

## **Total revalorization of high impact polystyrene (HIPS): enhancing styrene recovery and upcycling of the rubber phase**

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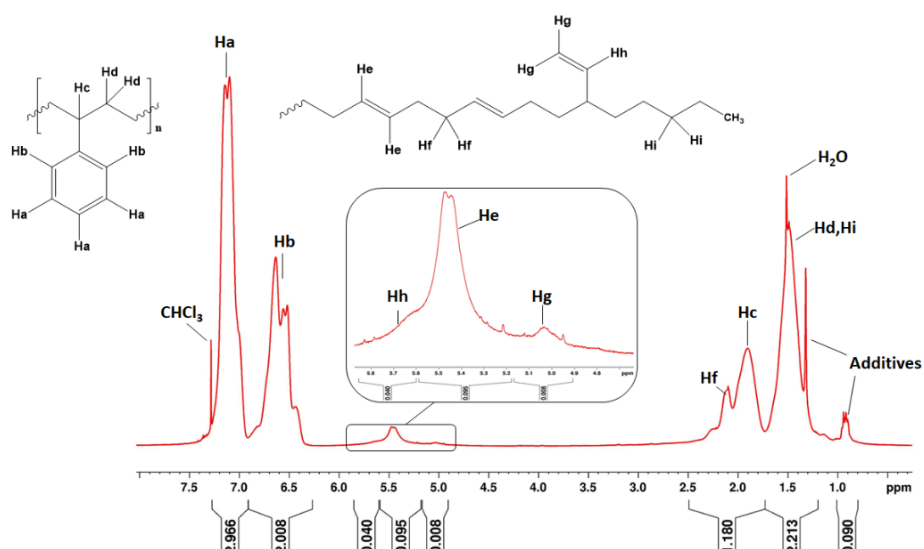
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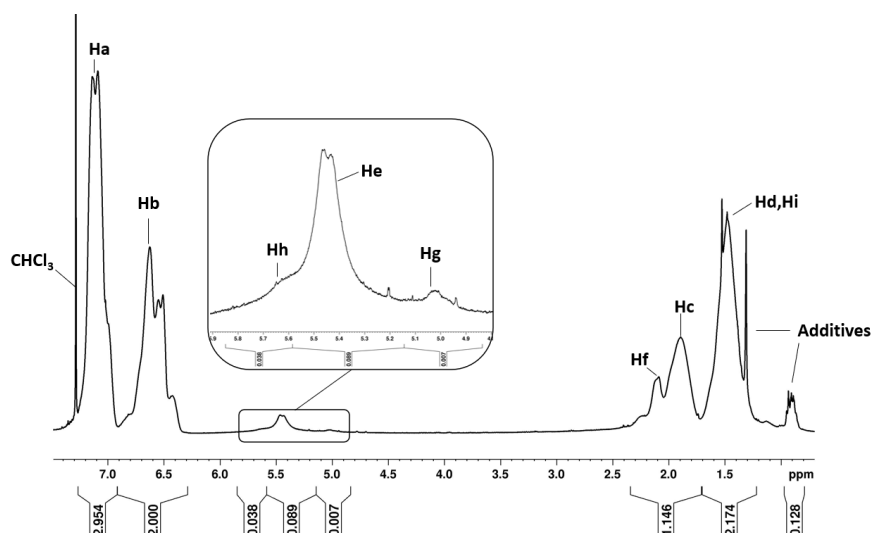
**Fig. S1 Pyrolysis reactor:** a) nitrogen gas flow dip-tube, b) stirring mechanism c) Pt-100 thermocouple, d) nitrogen flow tube, e) “heated” tube, f) condenser, g) walls of the condenser cooled by an ethylene glycol/water fluid, h) two-loop Eurotherm temperature control system, i) energy supply to the heating elements.



**Fig. S2 HIPS <sup>1</sup>H-NMR spectrum.** The major peaks are assigned in the spectrum (400MHz, CDCl<sub>3</sub>).<sup>1</sup> The PB relative area was calculated according to the following equation:

$$PB \text{ relative area} = \frac{2 \times AH_h + AH_e + AH_g}{AH_b + 2 \times AH_h + AH_e + AH_g} = \frac{0.183}{2.183} = 0.084$$

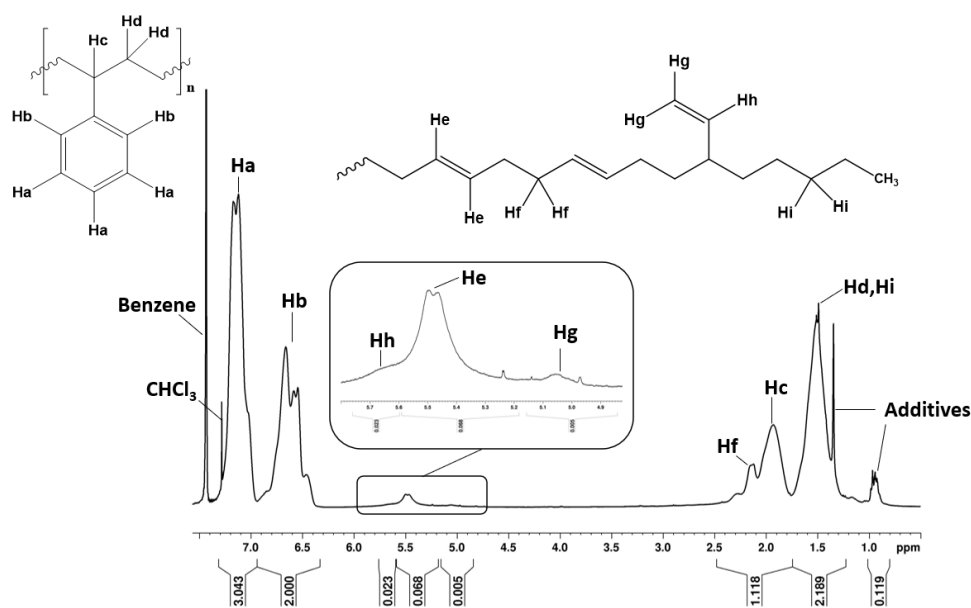
where  $AH_x$  = Area of the denoted proton. The PB relative area, which equals to 0.084, corresponds in a 8.5 wt.% PB content according to the nominal PB value included in the sample. Therefore, to correlate the relative area with the wt.% of PB in each sample, this ratio is multiplied by the factor  $\frac{8.5 \text{ wt.}\%}{0.084}$ . The PS wt.% is then calculated by subtracting the PB content from the 100 wt.% of the sample.



**Fig. S3 <sup>1</sup>H-NMR spectrum of the dried CHCl<sub>3</sub> supernatant solution.** The major peaks are assigned in the spectrum (400MHz, CDCl<sub>3</sub>).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(\text{wt.}\%) = \frac{2 \times AH_h + AH_e + AH_g}{AH_b + 2 \times AH_h + AH_e + AH_g} \times \frac{8.5 \text{ wt.}\%}{0.084} = \frac{0.172}{2.172} \times \frac{8.5 \text{ wt.}\%}{0.084} = 8.0 \text{ wt.}\%$$

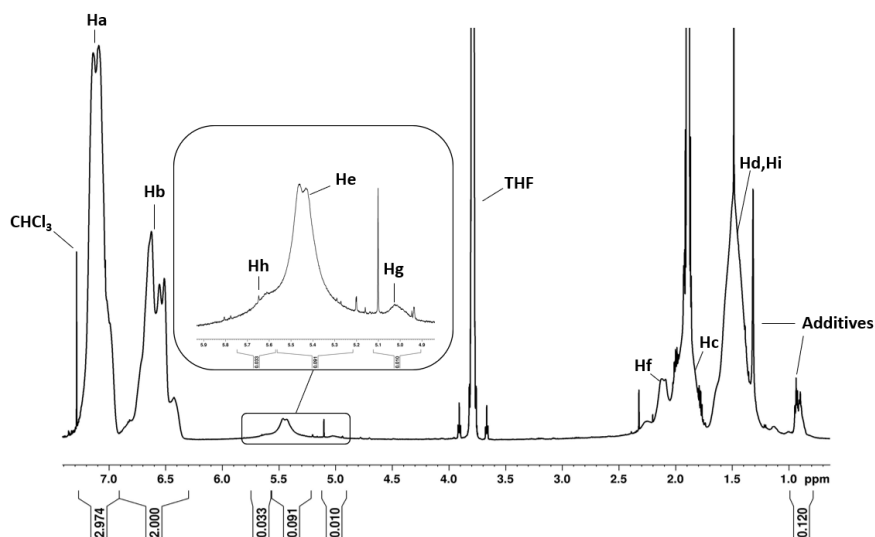
The PS wt.% is then calculated by subtracting the PB content from the 100 wt.% of the sample.



