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

Maksim E. Shivokhin, Daniel J. Read, Dimitris Kouloumasis, Rok Kocen, Flanco Zhuge,
Christian Bailly, Nikos Hadjichristidis, Alexei E. Likhtman

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 Mw = 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 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.

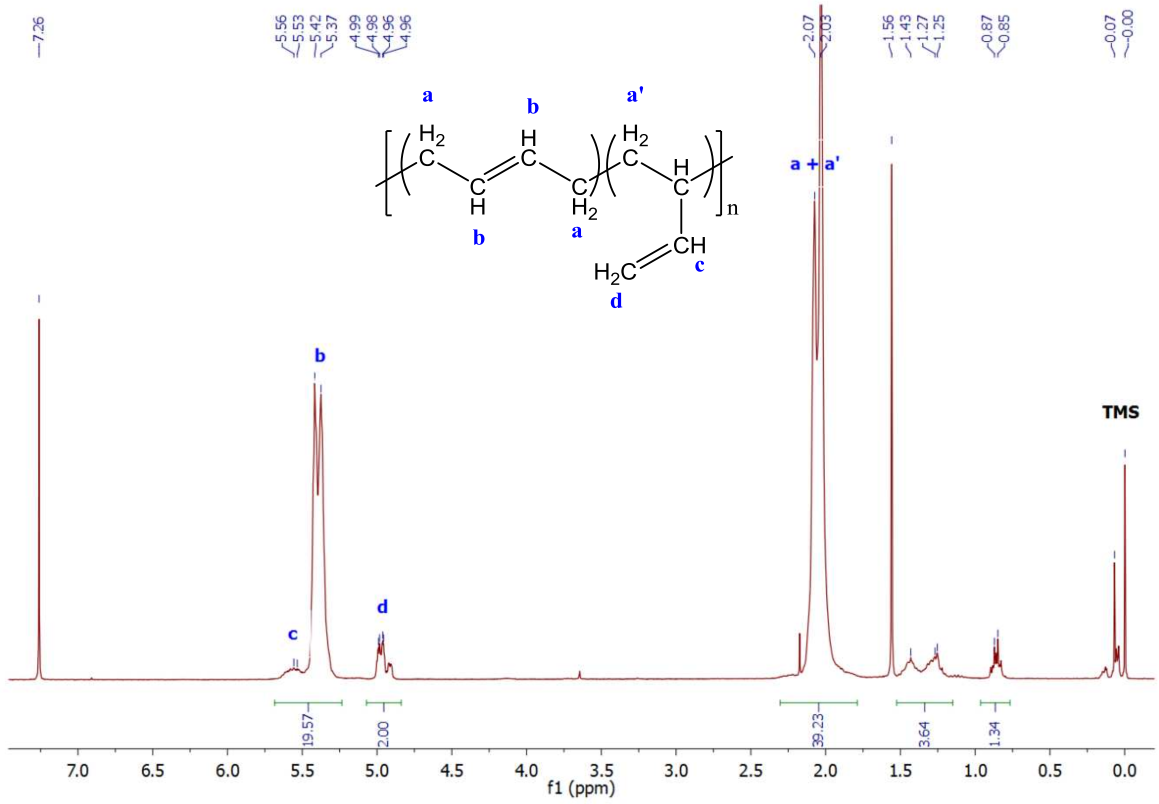

Figure S1. ^{1}H-NMR (300 MHz, $CHCl_3$-d, ppm) spectra of linear PBd with M_w = 6.9 kg/mol.

