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Depolymerization of polystyrene under ambient conditions

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Experimental details

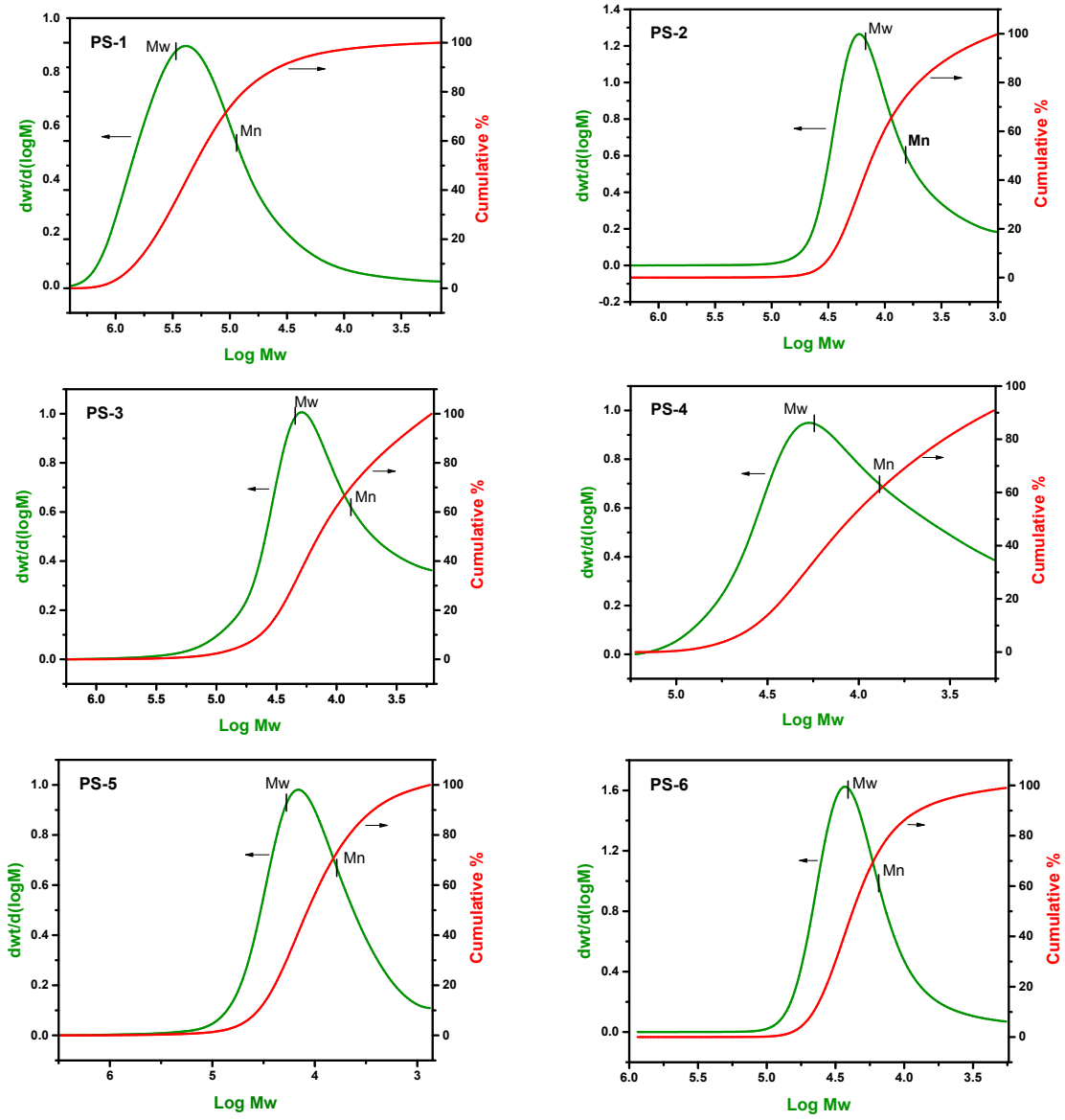
EPR experiments

Electron paramagnetic resonance (EPR) spectroscopy was performed on an X-band constant-wave Bruker Biospin ELEXSYS E580 system. EPR spectra were recorded at room temperature under ambient conditions.

The g-factor is analogous to the chemical shift in NMR and highly sensitive to the local environment of the radical species.[1] It is field independent and determined by calibrating the magnetic field and microwave frequency with an external standard, a gamma-irradiated quartz with a known concentration as g = 2.0004. Attenuation of the microwave power was calibrated on each sample.

