Electronic Supporting Information for

Understanding and controlling the glass transition of HTPB oligomers

Eleftheria Dossi,*[a] Jacob Earnshaw,[b] Laurence Ellison,[b] Gabriella Rabello dos Santos,[c] Hamish Cavaye,[d] Douglas J. Cleaver [b]

[a] Centre for Defence Chemistry, Cranfield University, Defence Academy of United Kingdom, Shrivenham, SN6 8LA, UK

[b] Materials and Engineering Research Institute, Sheffield Hallam University, City Campus, Howard Street, Sheffield, S1 1WB, UK

[c] Instituto Militar de Engenharia, Praca Gen Tiburcio, nr 80, Praia Vermelha (22290-270), Rio de Janeiro - RJ, Brasil

[d] Isis Neutron and Muon Source, Rutherford Appleton Laboratory, Science and Technology Facilities Council, Didcot, OX11 0QX, UK

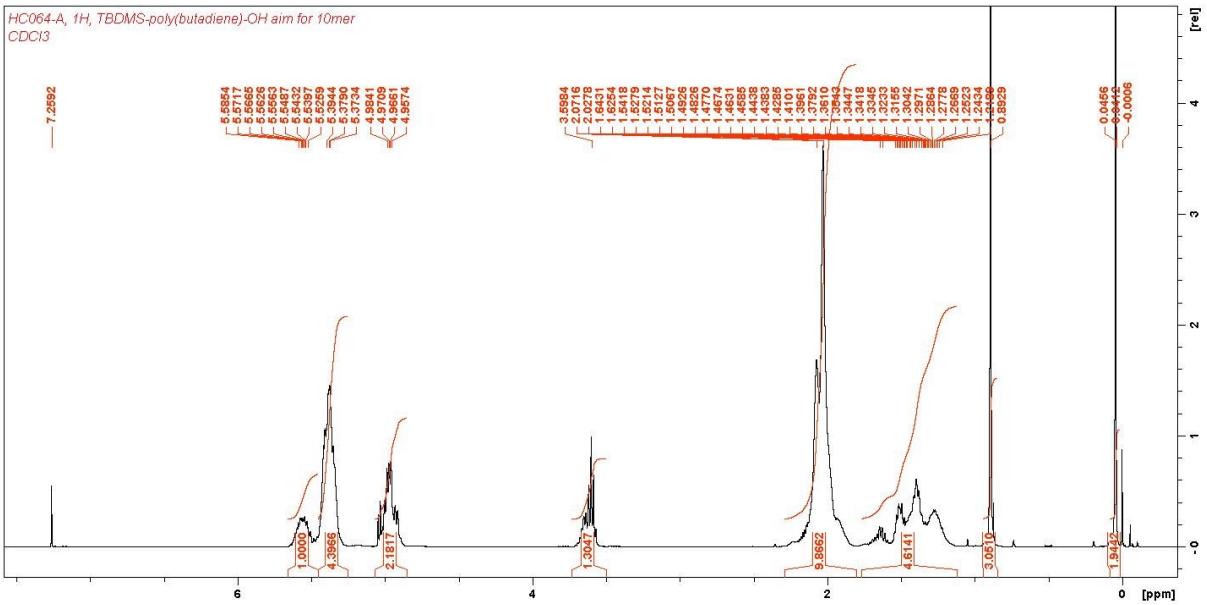

Fig. S1 **^{1}H-**NMR spectrum of MHTPB-Tol-25-10 in $CDCl_3$. The sample was made by polymerization of 1,3-butadiene (20 wt% solution in toluene) in toluene at 25 °C using 10 %mol initiator.

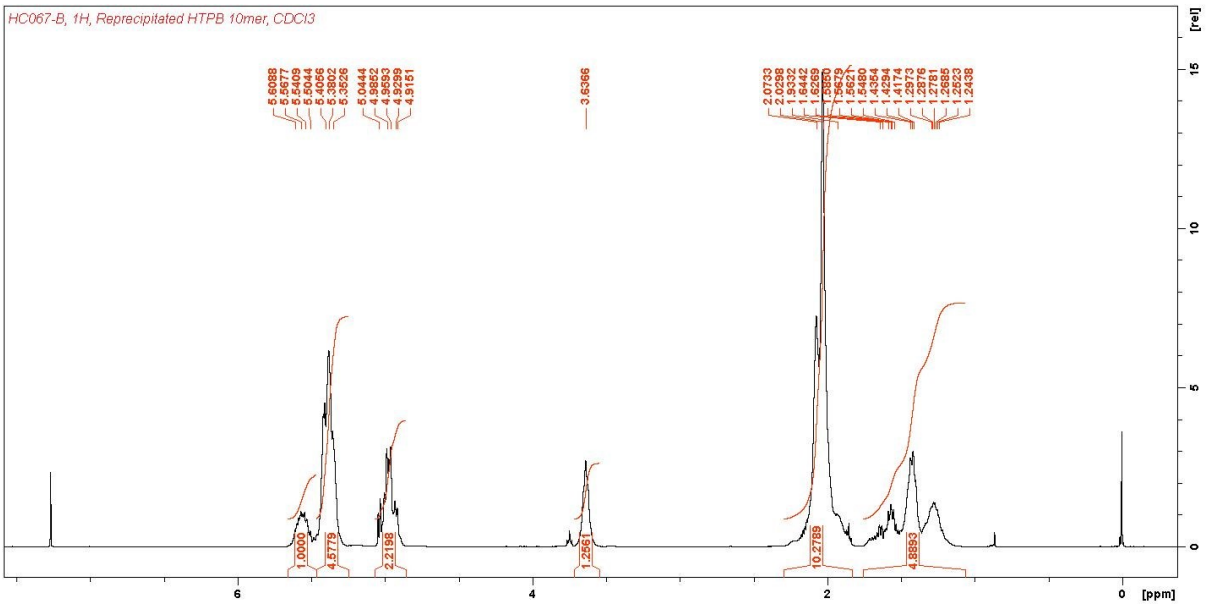

Fig. S2 **^{1}H-**NMR spectrum of HTPB-Tol-25-10 in $CDCl_3$. The sample was made by polymerization of 1,3-butadiene (20 wt% solution in toluene) in toluene at 25 °C using 10 %mol initiator.

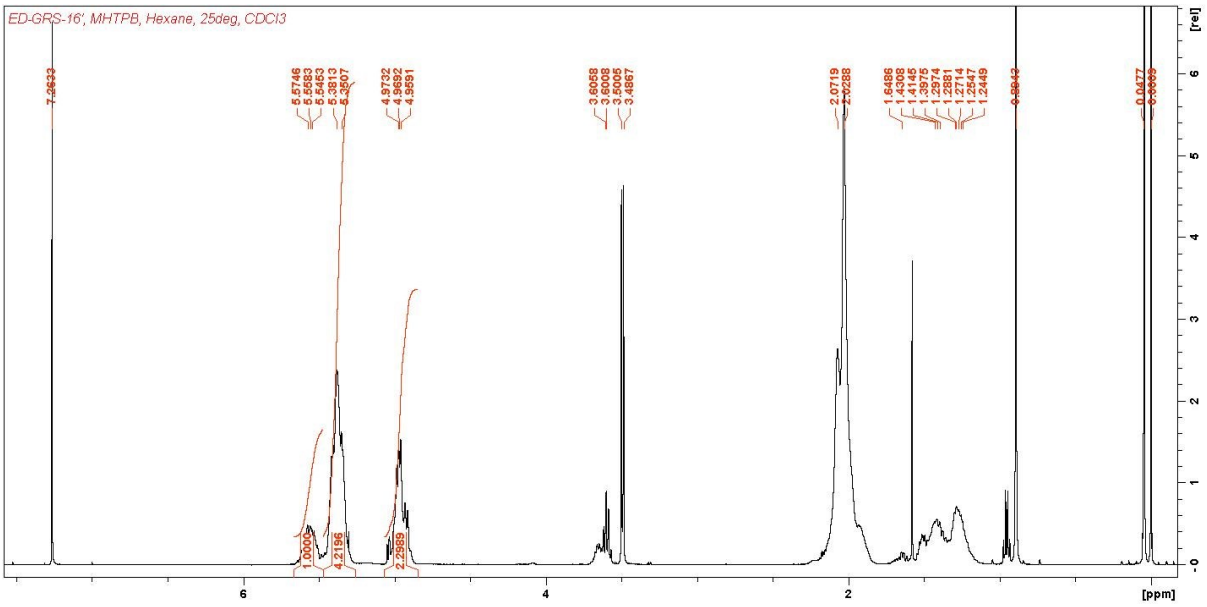

Fig. S3 ^{1}**H**-NMR spectrum of MHTPB-Hex-25 in $CDCl_3$. The sample was made by polymerization of 1,3-butadiene (15 wt% solution in hexane) in hexane at 25 ^{o}C using 10 %mol initiator.

