UNDERSTANDING EFFECT OF CONSTRAINT RELEASE ENVIRONMENT ON END-TO-END VECTOR RELAXATION OF LINEAR POLYMER CHAINS.

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Supporting Information

1. Experimental details

Materials.

The synthesis of the linear (M_w ~ 6.9 kg/mol and M_w ~ 50.0 kg/mol) Poly(butadiene)s (PBds) was achieved by anionic polymerization high vacuum techniques. All manipulations were performed, under high vacuum, in home-made glass reactors provided with break-seals for the addition of reagents and constrictions for removal of products. The reactors were preliminary washed with a benzene solution of nbutyllithium (Aldrich) followed by rinsing with benzene, the polymerization solvent. The purification of the monomer butadiene (99%, Aldrich), the solvent benzene (99.8%, Aldrich), the terminating agent methanol (99.9%, Aldrich) to the standards required for anionic polymerization, was performed according to well-established high-vacuum procedures.[1] Sec-Butyllithium (sec-BuLi), the initiator, was prepared in vacuo from sec-butylchloride (99.9%; Aldrich) and a lithium dispersion (99%, high sodium, Aldrich). Narrow distribution linear PBd with M_w ~ 305 kg/mol (PDI=1.08) (1,4 addition > 90%) has been purchased from Polymer Source, Inc.

Measurements.

^{1}H-NMR spectra were recorded on a 300 MHz Avance Bruker spectrometer at 25 °C. Chemical shifts are given in ppm downfield from tetramethylsilane (TMS).

Size exclusion chromatography (SEC) was carried out on a system composed of two PSS Gram columns (100 Å and 1000 Å) connected to a Waters 410 differential refractometer with $CHCl_3$/Et_3N/*i*-Propanol as the carrier solvent (25 °C, 1 mL min^{-1}). Polystyrene standards were used for calibration.

Differential scanning calorimetry (DSC) measurement was performed on a Mettler Toledo 822 calorimeter. The sample was placed in an aluminum capsule (40 mL). The DSC instrument was calibrated using an Indium standard. The sample was initially heated from -150°C to 0°C at 10°C/min under a nitrogen atmosphere, followed by cooling at the same rate immediately after heating. At last the sample was again heated from -150°C to 30°C at 10°C/min under a nitrogen atmosphere. The latter measurement was used to determine glass transition temperature, T_g, using midpoint Richardson method.

2. Results.

^{1}H-NMR.

