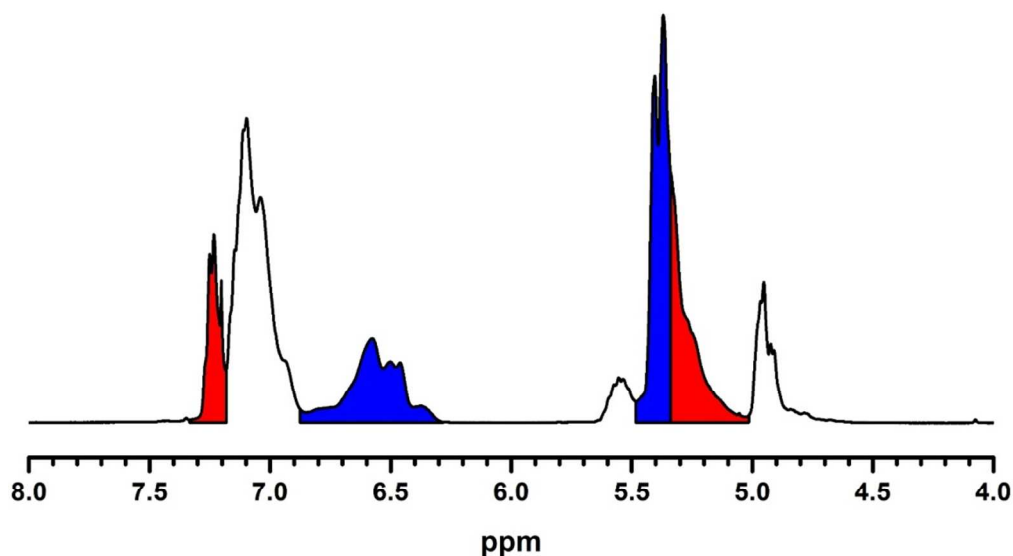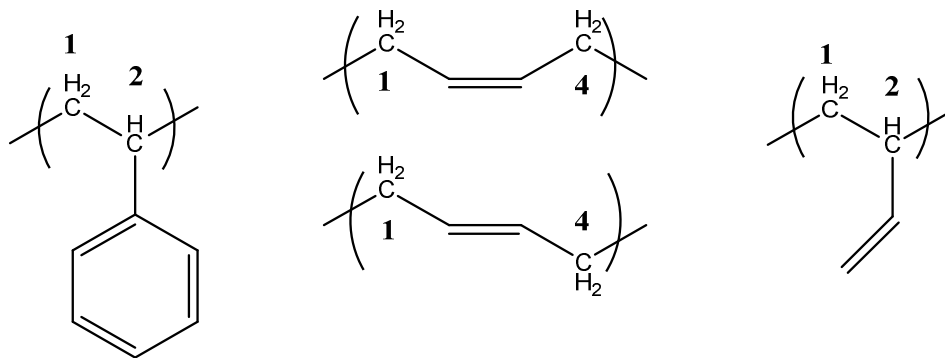

Figure S4. Representative 400 MHz ^{1}H solution NMR spectrum of an ITB copolymer (ITB-40 shown here) showing the approximate area of mixed monomer sequence signals in red. As more styrene monomers get incorporated adjacent to butadiene in the inverse-tapered region of the chain, the blocky styrene ortho-hydrogen signal from 6.2-6.8 ppm decreases, and the intensity from 7.1-7.3 ppm increases. Similarly, the butadiene signal from 5.0 to 5.4 also increases with increased taper fraction.

Table S1. Percent of the total NMR signal for the styrene and butadiene aromatic and olefinic signal regions, respectively, appearing as mixed monomer sequences (comonomers alpha to each other in the chain). Values are calculated using the regions highlighted in Figure S4, and tabulated versus the inverse-taper fraction f_T. Note the agreement in values between copolymers with the same f_T.

Copolymer	Sty signal in Sty-Bd sequence	Bd signal in Bd-Sty sequence	f_T
ITB-60	26.6%	33.0%	0.5
ITB-30	28.9%	32.5%	0.5
ITB-40	36.0%	40.5%	0.67
ITB-20	37.1%	39.0%	0.67
ITB-10	40.3%	38.8%	0.67

Table S2. Aliphatic ^{13}C solution NMR assignments for styrene-butadiene copolymers, highlighting sequence effect chemical shift changes as previously reported in the literature for random copolymers.[38,39] Assignments were confirmed using HSQC data shown in Figures S5, which includes the aromatic and olefinic regions. Symbols in the table: C, cis-1,4; T, trans-1,4; V, 1,2; S, styrene; B, cis-1,4 or trans-1,4. Capital letters denote the monomer assigned to the peak, using the labeling scheme below the table.