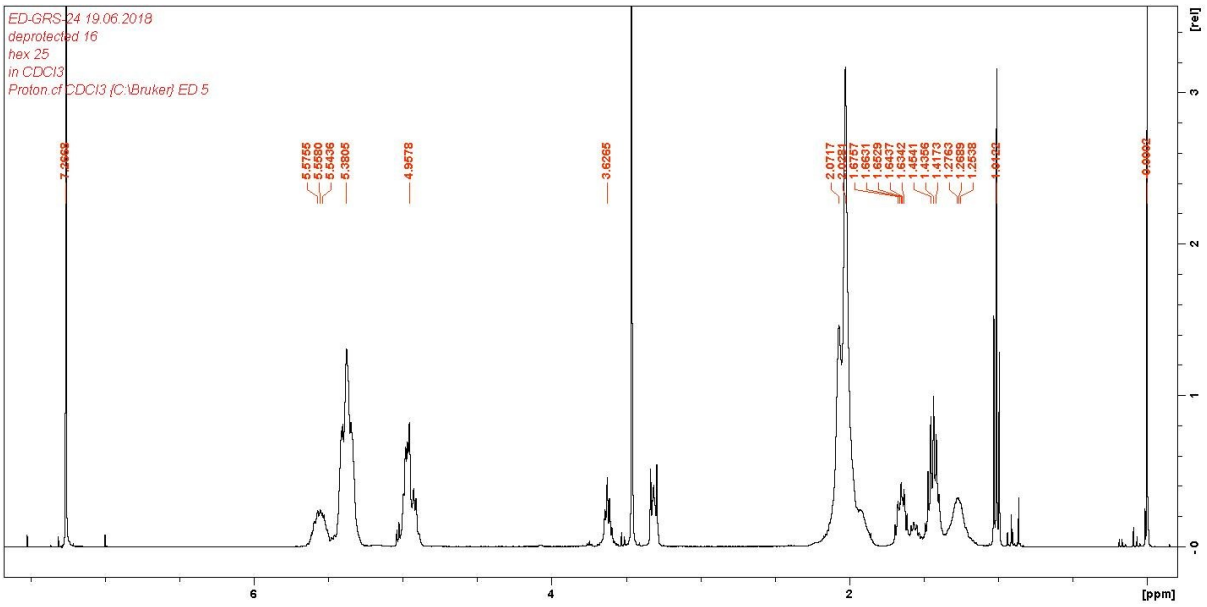

Fig. S4 ^{1}**H**-NMR spectrum of HTPB-Hex-25 in $CDCl_3$. The sample was made by polymerization of 1,3-butadiene (15 wt% solution in hexane) in hexane at 25 ^{o}C using 10 %mol initiator.

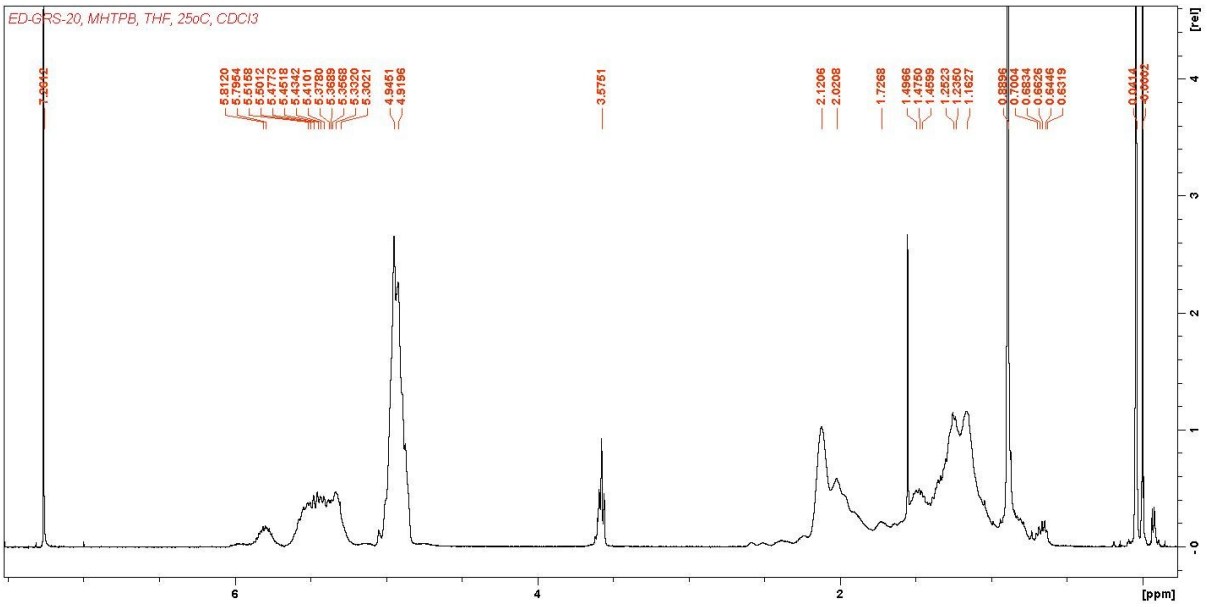

Fig. S5 ^{1}H-NMR spectrum of MHTPB-THF-25 in $CDCl_3$. The sample was made by polymerization of 1,3-butadiene (13 wt% solution in THF) in THF at 25 ^{o}C using 10 %mol initiator.

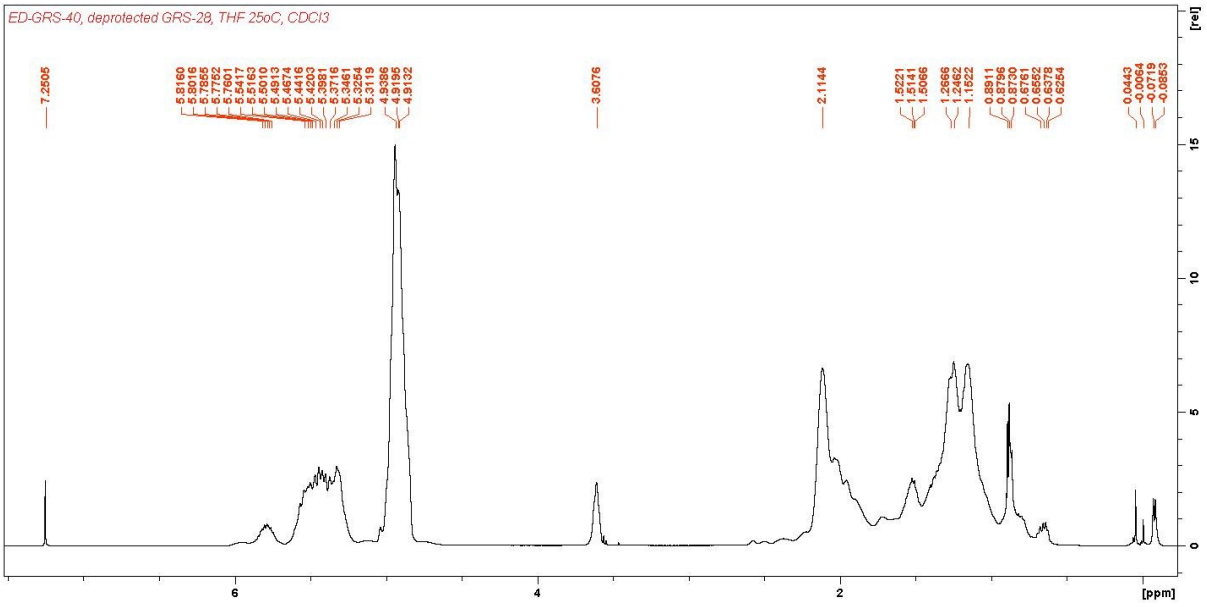

Fig. S6 ^{1}H-NMR spectrum of HTPB-THF-25 in $CDCl_3$. The sample was made by polymerization of 1,3-butadiene (13 wt% solution in THF) in THF at 25 ^{o}C using 10 %mol initiator.