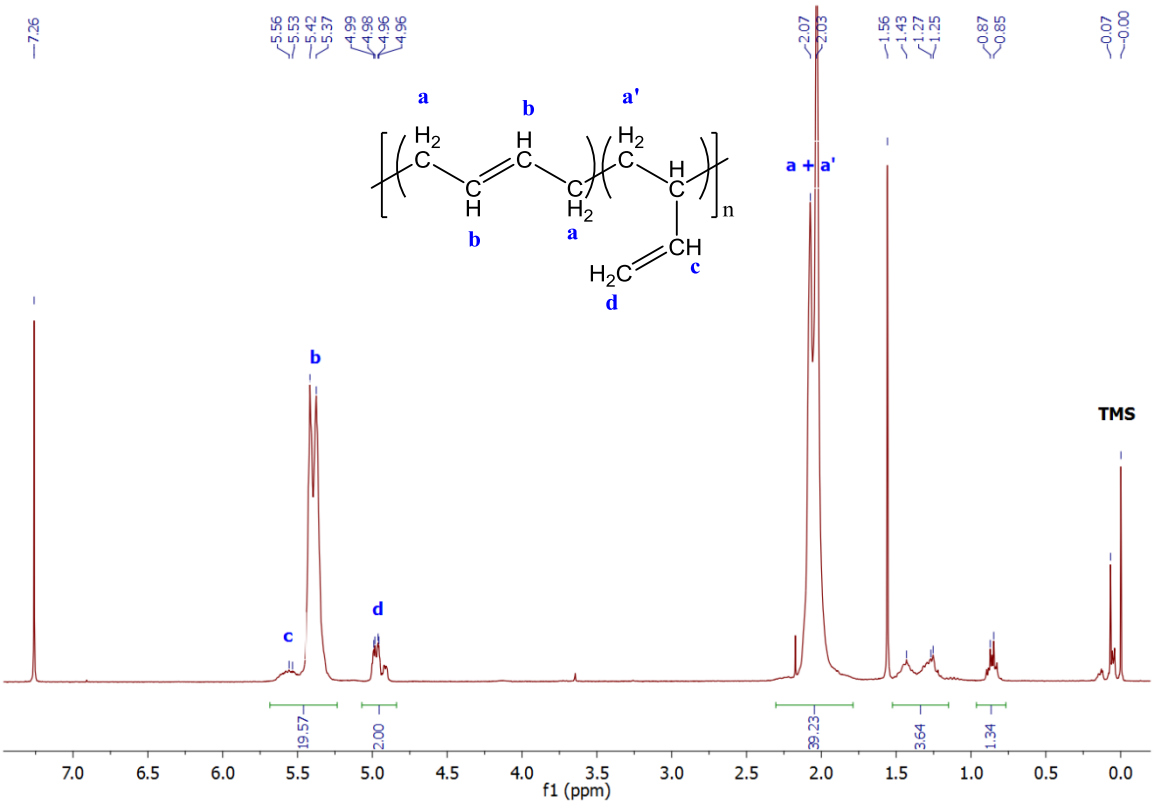

Figure S1. ^{1}H-NMR (300 MHz, $CHCl_3$-*d*, ppm) spectra of linear PBd with M_w ~ 6.9 kg/mol.

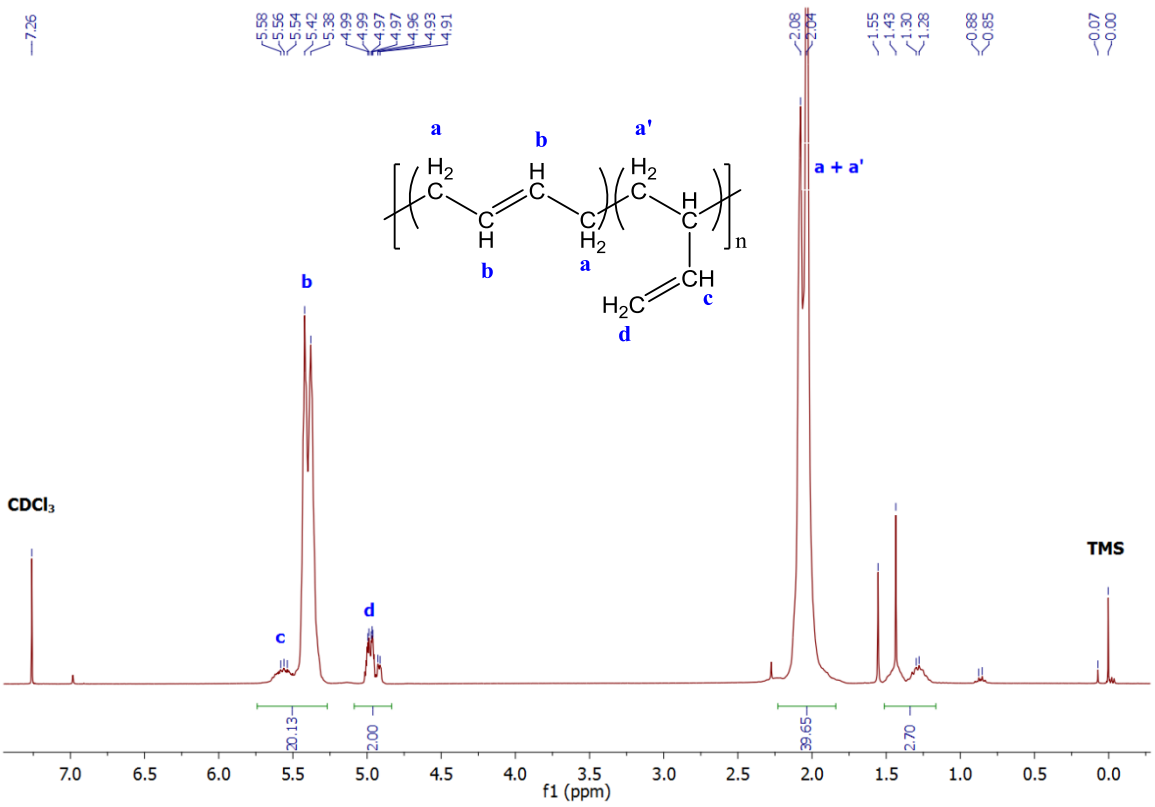

Figure S2. ^{1}H-NMR (300 MHz, $CHCl_3$-*d*, ppm) spectra of linear PBd with M_w ~ 50 kg/mol.

