

**A Thermally Crosslinked Functionalized Polydicyclopentadiene (*f*PDCPD)
with a High T_g and Tunable Surface Energy**

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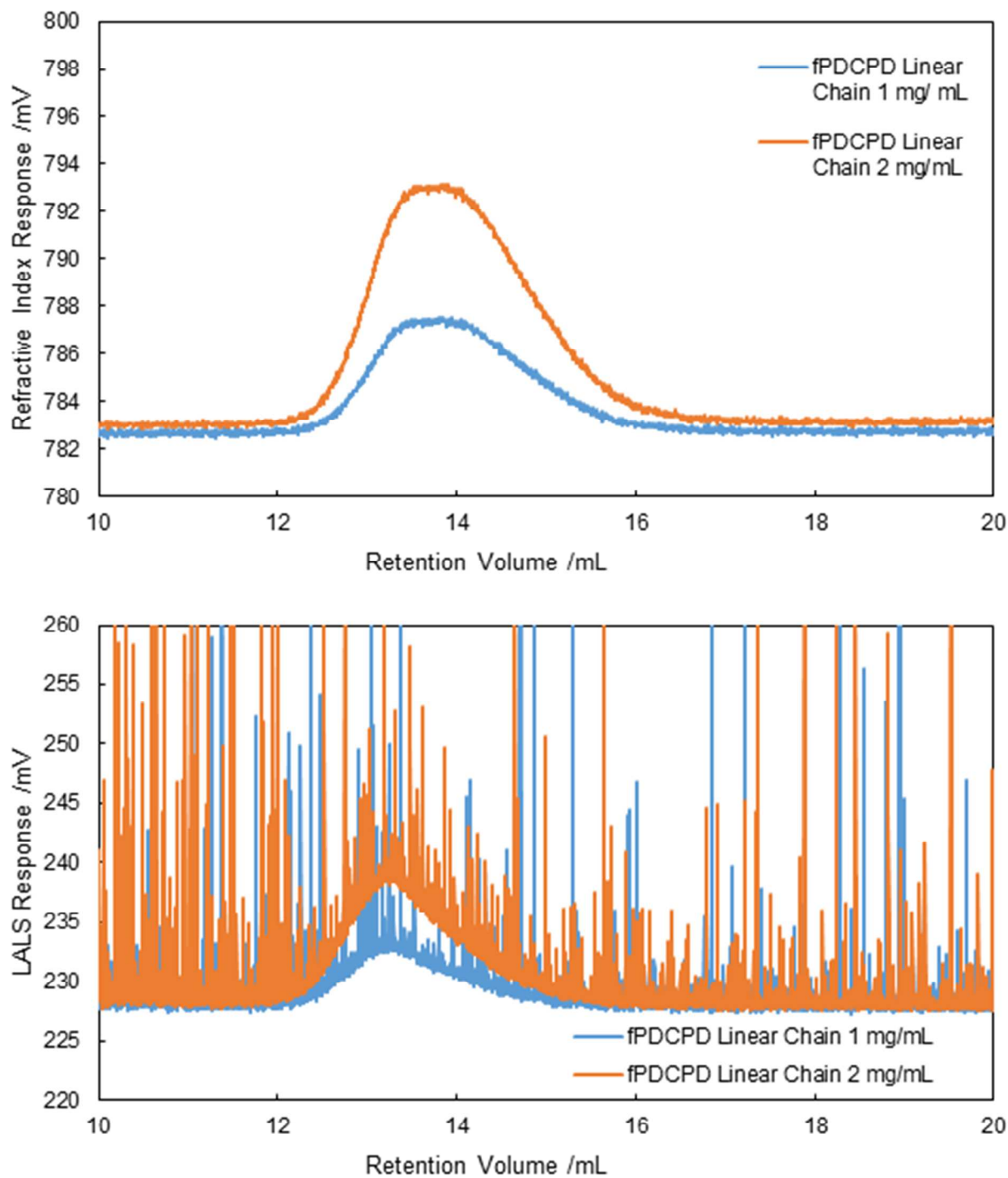


Figure S1A. GPC traces of a freshly-prepared (~4-hour-old) sample of polymer **5**. Top trace: refractive index detection. Bottom trace: low angle light scattering detection. Calculated data: 1 mg/mL sample: $M_w = 94445$ Da, $M_n = 39824$ Da, PDI = 2.37, $dn/dc = 0.103$; 2 mg/mL Sample: $M_w = 93290$ Da, $M_n = 47684$ Da, PDI = 1.96, $dn/dc = 0.108$.