Gel Permeation Chromatography

The molecular weight of the polystyrene materials was measured using gel permeation chromatography (GPC, Waters Breeze). Each sample was dissolved in chloroform before the measurements. Then, the solutions were filtered through 0.2 µm syringe PTFE filters. The GPC measurements were calibrated using

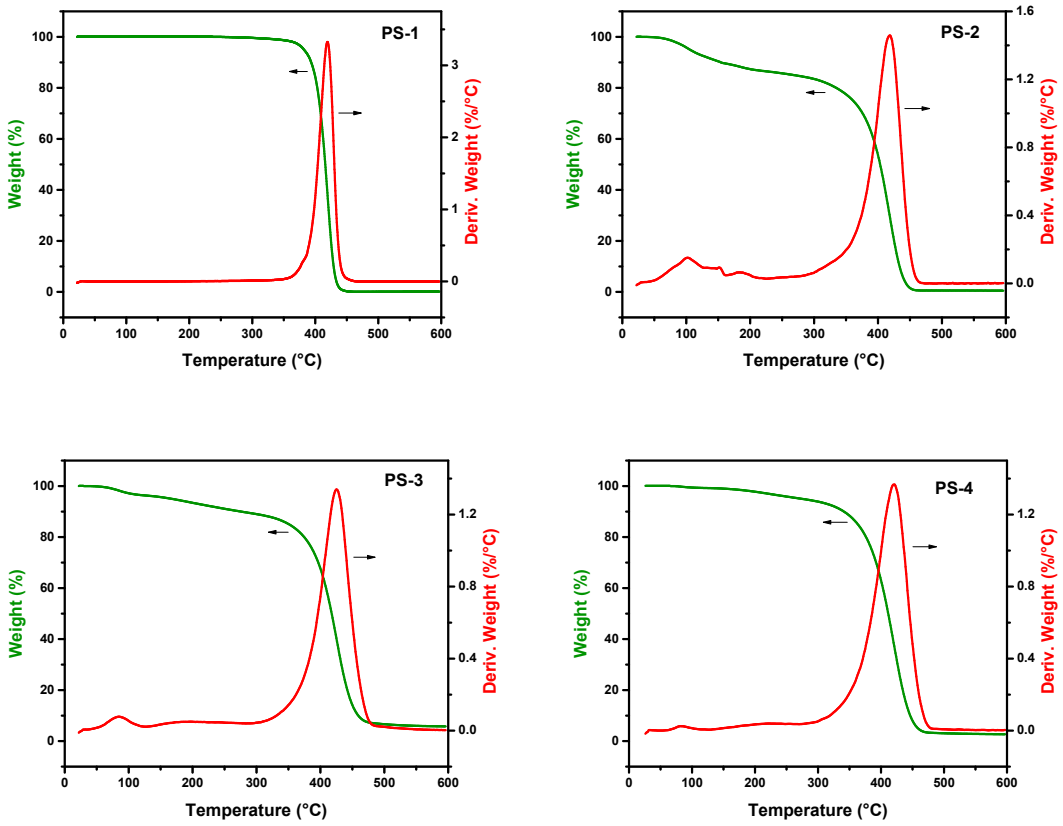


a polystyrene standard.

Figure S1. GPC data for the samples listed in Table 1, main text.

Thermogravimetric analysis

Thermogravimetric analysis (TGA), was conducted using a PerkinElmer TGA. All samples (~5 mg) were preheated at 25 °C for 10 min under a nitrogen atmosphere. Consequently, the samples were heated from room temperature to 600 °C at a heating rate of 10 °C/min.



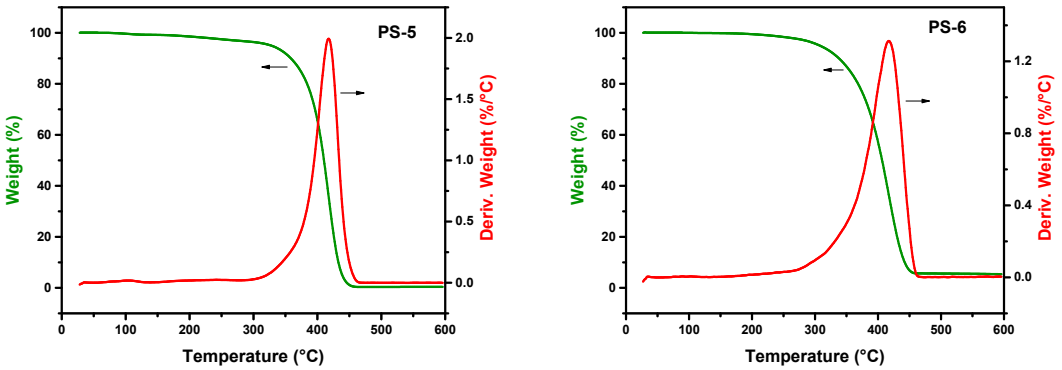


Figure S2. TGA data for the samples listed in Table 1, main text.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were conducted to obtain the glass transition of the PS materials. Samples (~5 mg) were analyzed using a DSC 2920 (TA Instruments) under a nitrogen atmosphere. Samples were heated from -50 °C to 200 °C at a heating rate of 20 °C/min to clear the thermal history, following by cooling and heating cycles. DSC measurements were not conducted for PS-2 and PS-3 due to the large mass loss of these samples.