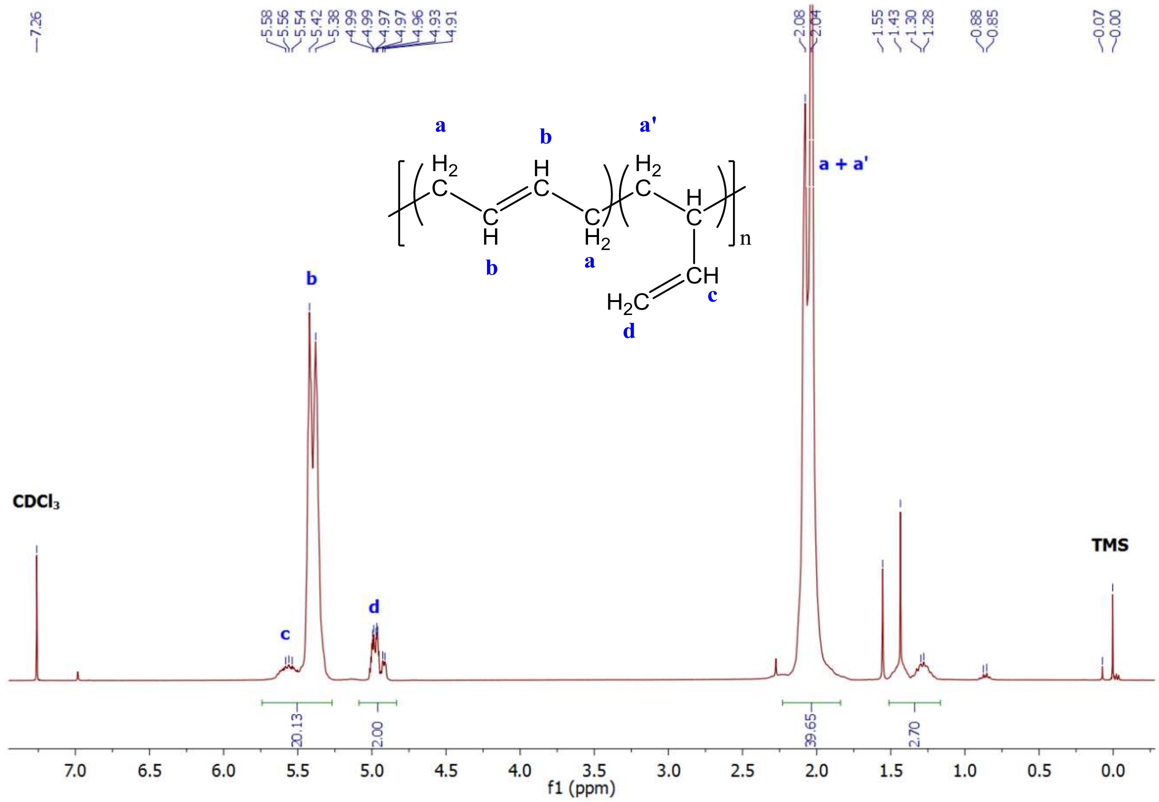

Figure S2. ^{1}H-NMR (300 MHz, $CHCl_3$-d, ppm) spectra of linear PBd with M_w = 50 kg/mol.