Video S1 HTPB311 - Four Temperatures Video Description

The following information describes the parameters for the molecular dynamics video associated with this publication 'Understanding and controlling the glass transition of HTPB oligomers'. The video displays 4 independent simulations taken from the same cooling sequence of 70 HTPB10_311 molecules. We show simulations from four different temperatures situated above and below the calculated glass transition temperature of 182K. Each simulation has been visualised and captured with the VMD (Visual Molecular Dynamics) software. In total, each simulation has 500 000 timesteps with every 200th timestep being captured, resulting in 2500 frames per video. All simulations have been performed in the constant-*NPT* ensemble, with the same molecule and visualisation state being identified for each temperature. The simulation cell contains a total of 7280 atoms (70 molecules) however the remaining 69 molecules have been omitted for clarity of the molecular motion of the individual, selected molecule.

In the 100K simulation (Top left), the structure of the HTPB oligomer is conformationally locked in place between its neighbours. This behaviour is characteristic to glassy nature of the HTPB system at this temperature where very few molecular degrees of freedom are available. As the simulated system is warmed to 200K (Top right) initial indications are apparent of the modes of molecular motion that first become available nearer the glass transition temperature. The terminal CH_3OH groups obtain some degree of rotational freedom and, within the main chain, there is some crankshaft motion at time-marks 00:28, 00:38 and 01:10 during the video. At 250K (Bottom Left) and crankshaft motion of the trans groups becomes more prolific and at 300K (Bottom Right) it can be observed throughout the simulation.

Table S1 Comparing conformation related parameters for HTPB10_311 and HTPB10_401.

T (K)	r_ee[1] [Å]		S1		S2		S3	
	HTPB_311	HTPB_401	HTPB_311	HTPB_401	HTPB_311	HTPB_401	HTPB_311	HTPB_401
120	19.944	20.203	3.572	3.547	10.357	9.565	53.615	55.673
130	19.968	20.243	3.572	3.550	10.386	9.585	53.673	55.778
140	19.996	20.287	3.576	3.565	10.395	9.566	53.894	55.953
150	19.993	20.275	3.575	3.552	10.393	9.593	53.938	55.980
160	20.022	20.307	3.584	3.566	10.398	9.557	54.003	56.004
170	19.987	20.364	3.566	3.567	10.377	9.582	53.885	56.112
180	19.941	20.423	3.580	3.551	10.381	9.558	53.834	56.471
190	20.014	20.402	3.591	3.573	10.339	9.568	54.006	56.369
200	20.126	20.441	3.601	3.576	10.409	9.578	54.347	56.603
210	20.216	20.428	3.620	3.557	10.400	9.552	54.509	56.691
220	20.101	20.487	3.603	3.561	10.411	9.568	54.413	56.837
230	20.166	20.586	3.655	3.627	10.502	9.587	54.644	57.244
240	20.205	20.632	3.686	3.645	10.490	9.505	54.651	57.376
250	20.270	20.630	3.543	3.623	10.463	9.609	55.026	57.274
260	20.186	20.471	3.606	3.659	10.578	9.840	54.601	56.214
270	20.318	20.587	3.630	3.612	10.617	9.835	54.375	56.517
280	20.158	20.548	3.674	3.582	10.483	9.817	54.631	56.480
290	20.079	20.504	3.643	3.556	10.395	9.944	55.275	56.541
300	20.067	21.074	3.381	3.527	10.707	9.757	55.492	58.490
400	18.848	20.815	3.290	3.322	10.952	9.858	52.459	60.498
500	19.095	20.832	3.371	3.272	10.493	10.261	52.629	59.420
600	20.326	19.844	3.317	3.398	10.146	10.399	56.614	54.890
700	19.242	20.305	3.406	3.390	10.173	10.265	52.783	56.617
800	19.128	19.599	3.464	3.467	10.176	10.124	50.870	53.627

1. r_ee is the end-to-end distance, S1, S2, S3 are the principal moments of the gyration tensor.

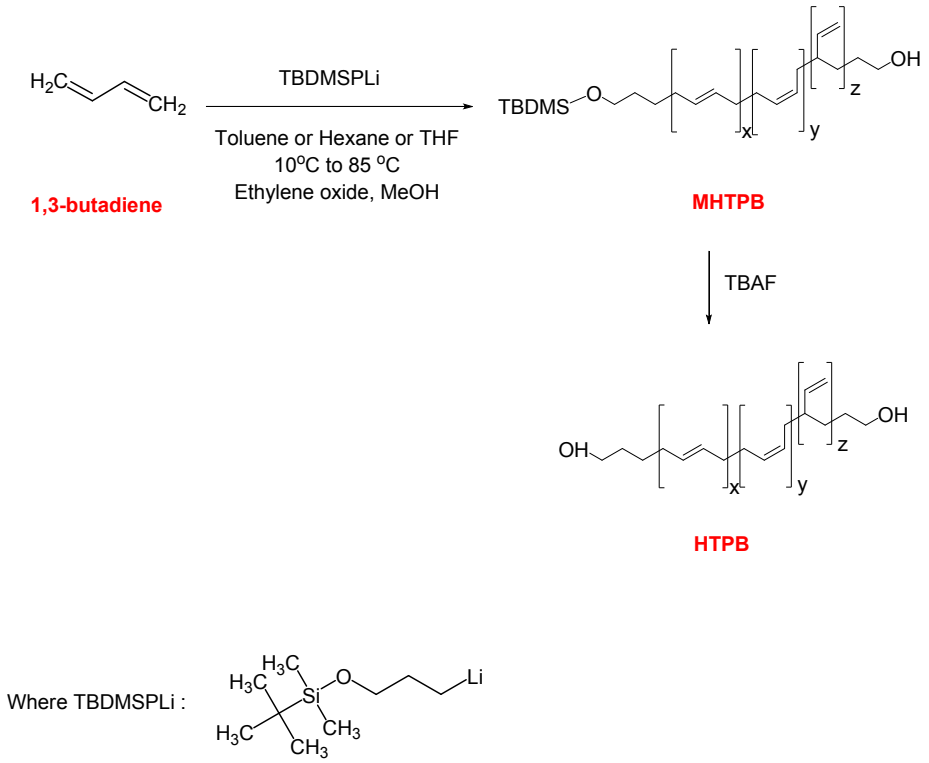

Fig. S7 Synthesis of MHTPB and HTPB in non-polar and polar solvents.

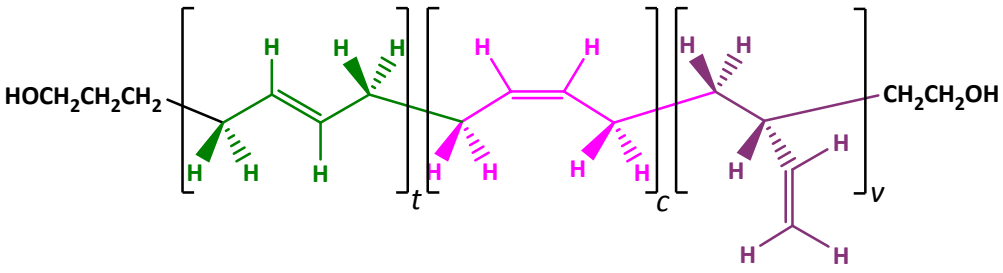

Fig. S8 Schematic representation of chemical structure of synthesised HTPB with *t*, *c* and *v* units randomly distributed in the main chain.