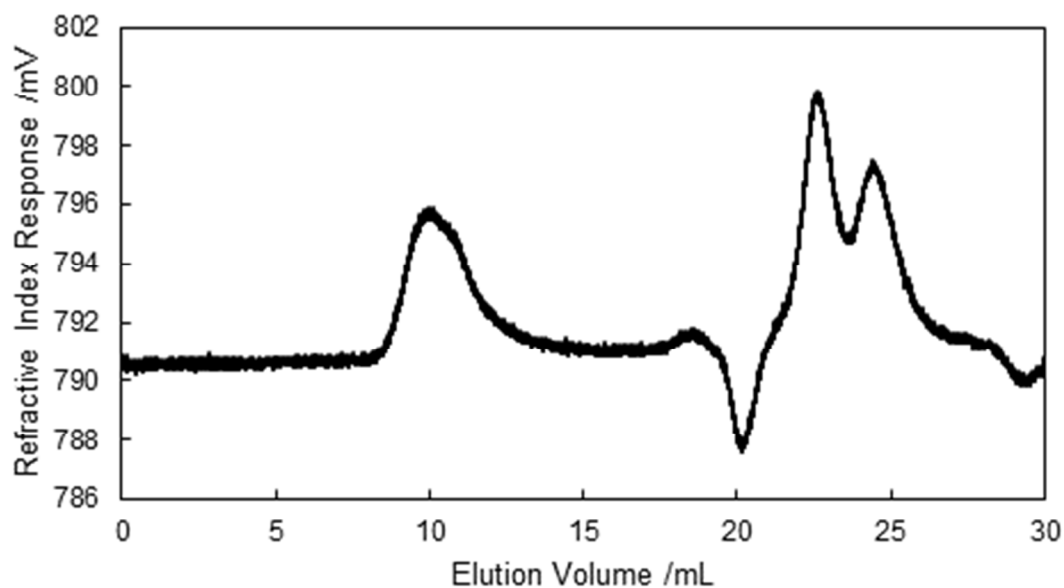
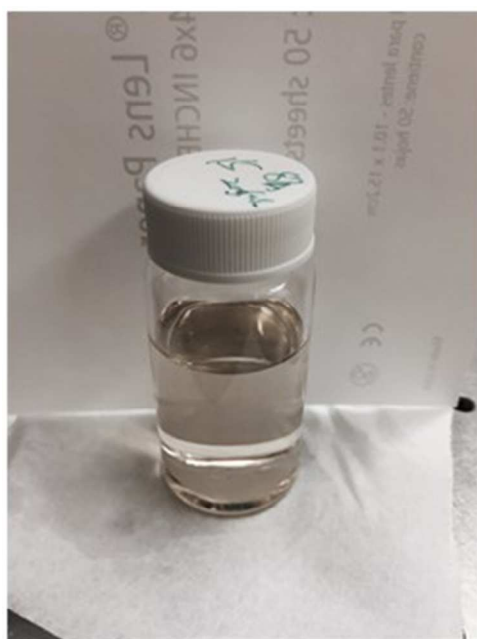
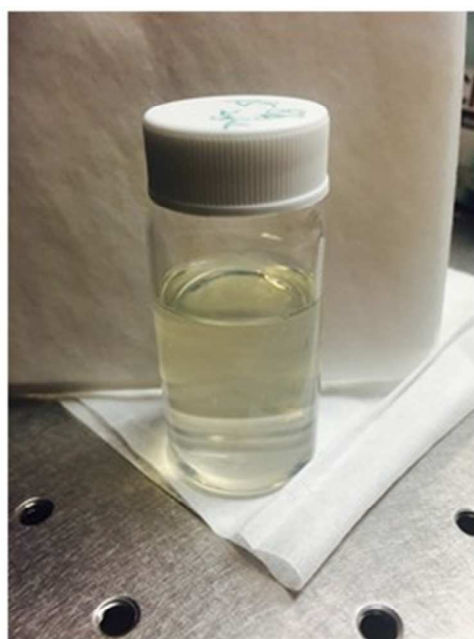


Figure S1B. GPC refractive index trace of a 2-day-old sample of polymer **5**. The peak at 10 mL elution volume corresponds to M_w and M_n values of 30036272 and 29802748 Da, respectively. The calculated PDI is $M_w/M_n = 1.008$, but this number is not particularly meaningful given the amount of oxidative crosslinking that the sample has evidently experienced prior to analysis.