**Fig. S4**  $^1\text{H-NMR}$  spectrum of the dried benzene supernatant solution. The major peaks are assigned in the spectrum (400MHz,  $\text{CDCl}_3$ ).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(\text{wt. \%}) = \frac{2 \times AH_h + AH_e + AH_g}{AH_b + 2 \times AH_h + AH_e + AH_g} \times \frac{8.5 \text{ wt. \%}}{0.084} = \frac{0.119}{2.119} \times \frac{8.5 \text{ wt. \%}}{0.084} = 5.7 \text{ wt. \%}$$

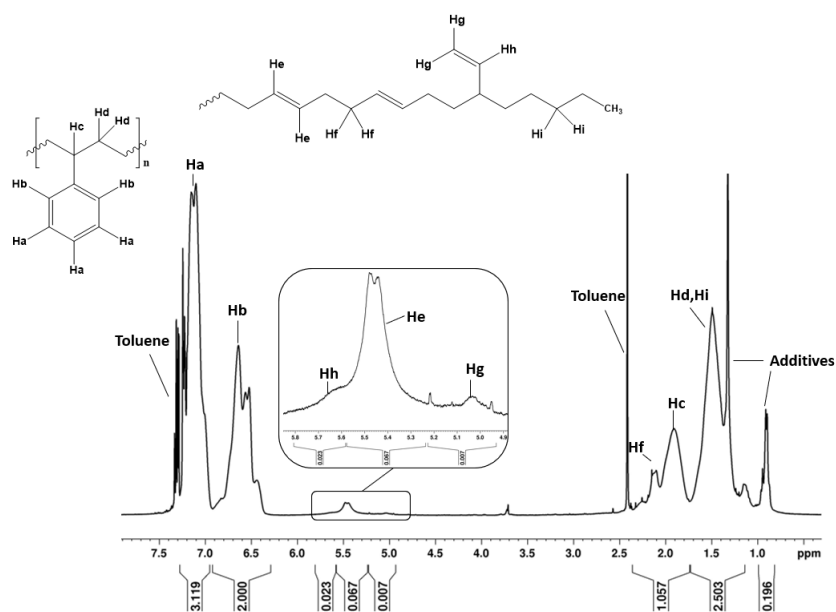
The PS wt.% is then calculated by subtracting the PB content from the 100 wt.% of the sample.



**Fig. S5**  $^1\text{H-NMR}$  spectrum of the dried THF supernatant solution. The major peaks are assigned in the spectrum (400MHz,  $\text{CDCl}_3$ ).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(\text{wt. \%}) = \frac{2 \times AH_h + AH_e + AH_g}{AH_b + 2 \times AH_h + AH_e + AH_g} \times \frac{8.5 \text{ wt. \%}}{0.084} = \frac{0.167}{2.167} \times \frac{8.5 \text{ wt. \%}}{0.084} = 7.8 \text{ wt. \%}$$

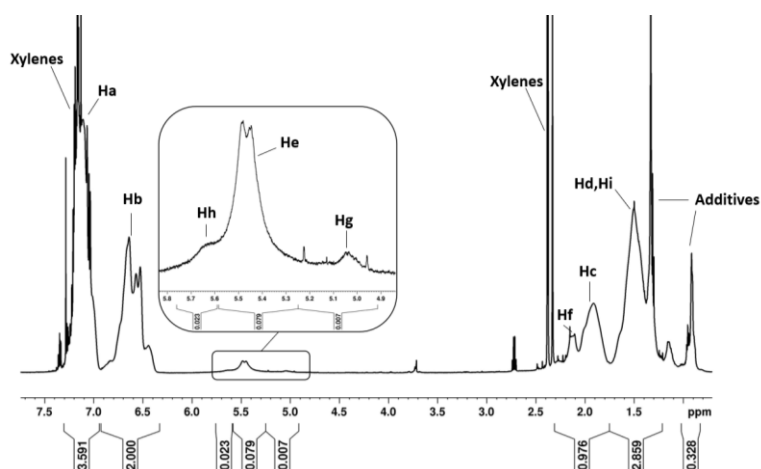
The PS wt.% is then calculated by subtracting the PB content from the 100 wt.% of the sample.



**Fig. S6**  $^1\text{H-NMR}$  spectrum of the dried toluene supernatant solution. The major peaks are assigned in the spectrum (400MHz,  $\text{CDCl}_3$ ).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(\text{wt. \%}) = \frac{2 \times AH_n + AH_e + AH_g}{AH_b + 2 \times AH_n + AH_e + AH_g} \times \frac{8.5 \text{ wt. \%}}{0.084} = \frac{0.120}{2.120} \times \frac{8.5 \text{ wt. \%}}{0.084} = 5.7 \text{ wt. \%}$$

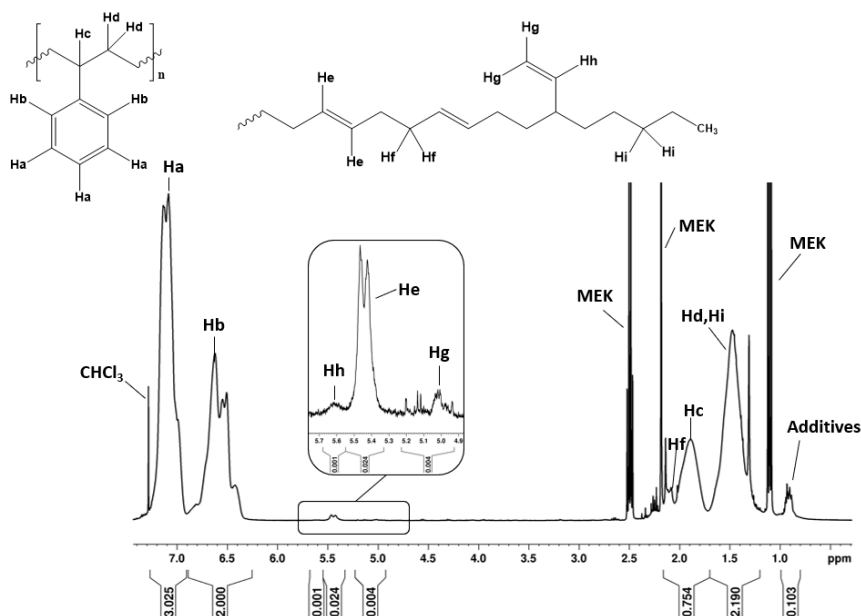
The PS wt.% is then calculated by subtracting the PB content from the 100 wt.% of the sample.



