Supporting Information

Multivalent hydrogen bonding block copolymers for strong and tough self-healing materials

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General information. Chemicals were purchased from Sigma-Aldrich, VWR or Fisher Scientific and used without further purification. Solvents used in reactions were from alumina filtration system. All glassware was flame dried before use, and reactions were carried out under nitrogen atmosphere. Extraction solvents were commercial grade. Flash Chromatography was performed using forced flow of the indicated solvent systems over Fisher silica gel (230 - 400 mesh). ^{1}H NMR spectra were taken on a 500MHz Bruker instrument. NMR chemical shifts were reported as values in ppm relative to deuterated solvents DMSO-*d6* (2.50), $CDCl_3$ (7.27) or DMF-*d7* (8.03, 2.92, 2.75). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hz and integration. Multiplets were reported over the range (in ppm) it appeared. ^{13}C NMR spectra were taken on a 125MHz Bruker instrument. Carbon NMR data were recorded relative to the solvent signals of DMSO-d_6 (39.51). Mass spectral data (ESI/MS) were obtained on a Micromass auto spec spectrometer. Gel permeation chromatography (GPC) was performed in THF (1 mL/min) using an Agilent LC 1100 Series equipped with a Polymer Laboratory's PLgel 5 μm mixed-C column to determine molecular weights and molecular weight distributions, Mw/Mn, of the bifunctional macroinitiators with respect to polymethylmethacrylate (PMMA) standards (Agilent Technologies, Inc.). Molecular weights of block copolymers were determined by size-exclusion chromatography (SEC) in DMF (1.0 mL/min) coupled with a Dawn DSP18 multi-angle light scattering detector (MALS, laser wavelength λ = 632 nm, Wyatt Technology, Santa Babara, CA) and a Refractometric Index (RI) detector (an Agilent 1100 SEC system with a Shodex OHpak SB 803-HQ column).

Synthesis of telechelic macroinitiator Br-PMMA-Br. The telechelic macroinitiator was synthesized according to Scheme 1a. Methyl methacrylate (MMA) (15.018 g, 150 mmol), ethylene glycol bis(2-bromoisobutyrate) (2Br^{i}Bu)[1] (54.0 mg, 0.15 mmol Br), and PMDETA (104.0 mg, 0.60 mmol) were dissolved in toluene (150 mL). The mixture was degassed with three freeze-pump-thaw cycles. After addition of CuBr (43.0 mg, 0.30 mmol), the mixture was heated at 70 °C for 24 h. Upon cooling, the polymer was precipitated in 1000 mL mixed solvent (methanol / water 9 : 1, v/v) twice. Filtered and washed the precipitate with water three times followed by methanol three times. The precipitate was dried at 60 °C under vacuum for 24 h to give 5.498 g of the telechelic PMMA macroinitiator **Br-PMMA-Br**: Mn: 49.2 KDa; PDI: 1.19 by GPC.

Synthesis of ABA block copolymers. The block copolymers **(PA-amide)-*b*-PMMA-*b*-(PA-amide)** were synthesized according to Scheme 1b. As an example, the synthesis for the block copolymer **BCP1** was described here. The linear macroinitiator **Br-PMMA-Br** (790.8 mg, 0.032 mmol Br), 5-acetylaminopentyl acrylate[2] (**5-AAPA**) (7.8003 g, 39.148 mmol), and PMDETA (13.6 mg, 0.078 mmol) were dissolved in DMF (20 mL). The mixture was degassed with three freeze-pump-thaw cycles. After addition of CuBr (5.6 mg, 0.039 mmol), the mixture was heated at 50 °C for 24 h. The monomer conversion was 35% determined by ^{1}H NMR spectroscopy. Upon cooling, the polymer was precipitated three times in ether to thoroughly remove any residual monomer. Catalyst was removed by passing a solution of the polymer in MeOH over a basic alumina plug. The dried polymer **BCP1** (3.344 g) was obtained by evaporating the methanol solution under vacuum at 110 °C for 48 h. Mn: 214 KDa; PDI: 1.35 by MALS.

