Supporting Information.

Materials. Polyethyleneglycol monomethylether methacrylate (PEGMA) (~475 Da), trifluoroethyl acrylate (tFEA) and ethyleneglycol dimethacrylate (EGDMA) were purchased from Sigma Aldrich and passed through an alumina column prior to use. Azobisisobutyronitrile (AIBN) was purchased from Acros scientific and recrystallised three times from ethanol before use. Solvents were purchased from Sigma Aldrich and used as received. Alkyne-terminated RAFT agent was synthesised as previously reported.[1]

Instrumental methods.

Standard ^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument using $CDCl_3$ as solvent. ^{1}H T_1 relaxation times were measured using the standard inversion-recovery pulse sequence as supplied by Bruker.

GPC-MALLS was carried out on a Waters GPC equipped with an RI detector and a Wyatt 8 angle DAWN MALLS detector. The polymers were eluted at 1 mL/min in tetrahydrafuran (THF). Dn/dc for each hyperbranched polymer was calculated by measuring the refractive index of a series of polymer dilutions in THF and was found to be 0.061.

Hyperbranch particle sizes in pure water were measured using a Malvern Zetasizer. The diameter that is recorded (Table 1) is a volume average and is the average result of 5 experiments.

Synthesis of Polymers.

P1 was synthesized as follows: 6g PEGMA (1.27×10^{-2} mol), 540 mg tFEA (3.5×10^{-2} mol), 14 mg AIBN (8.5×10^{-5} mol), 202 mg EGDMA (1.1×10^{-3} mol) and 348 mg alkyne-terminated RAFT agent (8.6×10^{-4} mol) were added to a 25 mL flask with 10 mL THF. The flask was sealed with a septum and the solution was purged with argon for 15 minutes before heating to 65 ^{o}C for 48 hours. After this time, the solution was diluted with THF and precipitated into hexane. The recovered solid was re-dissolved in THF and precipitated once more in hexane. The solid was then dissolved in a methanol/water mix (50:50) and dialysed against water for 3 days. The dialysed solution was freeze-dried to yield the pure polymer (P1) which was subsequently analysed by ^{1}H NMR (Figure S1). GPC-MALLS analysis: Mn =

21.0 kDa, Mw = 31.5 kDa, Đm = 1.5; NMR molecular weight: Mn = 6.3 kDa (Degree of polymerization (DP) = (peak a + peak b) / peak c); UV-VIS: 308 nm (thiocarbonylthio group).

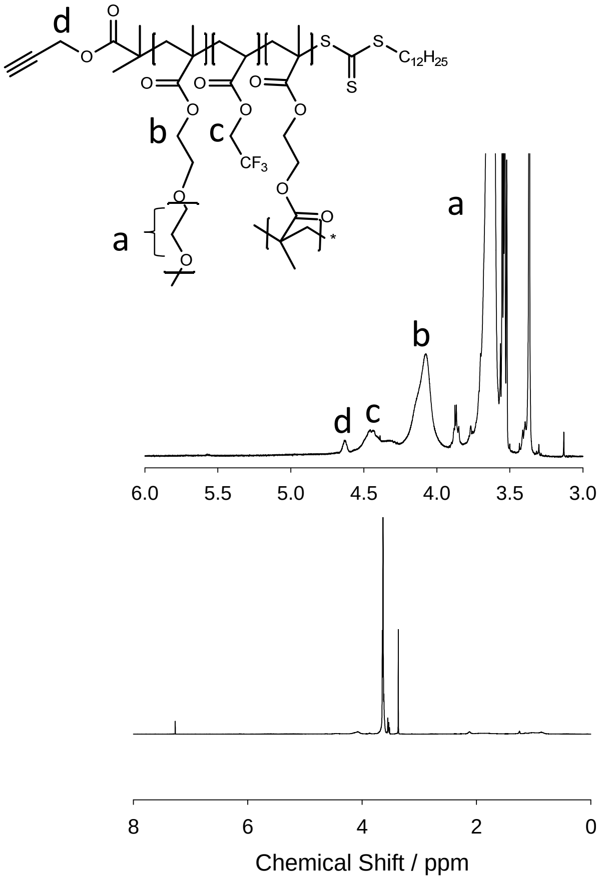

Fig S1. ^{1}H NMR spectrum of P1 using $CDCl_3$ as solvent. Peaks a and b refer to methylene protons from PEGMA and FEA repeat units, respectively, while peak c is due to the methylene protons immediately adjacent to the alkyne end-groups.