**Fig. S7**  $^1\text{H-NMR}$  spectrum of the dried xylenes supernatant solution. The major peaks are assigned in the spectrum (400MHz,  $\text{CDCl}_3$ ).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(\text{wt. \%}) = \frac{2 \times AH_n + AH_e + AH_g}{AH_b + 2 \times AH_n + AH_e + AH_g} \times \frac{8.5 \text{ wt. \%}}{0.084} = \frac{0.132}{2.132} \times \frac{8.5 \text{ wt. \%}}{0.084} = 6.3 \text{ wt. \%}$$

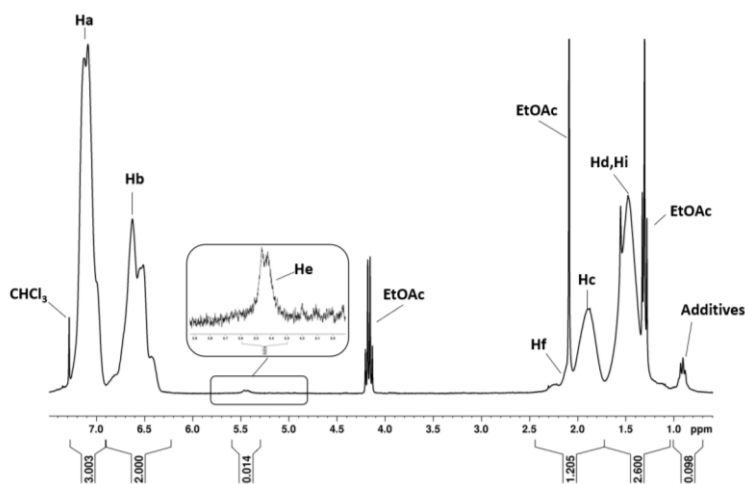
The PS wt.% is then calculated by subtracting the PB content from the 100 wt.% of the sample.



**Fig. S8**  $^1\text{H-NMR}$  spectrum of the dried MEK supernatant solution. The major peaks are assigned in the spectrum (400MHz,  $\text{CDCl}_3$ ).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(\text{wt. \%}) = \frac{2 \times AH_h + AH_e + AH_g}{AH_b + 2 \times AH_h + AH_e + AH_g} \times \frac{8.5 \text{ wt. \%}}{0.084} = \frac{0.03}{2.03} \times \frac{8.5 \text{ wt. \%}}{0.084} = 1.5 \text{ wt. \%}$$

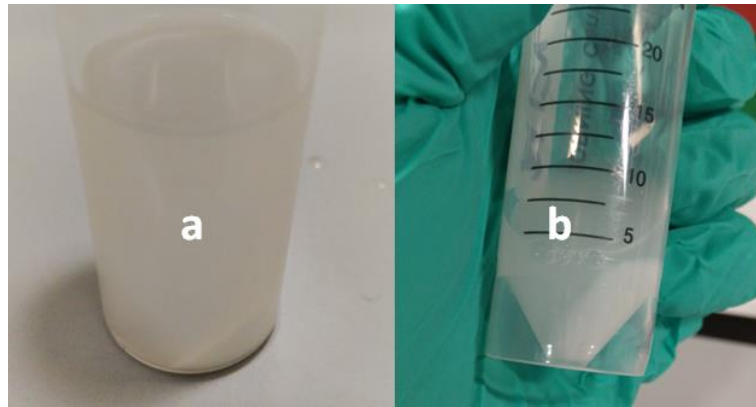
The PS wt.% is then calculated by subtracting the PB content from the 100 wt.% of the sample.



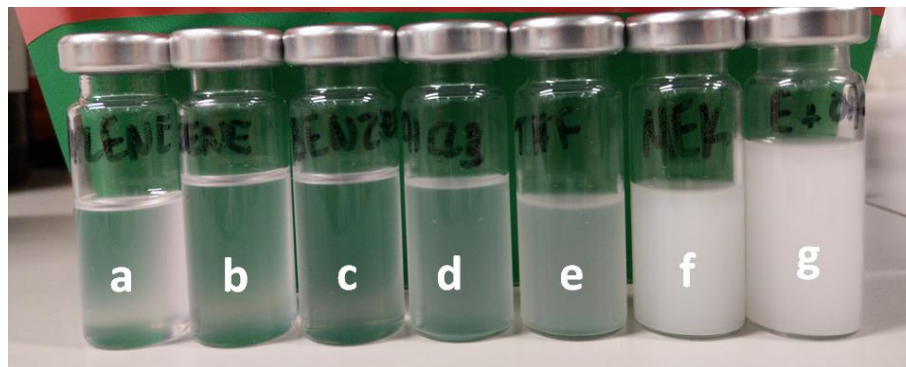
**Fig. S9**  $^1\text{H-NMR}$  spectrum of the dried EtOAc supernatant solution. The major peaks are assigned in the spectrum (400MHz,  $\text{CDCl}_3$ ).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(\text{wt. \%}) = \frac{AH_e}{AH_b} \times \frac{8.5 \text{ wt. \%}}{0.084} = \frac{0.014}{2.014} \times \frac{8.5 \text{ wt. \%}}{0.084} = 0.7 \text{ wt. \%}$$

The PS wt.% is then calculated by subtracting the PB content from the 100 wt.% of the sample.



**Fig. S10** Phases obtained after the centrifugation of HIPS dispersed in ethyl acetate (a), methyl ethyl ketone (b). The supernatant solutions contain the free PS matrix, while the white gel observed corresponds to the rubber phase of the HIPS sample.



**Fig. S11** HIPS dispersed in several solvents. (a) xylene, (b) toluene, (c) benzene, (d) CHCl<sub>3</sub>, (e) THF, (f) MEK, (g) EtOAc.

**Table S1 Hansen solubility parameters for several solvents and polymers<sup>2-5</sup>**

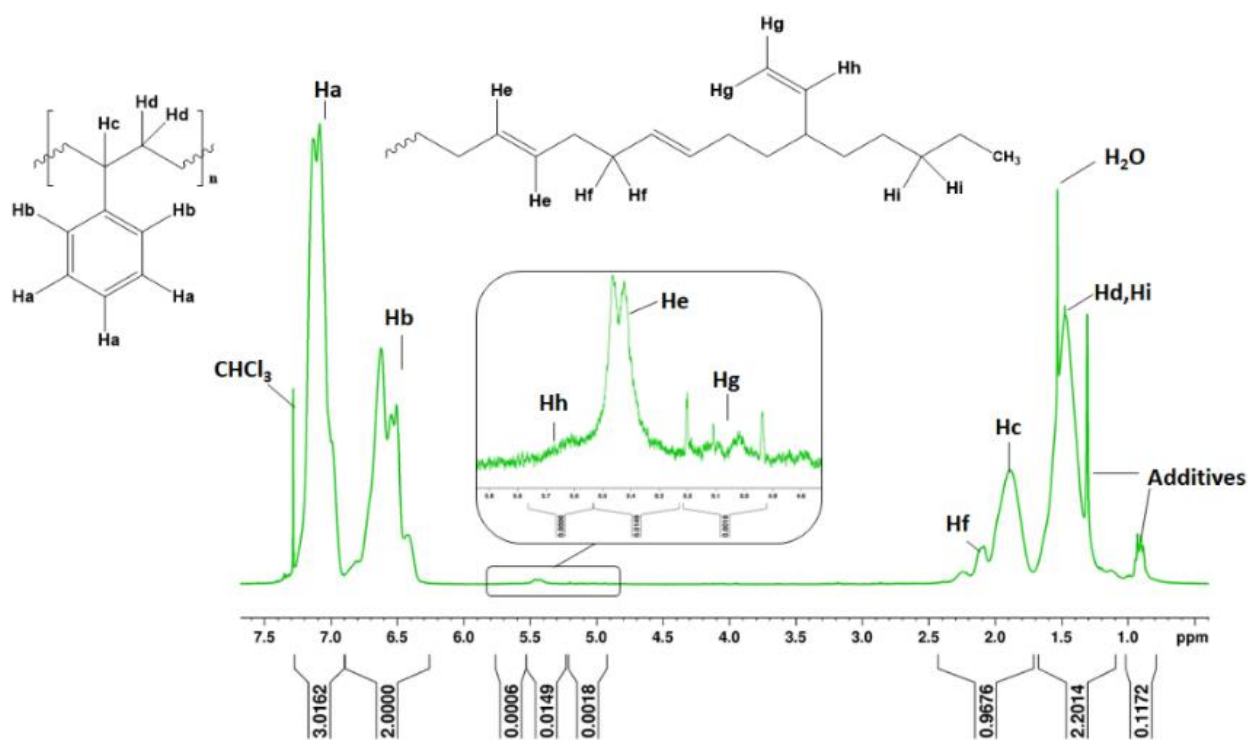
Solvent (S)	Dispersion(D)	Polar(P)	Hydrogen Bonding (H)
EtOAc	15.8	5.3	7.2
Toluene	18.0	1.4	2.0
Xylene	17.8	1.0	3.1
Benzene	18.4	0	2.0
MEK	16	9	5.1
THF	16.8	5.7	8.0
CHCl <sub>3</sub>	17.8	3.1	5.7
Polymer (P)			
Polystyrene (PS)	18.5	5.9	3.5
Styrene-butadiene rubber (SBR)	17.6	3.4	2.7
Polybutadiene	17.5	2.3	3.4