Table S2 Synthesis of MHTPB and HTPB samples, relative microstructure and T_g

Sample	Polymerisation Reaction[1]				Microstructure[2]			T_g[3] (°C)
	Solvent	T (°C)	Initiator (% mol)	Yield[4] (%)	Trans (1,4)	Cis (1,4)	Vinyl (1,2)	
MHTPB-Hex-25	Hexane	25	10	30	47	18	35	-85
HTPB-Hex-25				32	47	19	34	-74
MHTPB-Hex-35		35	10	55	49	19	32	-88
HTPB-Hex-35				100	49	19	32	-78
MHTPB-Hex-45		45	10	50	51	22	27	-87
HTPB-Hex-45				56	51	23	26	-80
MHTPB-Tol-10	Toluene	10	10	85	45	18	37	-79
HTPB-Tol-10				32	49	20	32	-81
MHTPB-Tol-25-30[5]		25	30	75	50	10	40	-89
HTPB-Tol-25-30[5]				30				-79
MHTPB-Tol-25-15[5]			15	40	52	18	30	-87
HTPB-Tol-25-15[5]				72				-81
MHTPB-Tol-25-10[5]			10	40	51	22	27	-87
HTPB-Tol-25-10[5]				51				-81
MHTPB-Tol-25			10	40	48	19	33	-84
HTPB-Tol-25				n.a.	48	19	33	-77
MHTPB-Tol-25-7[5]			7	63	52	22	26	-86
HTPB-Tol-25-7[5]				67				-82
MHTPB-Tol-25-3.5[5]			3.5	59	52	20	28	-88
HTPB-Tol-25-3.5[5]				88				-86
MHTPB-Tol-35		35	10	37	50	21	29	-86
HTPB-Tol-35				n.a.	49	21	30	-77
MHTPB-Tol-45		45	10	72	51	22	27	-89
HTPB-Tol-45				61	51	23	26	-84
MHTPB-Tol-55		55	10	61	52	23	25	-91
HTPB-Tol-55				45	52	24	24	-84
MHTPB-Tol-75		75	10	61	55	26	19	-95
HTPB-Tol-75				n.a	55	26	19	-90
MHTPB-Tol-85		85	10	100	56	26	18	-95
HTPB-Tol-85				72	56	26	18	-92
MHTPB-THF-25_1[6]	THF	25	10	83	14	0	86	-39
HTPB-THF-25_1[6]				74	4	0	96	-27
MHTPB-THF-25_2[6]				87	4	0	96	-32
HTPB-THF-25_2[6]				74	6	0	94	-24
MHTPB-THF-25_3[6]				87	4	0	96	-33
HTPB-THF-25_3[6]				55	6	0	94	-21
MHTPB-THF-45		45		77	6	0	94	-33
HTPB-THF-45				72	6	0	94	-27

1. From 1,3-butadiene in hexane (15 wt%), toluene (15 wt%) and THF (13 wt%).
2. From ^{1}H-NMR in $CDCl_3$.
3. From DSC, 40 µl aluminium pan, N_2 50 ml min^{-1}, -150 °C to 25 °C.
4. Very approximated yields of MHTPB products due to the low concentration of 1,3-butadiene in hexane, toluene and THF solutions.
5. From 1,3-butadiene in toluene (20 wt%).
6. Repeated synthesis.

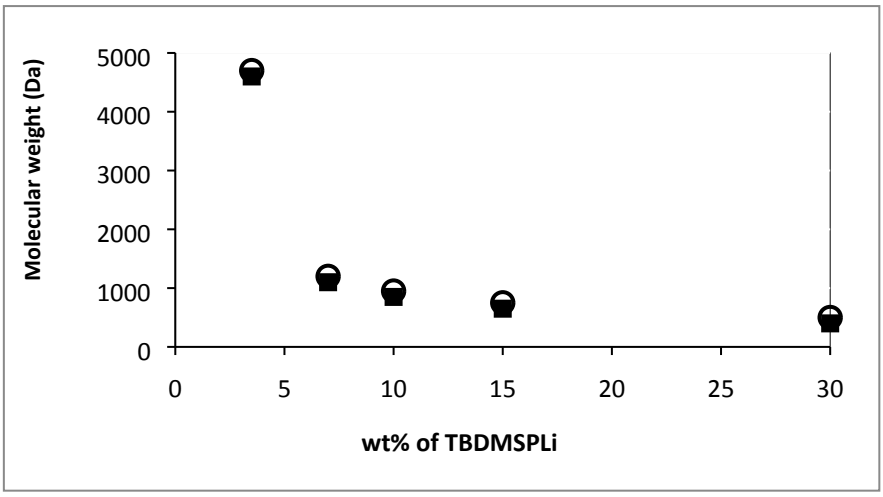

Fig. S9 Molecular weight of MHTPB (Circles) and HTPB (Squares) samples made in toluene at 25 ^{o}C, versus wt% of TBDMSPLi initiator calculated by ^{1}H NMR signals.

All synthetic MHTPB and HTPB samples were thermally characterised by DSC. The testing temperature was cycled two times between –150 and 30 °C. The glass transition temperature reported in Table S3 were determined from the second heating. An example of the cyclic thermogram is reported in Figure S9 and detailed single thermograms in Figure S10 to S13. To note that in all samples an endothermic relaxation observed during heating. [ref]

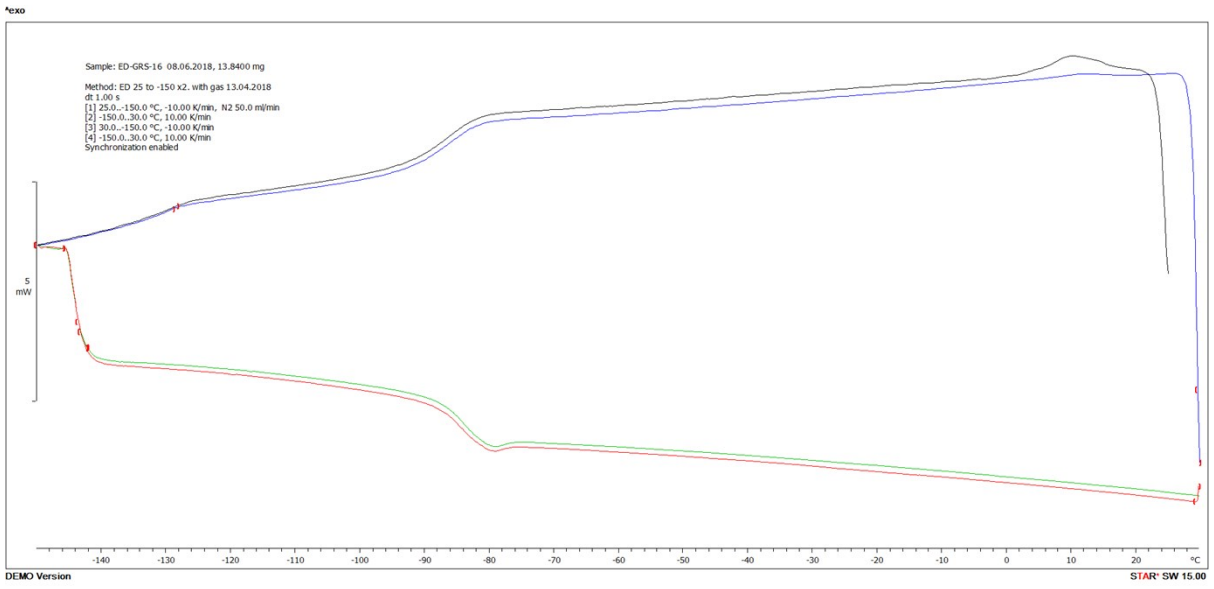

Fig. S10 Cyclic DSC thermograms of the glass transition of MHTPB-Hex-25 between -150 ^{o}C and 30 ^{o}C, at 10 ^{o}C min^{-1}.

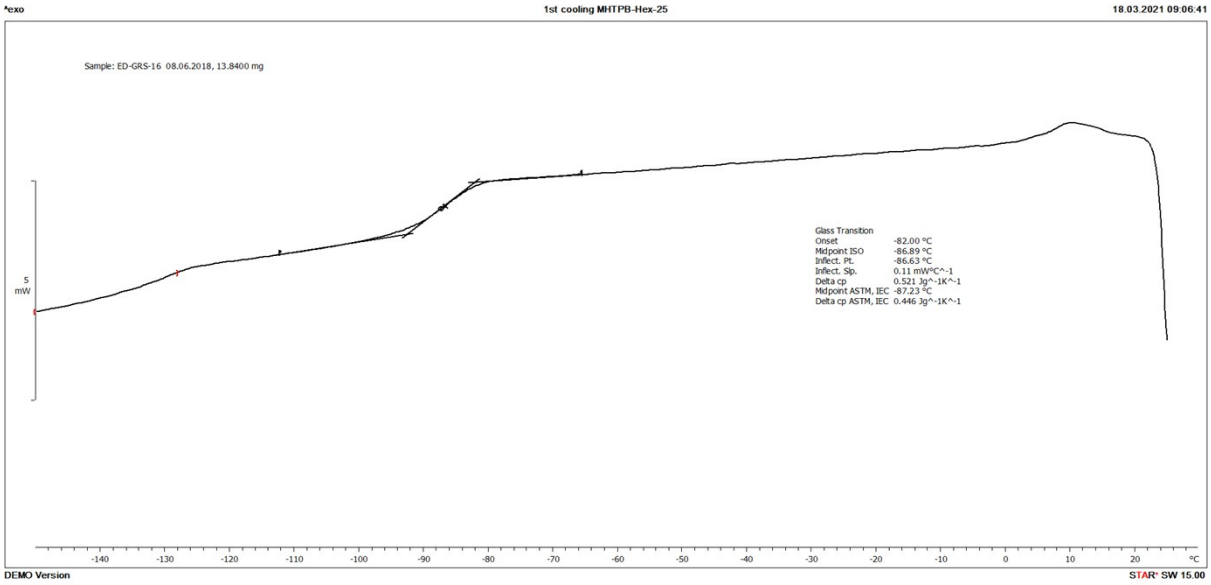

Fig. S11 DSC thermogram of the glass transition of MHTPB-Hex-25 between 30 °C and -150 °C, 1st cooling, at 10 °C min^{-1}.