P2 was synthesized using the same procedure as reported for P1, except double the amount of EGDMA (404 mg, 2 x 10^{-3} mol) and alkyne-terminated RAFT agent (696 mg, 1.7 x 10^{-3} mol) was used. GPC-MALLS analysis: Mn = 39.1 kDa, Mw = 66.0 kDa, Đm = 1.7; NMR molecular weight: Mn = 7.5 kDa; UV-VIS: 308 nm (thiocarbonylthio group).

Parahydrogen enrichment

Normal hydrogen with a purity of 5.0 was used as received from a commercial source (Westfalen AG, Münster, Germany). 95% enriched parahydrogen was generated by cooling thermal hydrogen down to 30 Kelvin with a closed-cycle cryostat setup (Advanced Research Systems, Macungie, PA, USA) in the presence of active charcoal as a catalyst for the otherwise symmetry forbidden conversion from ortho- to parahydrogen.

PHIP NMR experiments

10 mm NMR tubes were filled under argon atmosphere with 200 mg hyperbranched polymer and 10 mg (13.8mmol, 0.23 mol%) [1,4-bis(diphenylphosphino)butane](1,5-cyclooctadiene)rhodium(I) tetrafluoroborate as hydrogenation catalyst dissolved in 2600 mg of acetone-d6 (99.9% D). Parahydrogenation was carried out at elevated temperature and pressure in order to increase the conversion of the reaction. Therefore, the reaction tube was gently heated to 60°C in a water bath and then pressurized with 3.5 bar of para-H_2. Subsequently, the tube was shaken next to the magnet to start the hydrogenation and immediately inserted into the spectrometer. Shaking the tube outside of the magnet should create polarization in the ALTADENA spin state (ALTADENA = Adiabatic Longitudinal Transport After Dissociation Engenders Nuclear Alignment). The NMR experiments were performed with 300 MHz spectrometer using a Tecmag console. The resultant spectra are shown in Figure S2 and S3 for P1 and P2, respectively. In both cases the spectra are shown for the first and subsequent "shakes" with the hydrogenation catalyst to highlight the polarisation process.

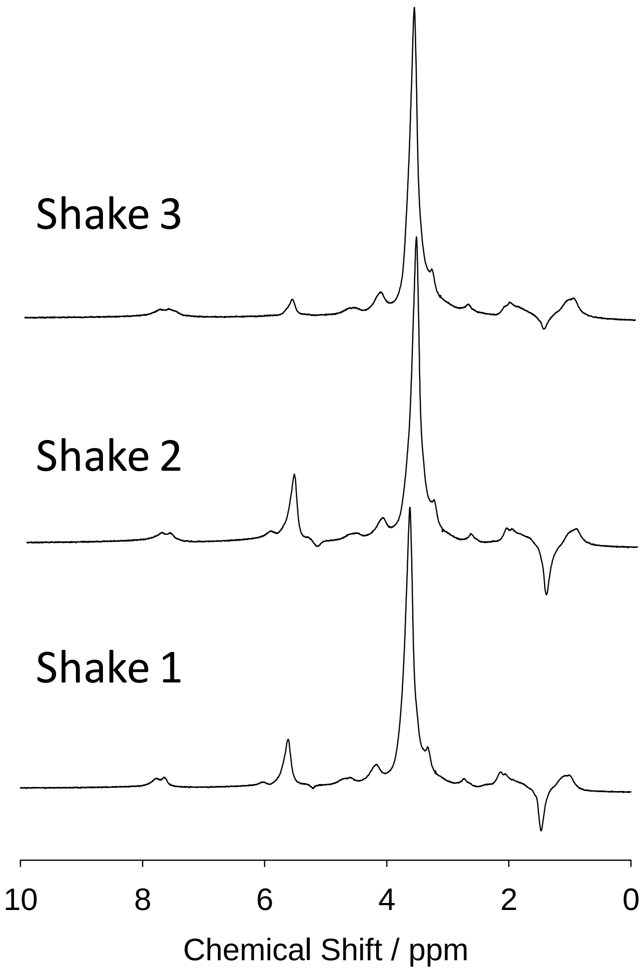

Fig S2. Comparison of the ^{1}H NMR spectr of P1 following PHIP enhancement after 1-3 "shakes" with the hydrogenation catalyst. Note the maximum polarisation is observed after the second shake.