To calculate  $R_a$  the following equation used:  $R_a^2 = 4(D_p - D_s)^2 + (P_p - P_s)^2 + (H_p - H_s)^2$ , and then the value  $R_a/R_o$  was calculated considering  $R_o(PS)=12.7$ ,  $R_o(SBR)=6.6$  and  $R_o(PB)=6.5$ .



**Fig. S12 Scale-up of the pre-fractionation procedure.** 10 g of HIPS and 350ml EtOAc in total were used.

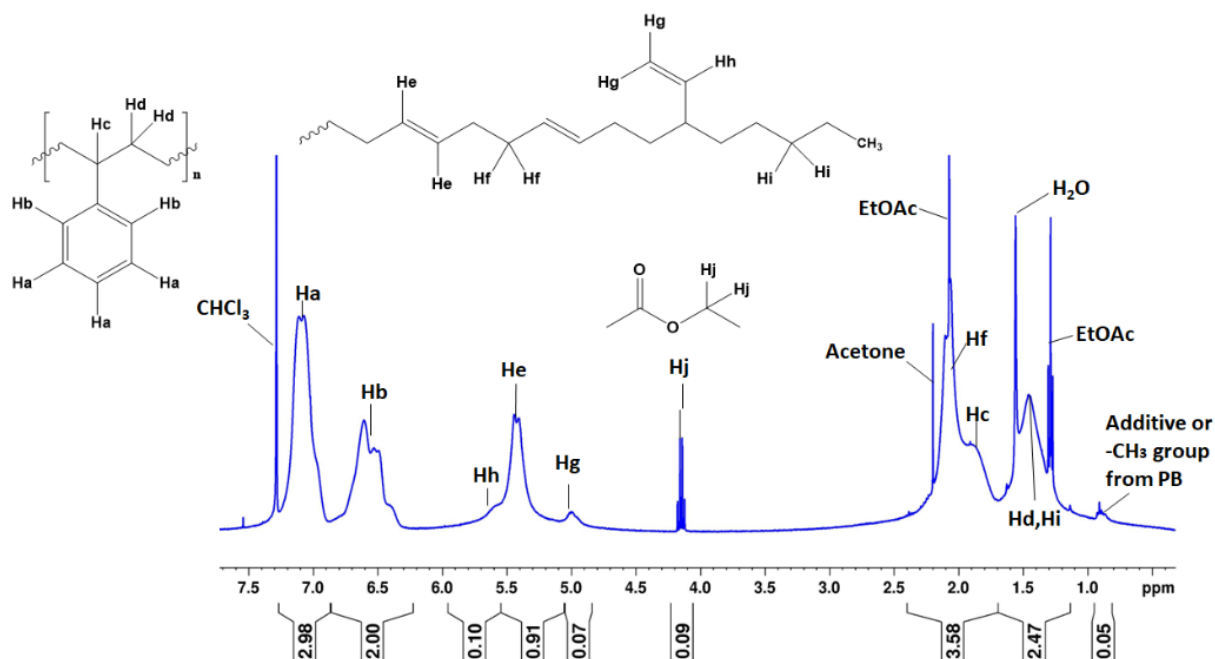




**Fig. S13** <sup>1</sup>H-NMR spectrum of PS-1. The major peaks are assigned in the spectrum (400MHz, CDCl<sub>3</sub>).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(wt\%) = \frac{2 \times AH_h + AH_e + AH_g}{AH_b + 2 \times AH_h + AH_e + AH_g} \times \frac{8.5 \text{ wt.}\%}{0.084} = \frac{0.0179}{2.0179} \times \frac{8.5 \text{ wt.}\%}{0.084} \times 100 = 0.9 \text{ wt.}\%$$

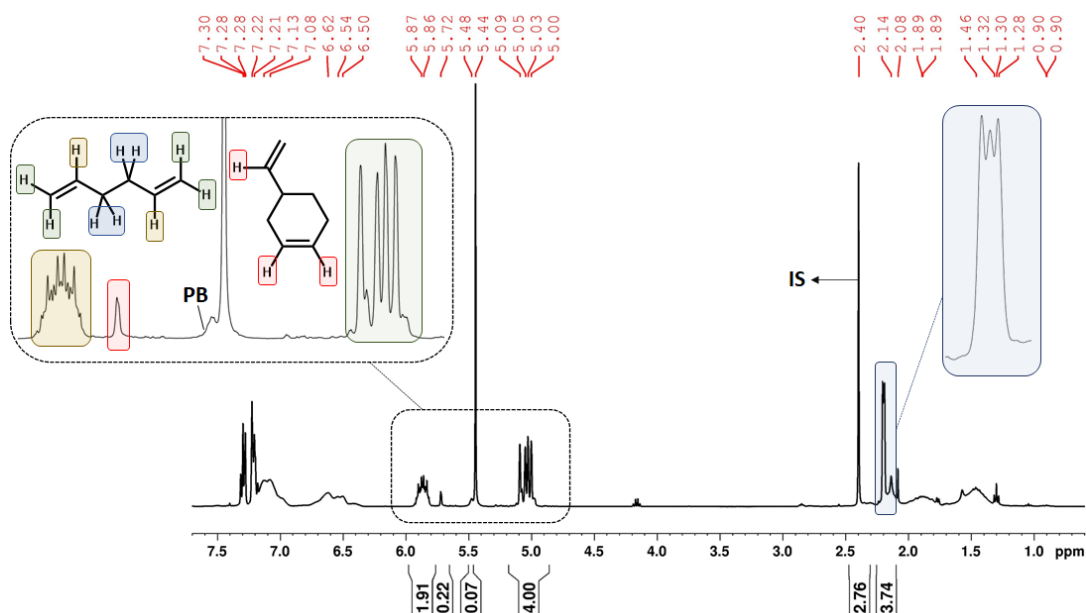
where  $AH_x$  = Area of the denoted proton. The PS wt.% is calculated by subtracting the PB content from the 100 wt.% of the sample.



**Fig. S14** <sup>1</sup>H-NMR spectrum of the rubber phase. The major peaks are assigned in the spectrum (400MHz, CDCl<sub>3</sub>).<sup>1</sup> The PB content was calculated according to the following equation:

$$PB(\text{wt. \%}) = \frac{2 \times AH_h + AH_e + AH_g}{AH_b + 2 \times AH_h + AH_e + AH_g} \times \frac{8.5 \text{ wt. \%}}{0.084} = \frac{1.18}{3.18} \times \frac{8.5 \text{ wt. \%}}{0.084} = 37.5 \text{ wt. \%}$$

where  $AH_x$  = Area of the denoted proton. The PS wt.% was calculated by subtracting the PB and EtOAc contents from the 100 wt.% of the sample.