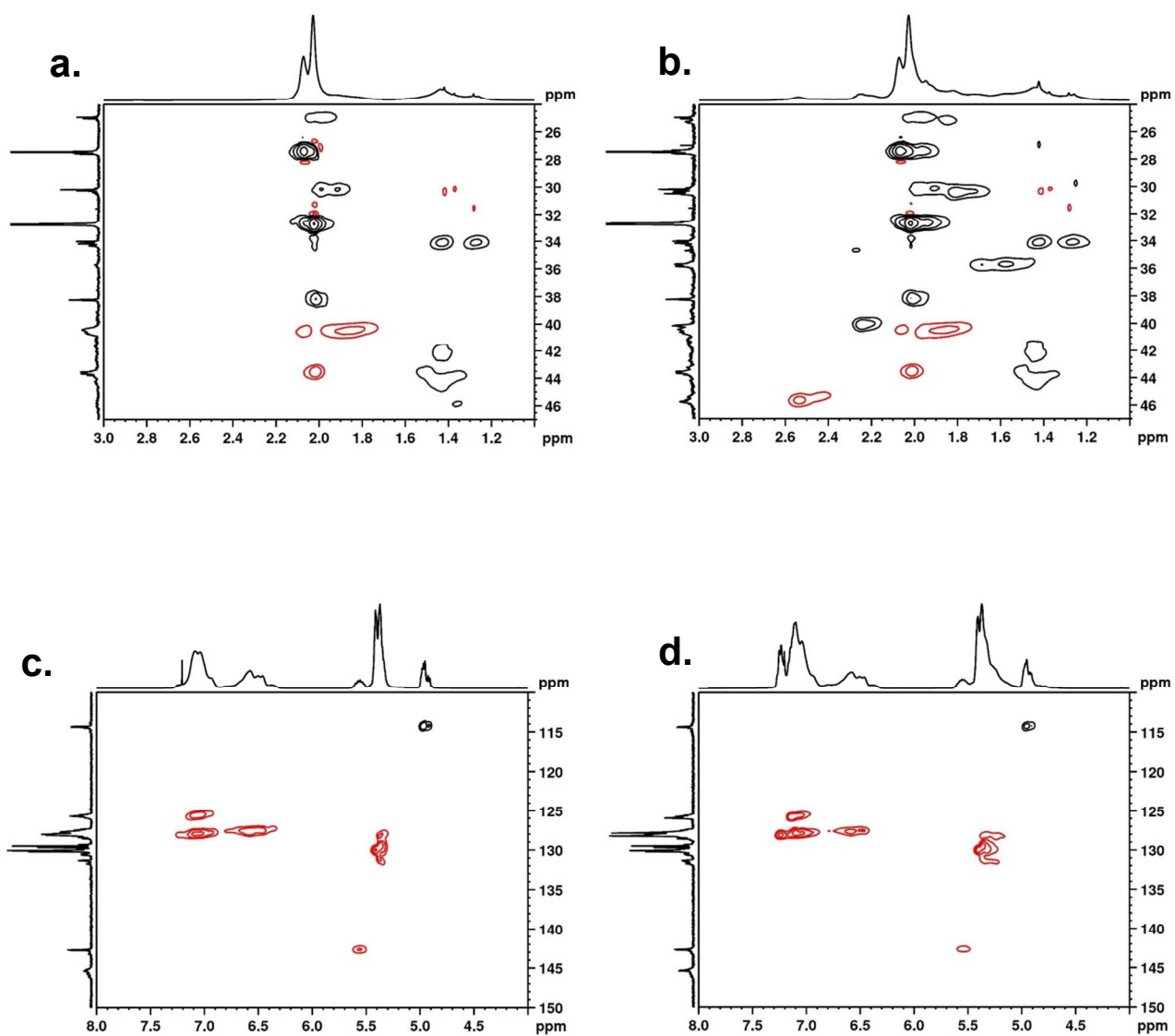| DB-20	ITB-40	Triad	Carbon	Segre[36]	Sato[37]
24.96	24.96	bCv, vCv, sCv	C4	25.07	24.9
	25.28	bCs, vCs, sCs	C4	25.40	25.2
	27.39	bCs	C1	27.55	---
27.49	27.49	bCb, bCv	C1 & C4, C1	27.55	27.32-27.44 (calc)
30.21	30.22	bTv, vTv, sTv	C4	30.16	30.1
30.41	30.53	bTs, vTs ,sTs	C4	30.51	30.4
	32.63	bTs	C1	32.74	---
32.75	32.75	vCb, vCv, vCs	C1	32.74	32.7
32.80	32.81	bTb, bTv	C1 & C4, C1	32.74	32.7
34.03	34.05	bVb	C1	34.25	33.9-34.3
	34.75	sCb, sCv, sCs	C1	34.8 (calc)	34.4-34.8
35.73	35.72	bSb	C1	35.88	35.4-36.0
38.26	38.27	vTb, vTv, vTs	C1	38.17	38.1
	40.19	sTb, sTv, sTs	C1	40.09*	40.1
40.43	40.45	sSs	C2	40.73	---
43.57	43.60	bVb, vVb, sVb	C2	43.51*	43.90-44.31 (calc)
	45.79	bSb	C2	45.82*	45.3-45.8

Figure S5. Representative 400 MHz ^{1}H solution NMR HSQC contour plots for the aliphatic region of (a) DB-20 and (b) ITB-10, and the olefinic/aromatic region of (c) DB-20 and (d) ITB-10. Signals from CH$_2$ and CH moieties are shown as black and red contours, respectively.
