# Supporting Information

## 3+2 Click Chemistry Approach to Tetrazine Containing Polymers

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Unless otherwise noted, all chemicals were used as received.

NMR data was collected on a Bruker Advance III 400 MHz NMR spectrometer at room temperature. Spectra were referenced to residual DMSO (2.50 ppm, 1H) or chloroform, $CDCl_3$ (7.26 ppm, 1H) with chemical shifts reported in δ values (ppm) and J values in hertz (Hz). The following abbreviations are used to describe peaks: d (doublet), brs (broad singlet), m (multiplet).

The GPC instrument used for this analysis is the Malvern OMNISEC (Westborough, MA, USA) equipped with quad detection: refractive index (RI), UV/Vis photoiode array (PDA), multi-angle light scattering and viscometer. A sample injection volume of 100 µL was used with a mobile phase flow rate of 1 mL/min. For all analyses, two serially coupled PL Gel Mixed C columns (Agilent Technologies, Palo Alto, CA, USA) were implemented.

DSC measurements were conducted on either: A) STD 650 (TA Instruments) coupled to a Discovery II quadruple mass spectrometer (TA Instruments) or B) DSC Q-2000 from TA Instruments.

A TA Instruments DHR-3 Discovery Hybrid Rheometer was used to measure the storage (G' [Pa]) and loss (G" [Pa]) moduli evolution for the GAP-P:BPT and GAP:BPT systems at an elevated temperature to observe time to gelation. The rheometer was equipped with a Peltier plate attachment for regulating sample temperature, and the geometry used for these experiments was a set of smooth 25 mm aluminum disposable parallel plates. Samples were prepared by mixing the components in a FlackTek DAC 330-100-PRO dual axis centrifugal mixer. After mixing, the GAP-P and GAP mixtures were loaded into the rheometer and tested for 360 min and 300 min at 60 ºC, respectively. The samples were measured with a constant oscillation where the strain amplitude was 0.25% with a strain rate of 10 $s^{-1}$.

Synthetic Procedures

Compounds **5** and **7** were synthesized as previously reported.[15, 16] Caution! The compounds and polymers presented are highly energetic with sensitivity to various stimuli. While we encountered no issues while working with this material, proper protective measures (Kevlar® gloves, face shield, and grounded equipment) should still be used at all times. The 3+2 cycloaddition between alkyne and azide moieties is highly exothermic and should only be undertaken in small amounts with sufficient heat-dissipation to avoid ignition during reaction.

**3,6-propargyloxy-1,2,4,5-tetrazine (4):** To propargyl alcohol (10 mL) is added freshly powdered $K_2CO_3$ (0. 40 g, 2.89 mmol) was added. The mixture was stirred at ambient temperature. 3,6-(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine (5.4 g, 20 mmol) were then added. The mixture was heated to 70 ºC and the mixture became a solution. The reaction was stirred 30 min at 70 ºC, cooled to ambient temperature and water (50 mL) was added. A red-orange precipitate was formed. The product was filtered, washed with water and air-dried to provide 2.8 g (74% yield) of product. FTIR $cm^{-1}$ 3260, 2130, and 1320. $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 3.64 (d, *J* = 2.4 Hz,

1H) and 5.72 (d, $J$ = 2.4 Hz 2H). $^{13}$C NMR (400 MHz, DMSO-d$_6$) δ 67.1, 87.3, 176.2, 215.7. Elemental analysis Calc'd C, 50.53, H, 3.18, 29.46. Found C, 50.51, H, 3.19, N, 29.448.

**Polymer (8):** To 2,2-azidomethyl-1,3 propane diol (**6**) (0.093 g, 0.500 mmol) 3,6-propargyloxy-1,2,4,5-tetrazine (**4**) (0.086 g, 0.452 mmol) was added, followed by copper iodide (0.002 g, 0.010 mmol). The mixture was stirred for one minute (X2) at ambient temperature.  The mixture was slowly heated in increments of 10 °C to 60 °C. The reaction was held at 60 °C for 24 hours. A dark burgundy solid was formed.  The product was air-dried to provide 0.078 g of material.

**Polymer (10):** To a vessel containing 3,6-propargyloxy-1,2,4,5-tetrazine (**4**) (0.203 g, 1.07 mmol), 2-hydroxy-1,3-diazido-propane (**9**) (0.167 g, 1.17 mmol) was added, followed by copper iodide (0.005 g, 0.026 mmol). The mixture was stirred for one minute (X2) at ambient temperature.  The mixture was slowly heated in increments of 10 °C to 60 °C. The reaction was held at 60 °C for 24 hours. A dark burgundy solid was formed.  The product was air-dried to provide 0.332 g of material.

General crosslinking procedure:

**Polymer (10):** To a vessel containing GAP or GAP-plasticizer, 3,6-Propargyloxy-1,2,4,5-tetrazine (**4**) was added, followed by catalytic copper iodide (see table for amounts). The mixture was stirred for one minute (X2) at ambient temperature.  The mixture was slowly heated to 60 °C. The reaction was held at 60 °C for 2 hours and cured overnight at room temperature. A dark burgundy solid was formed.

| Reaction (ratio % (**4**): GAP) | 3,6-propargyloxy-1,2,4,5-tetrazine (**4**) | glycidyl azide polymer (GAP) | Copper iodide |
|---|---|---|---|
| A (3.15%) | 0.107 g (0.562 mmol) | 3.394 g | 0.003 g (0.016 mmol) |
| B (6.16%) | 0.209 g (1.099 mmol) | 3.393 g | 0.002 g (0.010 mmol) |
| C (9.92%) | 0.316 g (1.662 mmol) | 3.185 g | 0.005 g (0.026 mmol) |

| Reaction (ratio % (**4**): GAPp) | 3,6-propargyloxy-1,2,4,5-tetrazine (**4**) | glycidyl azide polymer plasticizer (GAPp) | Copper iodide |
|---|---|---|---|
| D (3.09%) | 0.105 g (0.552 mmol) | 3.395 g | 0.004 g (0.021 mmol) |
| E (6.15%) | 0.209 g (1.099 mmol) | 3.396 g | 0.002 g (0.010 mmol) |
| F (9.89%) | 0.315 g (1.656 mmol) | 3.186 g | 0.006 g (0.031 mmol) |
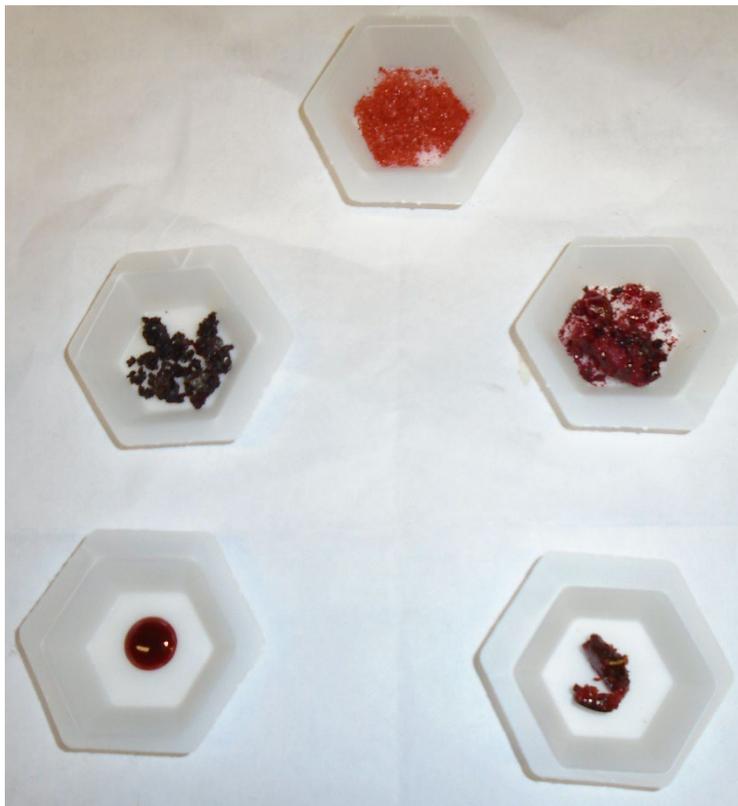
**S1.** Photograph of compound **4** (top), polymer **8** (second row, left), polymer **10** (second row, right), polymer **6** (third row, left), and polymer **6p** (third row right).