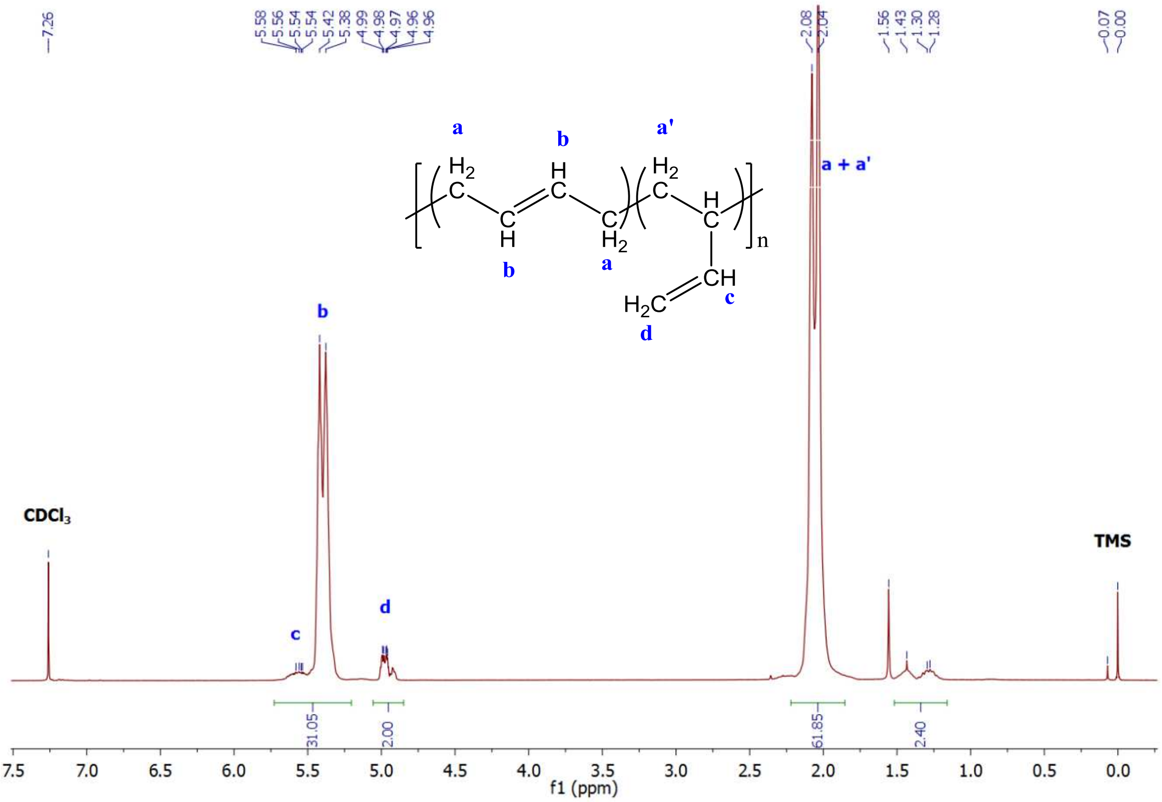

Figure S3. ^{1}H-NMR (300 MHz, $CHCl_3$-d, ppm) spectra of linear PBd with M_w = 305 kg/mol.

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

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.

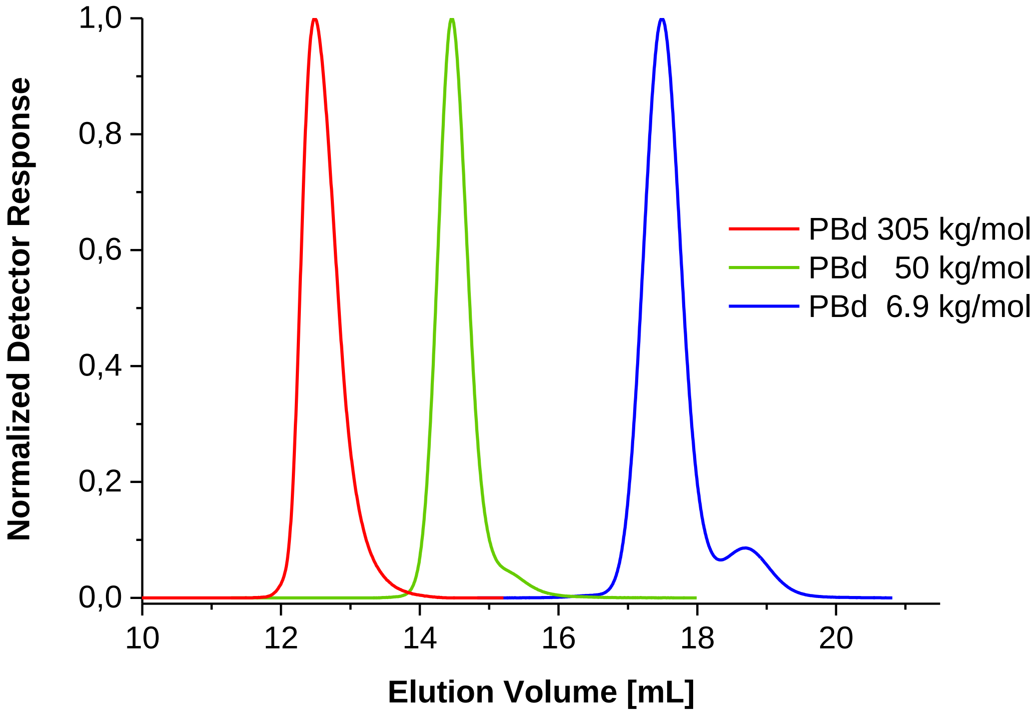

Figure S4. SEC traces of linear Poly(butadiene)s with M_w = 6.9 kg/mol (blue), M_w = 50 kg/mol (green) and M_w = 305 kg/mol (red).

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 thermographs.

