

Efficient Free-Radical Cyclopolymerization of Oriented Styrenic Difunctional Monomers

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Table S1. Optimization of reaction conditions for the synthesis of monomers **3a** and **3b**.^[a]

Entry	Reagent	Solvent/Base	Time (h)	Yield%(Product) ^[b]
1	2a	Toluene/NaH	24	1.5(3a)
2	2a	THF/NaH	3	11(3a)
3	2a	THF/ <i>t</i> -BuOK	5.5	16(3a)
5	2b	THF/ <i>t</i> -BuOK	5.5	53(3a)
6	2b	THF/ <i>t</i> -BuOK	5.5	65(3b)

^[a] All reactions were conducted with 2 molar equivalent of vinyl benzyl halide vs malonate **1a** or **1b** at 65°C. ^[b] Isolated yields.

Table S2. Cyclopolymerization of monomer **8** to yield polymer **9** under free radical conditions using Benzoyl peroxide as the initiator.^a

Entry	Monomer	[M]/ [%BPO] ^b	Time (h)	M_n^c	PDI ^c	DP ^d	Yield% ^d
1	8	0.05/4	48	7490	1.65	18	21
2	8	0.1/4	48	13700	2.6	34	26
3	8	0.15/4	48	16750	11.0	41	26

a) Polymerizations were run at 70°C in Toluene. b) [M] refers to the monomer concentration, and . c) As determined by GPC relative to polystyrene standards. PDI = polydispersity. c) Degree of polymerization calculated on the basis of the average number molecular weight. d) Yield determined on the basis of the molecular weight of monomer. The solvent used for polymer purification was MeOH.

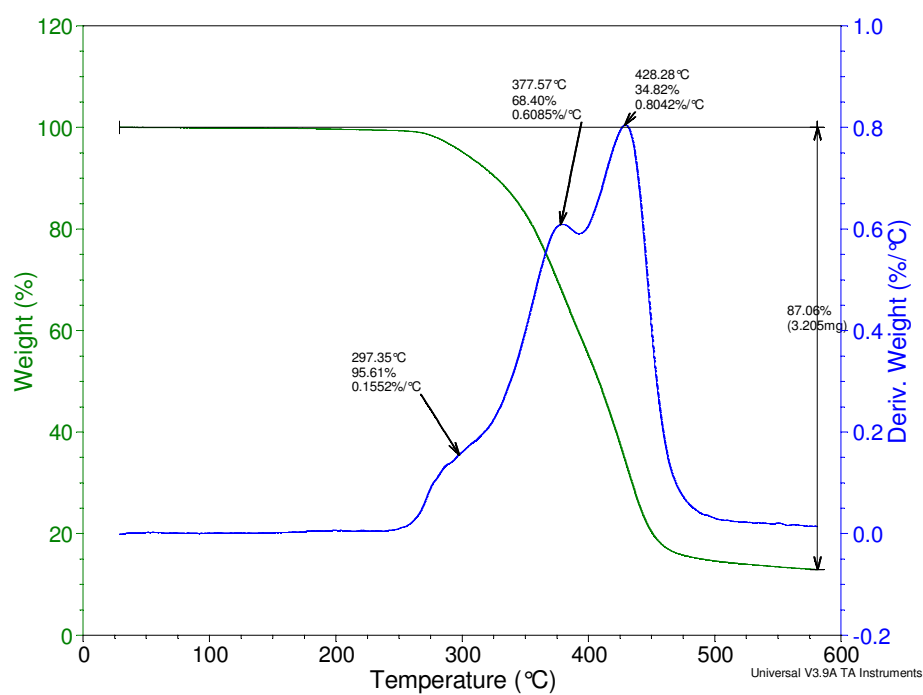


Figure S1. TGA profile and derivative weight loss (blue) for cyclopolymer 9.