AFM studies. Atomic force microscopy (AFM) was performed on a MFP-3D-SA AFM instrument (Asylum Research, Santa Barbara, CA) using silicon tips (type AC240TS) with a spring constant of 2 N/m at a resonance frequency of 70 kHz. All measurements were carried out in tapping (AC) mode. The samples were spin-coated from DMF solution (1 mg/mL) on mica substrates. The solvent was removed under high vacuum overnight at 40 °C.

Differential Scanning Calorimetry (DSC). DSC was performed on a TA Instruments Q2000 using standard heat-cool-heat experiments on ~5 mg of sample between -80 and 200 °C. The heating rate was 10 °C/min. The glass transition temperatures (T_g) were reported at the inflection point of the heat capacity jump of the second heating run.

Mechanical studies. Mechanical testing was performed on an Instron 3365 machine. Samples were prepared by hot-pressing the resin into Teflon moulds (30 mm x 7 mm x 2 mm). The specimens were extended at 100 mm/min at room temperature. Each measurement was repeated at least three times. Young's modulus (E) was determined from the initial slope of the stress-strain curves. Self-healing specimens were prepared by cutting the film in half, gently pushing two interfaces together for a minute and letting the fixed film heal for a certain time.

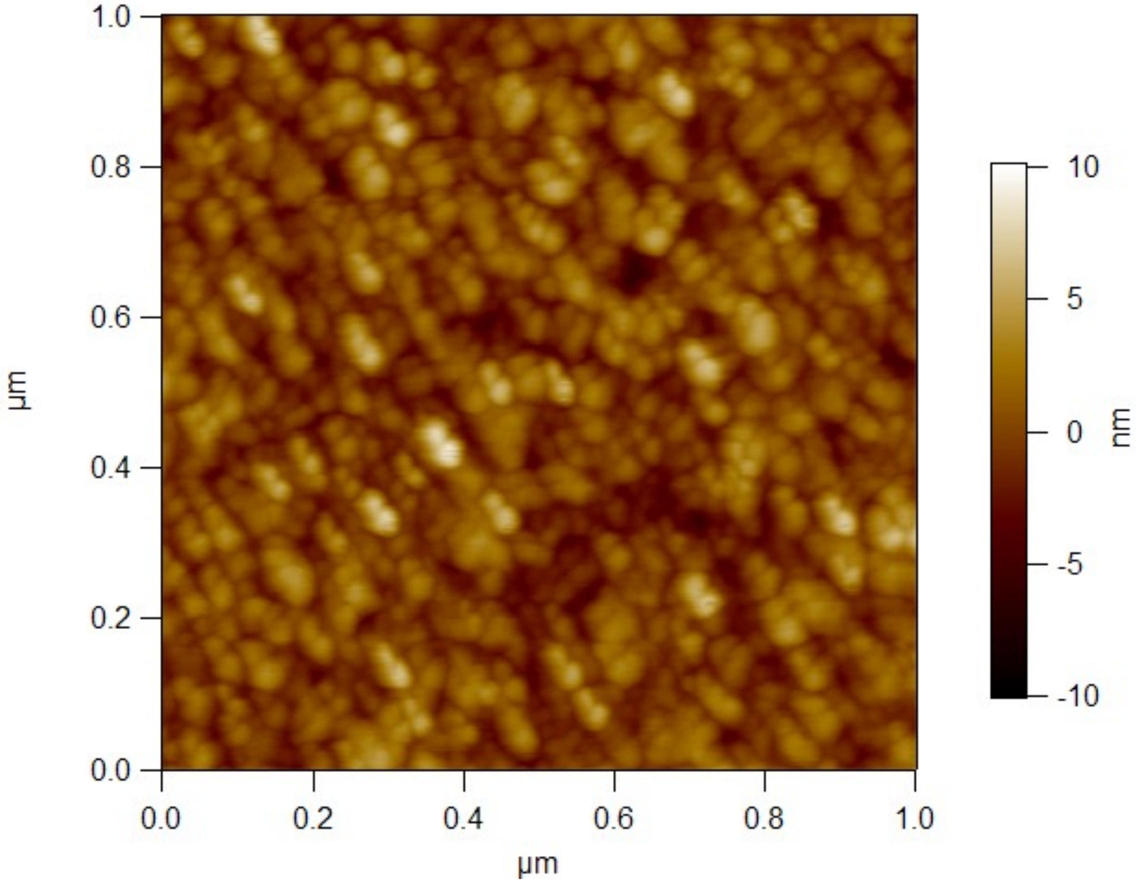


Figure S1. AFM image of the block copolymer **BCP3**.

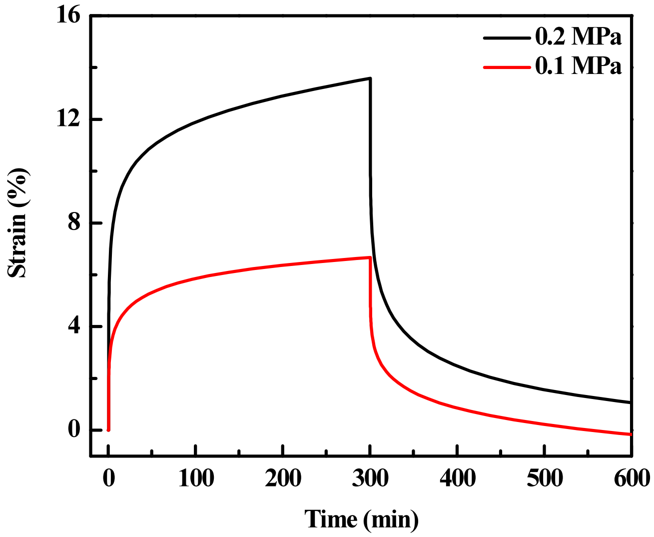


Figure S2. The creep-recovery behaviour of **BCP1** at different stress.