**Fig. S15**  $^1\text{H-NMR}$  of the crude ethenolysis mixture (starting material: rubber phase).<sup>6</sup> Toluene (50  $\mu\text{L}$ ) was used as internal standard (IS). The mmol of each product were calculated using equation 1:

$$X_{mmol} = \frac{nH_{IS}}{nH_x} \times \frac{A_x}{A_{IS}} \times mmol_{IS} \quad (\text{equation 1})$$

Where  $nH_{IS}$  is the number of protons corresponding to the IS signal (3 protons, peak at 2.4 ppm),  $nH_x$  the number of protons corresponding to the product signal,  $A_x$  the area of the product,  $A_{IS}$  the area of the IS, and  $mmol_{IS}$  the number of mmoles of the IS. Calculations were carried out with non-overlapping signals. Thus, in the case of 1,5-hexadiene using the signal of the protons marked in yellow:

$$1,5\text{-hexadiene}_{mmol} = \frac{3}{2} \times \frac{1.91}{2.76} \times 0.471 = 0.49 \text{ mmol}$$

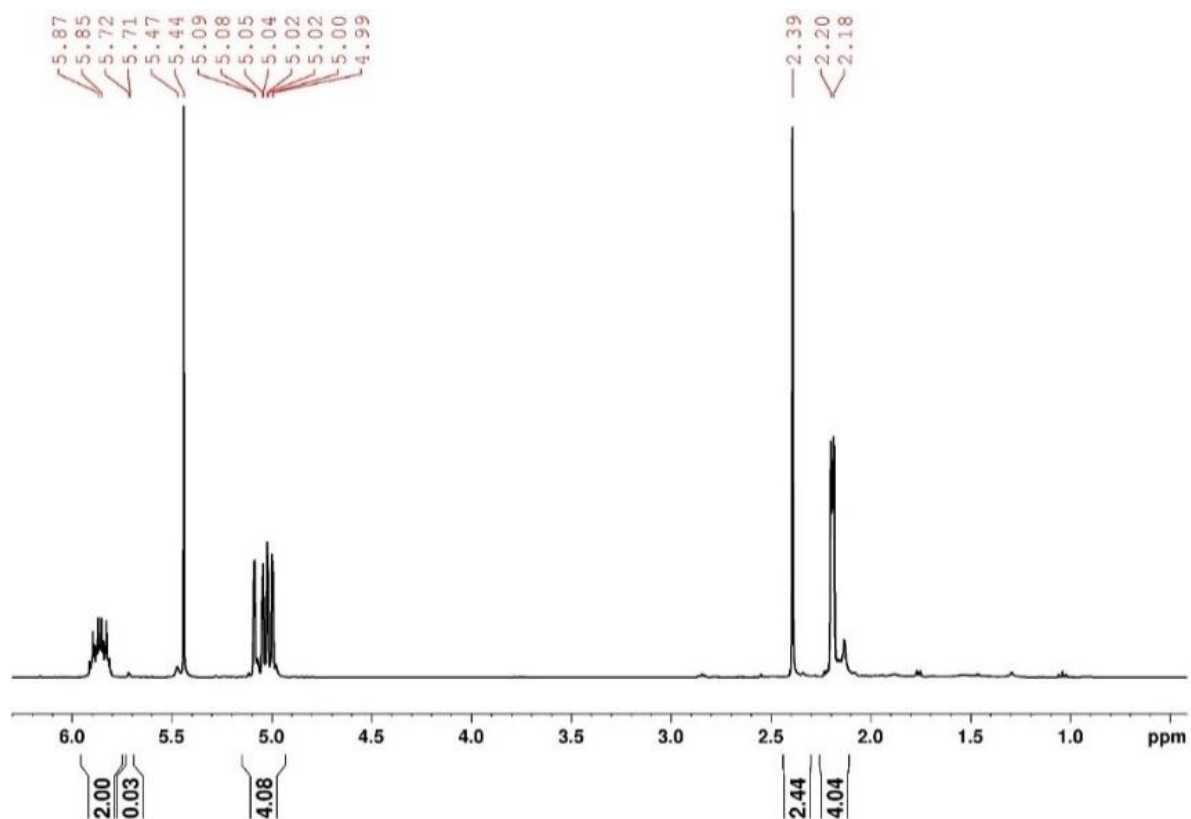
Analogously,  $4\text{-vinylcyclohexene}_{mmol} = 0.038\text{mmol}$ . The PB content of the rubber phase was calculated (37.5 wt.%) and 120 mg of the rubber were used. Hence, 45 mg of PB are included in the rubber phase, and the starting amount (mmol) of PB is equal to:

$$PB_{mmol} = \frac{45\text{mg}}{54\frac{\text{g}}{\text{mol}}} = 0.83 \text{ mmol}$$

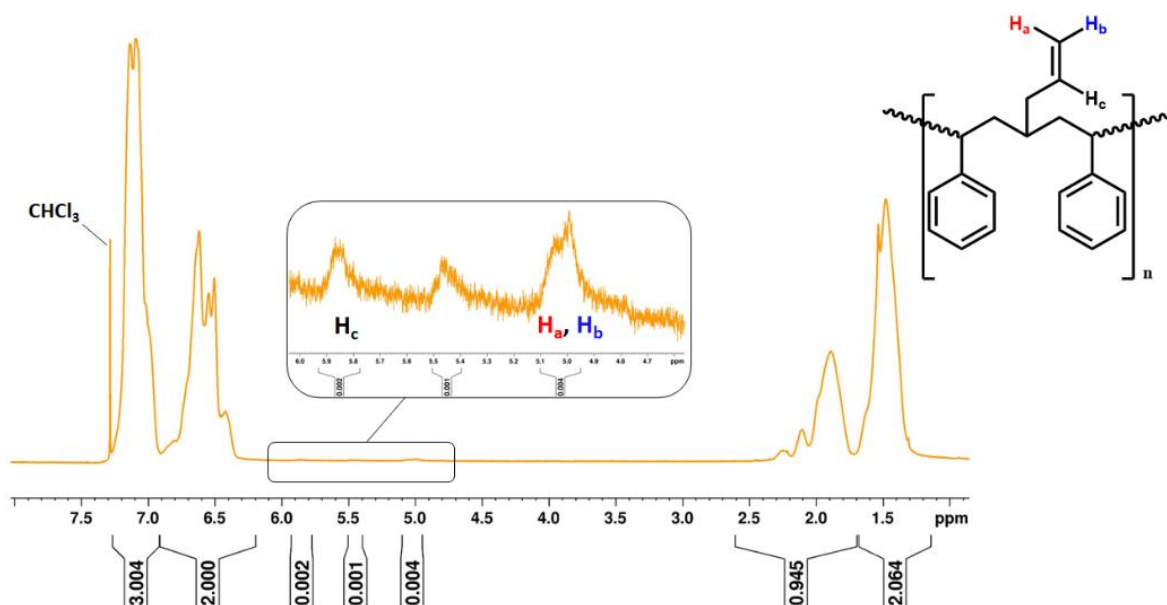
Therefore the yields of 1,5-hexadiene and 4-vinylcyclohexene can be calculated by equations 2 and 3.

$$1,5\text{-hexadiene}_{yield} = \frac{1,5\text{-hexadiene}_{mmol}}{PB_{mmol}} \times 100 = \frac{0.49}{0.83} \times 100 = 59.0\% \quad (\text{equation 2})$$

$$4\text{-vinylcyclohexene}_{yield} = \frac{4\text{-vinylcyclohexene}_{mmol}}{PB_{mmol}} \times 100 = \frac{0.038}{0.83} \times 100 = 4.6\% \quad (\text{equation 3})$$



**Fig. S16**  $^1\text{H-NMR}$  after ethenolysis of PB molecular weight 200 kDa.<sup>6</sup> The starting amount of PB was 44 mg (0.81 mmol using the molecular weight of the single unit). Using equation 1,  $1,5\text{-hexadiene}_{\text{mmol}} = 0.58$  mmol,  $4\text{-vinylcyclohexene}_{\text{mmol}} = 0.0058$  mmol, and therefore the yields are 72% and 0.58%, respectively, following equations 2 and 3.