Day 1



Day 3

Figure S2. Comparison between freshly prepared polymer **5** solution and 3-day-old suspension. We attribute the appearance of cloudiness to the precipitation of oxidatively crosslinked polymer.

Table S1. Measured Contact Angles for *f*PDCPD and PDCPD.

polymer	left (°)	right (°)	overall (°)
methyl ester (H ₂ O)	87.0 ± 1.1	87.4 ± 0.8	87.2 ± 0.9
carboxylate salt (H ₂ O)	63.3 ± 3.0	63.9 ± 2.2	63.6 ± 2.5
carboxylic acid (H ₂ O)	28.8 ± 1.1	29.2 ± 1.2	29.0 ± 1.1
methyl ester (CH ₂ I ₂)	46.0 ± 0.8	45.6 ± 1.0	45.8 ± 0.9
carboxylate salt (CH ₂ I ₂)	46.1 ± 1.7	46.6 ± 1.5	46.4 ± 1.5
carboxylic acid (CH ₂ I ₂)	52.0 ± 1.6	52.4 ± 1.3	52.2 ± 1.4
PDCPD (H ₂ O)	119.4 ± 1.2	120.1 ± 1.5	119.8 ± 1.3



Figure S3. Apparatus used for the preparation of slides half coated with polymer **6** and half with polymer **7**. Glass cover slips were first spin coated with linear polymer **5**, then incubated in a 180 °C oven under vacuum overnight to provide crosslinked polymer **6**. The slides were then supported by clips and partially immersed in a solution of methanolic NaOH to facilitate (partial) hydrolysis of surface ester groups.

Figure S4. ^1H NMR spectrum for compounds **3** and **4** (prepared as a mixture).

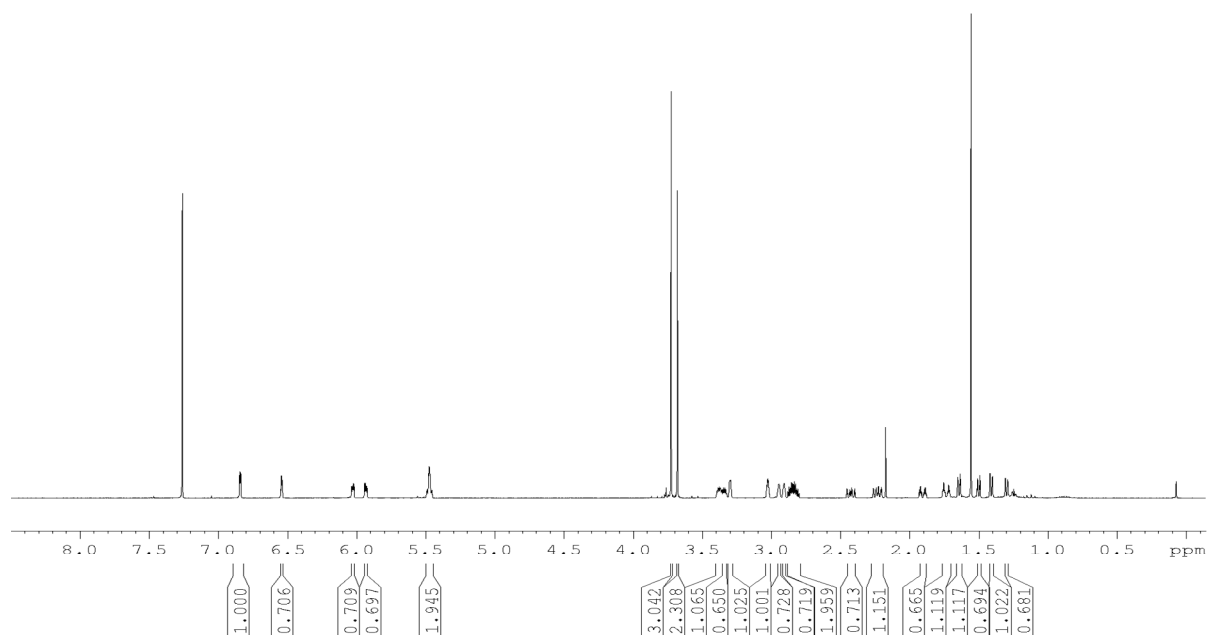


Figure S5. ^{13}C NMR spectrum for compounds **3** and **4** (prepared as a mixture).