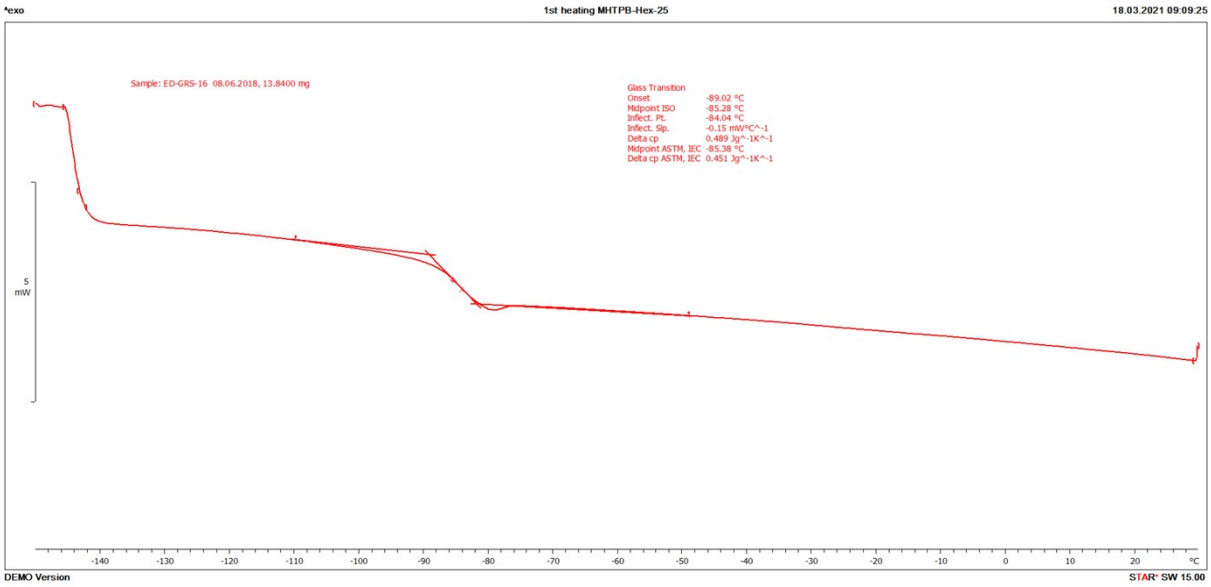

Fig. S12 DSC thermogram of the glass transition of MHTPB-Hex-25 between -150 °C and 30 °C, 1st heating, at 10 °C min^{-1}.

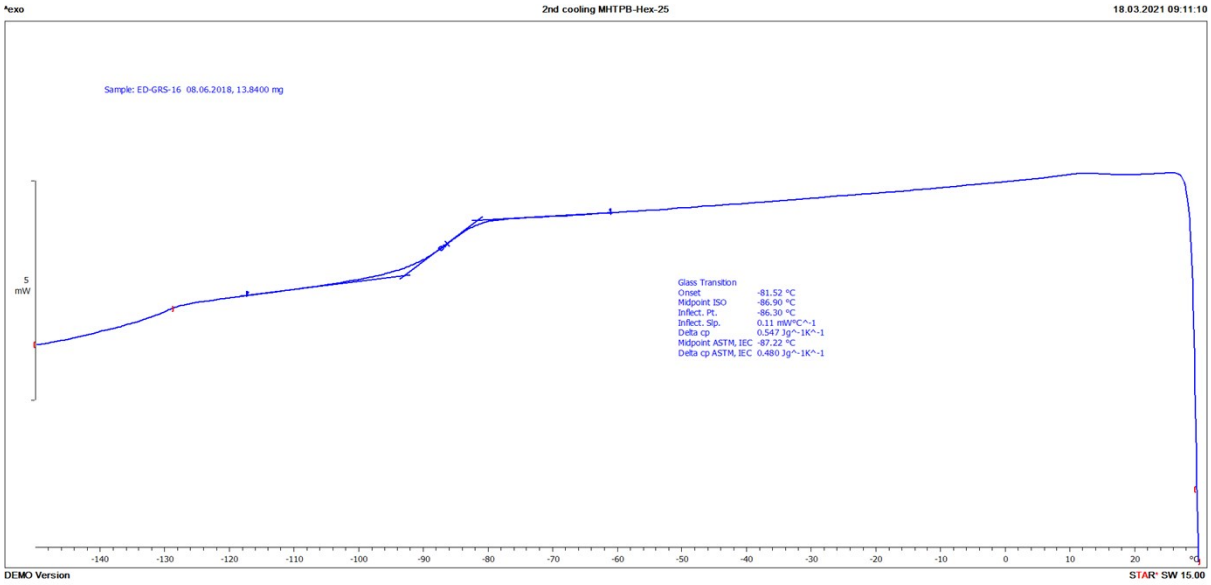

Fig. S13 DSC thermogram of the glass transition of MHTPB-Hex-25 between 30 °C and -150 °C, 2nd cooling, at 10 °C min^{-1}.

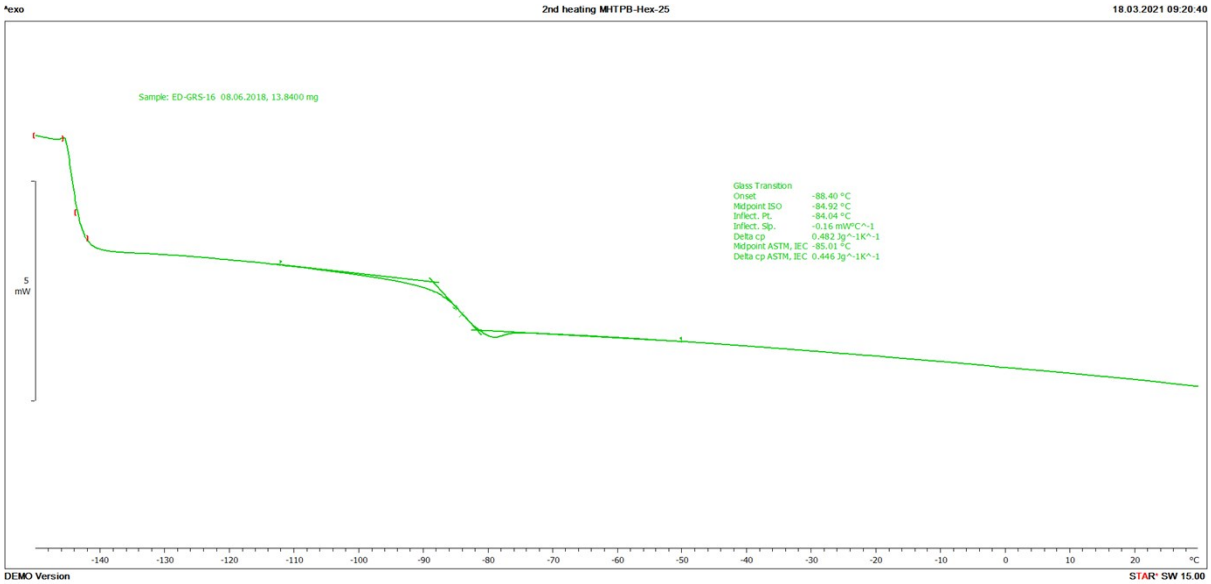

Fig. S14 DSC thermogram of the glass transition of MHTPB-Hex-25 between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}.