Bis propargyloxy tetrazine small scale
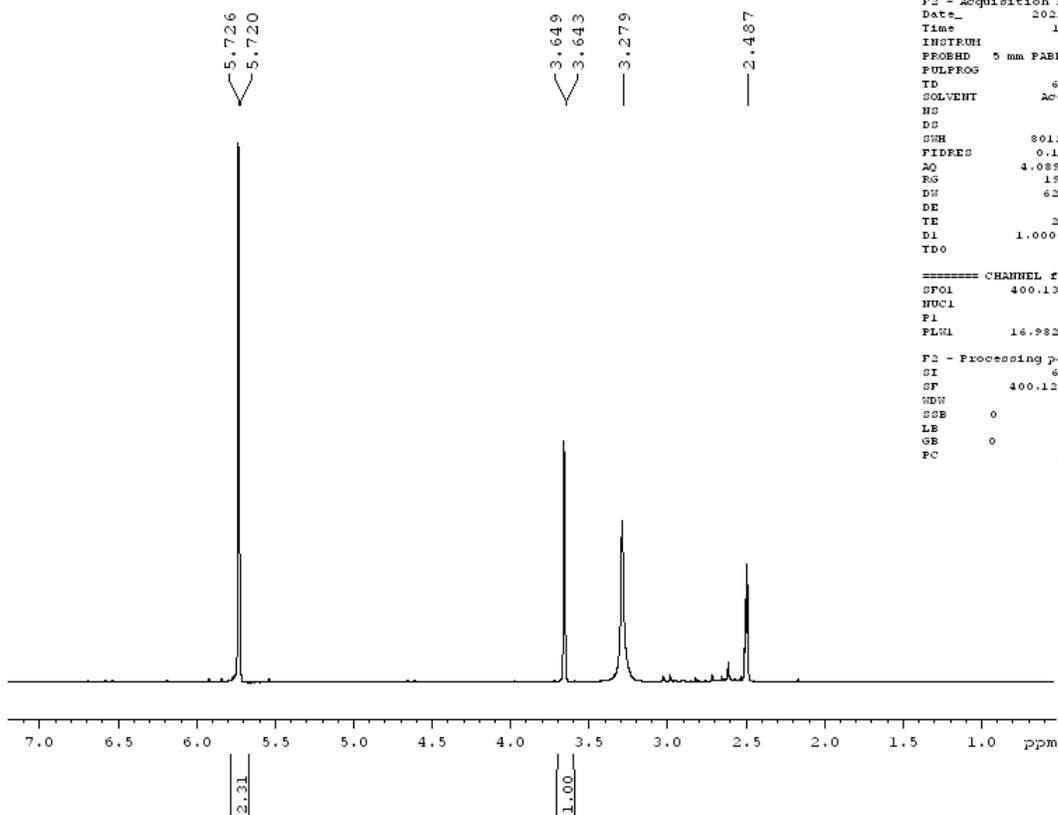
Current Data Parameters
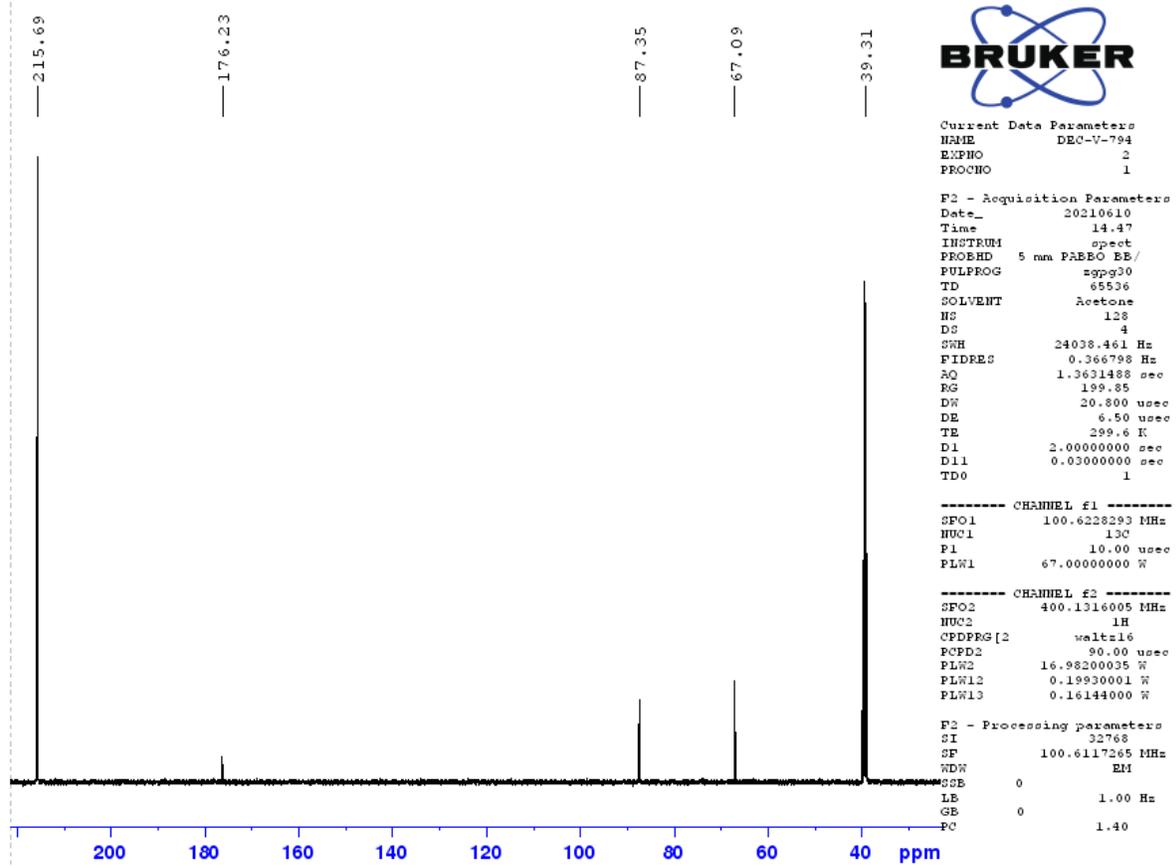NAME        DEC-V-794
EXPNO           1
PROCNO          1