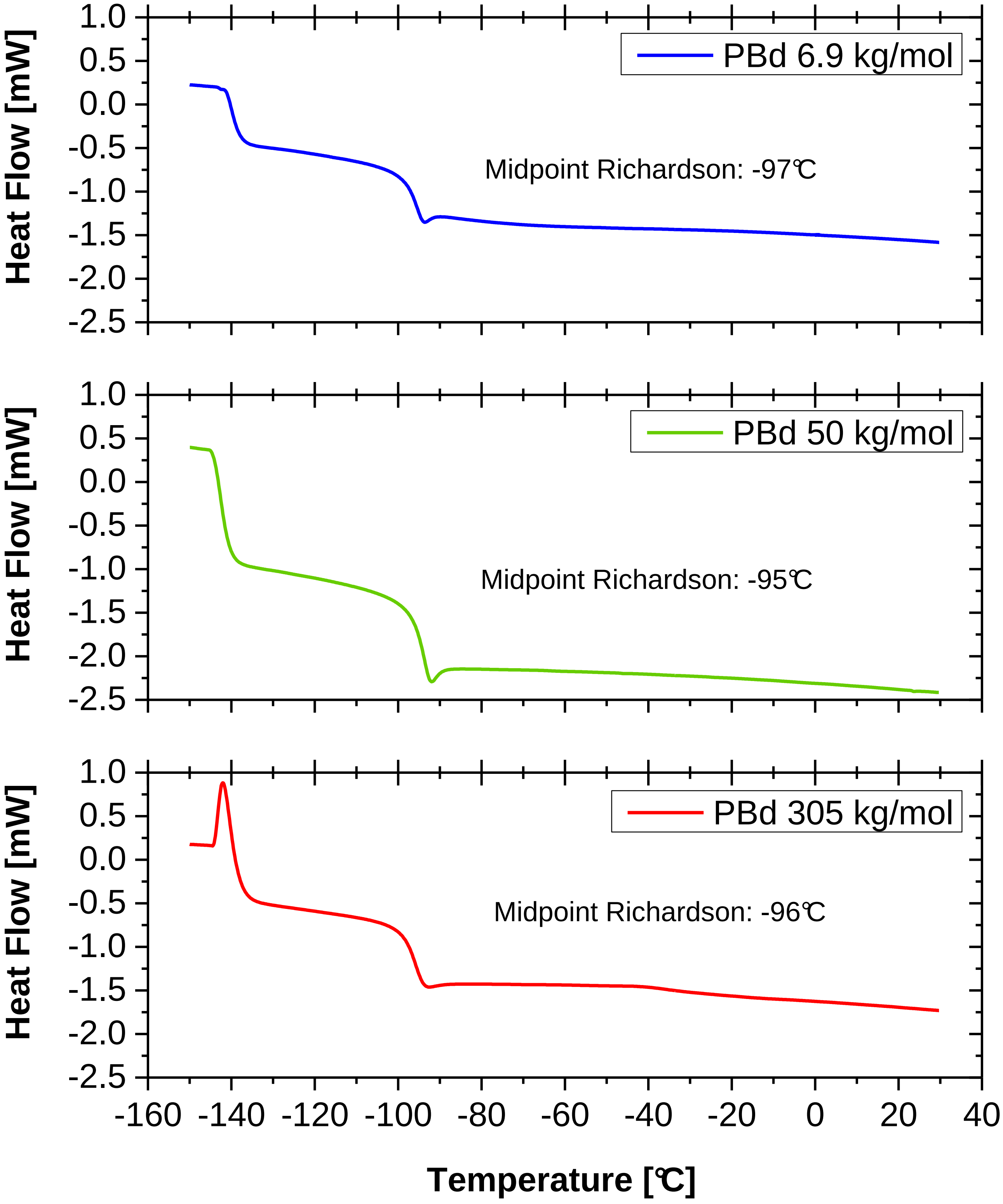
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
Heat Flow [mW]
PBd 6.9 kg/mol
Midpoint Richardson: -97℃
PBd 50 kg/mol
Midpoint Richardson: -95℃
PBd 305 kg/mol
Midpoint Richardson: -96℃
-160
-140
-120
-100
-80
-60
-40
-20
0
20
40
Temperature [℃]

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.