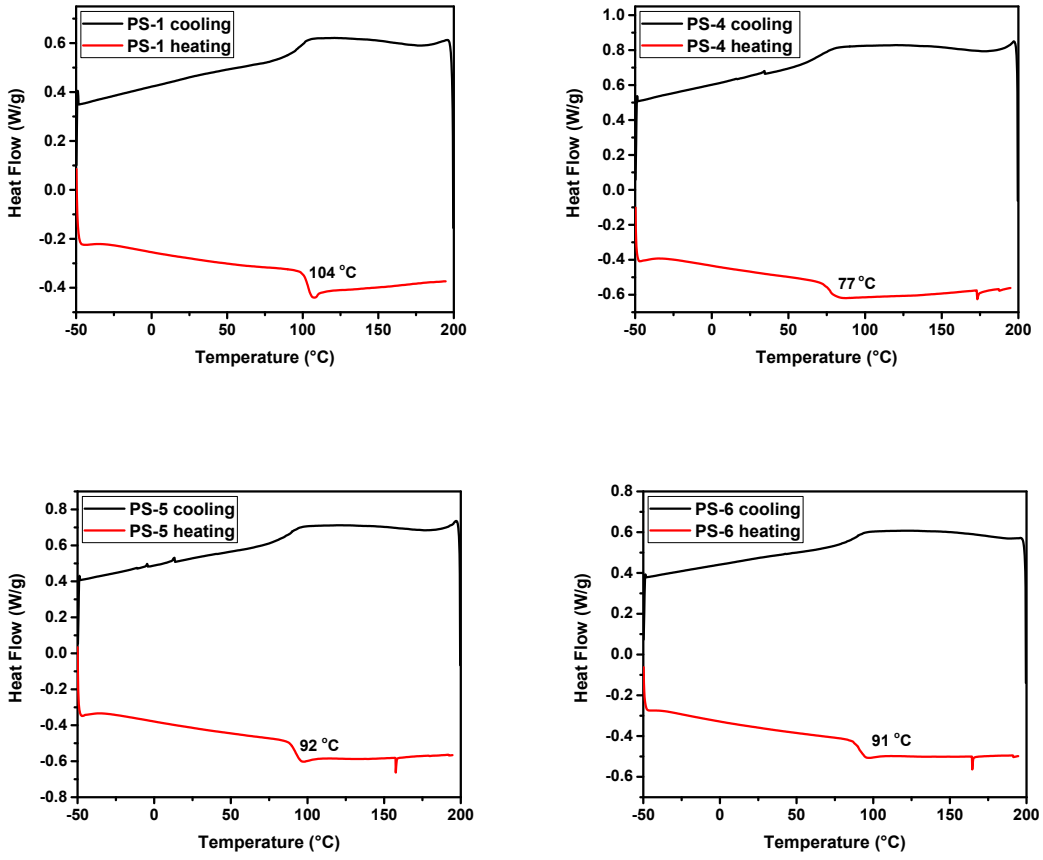


Figure S3. DSC data for the samples listed in Table 1, main text.