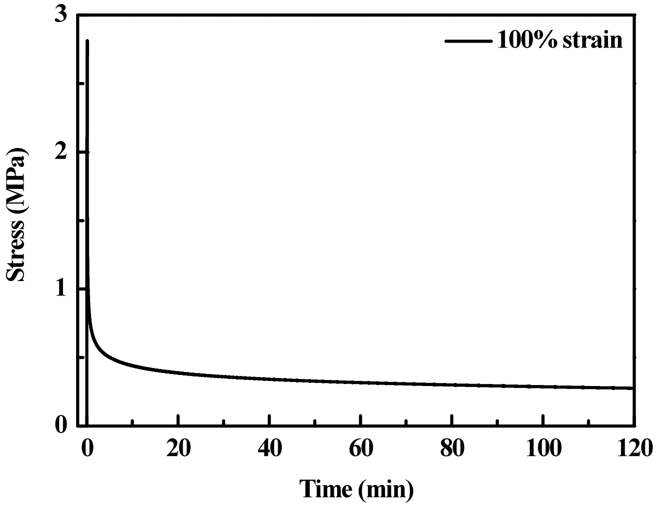
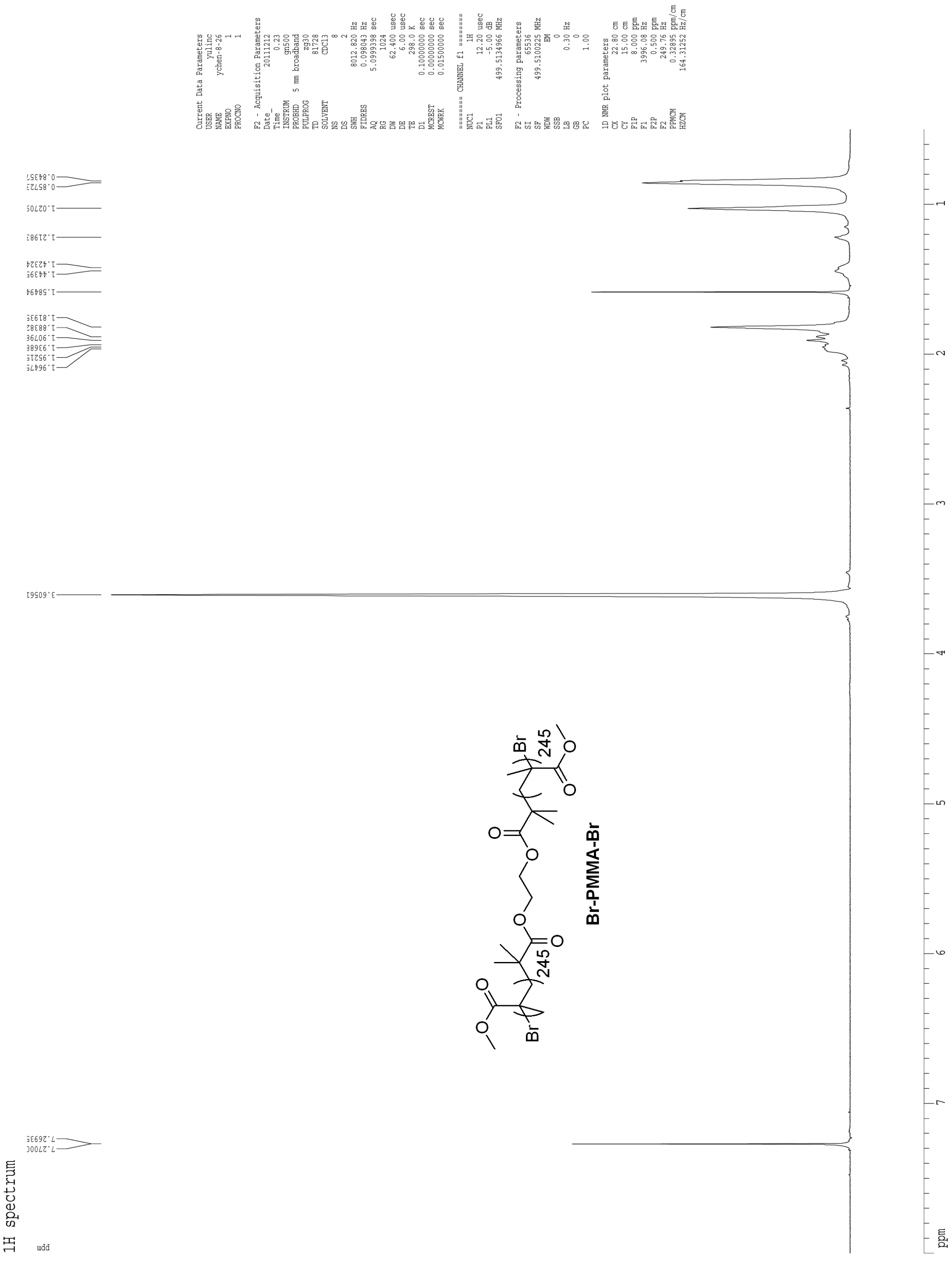


Figure S3. The stress-relaxation of **BCP1** at 100% strain.

List of ^{1}H NMR Spectra for the macroinitiator and the block copolymers



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NAME            ychen-8-26
EXPNO                    1
PROCNO                   1

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Time                  0.23
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PROBHD   5 mm broadband
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0999398 sec
RG                    1024
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.20 usec
PL1                  -5.00 dB
SFO1           499.5134966 MHz

F2 - Processing parameters
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SF             499.5100225 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
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CY                   15.00 cm
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F1                 3996.08 Hz
F2P                  0.500 ppm
F2                  249.76 Hz
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Figure S4. ^{1}H NMR spectrum of the telechelic macroinitiator **Br-PMMA-Br**.