F2 - Acquisition Parameters
Date_        20210610
Time           14.36
INSTRUM        spect
PROBHD   5 mm PABBO BB/
PULPROG         zg30
TD             65536
SOLVENT      Acetone
NS               16
DS                2
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ       4.0894465 sec
RG            199.85
DW         62.400 usec
DE           6.50 usec
TE           298.8 K
D1       1.00000000 sec
TD0               1

======== CHANNEL f1 ========
SFO1     400.1324710 MHz
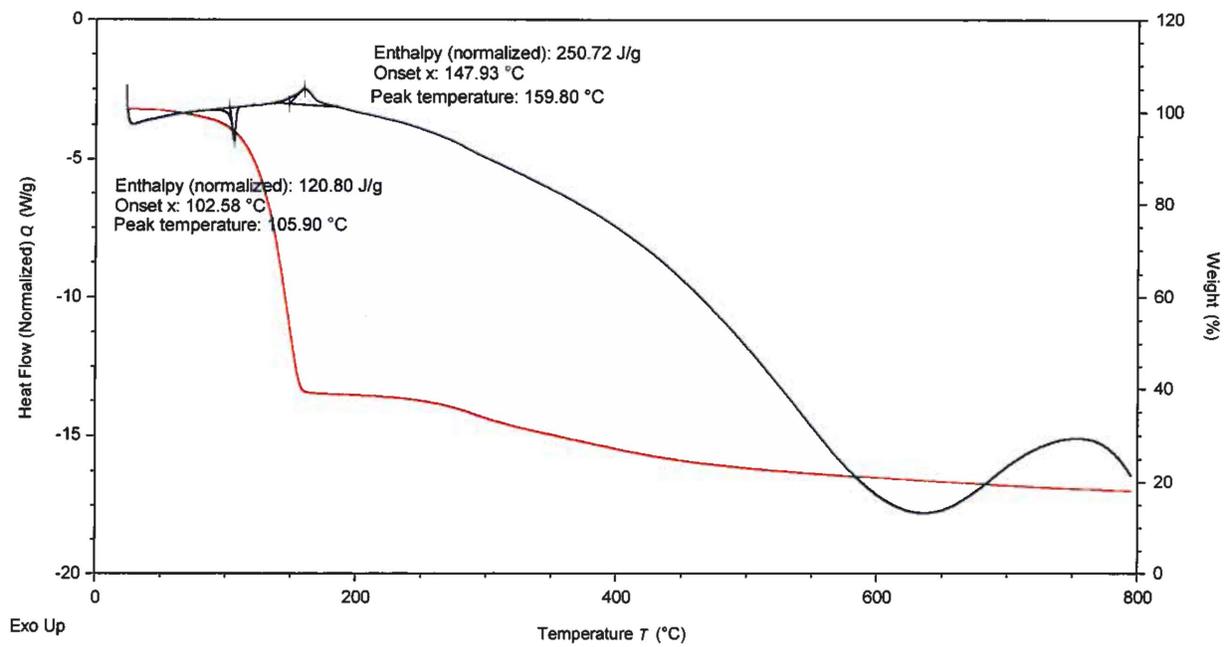NUC1             1H
P1          9.75 usec
PLW1    16.98200035 W

F2 - Processing parameters
SI             65536
SF       400.1298326 MHz
WDW              EM
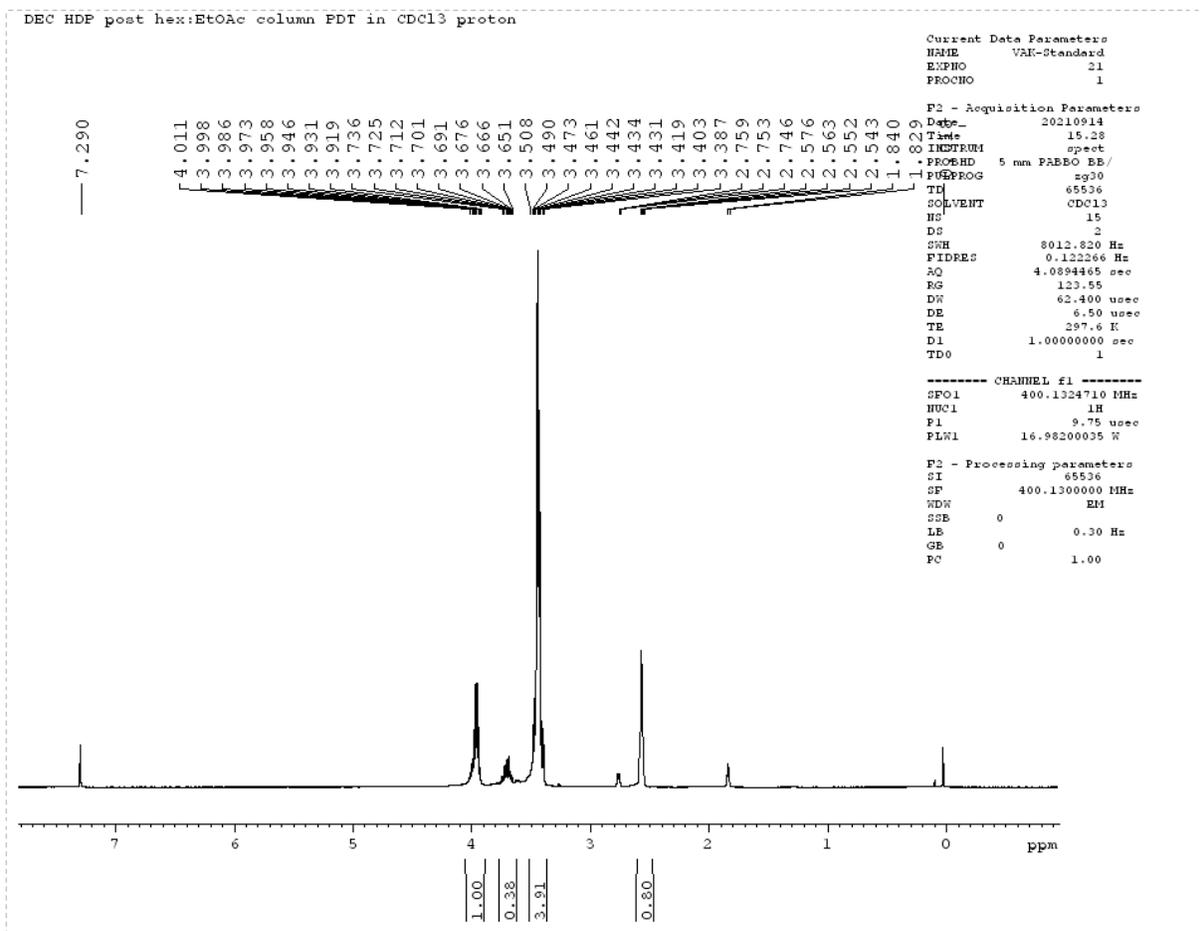SSB         0
LB          0.30 Hz
GB          0
PC          1.00