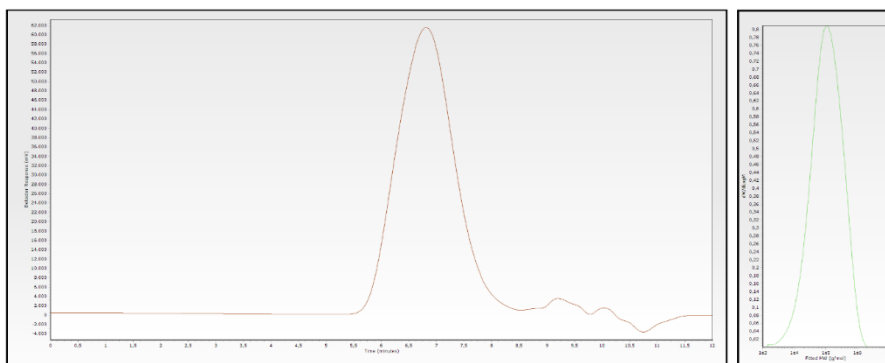


**Fig. S17**  $^1\text{H-NMR}$  spectrum of PS-2. The major peaks are assigned on the spectrum (600MHz,  $\text{CDCl}_3$ ).<sup>7</sup> Besides  $\text{H}_a$ ,  $\text{H}_b$ ,  $\text{H}_c$ , the signal in between them could be attributed to lower molecular weight PB which remained on the PS backbone or co-precipitated upon MeOH addition. The PB content was calculated by the equation:

$$PB(\text{wt.}\%) = \frac{0.001}{2.000 + 0.001} \times \frac{8.5 \text{ wt.}\%}{0.084} = \frac{0.001}{2.001} \times \frac{8.5 \text{ wt.}\%}{0.084} = 0.05 \text{ wt.}\%$$

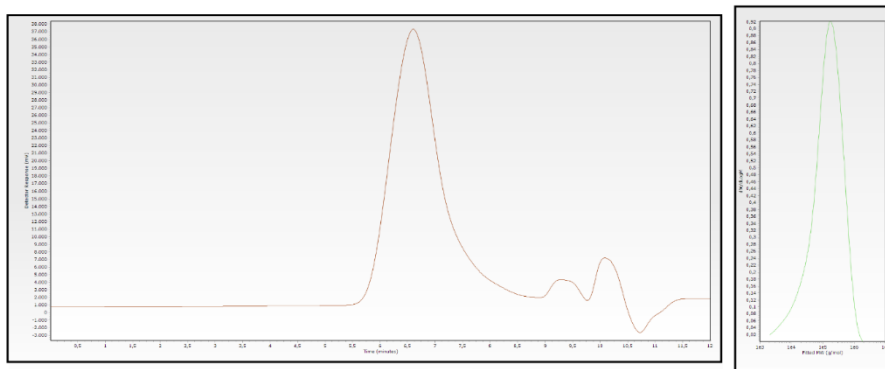
The PS wt.% was calculated by subtracting the PB content from the 100 wt.% of the sample. To precipitate the unreacted PS, MeOH was added as anti-solvent. The precipitated PS was washed three times with MeOH, dried, and weighed. Based on Table S2, supporting information, 120 mg rubber phase contain 75 mg of PS, out of which 65 mg of dried unreacted PS were recovered, which was denoted as PS-2.

$$\text{Overall mass recovery efficiency} = \frac{65}{75} \times 100 = 87 \%$$



Sample	Mp	Mn	Mw	Mv	Mz	Mz+1	PD
PS-1	106809	51801	179964	154806	411745	674356	3.474

**Fig. S18 GPC results of PS-1 (polystyrene isolated from HIPS).** Additional peaks at 9.2 and 10.1 minutes correspond to compounds of low molecular weight and they probably originate from the known additives in the HIPS sample.

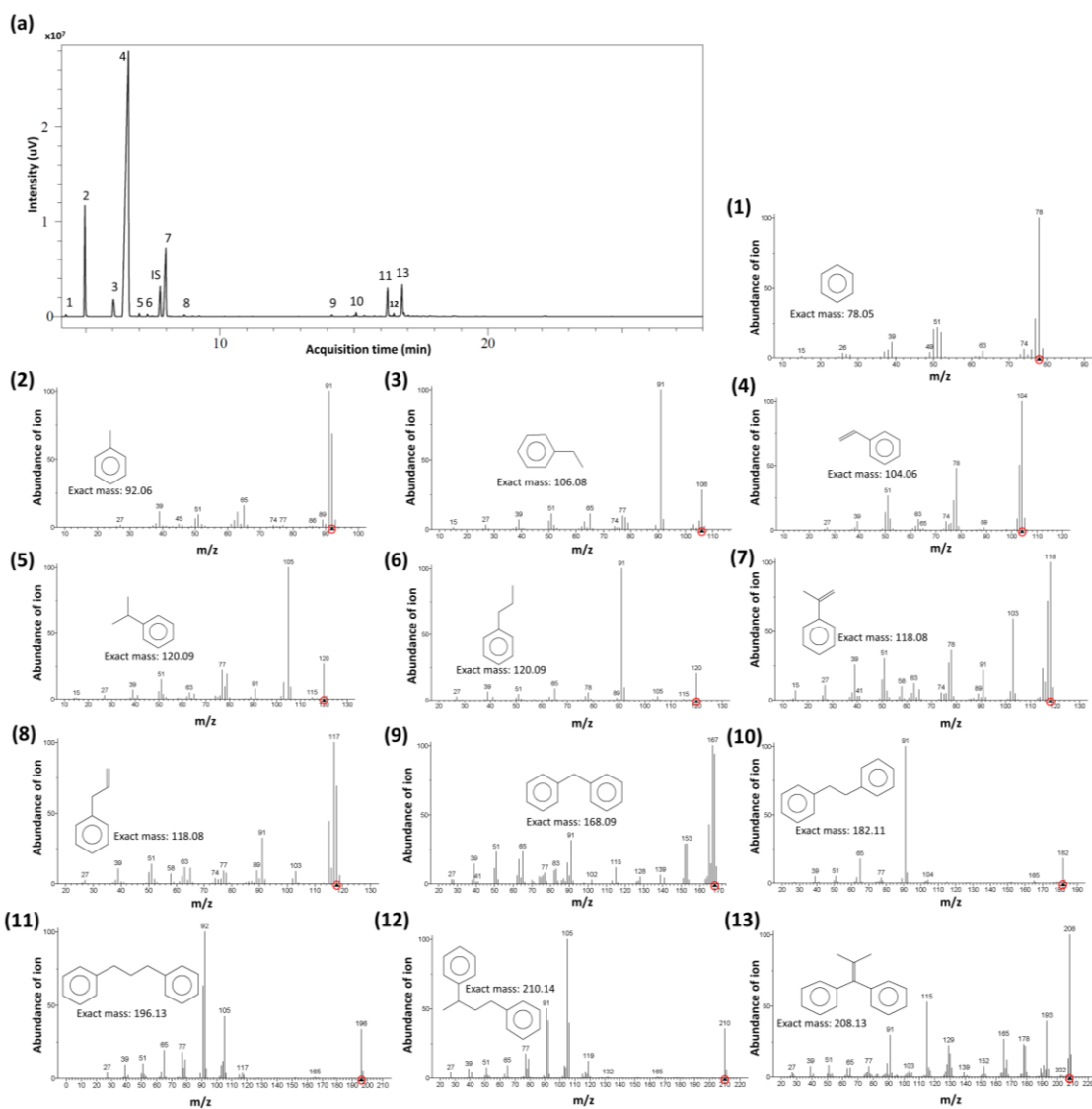


Sample	Mp	Mn	Mw	Mv	Mz	Mz+1	PD
PS-2	174856	53936	216897	190760	427794	648361	4.021