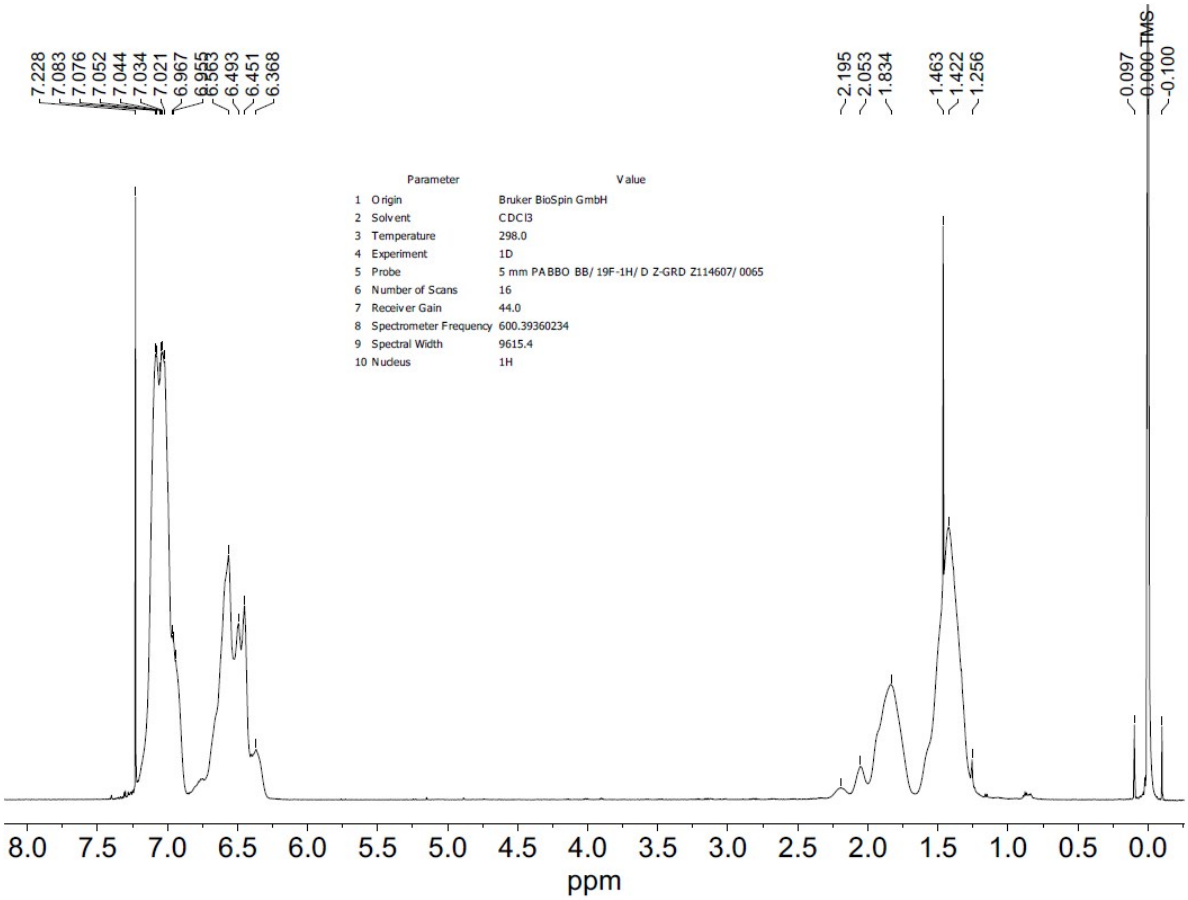


Figure S4. NMR spectrum of commercial polystyrene (PS-1). ^{1}H solution NMR spectrum of commercial polystyrene (Sigma-Aldrich, Cat. # 182427**)** in $CDCl_3$ (Acros Organics, Cat Nr. AC209560250, TMS as internal standard).

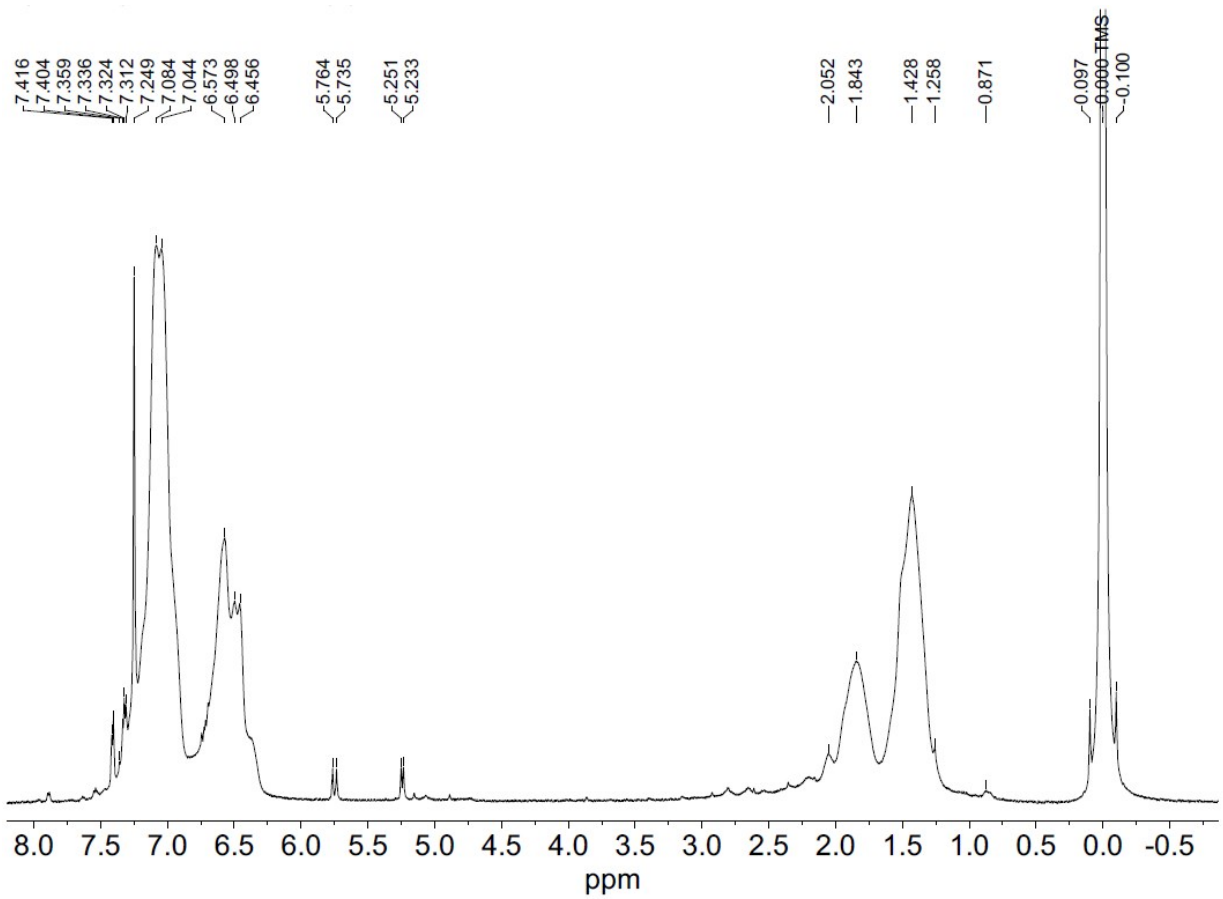


Figure S5. NMR spectrum of ball milled polystyrene (PS-3). ^{1}H solution NMR spectrum of commercial polystyrene (Sigma-Aldrich, Cat. # 182427) ball milled in a hardened steel processing set in air for 12 hours (solvent: $CDCl_3$, Acros Organics, Cat Nr. AC209560250, contains TMS as internal standard). Peak broadening in this case is attributed to the presence of a minor magnetic impurity introduced during the milling.