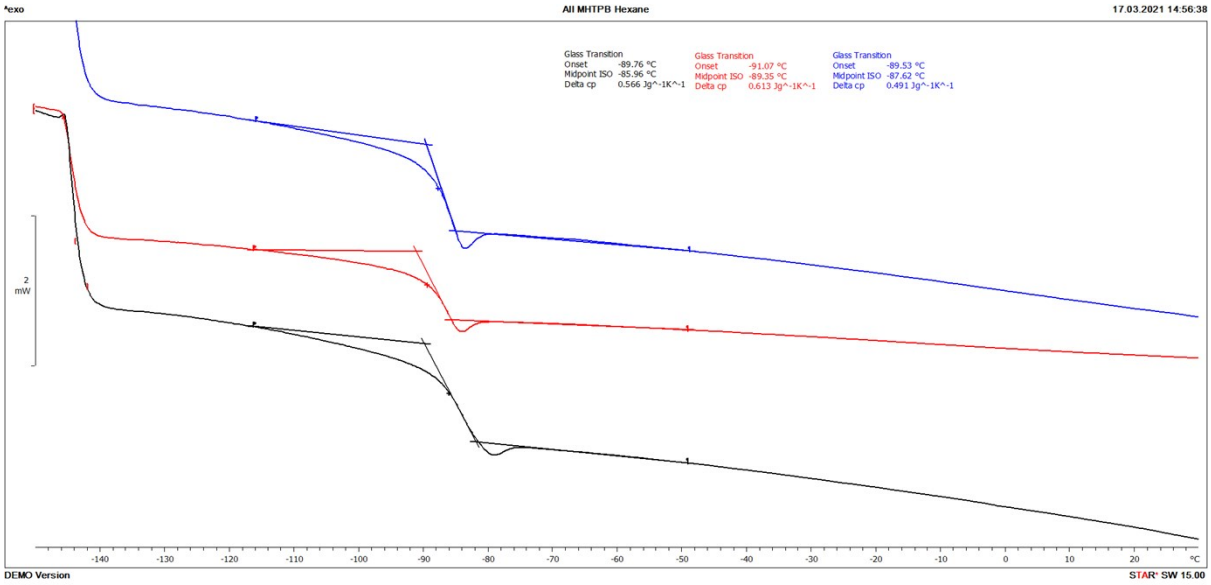

Fig. S15 DSC thermograms of the glass transition of MHTPB-Hex-25 (Black line), MHTPB-Hex-35 (Red line) and MHTPB-Hex-45 (Blue line) between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}. All samples were made from 15% 1,3-butadiene solution in hexane.

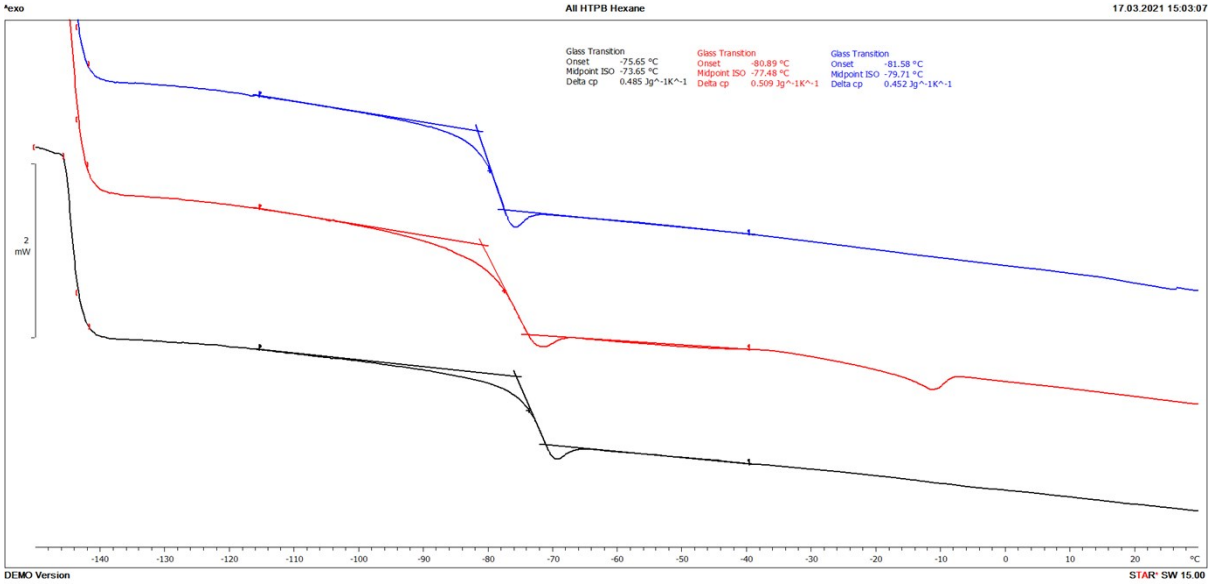

Fig. S16 DSC thermograms of the glass transition of HTPB-Hex-25 (Black line), HTPB-Hex-35 (Red line) and HTPB-Hex-45 (Blue line) between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}. All samples were made from 15% 1,3-butadiene solution in hexane.

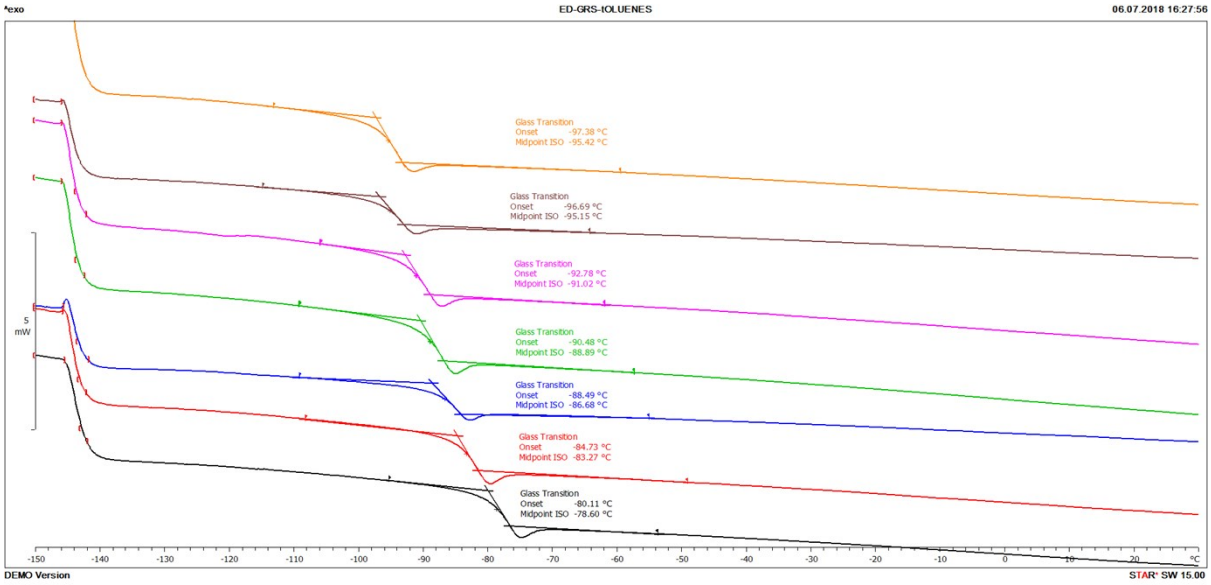

Fig. S17 DSC thermograms of the glass transition of MHTPB-Tol-10 (Black line), MHTPB-Tol-25 (Red line), MHTPB-Tol-35 (Blue line), MHTPB-Tol-45 (Green line), MHTPB-Tol-55 (Purple line), MHTPB-Tol-75 (Brown line) and MHTPB-Tol-85 (Orange line) between -150 ^{o}C and 30 ^{o}C ,2nd heating, at 10 ^{o}C min^{-1}. All samples were made from 15% 1,3-butadiene solution in toluene.