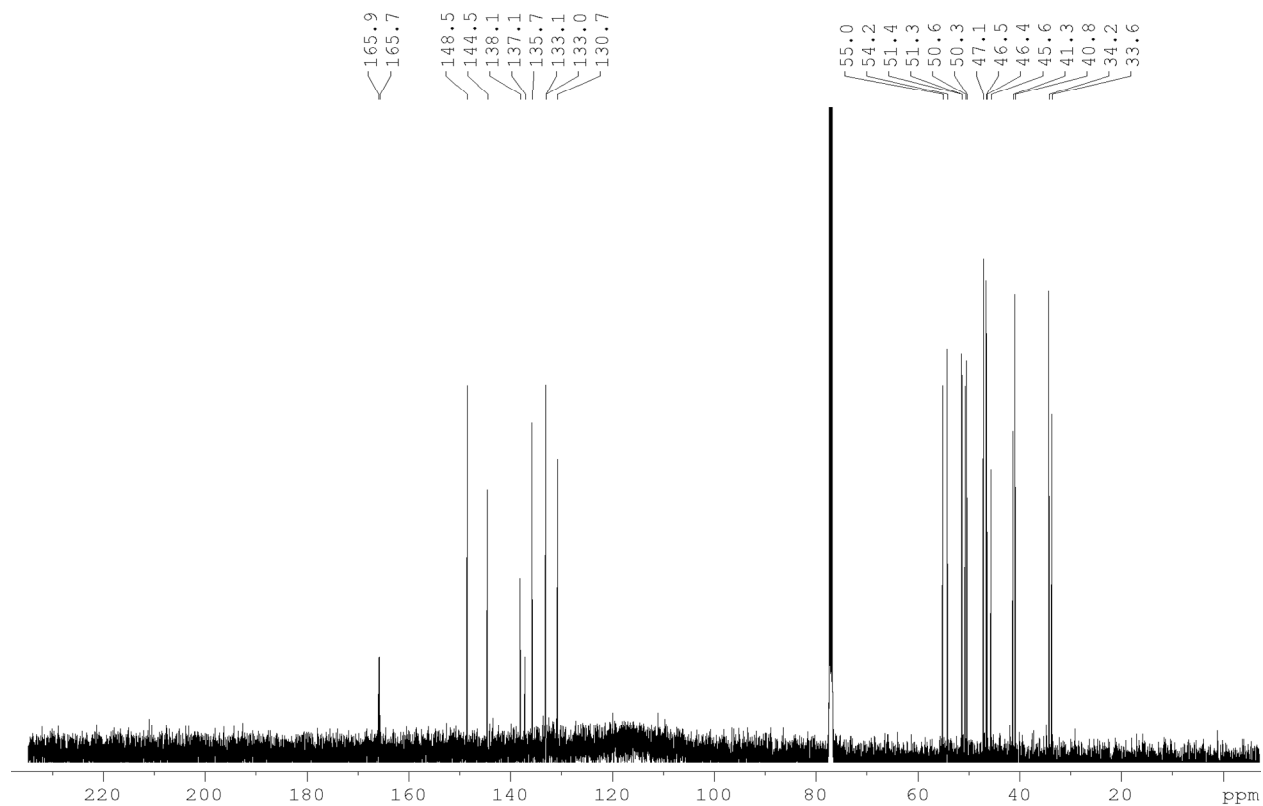


Figure S6. ^1H NMR spectrum for partially purified compound **3**.

(recovered ether supernatant from the synthesis of polymer **5**; contains solvent impurity)