5.726
5.720

3.649
3.643
3.279

2.487



7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   ppm

2.31

1.00

**S2.** 1H NMR of **4** in DMSO-d$_6$.

5

Bis propargyloxy tetrazine small scale



215.69
176.23
87.35
67.09
39.31

**S3.** $^{13}$C NMR of **4** in DMSO-d$_6$.

Enthalpy (normalized): 250.72 J/g
Onset x: 147.93 °C
Peak temperature: 159.80 °C

Enthalpy (normalized): 120.80 J/g
Onset x: 102.58 °C
Peak temperature: 105.90 °C

Exo Up

**S4.** DSC data of compound **4**.

**S5.** ^{1}H NMR of **9** in CDCl₃. Residual ethyl acetate contamination.
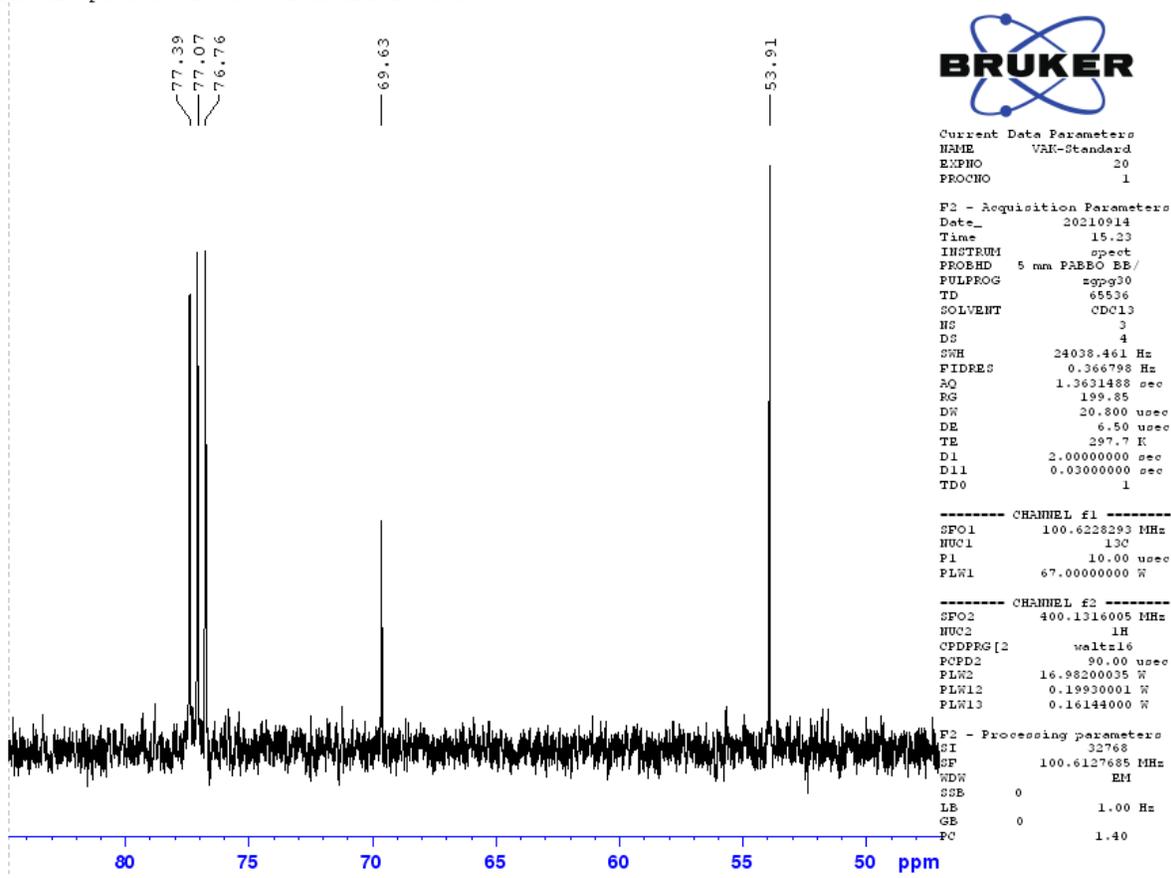