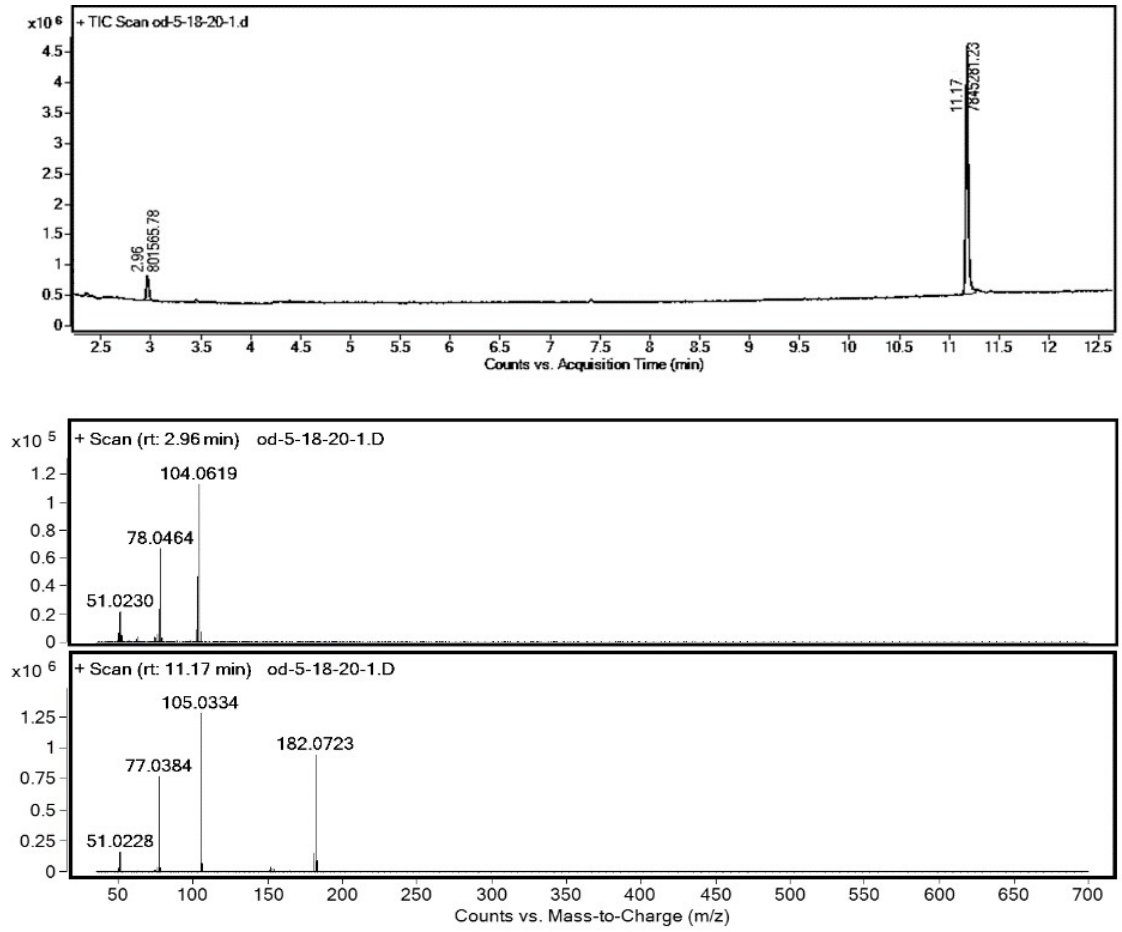


Figure S6. GC-MS evaluation of the ball milled polystyrene (PS-3). GS traces and MS spectra obtained for commercial polystyrene (Sigma-Aldrich, Cat. # 182427) ball milled in a hardened steel set in air for 12 hours. Methanol soluble components were extracted from 0.0154 g of the milled sample using 5.2674 g of methanol, combined with 0.0145 g of benzophenone in 10.1249 g of methanol, centrifuged, and the clear solution formed was analyzed using Agilent 7250 GC/Q-TOF Quadrupole Time-of-Flight GC-MS system. The amount of styrene in the sample was calculated from integrated peak areas that correspond to two main products in the sample, e.g., styrene (retention time 2.96 min) and benzophenone (retention time 11.17 min), whose mass spectra are shown as well.