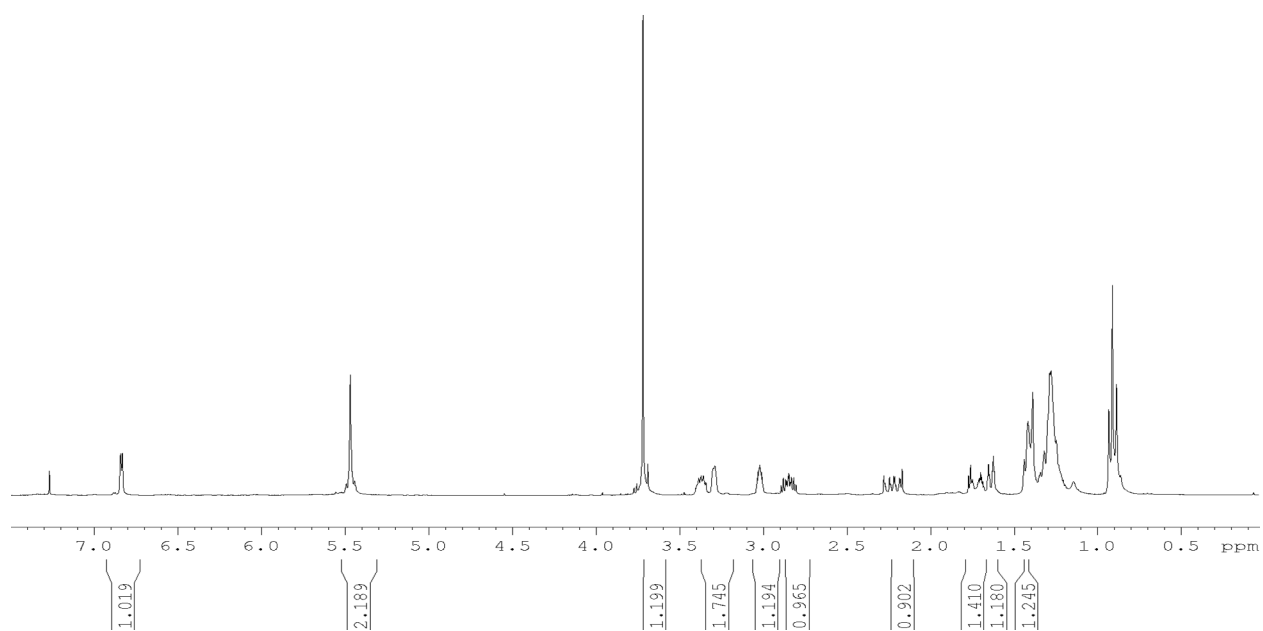


Figure S7. ^1H NMR spectrum for partially purified compound **4**.

(from conjugate addition of benzyl amine to the mixture of **3** and **4**; contains minor impurities)

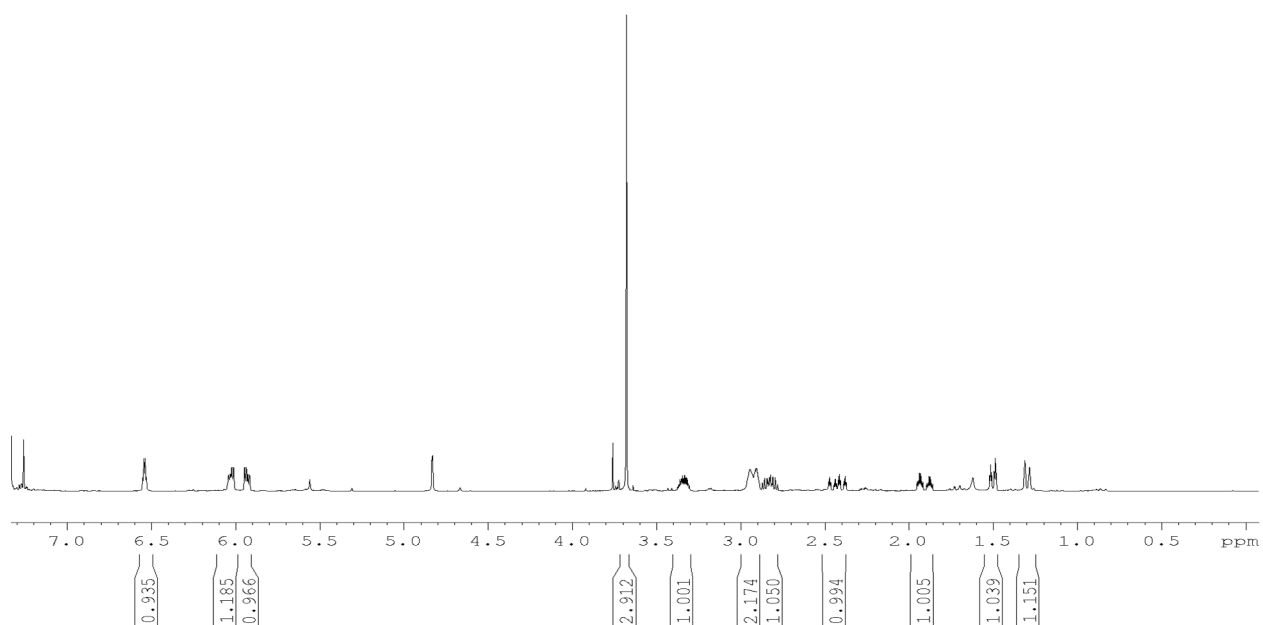


Figure S8. ^1H NMR spectrum for linear polymer **5**.