**S6.** $^{13}C$ NMR of **9** in CDCl3.
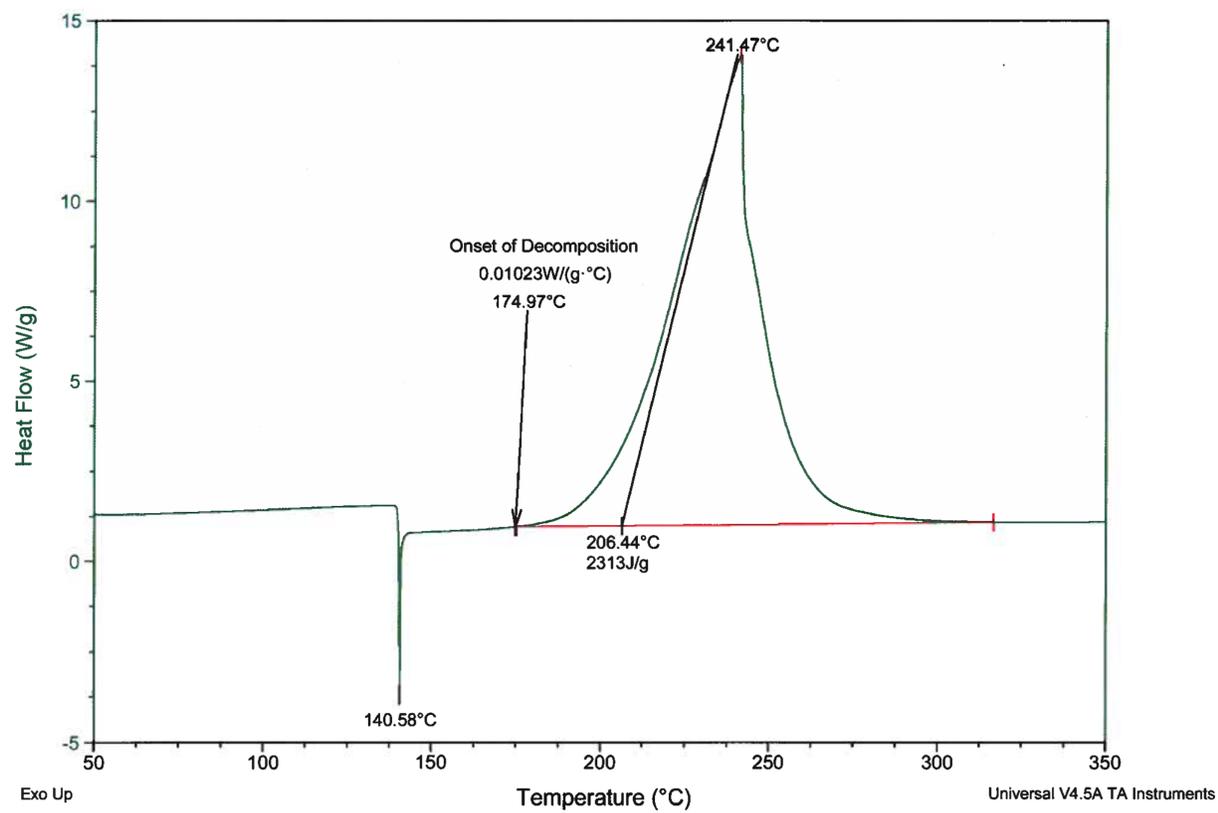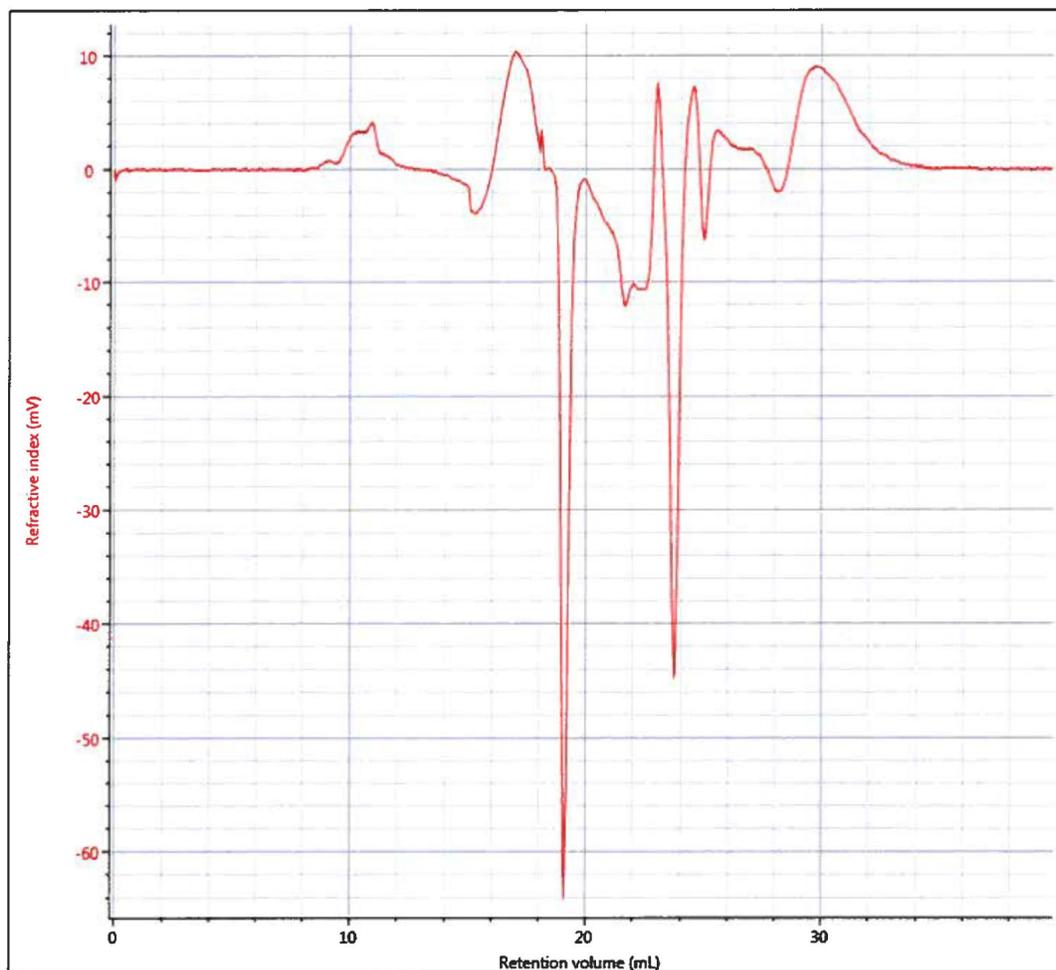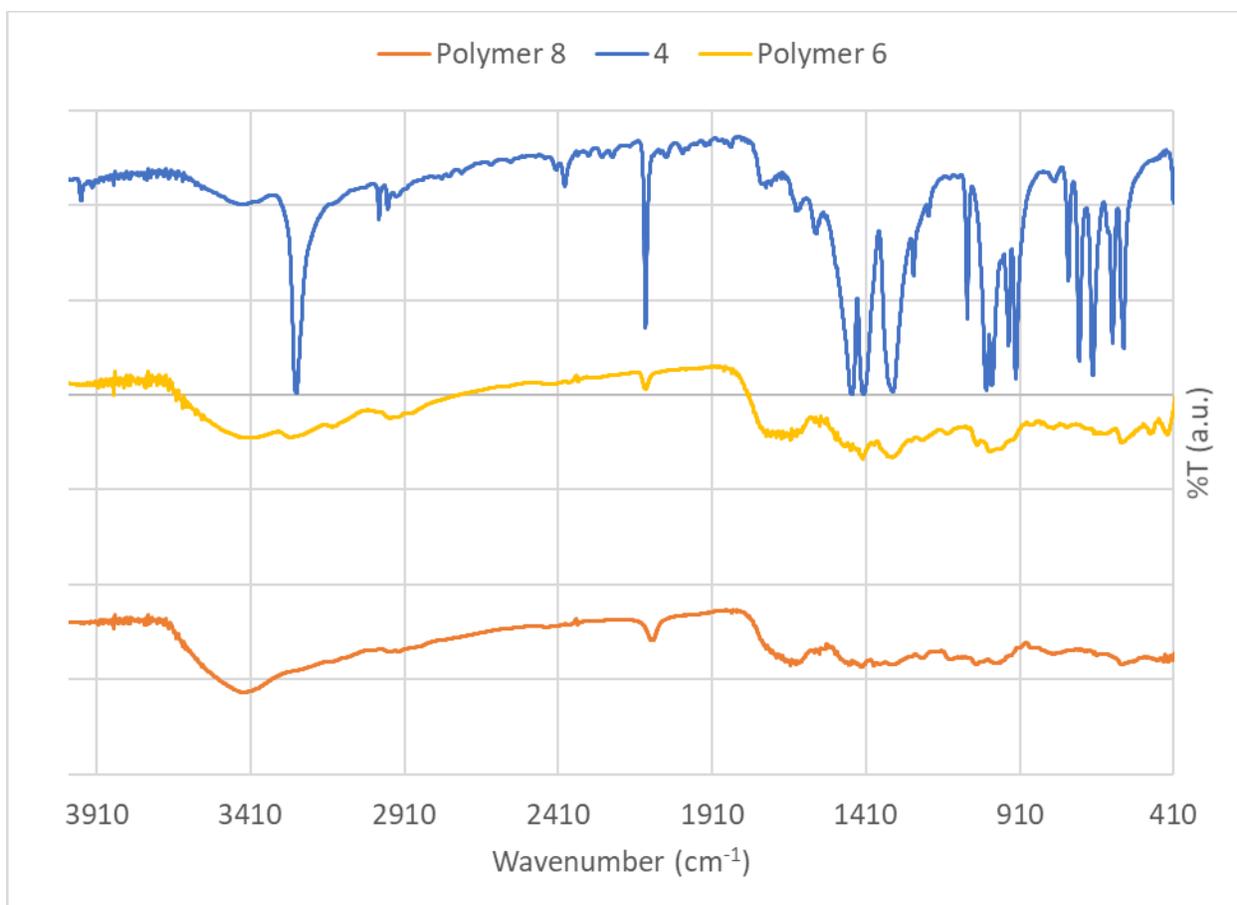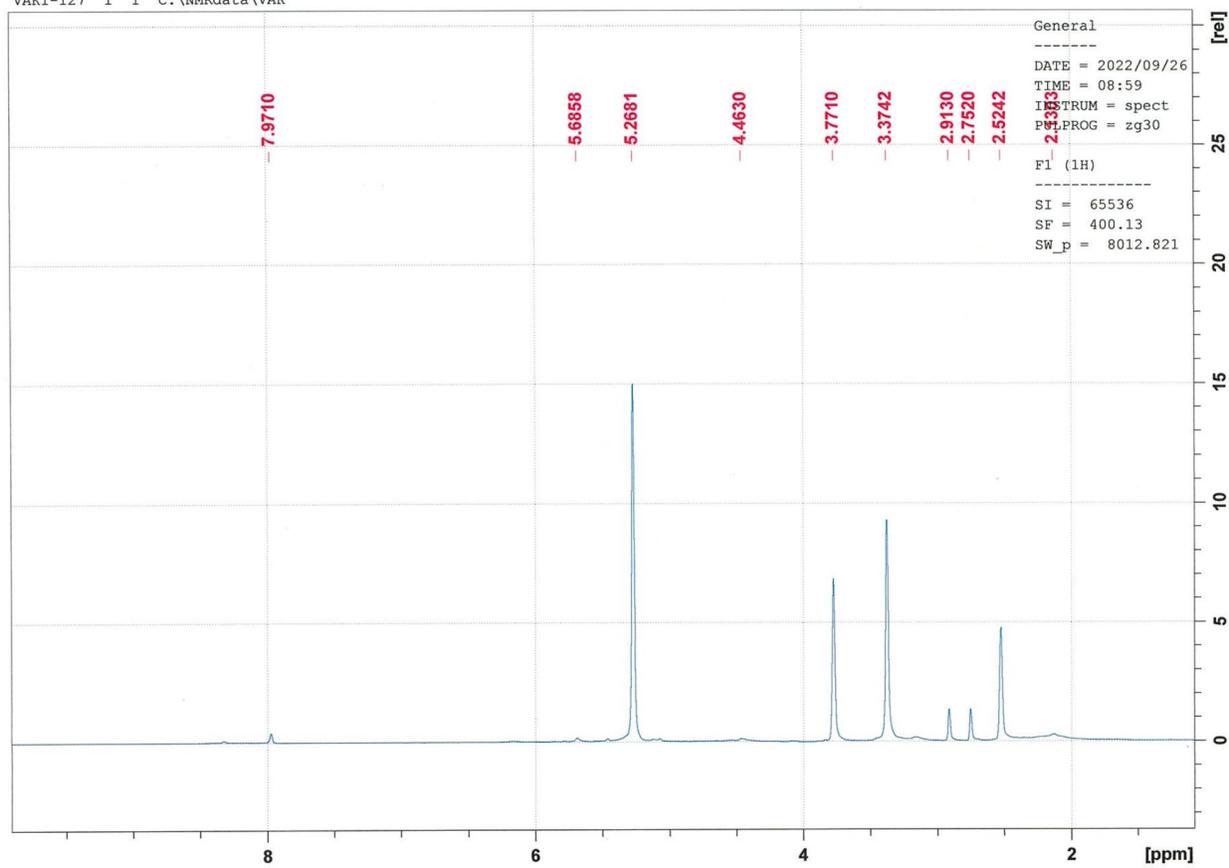
**S7**. DSC data of compound **9**.
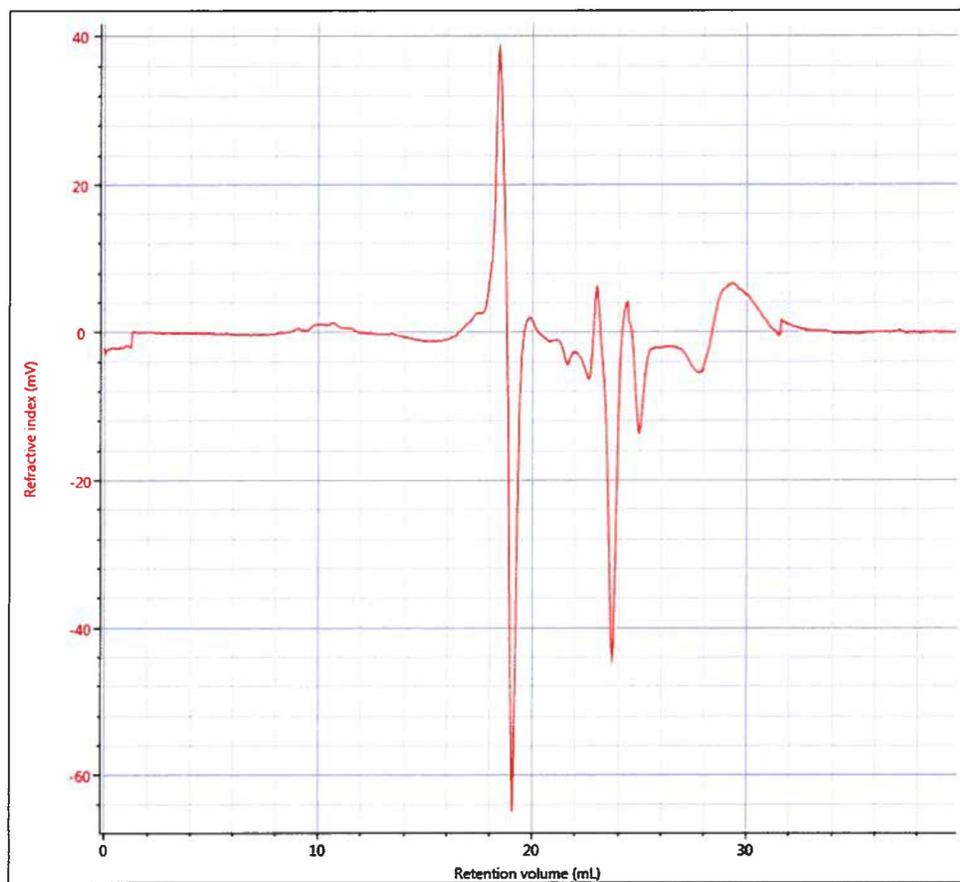
**S8.** GPC retention data of polymer **8**.