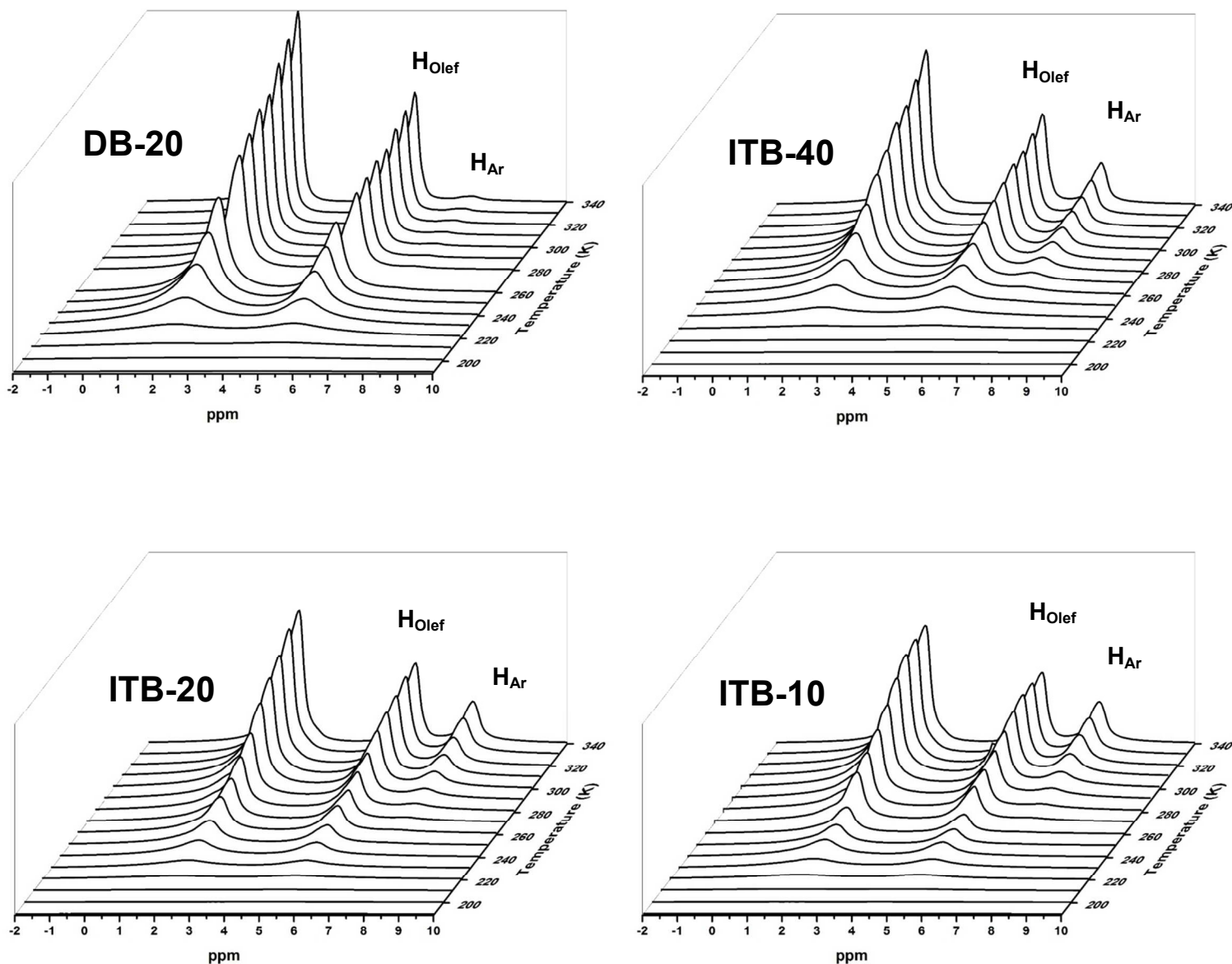
Figure S6. Variable-temperature ^{1}H MAS NMR spectra on solid copolymers acquired from 190-340 K. **NOTE** the reversed chemical shift axis to more easily observe the aromatic signal. Each stack plot is labeled according to the scheme in the text. For convenience, the DB-20 and ITB-40 are reproduced here, as shown in Figure 3 of the paper. Note the different temperatures at which butadiene olefinic and styrene aromatic peaks appear, and the differences in temperature-dependent linewidths between copolymers.