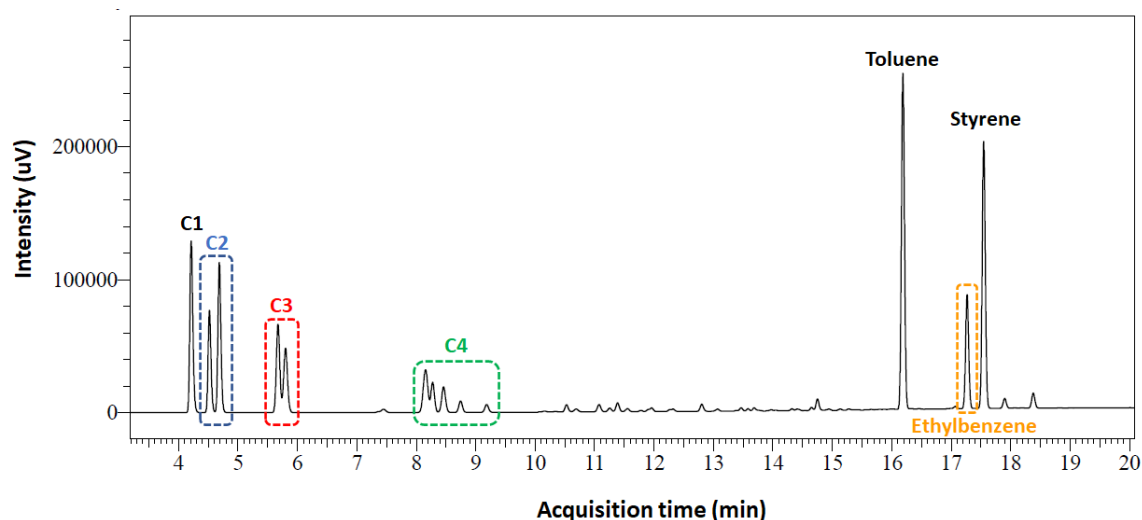
**Fig. S19 GPC results of PS-2 (polystyrene isolated after ethenolysis).** Additional peaks at 9.2 and 10.1 minutes correspond to compounds of low molecular weight and they are probably originate from the known additives in the HIPS sample.

**Table S2. Composition of the samples tested in this study.** The wt.% percentages were calculated by <sup>1</sup>H-NMR by dissolving 20 mg of sample in 0.6 mL of CDCl<sub>3</sub>.

Sample	PS (wt.%)	PB (wt.%)
PS-192	100	-
PS-1	99.1	0.9
PS-2	99.95	0.05
Rubber phase	62.5	37.5



**Fig. S20 Gas Chromatography-Mass Spectrometry (GC-MS) analysis of the pyrolysis liquid.** (a) Gas chromatogram after the pyrolysis of PS-192 sample (1) - (13) Mass spectra of the corresponding peaks.



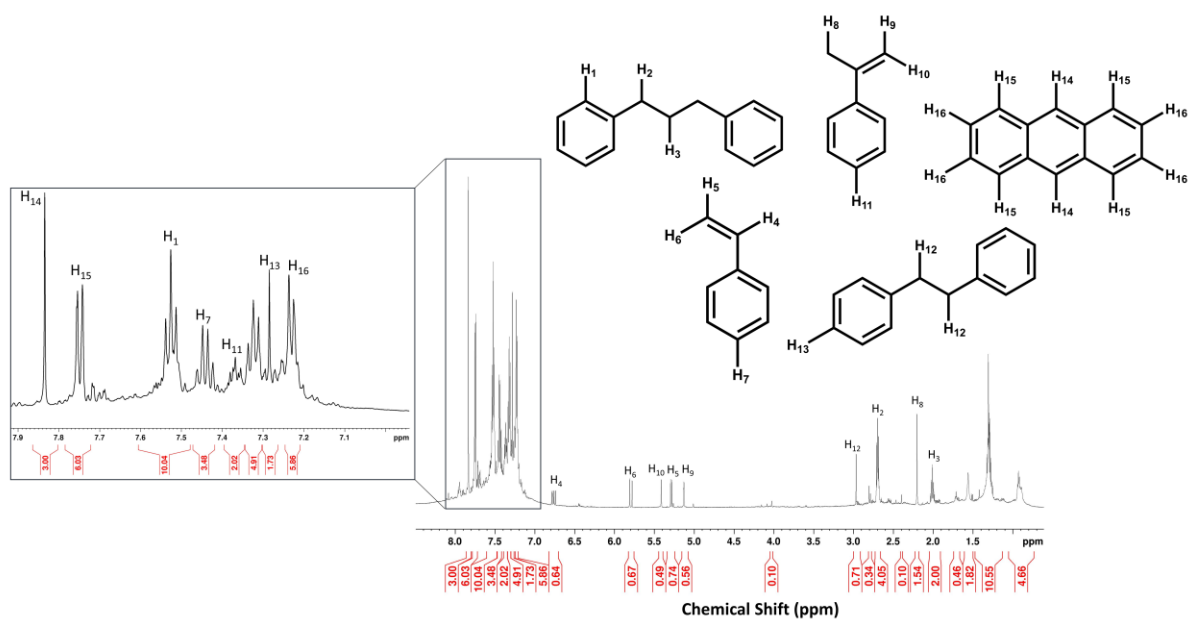
**Fig. S21 Representative chromatogram (HIPS sample) in the analysis of gases/losses during the pyrolysis experiments.**