**S9.** GPC retention data of polymer **10**.

**S10.** FT-IR data of compounds **4, 8,** and **10**.

General
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DATE = 2022/09/26
TIME = 08:59
INSTRUM = spect
PULPROG = zg30

F1 (1H)
-------------
SI =   65536
SF =    400.13
SW_p =  8012.821

7.9710

5.6858
5.2681

4.4630

3.7710

3.3742

2.9130
2.7520
2.5242

2.333

**S11.** H1 NMR of polymer **8** in DMSO
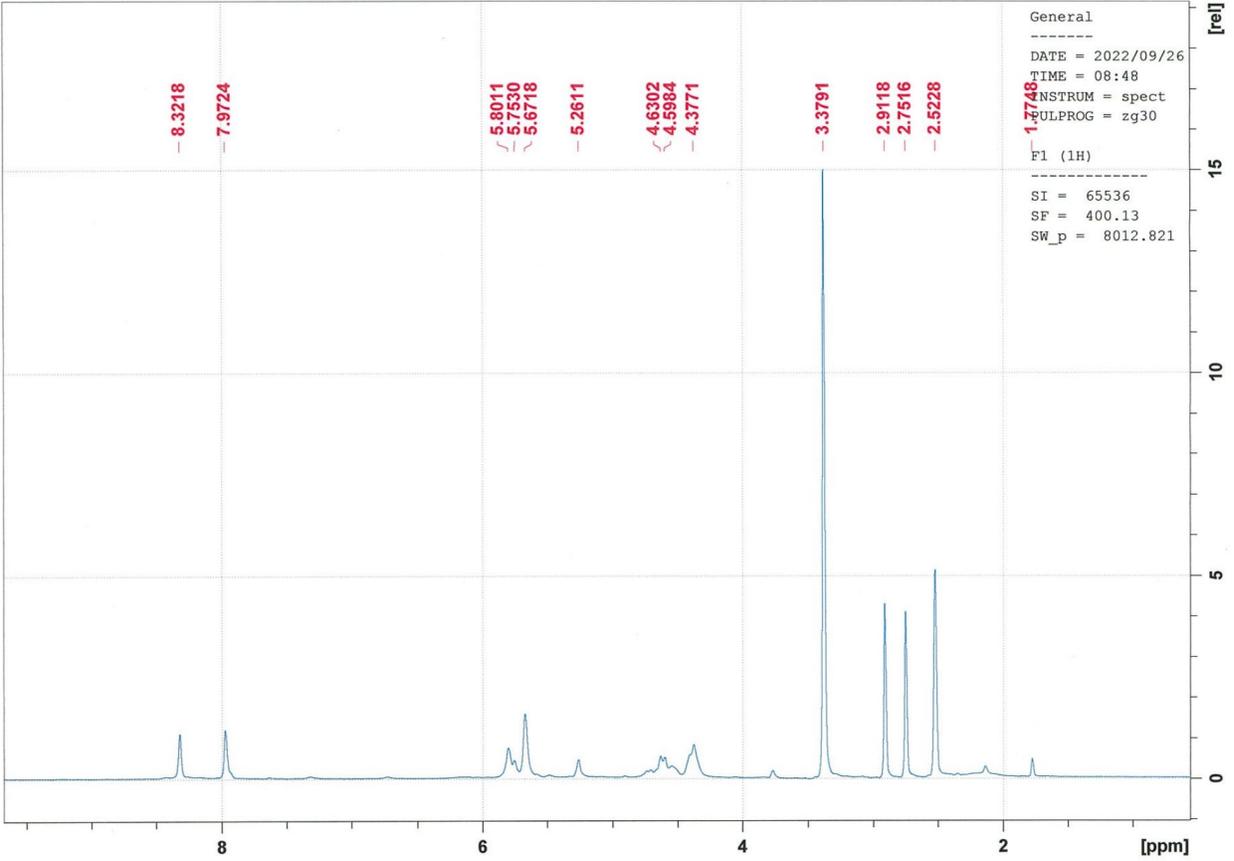
**S12.** H1 NMR of polymer **10** in DMSO.
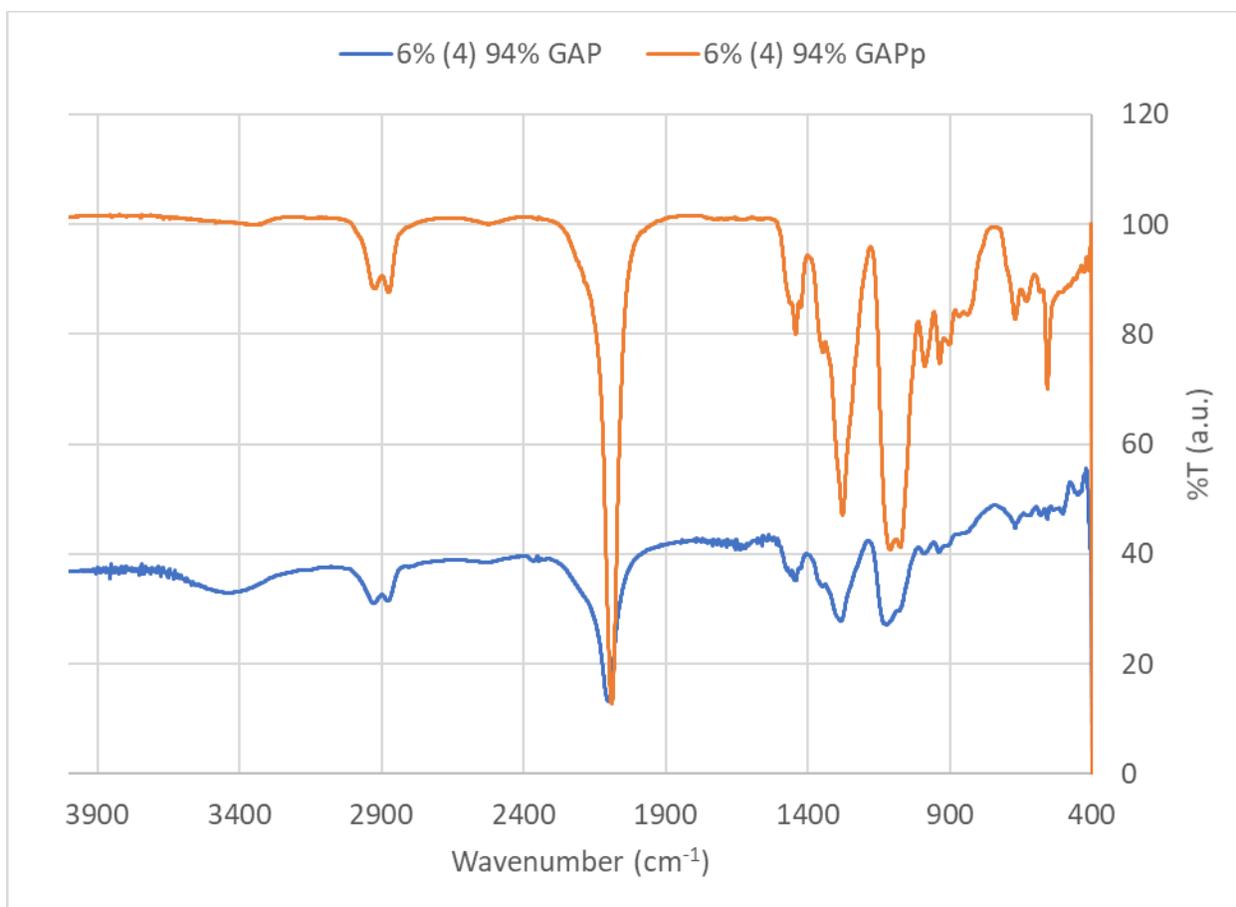
**S13.** FT-IR polymer **6** and **6p**. Ratios of **4** to GAP/GAPp listed.