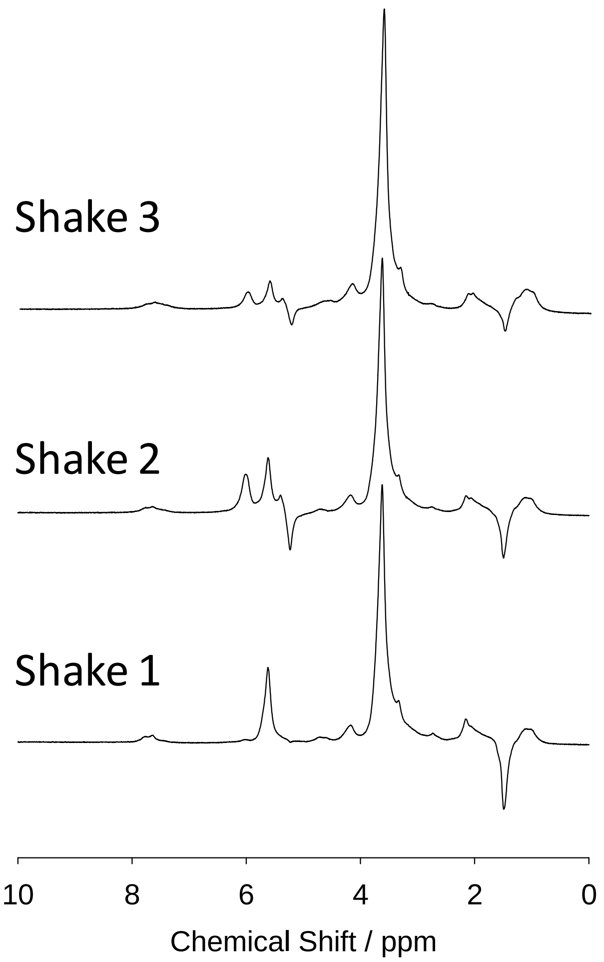

Fig S3. Comparison of the ^{1}H NMR spectra of P2 following PHIP enhancement after 1-3 "shakes" with the hydrogenation catalyst. Note the maximum polarisation is again observed after the second shake. The polarised signal of the single alkene proton is of the same order of magnitude as the thermally polarised protons within the whole polymer.

A spectrum of the catalyst in the absence of polymer following exposure to p-H_2 was also taken for comparison and is shown in Figure S4.

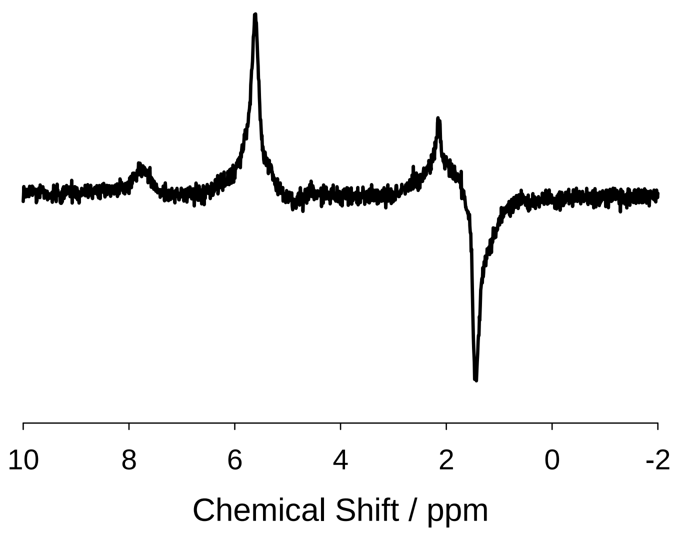

Figure S4. ^{1}H spectrum of solution following reaction of catalyst with parahydrogen in acetone. Spectrum was taken in the absence of polymer to show conversion of cyclooctene to cyclooctane.