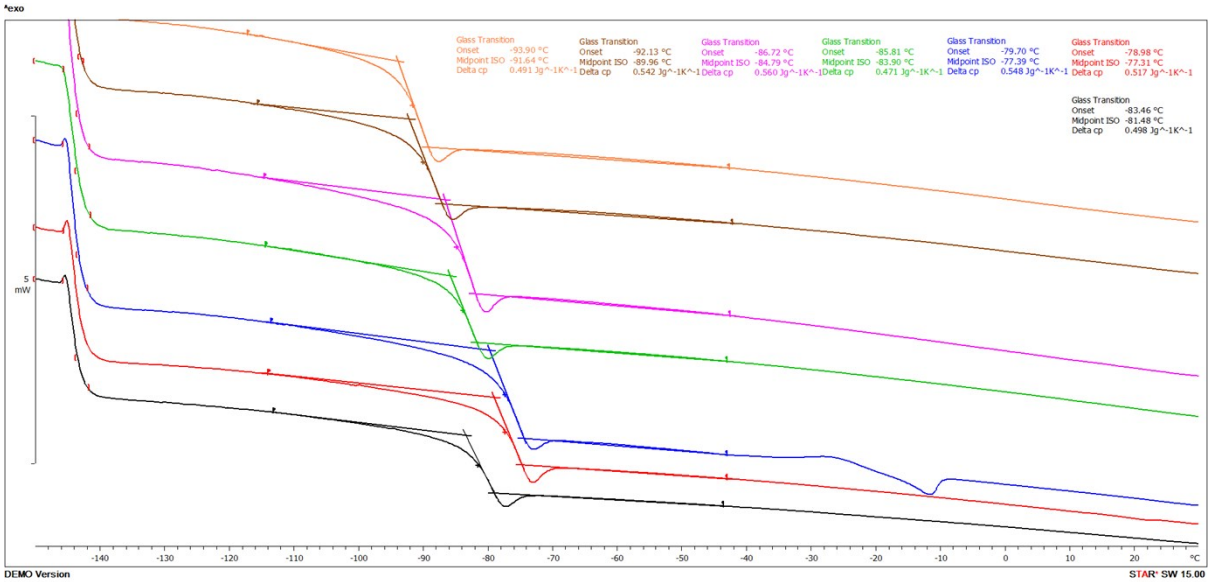

Fig. S18 DSC thermograms of the glass transition of HTPB-Tol-10 (Black line), HTPB-Tol-25 (Red line), HTPB-Tol-35 (Blue line), HTPB-Tol-45 (Green line), HTPB-Tol-55 (Purple line), HTPB-Tol-75 (Brown line) and HTPB-Tol-85 (Orange line) between -150 ^{o}C and 30 ^{o}C, 2nd heating, at 10 ^{o}C min^{-1}. All samples were made from 15% 1,3-butadiene solution in toluene.

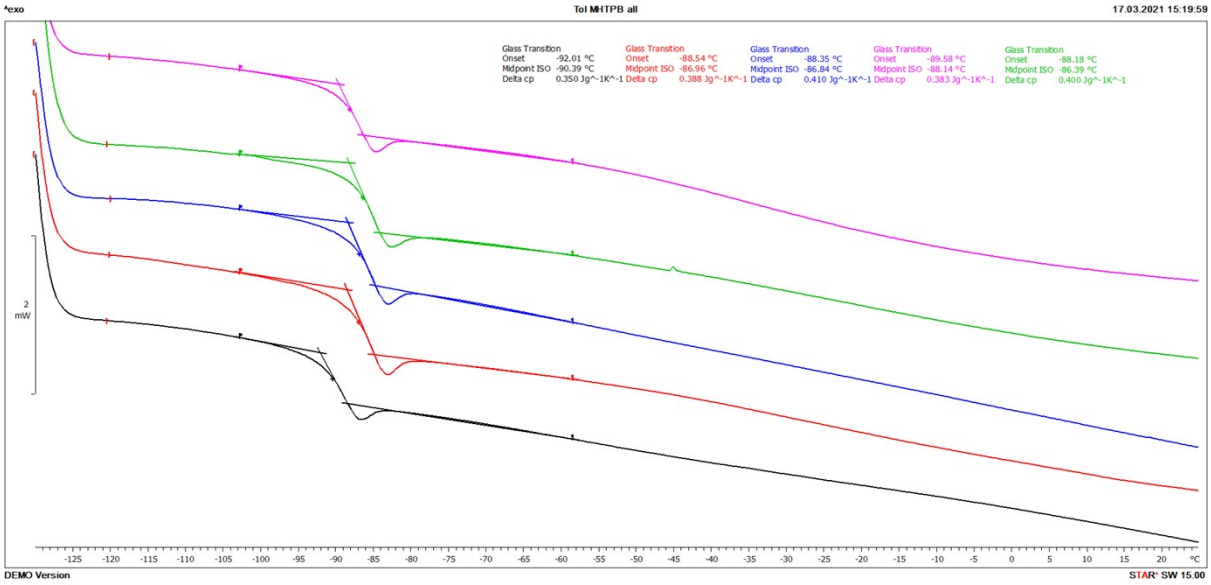

Fig. S19 DSC thermograms of the glass transition of MHTPB-Tol-25-30 (Black line), MHTPB-Tol-25-15 (Red line), MHTPB-Tol-25-10 (Blue line), MHTPB-Tol-25-7 (Green line) and MHTPB-Tol-25-3.5 (Purple line) between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}. All samples were made from 20% 1,3-butadiene solution in toluene and variable amounts of initiator.

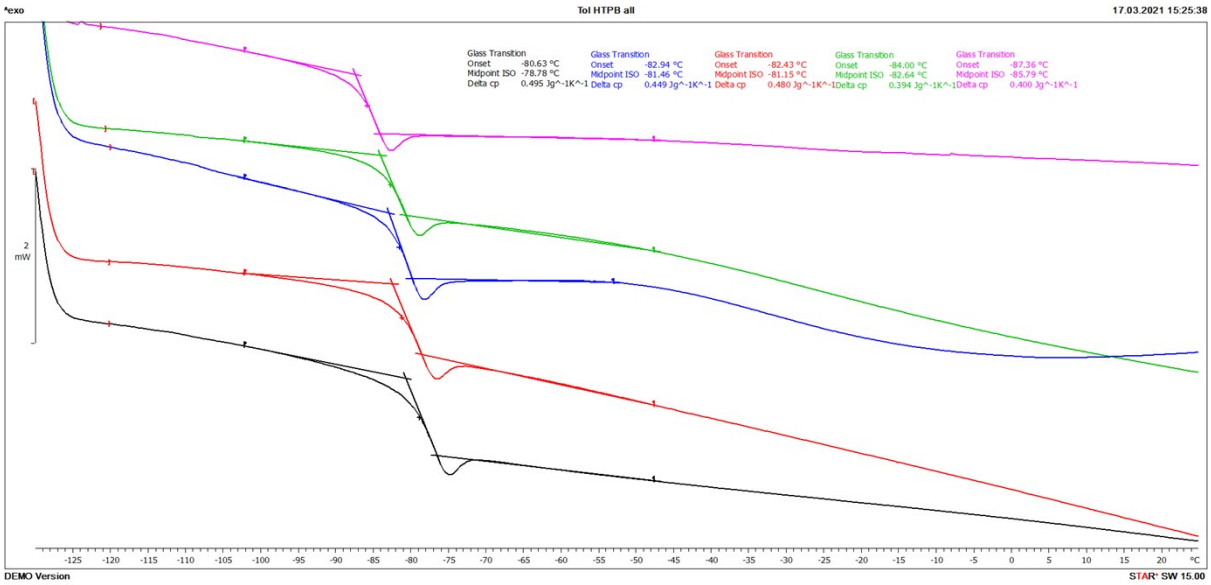

Fig. S20 DSC thermograms of the glass transition of HTPB-Tol-25-30 (Black line), HTPB-Tol-25-15 (Red line), HTPB-Tol-25-10 (Blue line), HTPB-Tol-25-7 (Green line) and HTPB-Tol-25-3.5 (Purple line) between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}. All samples were made from 20% 1,3-butadiene solution in toluene and variable amounts of initiator.

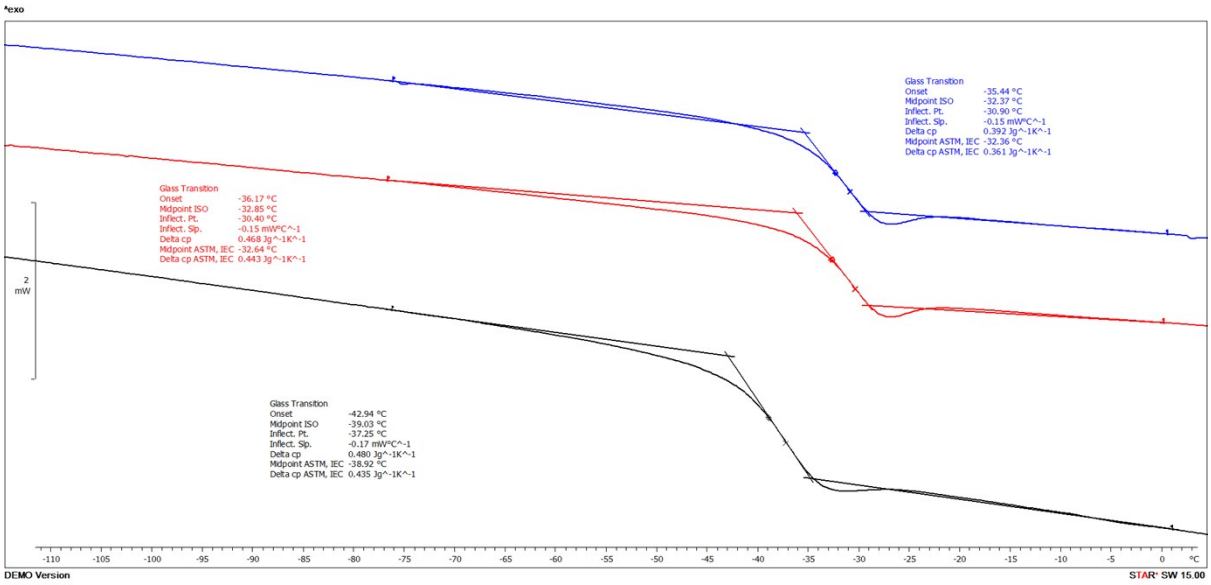

Fig. S21 DSC thermograms of the glass transition of MHTPB-THF-25_1 (Black line), MHTPB-THF-25_2 (Red line) and MHTPB-THF-25_3 (Blue line) between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}. All samples were made from 13% 1,3-butadiene solution in THF.