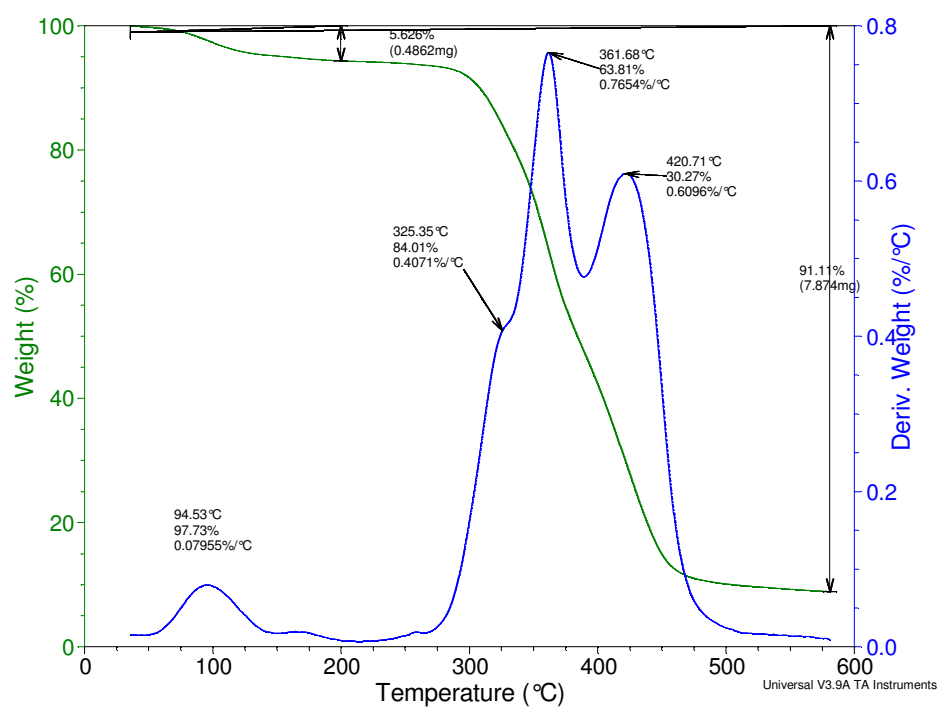


Figure S2. TGA profile and derivative weight loss (blue) for cyclopolymer 11.

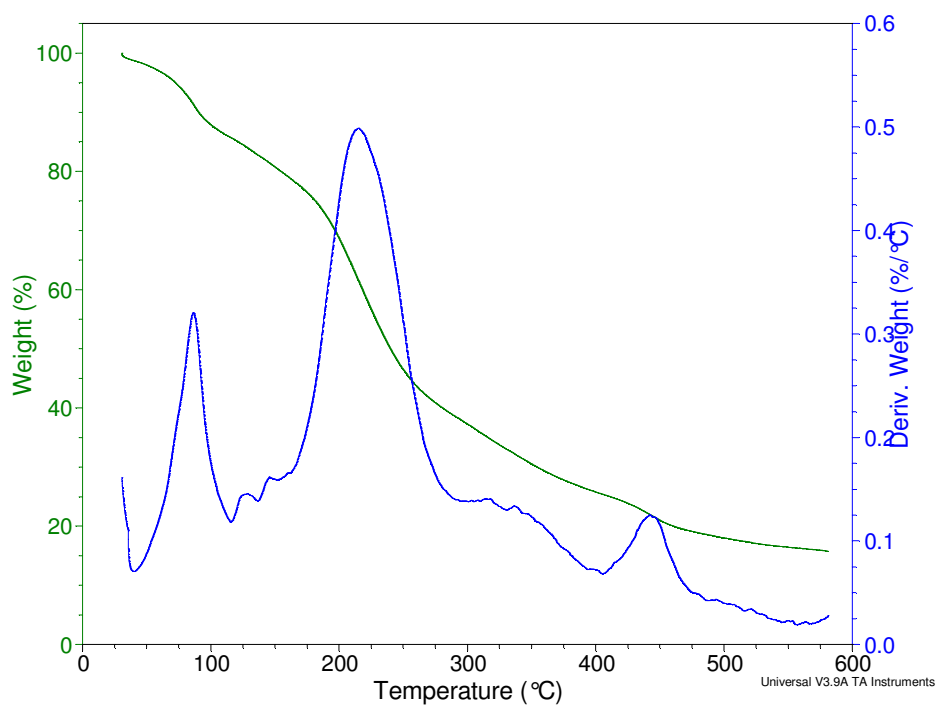


Figure S3. TGA profile and derivative weight loss (blue) for cyclopolymer **9** in the presence of a catalytic amount of solid *p*-toluenesulfonic acid.