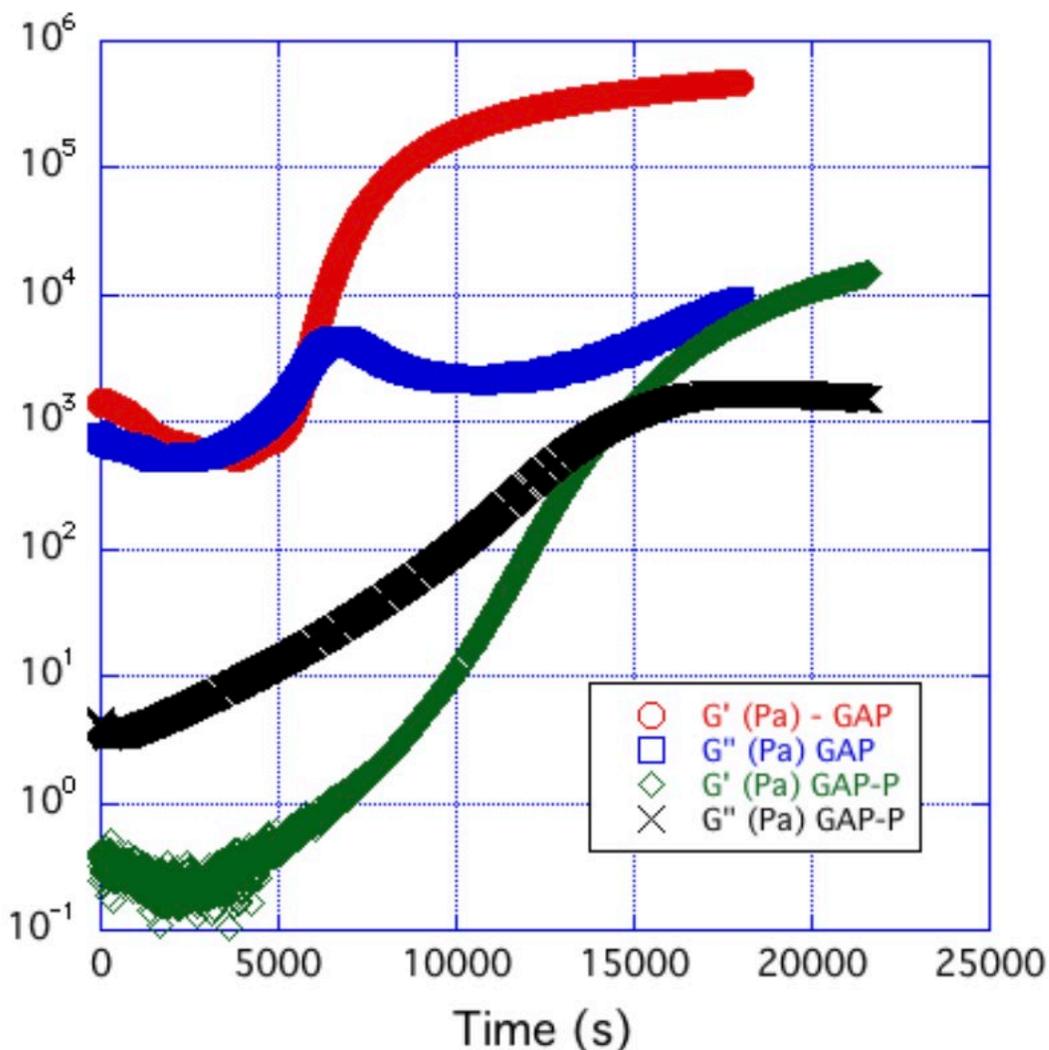**S14.** Rheometry data for gelation of polymers **6** (red and blue) and **6p** (green and black).


Single crystal X-ray analysis of **4**

$C_8H_6N_4O_2$, FW = 190.17, monoclinic, $P2_1/c$, a = 8.5211(4) Å, b = 6.8626(3) Å, c = 7.5560(4) Å, $\alpha$ = 90°, $\beta$ = 101.5330(10)°, $\gamma$ = 90°, V = 432.93(4) Å³, Z = 2, $\rho_{calc}$ (293K) = 1.459 Mg/m³, $\mu$ = 0.110 mm⁻¹, $F$(000) = 196, $R_1$ = 0.0369 for 946 observed (I > 2σI) reflections and 0.0494 for all 1223 reflections, Goodness-of-fit = 1.044, 64 parameters.

A clear orange block crystal of dimensions 0.253 x 0.247 x 0.028 mm was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated $MoK_\alpha$ radiation (λ= 0.71073). Data was collected at room temperature (20°C).

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].[1] Data Reduction was performed using *SAINT* [v8.34A][2] and *XPREP* [v2014/2][3]. Corrections

were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].[4] The structure was solved and refined with the aid of the program SHELXL-2014/7.[5] The full-matrix least-squares refinement on $F^2$ included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were located from the difference electron-density maps and added using a riding model.

**Table 1**. Crystal data and structure refinement for **4**.

| | |
|---|---|
| Identification code | chav180 |
| Empirical formula | $C_8H_6N_4O_2$ |
| Formula weight | 190.17 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | a = 8.5211(4) Å $\quad$ $\alpha$= 90°. |
| | b = 6.8626(3) Å $\quad$ $\beta$= 101.5330(10)°. |
| | c = 7.5560(4) Å $\quad$ $\gamma$ = 90°. |
| Volume | 432.93(4) Å$^3$ |
| Z | 2 |
| Density (20°C) | 1.459 Mg/m$^3$ |
| Absorption coefficient | 0.110 mm$^{-1}$ |
| F(000) | 196 |
| Crystal size | 0.253 x 0.247 x 0.028 mm$^3$ |
| Theta range for data collection | 2.439 to 29.993°. |
| Index ranges | -11<=h<=11, -9<=k<=8, -10<=l<=10 |
| Reflections collected | 4930 |
| Independent reflections | 1223 [$R_{int}$ = 0.0188] |
| Completeness to theta = 25.242° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7460 and 0.6920 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1223 / 0 / 64 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0369, $wR_2$ = 0.0965 |
| R indices (all data) | $R_1$ = 0.0494, $wR_2$ = 0.1039 |
| Largest diff. peak and hole | 0.190 and -0.190 e.Å$^{-3}$ |

**Table 2**. Atomic coordinates  x $10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2$x $10^3$)

for **4**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

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|        | x       | y       | z       | U(eq)  |
|--------|---------|---------|---------|--------|
| C(1)   | 9618(2) | 2159(2) | 8702(2) | 51(1)  |
| C(2)   | 8628(1) | 3242(2) | 8980(2) | 40(1)  |
| C(3)   | 7420(1) | 4580(2) | 9377(2) | 43(1)  |
| O(4)   | 5824(1) | 4071(1) | 8393(1) | 45(1)  |
| C(5)   | 5445(1) | 4561(2) | 6651(1) | 33(1)  |
| N(6)   | 3945(1) | 4104(1) | 5869(1) | 38(1)  |
| N(7)   | 3480(1) | 4565(1) | 4142(1) | 37(1)  |

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1.  Bruker (2015). APEX3 v2015.5-2. Bruker AXS Inc., Madison, Wisconsin, USA.
2.  Bruker (2013). SAINT v8.34A. Bruker AXS Inc., Madison, Wisconsin, USA.
3.  Bruker (2014). XPREP v2014/2. Bruker AXS Inc., Madison, Wisconsin, USA.
4.  Bruker (2014). SADABS v2014/5, Bruker AXS Inc., Madison, Wisconsin, USA.
5.  Sheldrick, G. M. (2014). SHELXL-2014/7. University of Göttingen, Germany.