**Table S3 Composition of the gases/losses. Pyrolysis of PS-192, HIPS and PS-1.**

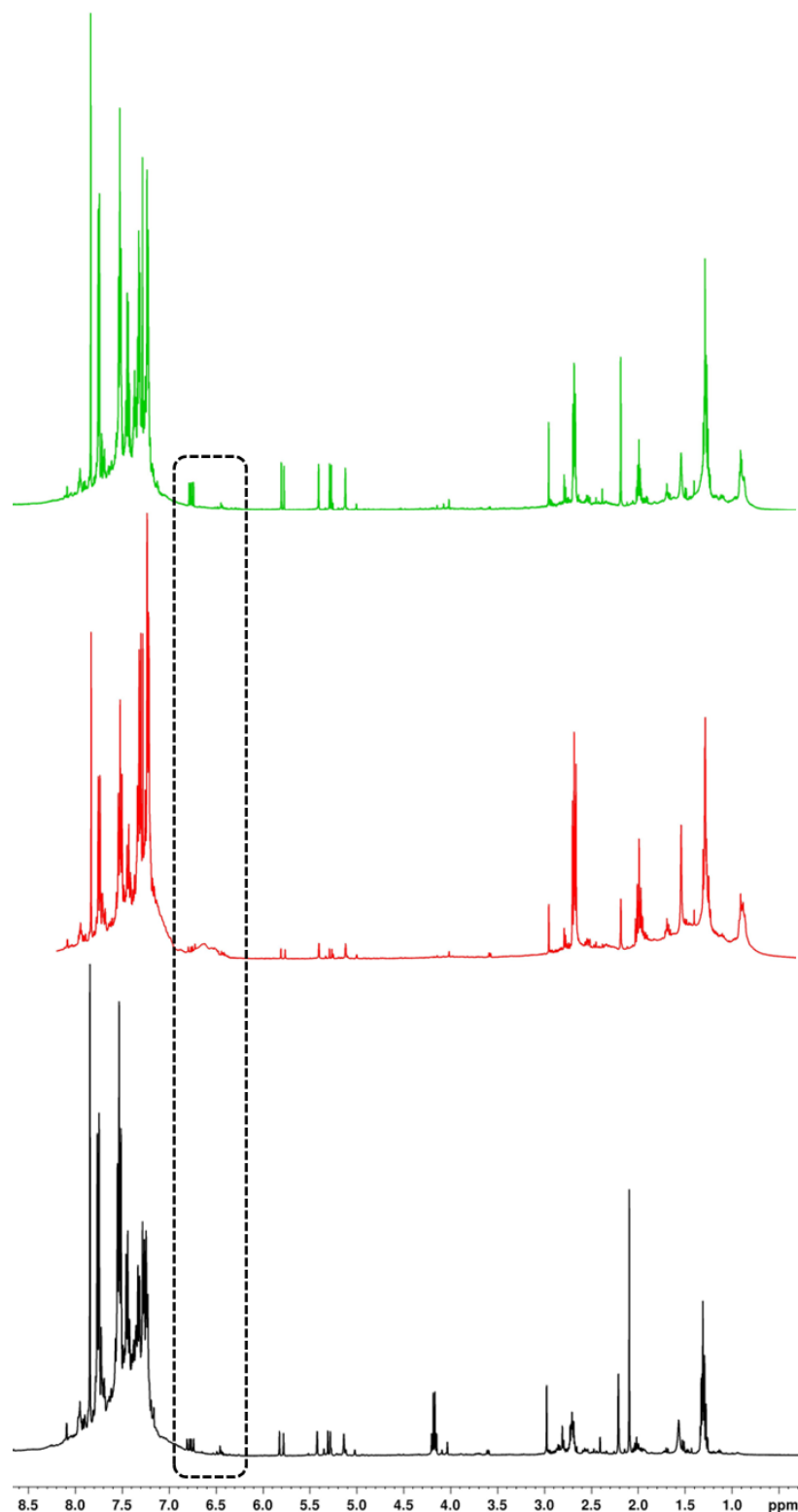
Sample	C1	C2	C3	C4	Aromatics	Styrene	Others
PS-192	17%	10%	3%	2%	29%	33%	6%
HIPS	33%	24%	12%	8%	12%	7%	4%
PS-1	23%	16%	9%	8%	21%	18%	5%

The composition of the gasses/losses was determined by GC-FID on a Shimadzu GC 2014 instrument equipped with a SH-I-1MS column and an FID detector. Gases were collected in a 1 L Tedlar bag connected to the ventilation line throughout the reaction. The peaks between 10-15 minutes and 18-20 minutes are denoted as “others” in table S3.

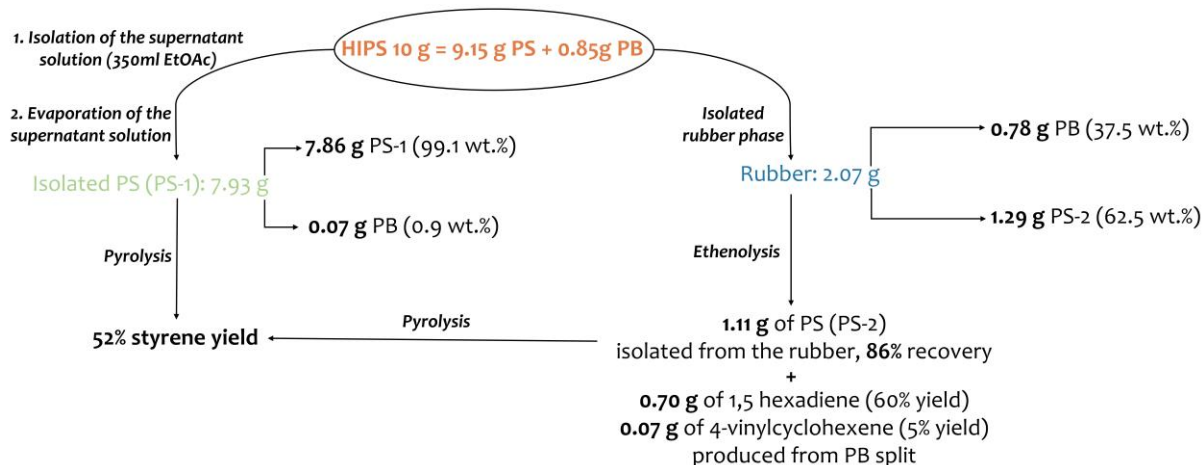




**Fig. S22 <sup>1</sup>H-NMR spectrum of the solid residue and major products.** The spectrum presented corresponds to the solid residue in the pyrolysis of PS-1 (600MHz, CDCl<sub>3</sub>). The pyrolysis residue was dissolved in CDCl<sub>3</sub> and then filtered (in order to remove the char particles) before GC-MS and <sup>1</sup>H-NMR analyses. Peaks at 1.4 ppm and 0.9 ppm correspond to the known additives in HIPS sample.



**Fig. S23** <sup>1</sup>H-NMR spectra of the solid residues isolated after the end of pyrolysis. The main difference is observed at 6.7 ppm where in the cases of the residues of PS-192 (black spectrum) and PS-1 (green spectrum) there is no peak related with the presence of PB after the end of the process. In contrast, it can be observed that in the spectrum obtained from the HIPS residue (red spectrum) at 6.7 ppm there is a wide peak that indicates the presence of degraded PB parts<sup>8</sup> in the solid residue of this reaction (600MHz, CDCl<sub>3</sub>).



**Fig.S24 Overall yields throughout the entire HIPS fractionation process.** First the HIPS sample was dispersed in a total amount of 350 ml EtOAc, which was used as the fractionation solvent. After centrifugation, the supernatant solution was collected, evaporated and the “free” PS (PS-1, 7.93 g) was isolated. Next the rubber (2.07 g) was used as a starting material in the ethenolysis metathesis, producing 60% of 1,5-hexadiene (0.70 g) as major compound due to the split of PB, while the “grafted” PS (PS-2, 1.11 g, 86% recovery) was precipitated using MeOH as an anti-solvent in the crude ethenolysis mixture. Both PS-1 and PS-2 were thermally degraded leading to a pyrolysis oil with 70% styrene selectivity and 52% overall styrene yield.

## References

- 1) N. Makhiyanov, Determination of configurational isomers in polybutadienes by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, *Polym. Sci. Ser. A*, 2012, 54 (2), pp. 69–80.
- 2) B.A. Miller-Chou and J. L. Koenig, A review of polymer dissolution, *Progress in Polymer Science*, 2003, 28 (8), pp. 1223-1270.
- 3) Retrieved from: <https://www.hansen-solubility.com/HSP-science/sphere.php>.
- 4) C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook, 2nd Edition*, CRC Press, Boca Raton, 2007, pp.34-36, 493-494.
- 5) Available at: <https://hansen-solubility.com/HSP-science/Hildebrand-parameters.php>.
- 6) M.D. Watson and K.B. Wagener, Acyclic diene metathesis (ADMET) depolymerization: ethenolysis of 1,4-polybutadiene using a ruthenium complex, *J. Polym. Sci. A Polym. Chem.*, 1999, 37 (12), pp. 1857–1861.
- 7) D. Michel, W. Böhlmann, J. Roland and S. Mulla-Osman, Study of conformation and dynamics of molecules adsorbed in zeolites by  $^1\text{H}$ -NMR, *Lect. Notes Phys.*, 2004, 634, pp.232-236.
- 8) B. Schneider, D. Doskočilová, J. Štokr and M. Svoboda, Study of thermal degradation of polybutadiene in inert atmosphere: 1. Evidence of temperature and time of heating in i.r. and n.m.r. spectra, *Polymer*, 1993, 34 (2), pp. 432-436.