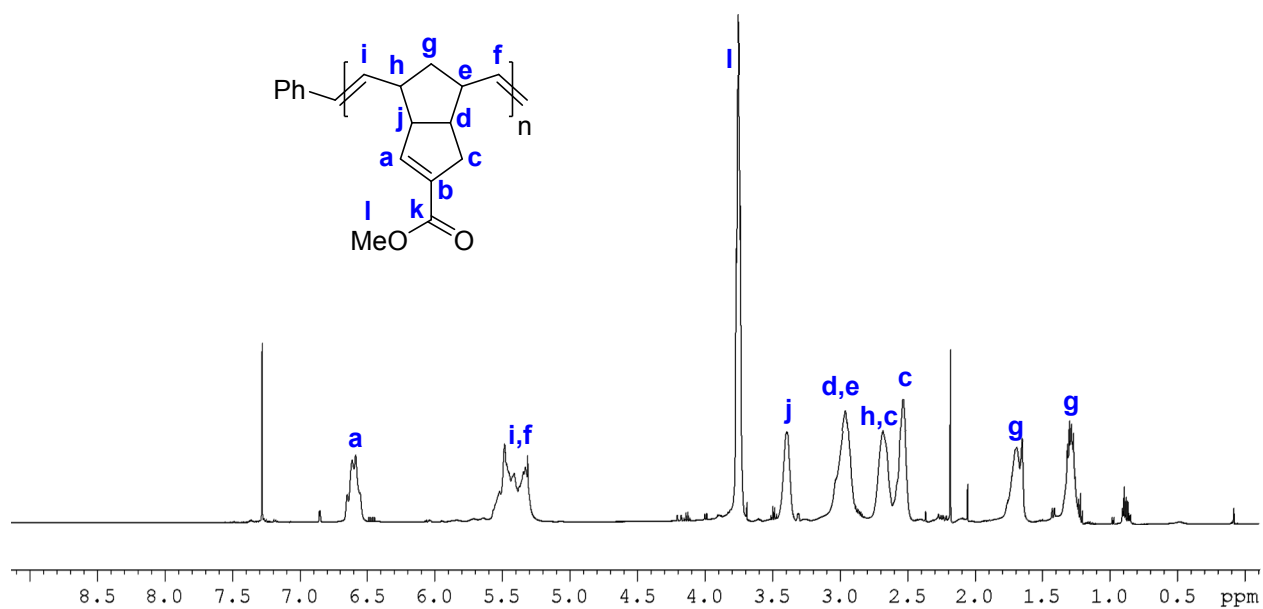


Figure S9. ^{13}C NMR spectrum for linear polymer **5**.