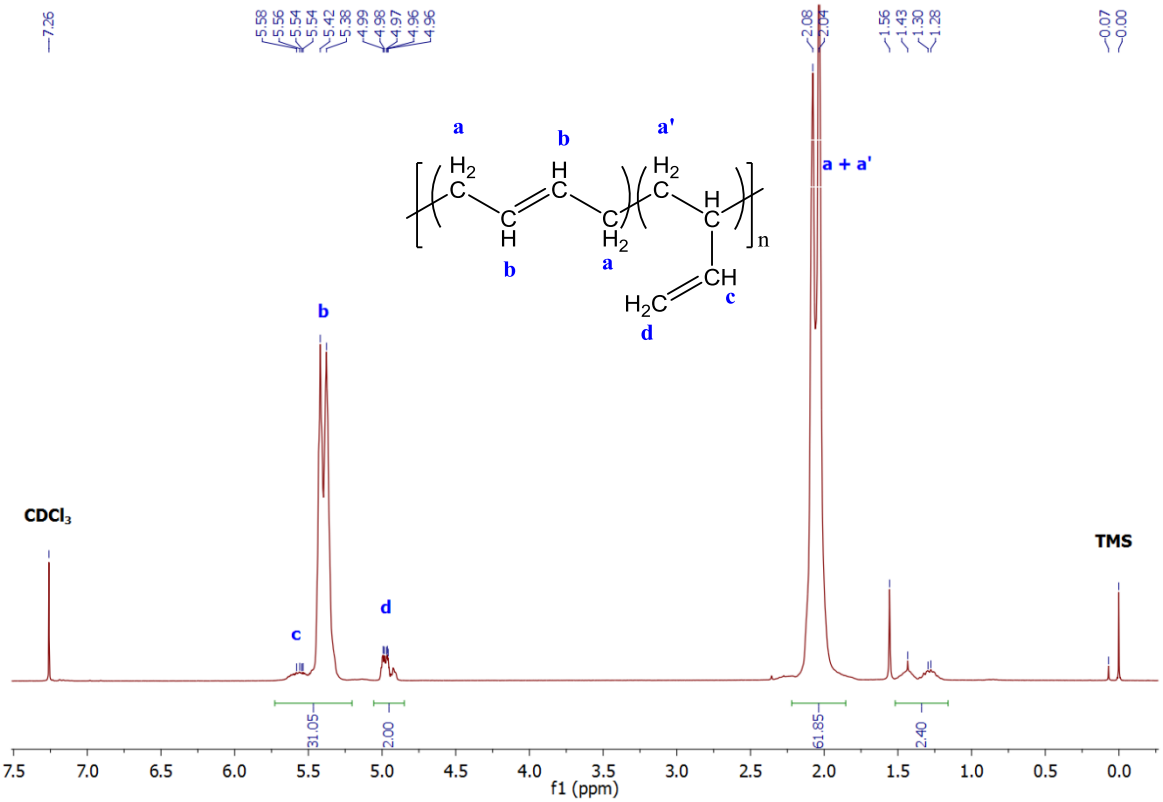

Figure S3. ^{1}H-NMR (300 MHz, $CHCl_3$-*d*, ppm) spectra of linear PBd with M_w ~ 305 kg/mol.