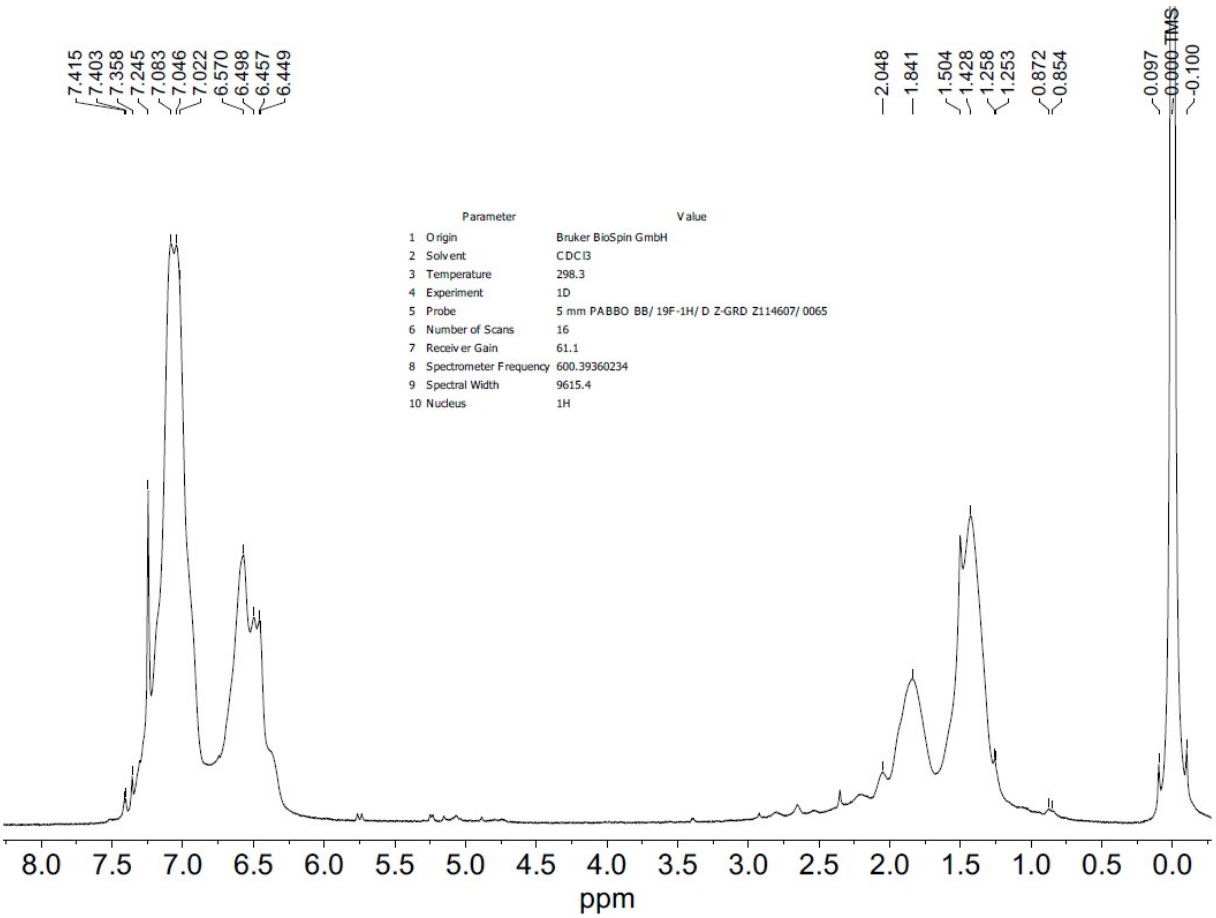


Figure S7. NMR spectrum of polystyrene ball milled under argon (PS-4). ^{1}H solution NMR spectrum of commercial polystyrene (Sigma-Aldrich, Cat. # 182427**)** ball milled in a hardened steel processing set under argon for 12 hours (solvent: $CDCl_3$, Acros Organics, Cat Nr. AC209560250, contains TMS as internal standard). Peak broadening in this case is attributed to the presence of a minor magnetic impurity introduced during the milling.