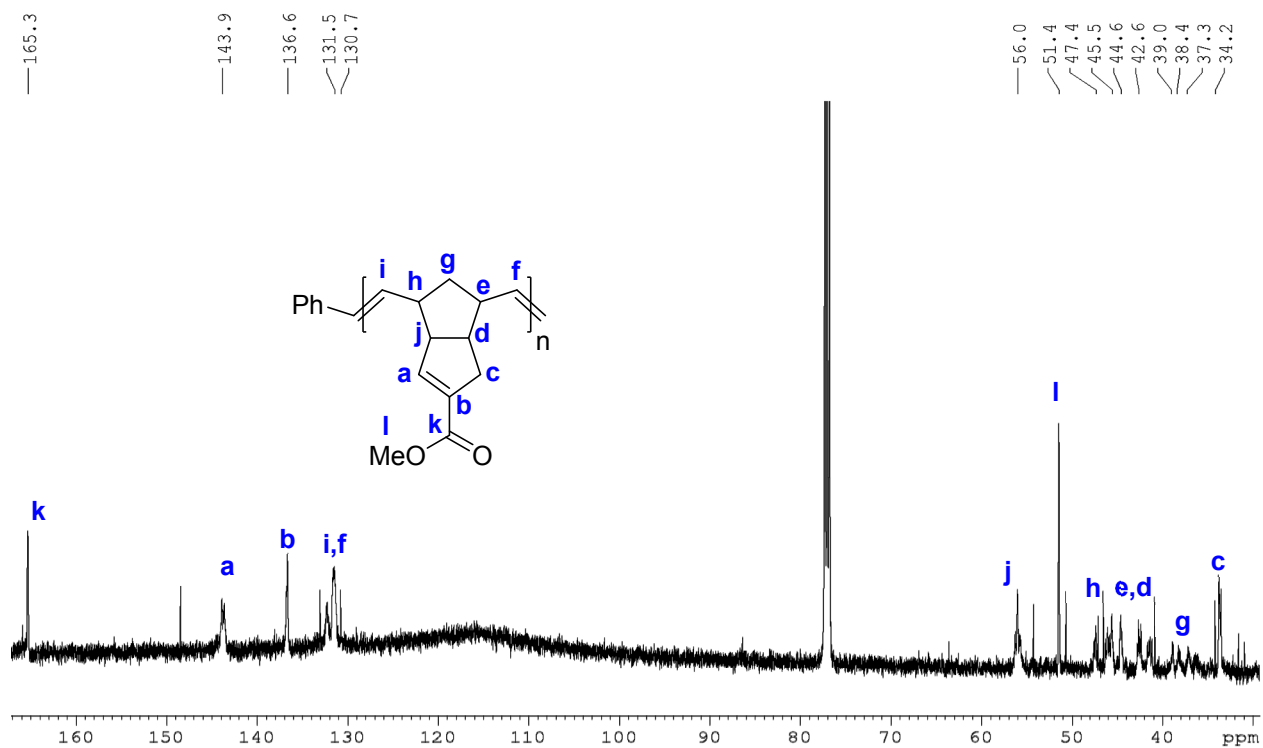


Figure S10. HSQC spectrum for linear polymer **5**.

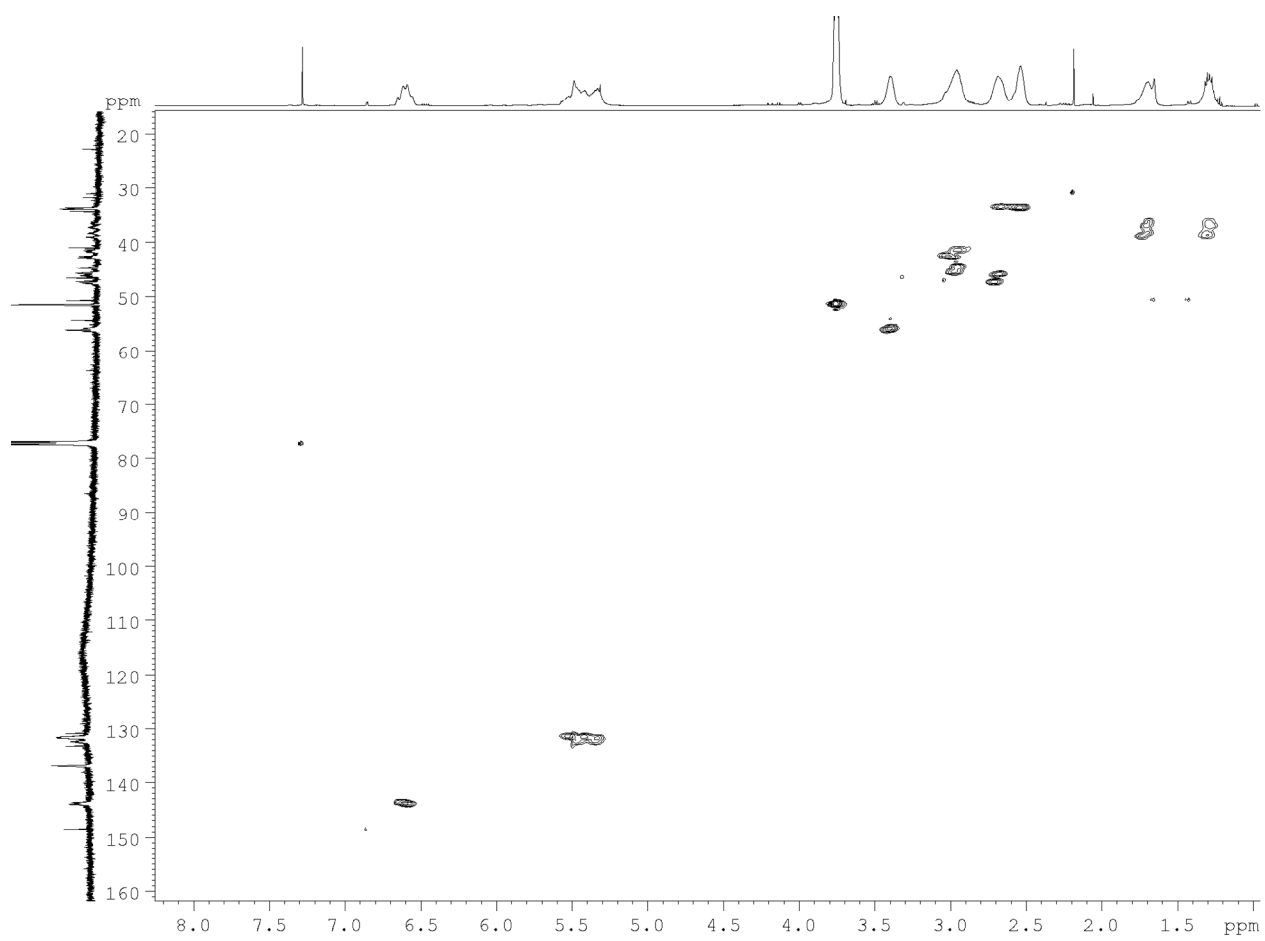


Figure S11. COSY spectrum for linear polymer **5**.