The total molar content of 1, 2 - structure and 1, 4 - structure of PBd can be calculated from ^{1}H-NMR spectrum:

$$C_{1,2\text{-structure}} = \frac{Integral\,(d)/2}{\frac{Integral\,(b+c) - Integral\,(d)/2}{2} + Integral(d)/2}$$

and $C_{1,4\text{-structure}} = 1 - C_{1,2\text{-structure}}$

The content of 1,2 – structure and 1,4 – structure are calculated as:

- PBd 6.9kg/mol : $C_{1,4\text{-structure}}$ = 90.3 ± 1% and $C_{1,2\text{-structure}}$ = 9.7 ± 1%
- PBd 50kg/mol : $C_{1,4\text{-structure}}$ = 90.6 ± 1% and $C_{1,2\text{-structure}}$ = 9.4 ± 1%
- PBd 305kg/mol : $C_{1,4\text{-structure}}$ = 93.2 ± 1 -% and $C_{1,2\text{-structure}}$ = 6.8 ± 1%

PBd with M_w ~ 305 kg/mol (from Polymer Source Inc.) displays a lower by approximately 3% content of 1,2 structure compared to the synthesized PBds.

SEC chromatograms.

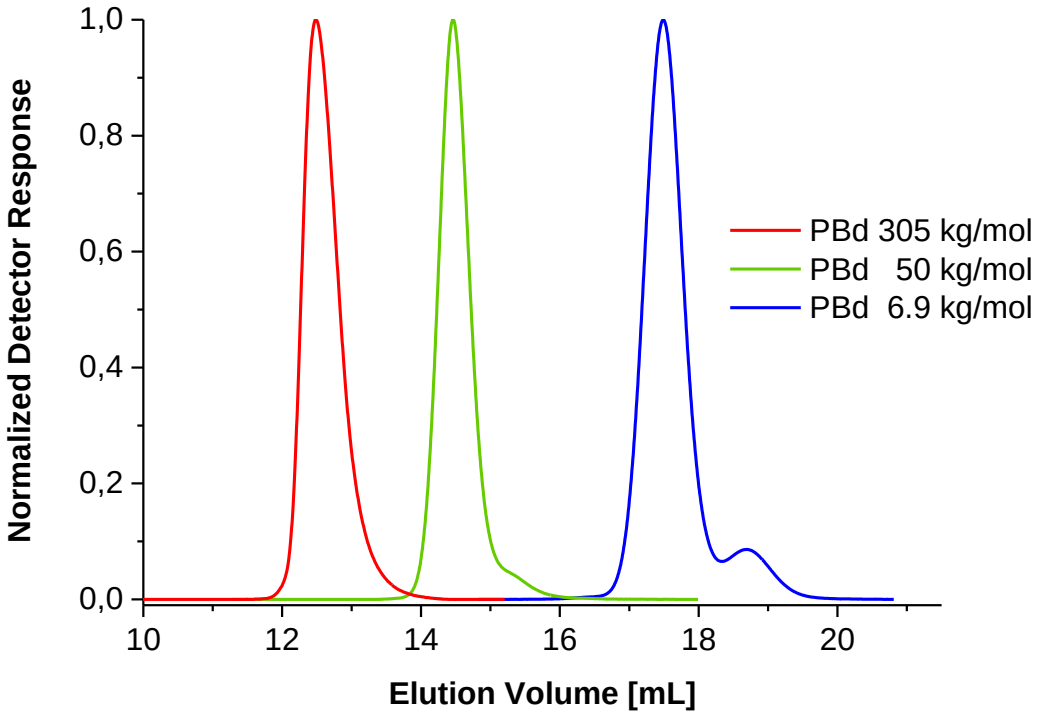

Figure S4. SEC traces of linear Poly(butadiene)s with M_w ~ 6.9 kg/mol (blue), M_w ~ 50 kg/mol (green) and M_w ~ 305 kg/mol (red).

Linear PBd with M_w ~ 305 kg/mol and M_w ~ 50 kg/mol display unimodal peak whereas PBd with PBd ~ 6.9 kg/mol displays a slight shoulder at low molecular weight end. Polystyrene standards were used for calibration to determine PDI:

Sample	**PDI**
PBd 6.9 kg/mol	1.08
PBd 50 kg/mol	1.06
PBd 305 kg/mol	1.08

DSC thermograms.