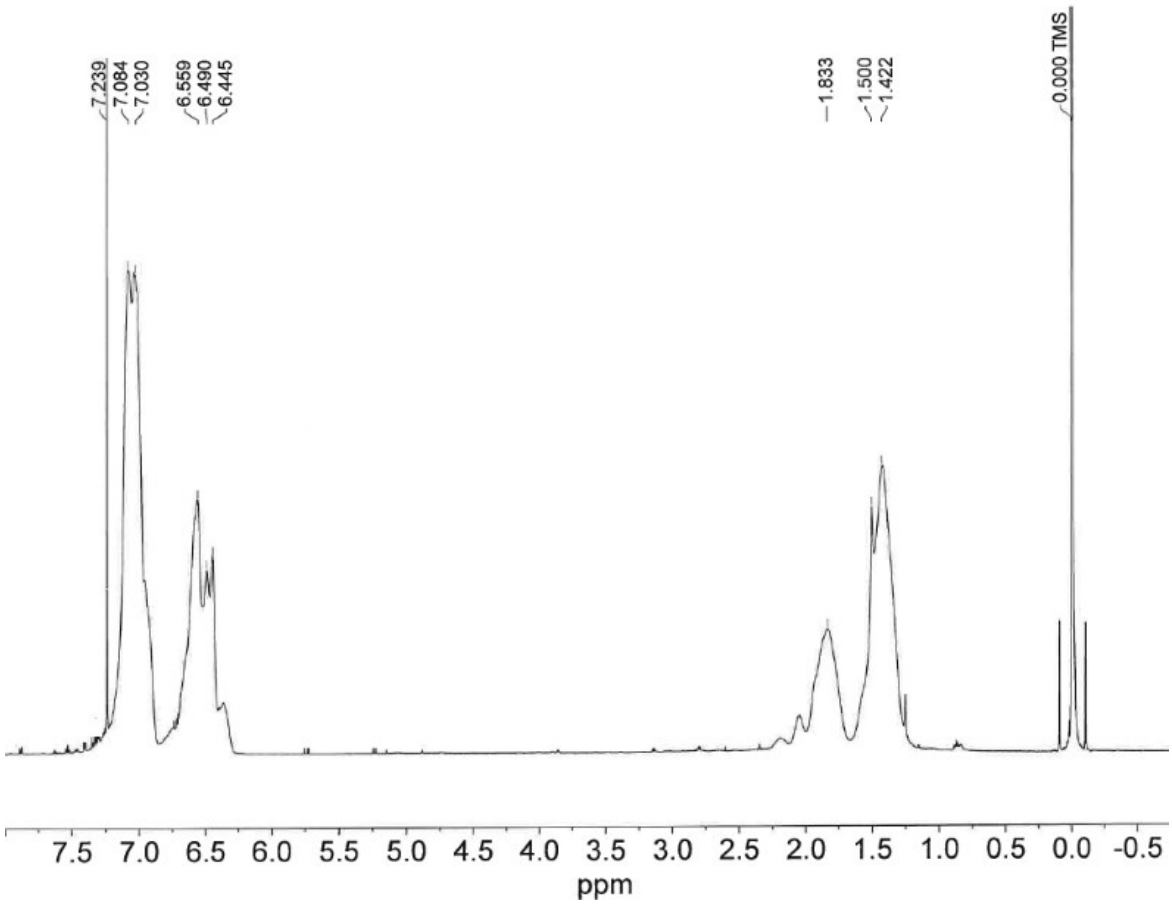


Figure S8. NMR spectrum of ball milled polystyrene (PS-6). ^{1}H solution NMR spectrum of commercial polystyrene (Sigma-Aldrich, Cat. # 182427) ball milled in a silicon nitride set in air for 12 hours (solvent: $CDCl_3$, Acros Organics, Cat. # AC209560250, contains TMS as internal standard).

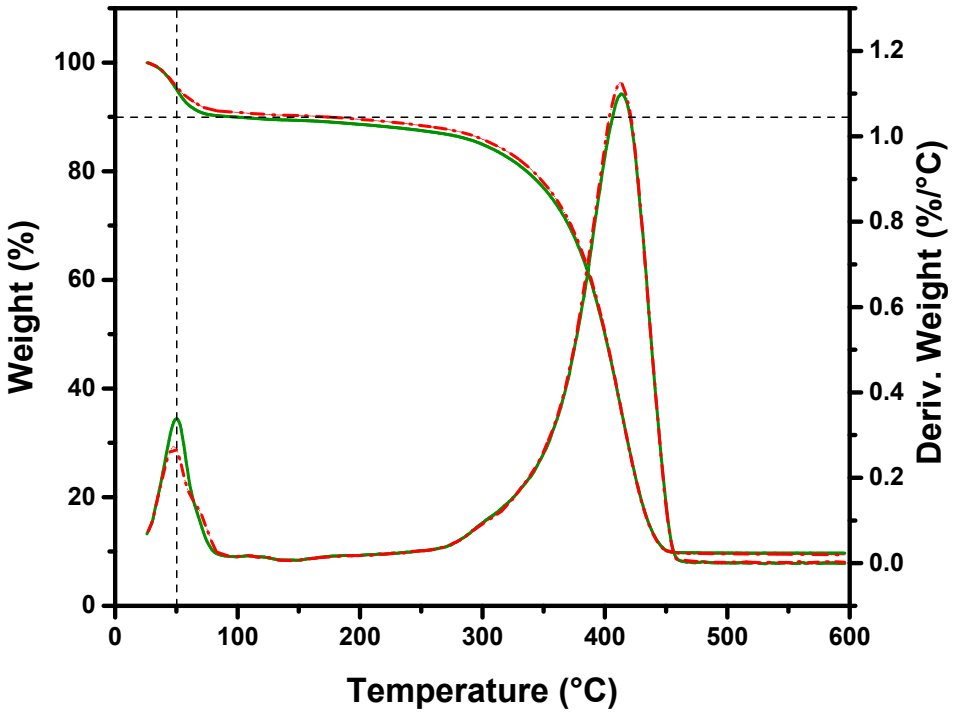


Figure S9. Mixture of polystryrene and ammonium carbonate. TGA plots of a mixture of polystyrene (Sigma-Aldrich, Cat. # 182427) and ammonium carbonate (Alfa Aaesar, Cat. Nr. AA 1298009) combined in 2:1 weight ratio and ball milled in a hardened steel setup for 12 hours. The ammonium carbonate (~10 wt.%, decomp. 58 °C) is still present in the material, confirming that the sample temperature remained below 60 °C throughout the milling process.