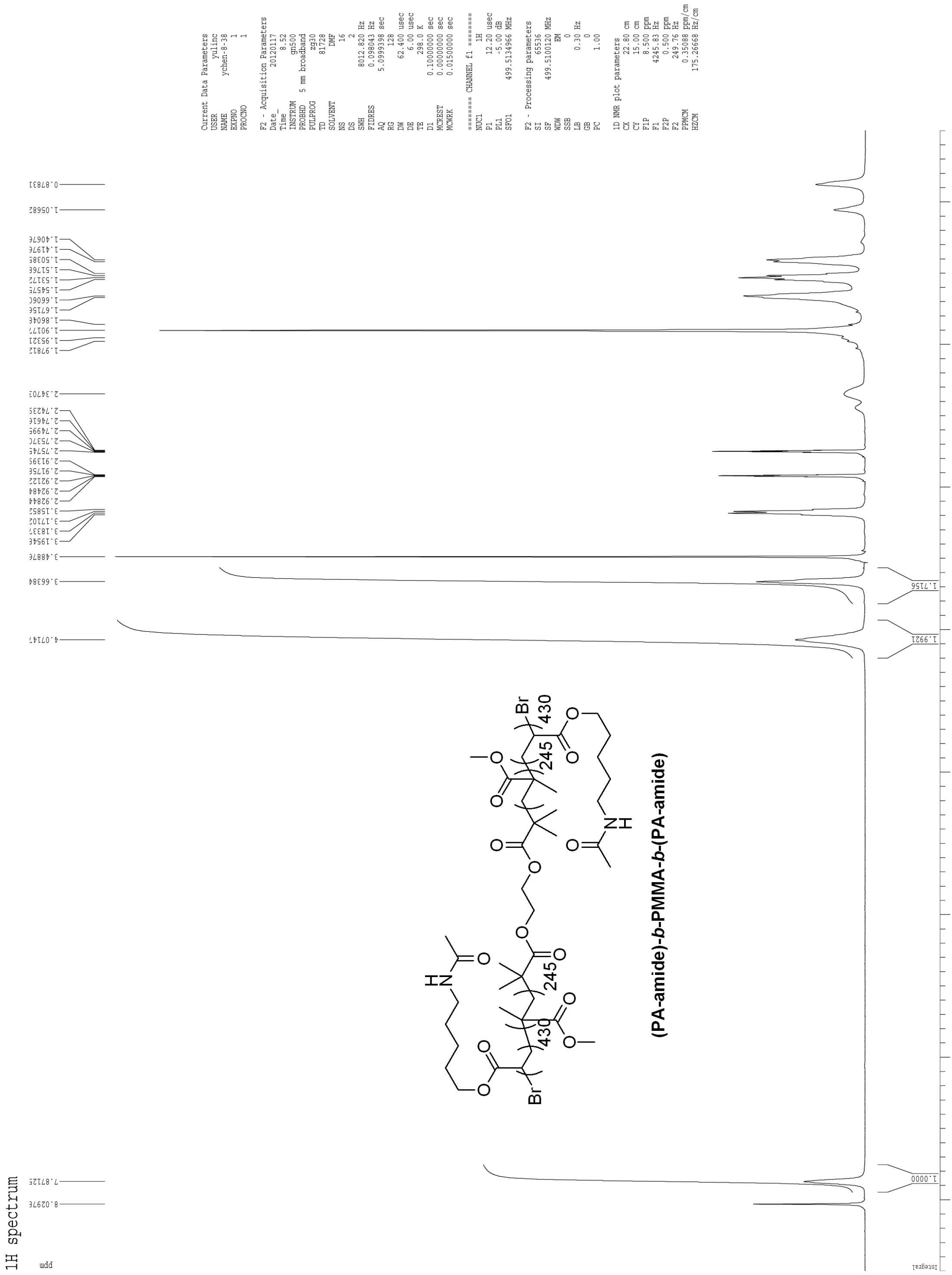

Figure S5. ^{1}H NMR spectrum of the ABA block copolymer **BCP1**.