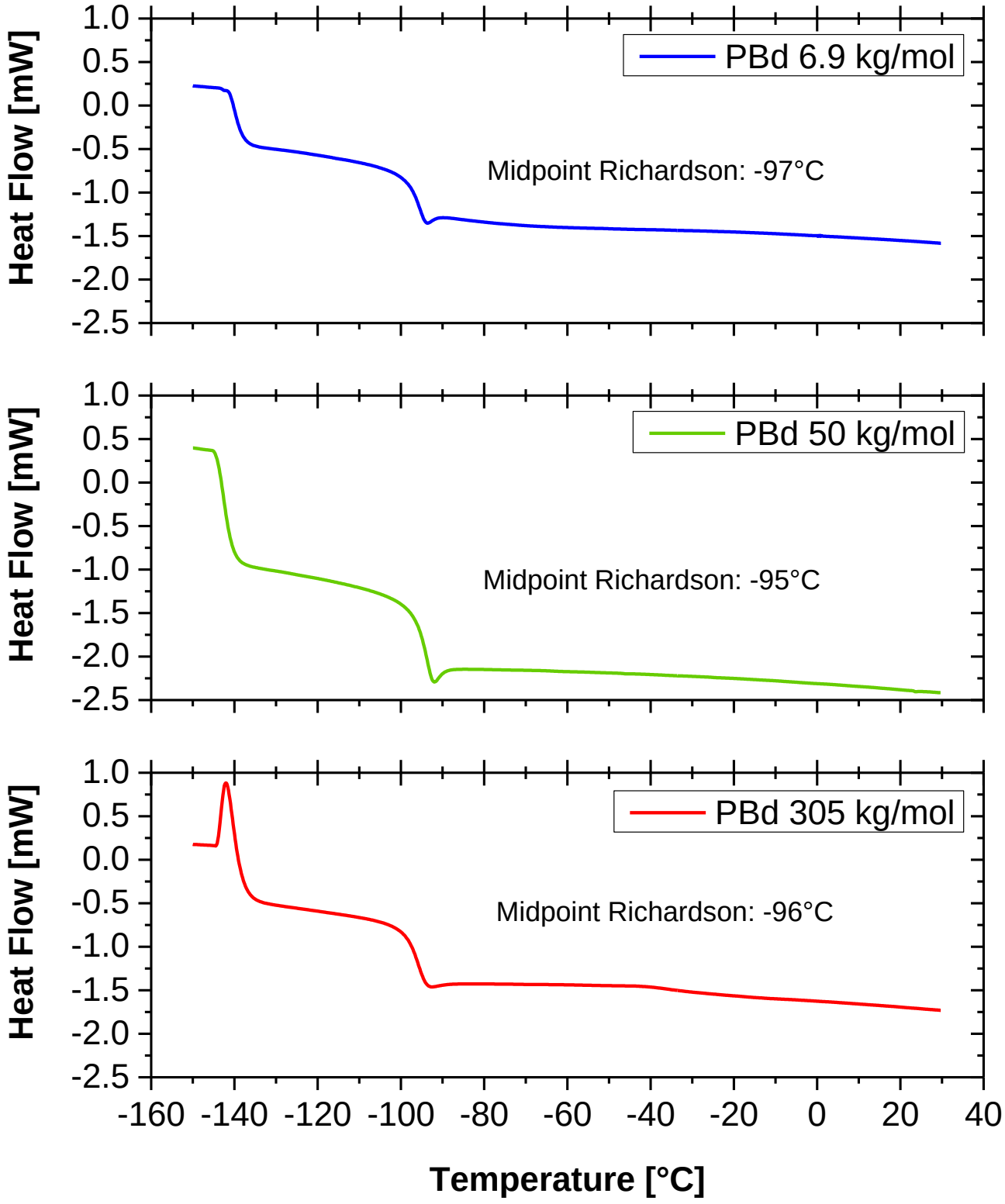

Figure S5. DSC curves of linear Poly(butadiene)s. **Top** with M_w ~ 6.9 kg/mol (blue), **middle** M_w ~ 50 kg/mol (green) and **bottom** M_w ~ 305 kg/mol (red).

The measured T_g of the "gel" chains is lower with respect to two other samples, and if the microstructure is the same we would expect an increase of T_g with M_w.

References.

1. Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. Anionic Polymerization: High Vacuum Techniques *J. Polym. Sci.-Polym. Chem.* **2000**, *38*, 3211-3234.