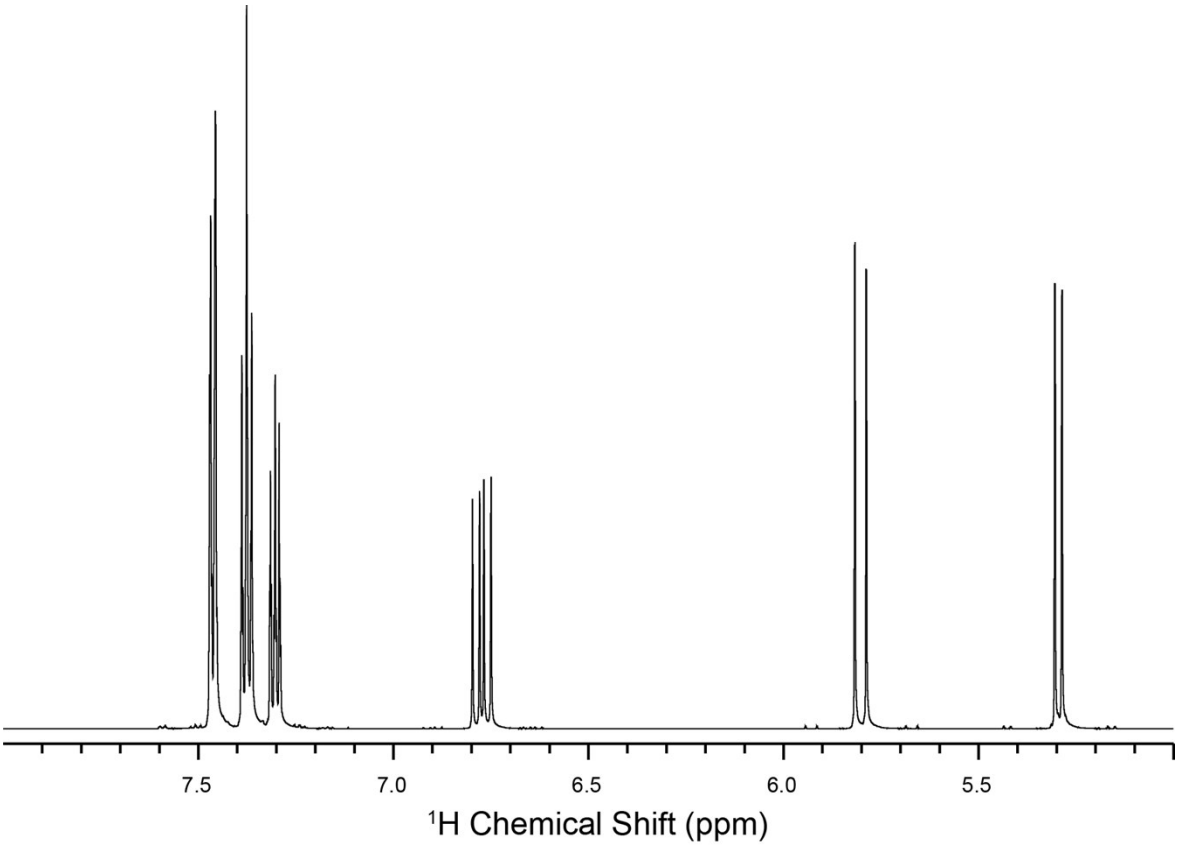


Figure S10. NMR spectrum of commercial styrene (Sigma-Aldrich, Cat. #45993; solvent: $CDCl_3$, Acros Organics, Cat Nr. AC209560250, contains TMS as internal standard).

Calculations of Molecular Weight from T_g:

w is weight fraction of a component

$Ln\,T_{gmix} = w_{monomer} \times Ln\,T_{gmonomer} + w_{polymer} \times Ln\,T_{gpolymer}$

T_{gmix}: from DSC

$T_{gmonomer} = 150K$ from literature[2]

$w_{monomer}$: $from\ TGA\ (Boiling\ point\ of\ styrene\ monomer\ is\ 145°C)$

$w_{polymer} = 1 - w_{monomer}$

Find $T_{gpolymer}$

$T_g(K) = 373 - \frac{1.8 \times 10^5}{M_n}$ => Molecular weight of polymer is found.[3]

References

1. (a)EPR Spectroscopy: Fundamentals and Methods. Eds.: D. Goldfarb and S. Stoll, Wiliey, 2018, 648 p;

(b) *chem.libretexts.org.*

2. P. Claudy, J. M. Létoffé, Y. Camberlain, J. P. Pascault, *Polymer Bulletin* 1983, **9**, 208-215.

23. L. H. Sperling, *Introduction to the physical polymer science*, 3rd ed., Wiley-Intersci., 2001.

Table S1. Calculation of molecular weight from DSC data for the samples listed in Table 1, main text.

Sample	W monomer (TGA)	T_g mixture, °C, (DSC)	T_g mixture K	T_g monomer K [2]	W polymer	T_g polymer, K	T_g polymer °C	Molecular weight
PS-2	0.0939			150	0.9061			
PS-3	0.0412			150	0.9588			
PS-4	0.0093	77	350	150	0.9907	353.22	**80**	**9102**
PS-5	0.0079	92	365	150	0.9922	367.49	**94.5**	**32643**
PS-6	0.0014	91	364	150	0.9986	364.11	**91**	**20240**