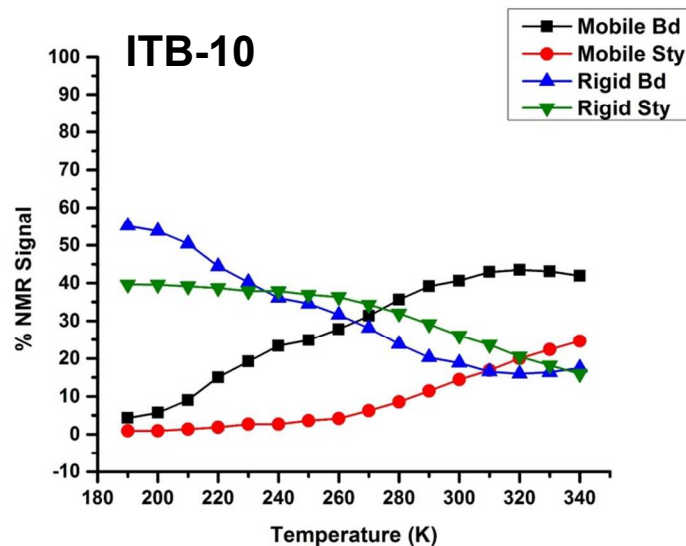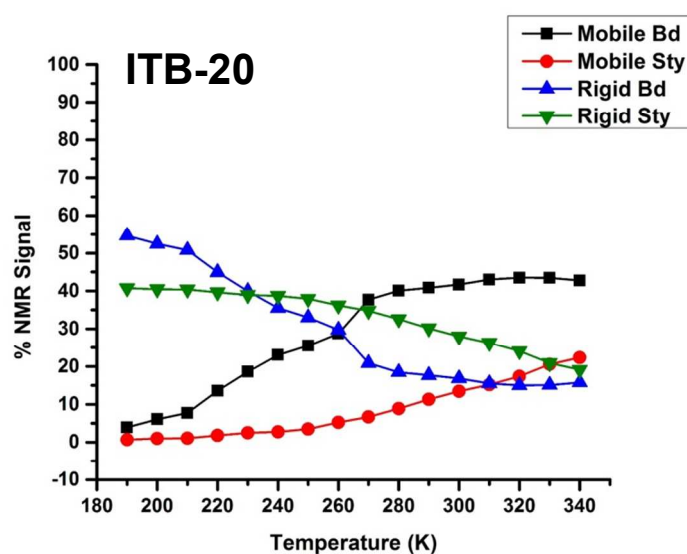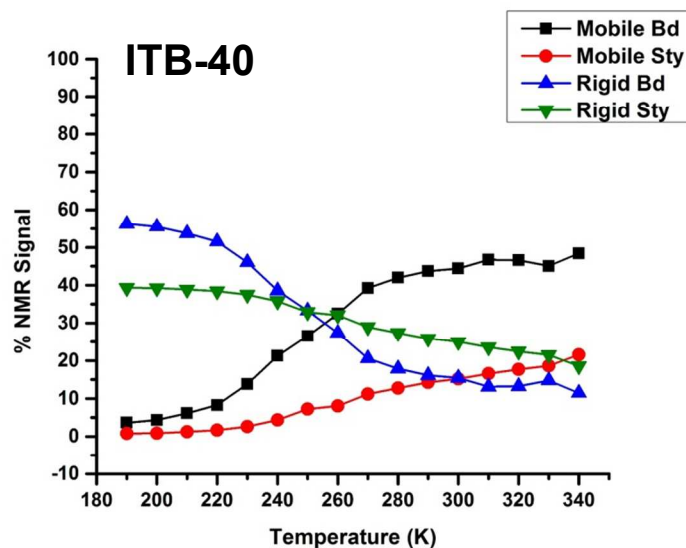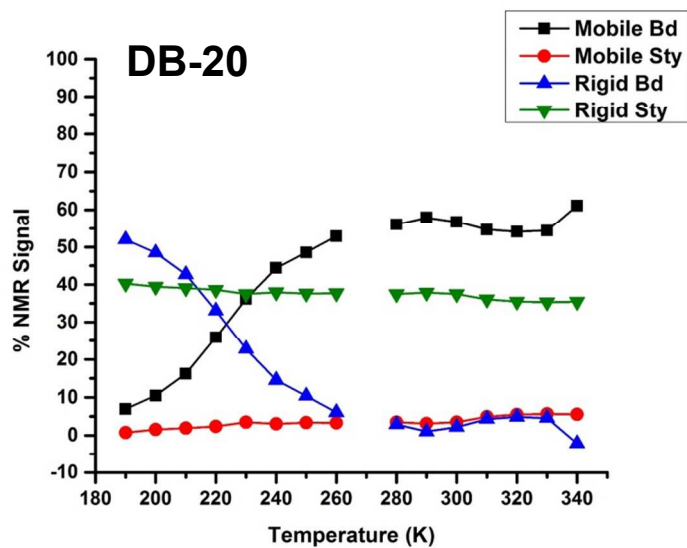
Figure S7. Plots showing temperature dependence of individual rigid versus mobile styrene and butadiene chain segments, extracted from data like that shown in Figure 2 of the manuscript