For the most promising hyperbranched polymer P2 we repeated the PHIP experiment with optimized reaction conditions to obtain an even higher signal enhancement (Figure S5). Therefore, we altered the polymer to catalyst ratio such that we decreased the amount of polymer by a factor of 4 (i.e. we used only 50 mg polymer for the experiment, all other reaction parameters were kept the same). This was done in order to decrease the poisoning of the catalyst by the polymer in order to get a better hydrogenation of the triple bond of the polymer. Moreover, we were able to reduce the transfer time of the hyperpolarized sample into the spectrometer slightly to 5s (instead of 6s for the other experiments). These measures led to an improved signal enhancement of 3840 for P2. This highlights the challenges associated with parameter optimisation when applying PHIP enhancement to polymers, but also gives insight into the potential of this technique for molecular imaging in the future.

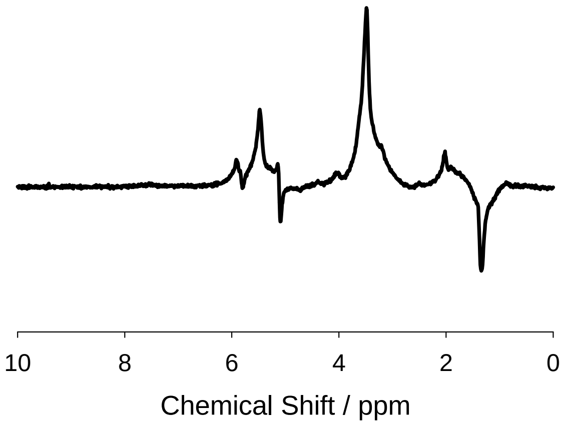

Figure S5. ^{1}H NMR spectrum of P2 following PHIP enhancement using optimised mixing conditions.

Determination of Enhancement.

It was not possible to measure a thermally polarized spectrum of the hyperbranched polymer after the PHIP reaction in which the peaks of the generated double bond were visible (2 days of signal averaging (16k scans) were not sufficient). This illustrates the small conversion of the PHIP reaction and the very small amount of hyperpolarized spins compared to the rest of the polymer. Therefore we had to determine the signal enhancement of the experiments by using an internal reference in the spectra and chose the peak labelled with b (4.16 ppm) in Figure S1 which represents a methylene group within the monomer repeat unit of the polymer. For P1 and P2 the amount of this methylene group per alkyne group is 14 and 16, respectively. In the following we calculate exemplarily the signal enhancement of the second shake of the PHIP experiments with P2 (second trace in figure S3).

i) The integrals of one hyperpolarized (6.05 ppm) and the reference peak (4.16 ppm) are determined and the ratio of them is calculated. This is for this particular experiment 2.4.

ii) It must be considered how many protons give rise to the respective signals: For the hyperpolarized peak it is only one and for the thermal one we have 16 methylene groups which consist of 2 protons each, therefore the thermal signal originates from 32 protons.

iii) The conversion of the hydrogenation reaction must be taken into account (i.e. the number of hyperpolarized molecules and therefore protons), we estimate 5% conversion for the hyperbranced polymer.

Finally, the total enhancement of this experiment can then be calculated: 2.4*32*20=1536.

To determine the signal enhancement due to PHIP, the level of catalyst efficiency is required (see iii). If a thermally polarized reference spectrum with visible product peaks can be acquired, the conversion of the hydrogenation can be calculated from the integrals of the product peaks. However, this was not possible for the hyperbranched polymers due to the very low concentration of hydrogenation product that is formed. Therefore the conversion was determined by measuring the degree of hydrogenation that was observed for a model molecule, 1-hexyne, with this particular catalyst. Under the same conditions of temperature, pressure and catalyst concentration, 1-hexyne was consistently hydrogenated to less than 5% efficiency as measured by ^{1}H NMR. Thus, we have assumed in all our calculations that ~5% of alkyne groups in the polymer are hydrogenated using this catalyst.

References.

1. Quemener, D.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Chemical Communications (Cambridge, United Kingdom)* **2006**, (48), 5051-5053.