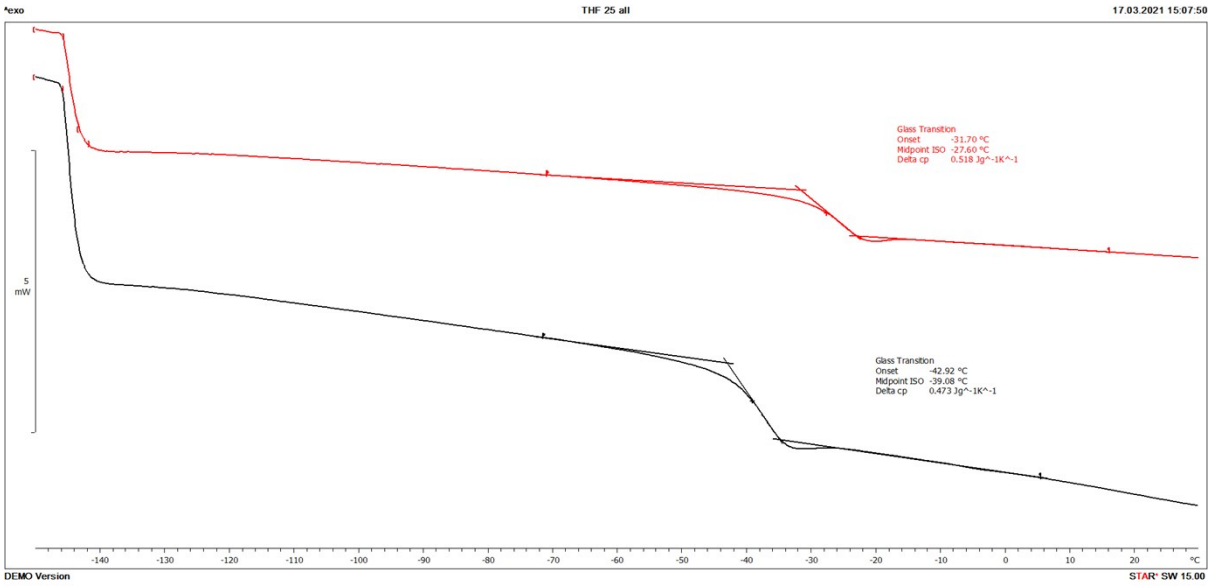

Fig. S22 DSC thermograms of the glass transition of MHTPB-THF-25_1 (Black line), and HTPB-THF-25_1 (Red line) between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}. All samples were made from 13% 1,3-butadiene solution in THF.

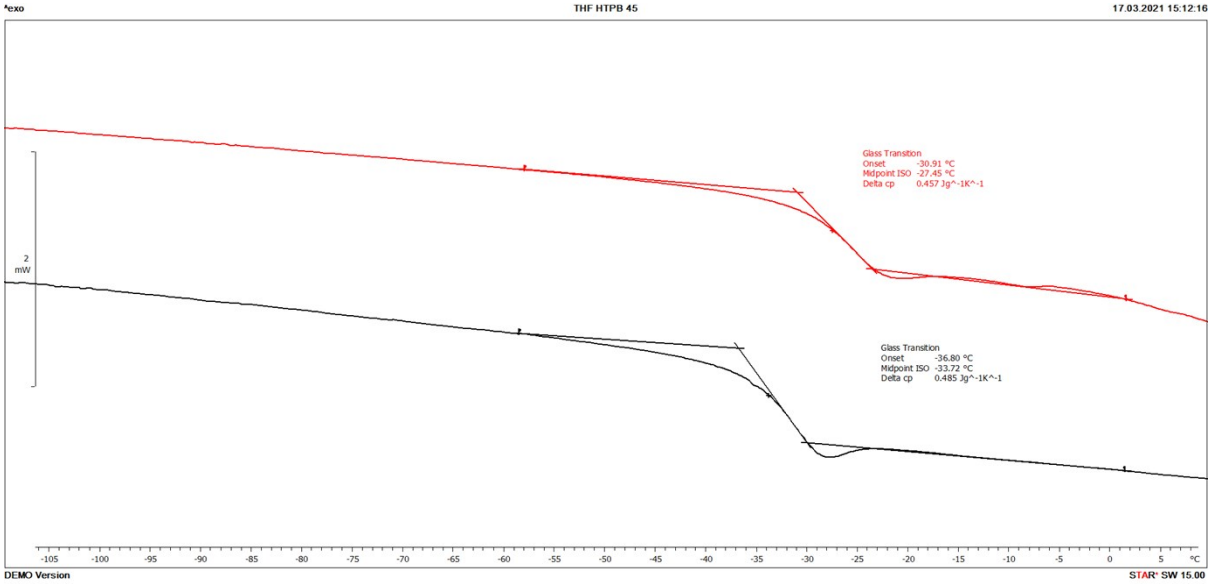

Fig. S23 DSC thermograms of the glass transition of MHTPB-THF-45 (Black line), and HTPB-THF-45 (Red line) between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}. All samples were made from 13% 1,3-butadiene solution in THF.

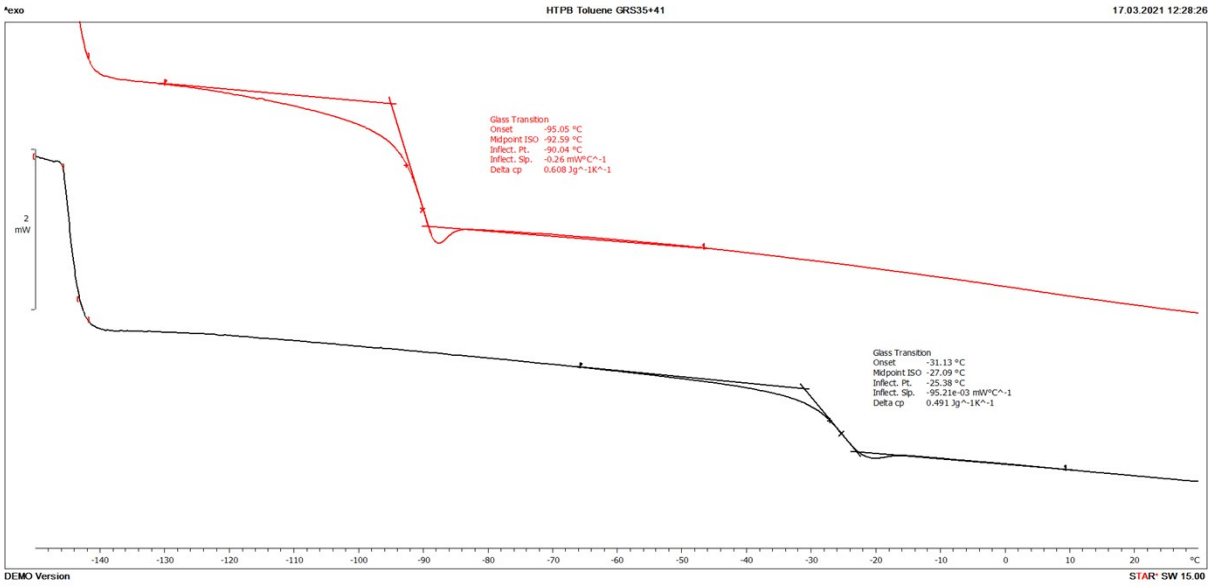

Fig. S24 DSC thermograms of the glass transition of HTPB-THF-25_1 (Black line), and HTPB-Tol-85 (Red line) between -150 °C and 30 °C, 2nd heating, at 10 °C min^{-1}.