and Figure S6 above, using signal intensity fractions in the isotropic region of the spectrum.
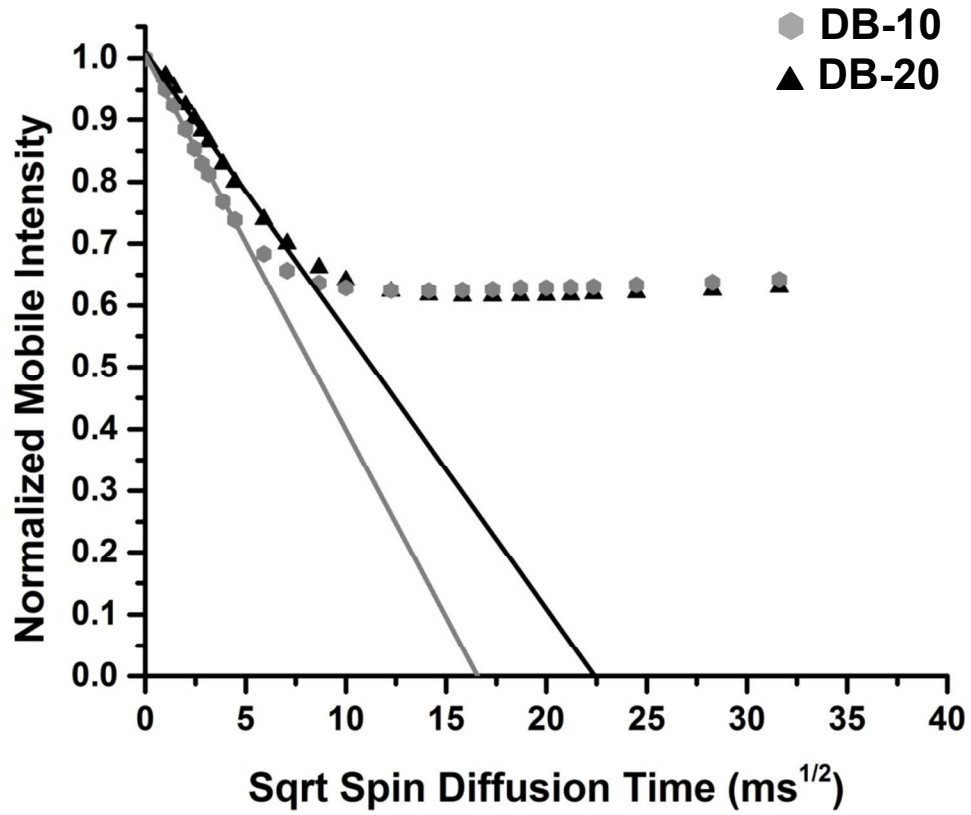
Figure S8. Spin-diffusion data for the DB-10 and DB-20 copolymers, showing how the initial polarization transfer rate is used to determine the characteristic spin-diffusion time constant $\tau_m^{0.5}$.