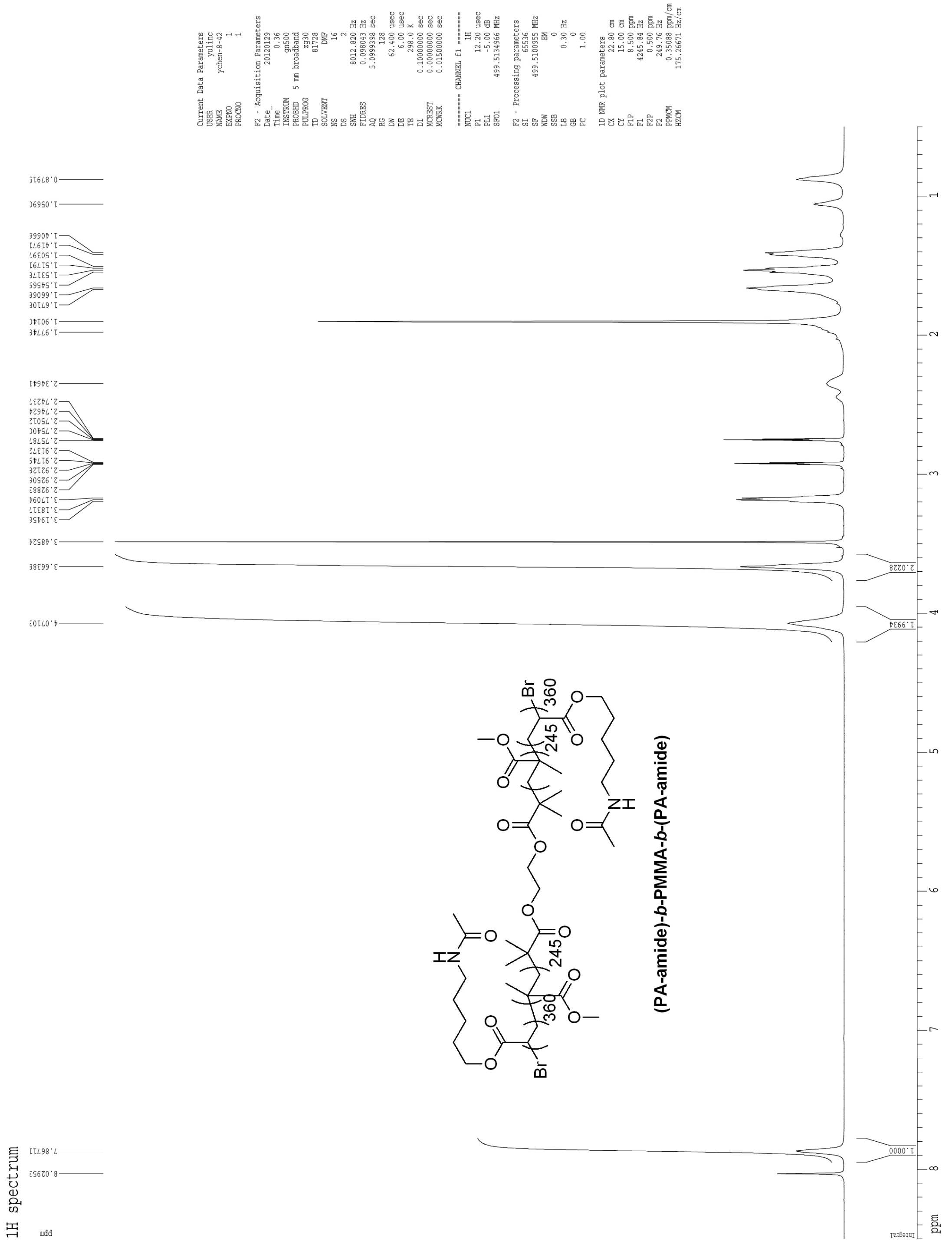

Figure S6. ^{1}H NMR spectrum of the ABA block copolymer **BCP2**.