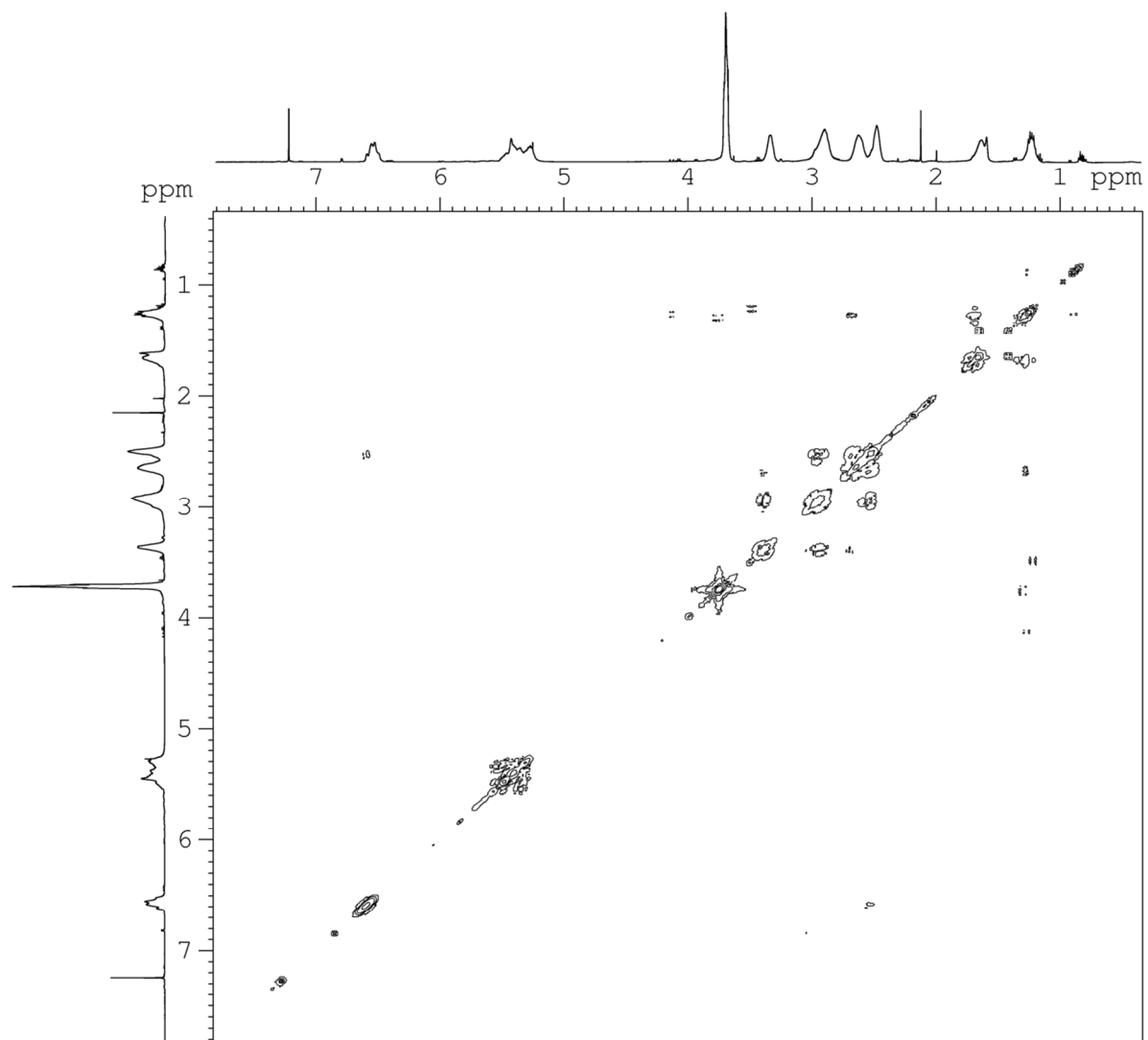


Figure S12. Estimated molecular weight of **5** by NMR (in CD_2Cl_2).