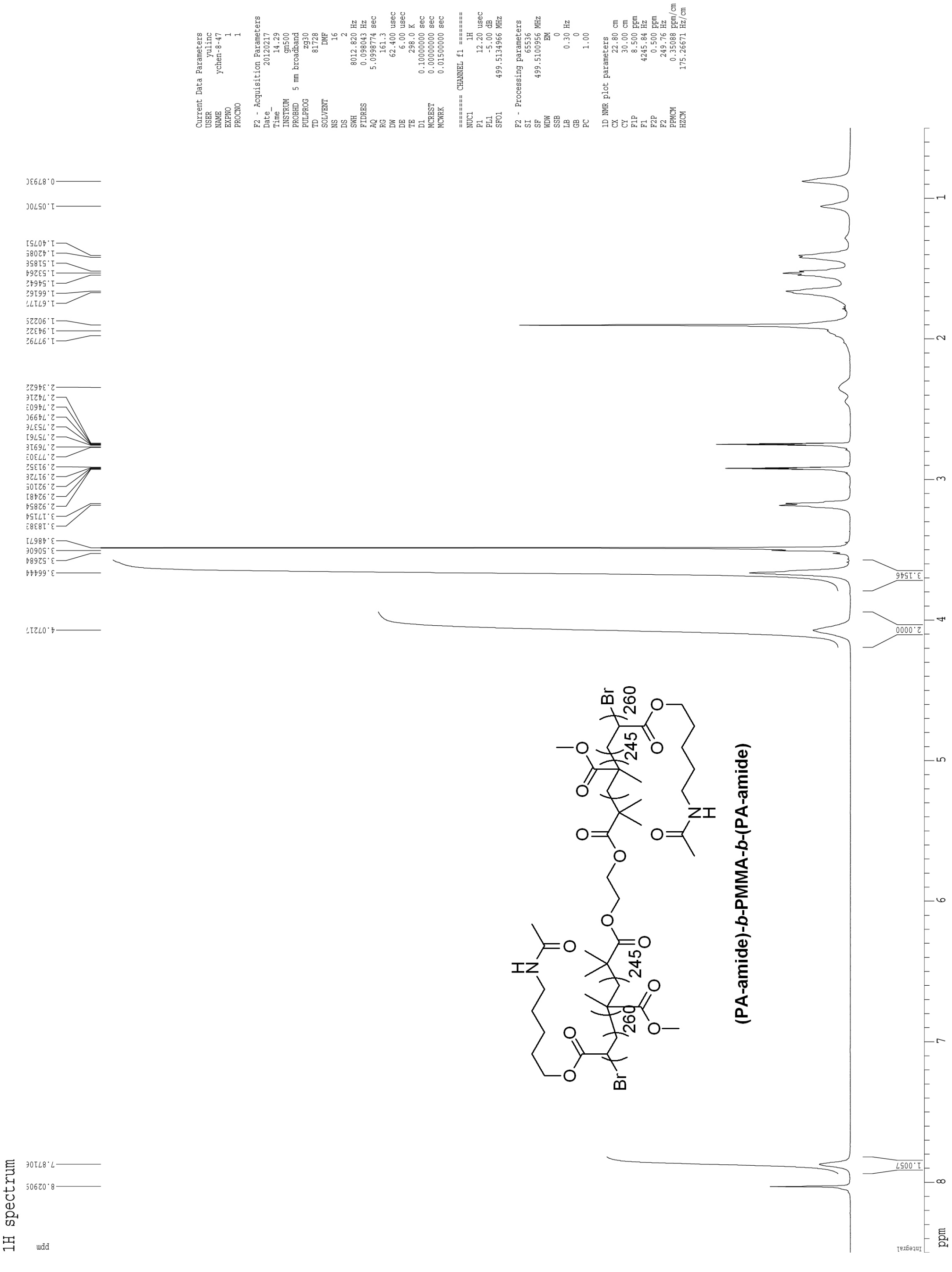

Figure S7. ^{1}H NMR spectrum of the ABA block copolymer **BCP3**.

References

1 K. Matyjaszewski, P. J. Miller, J. Pyun, G. Kickelbick, S. Diamanti, *Macromolecules*, 1999, **32**, 6526−6535.

2 Y. Chen, A. M. Kushner, G. A. Williams, Z. Guan, *Nat. Chem.,* 2012, **4**, 467−472.