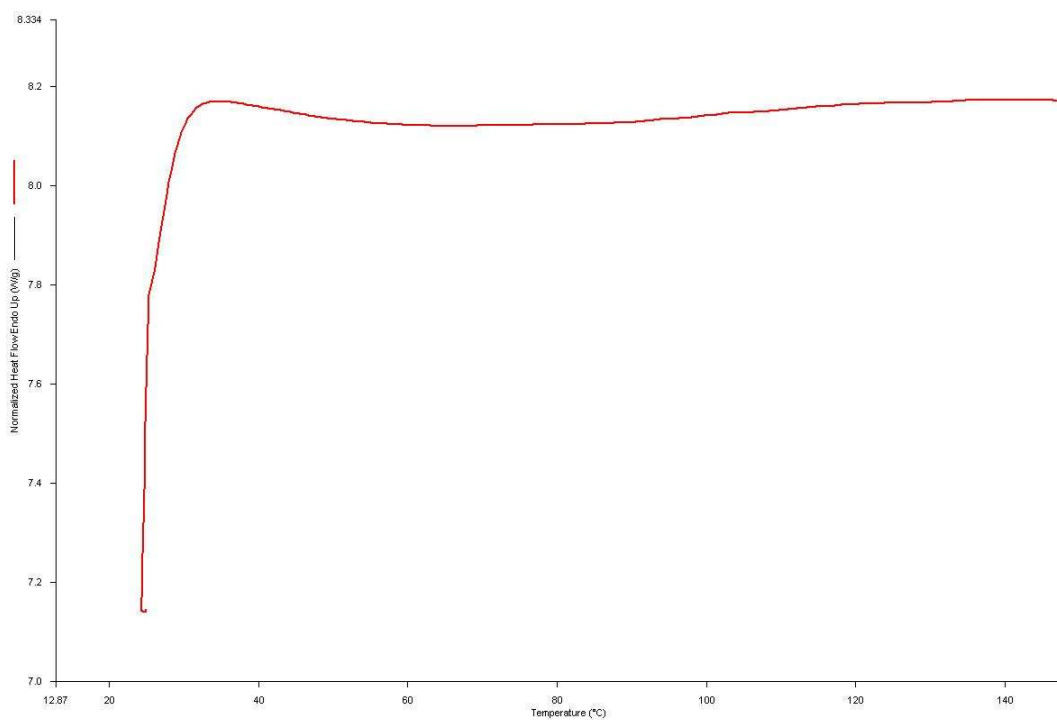


Figure S4. DSC thermogram for polymer **9** (second scan: from 25 to 150°C, 25°C/min).

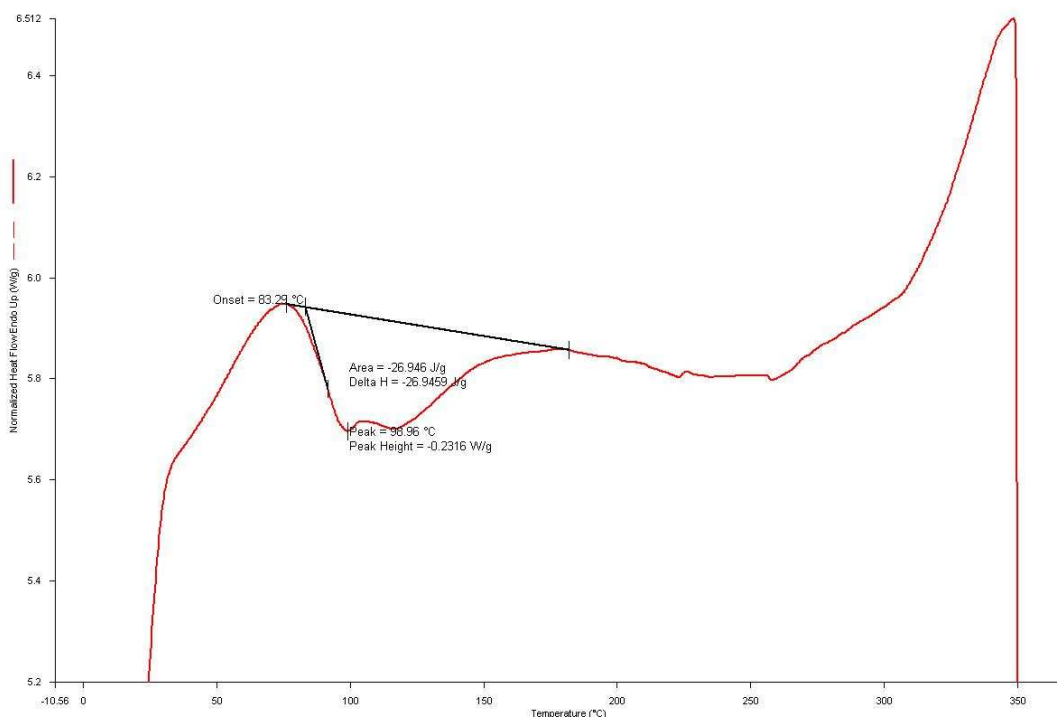


Figure S5. DSC thermogram for polymer **11** (first scan: from 25 to 350°C, 25°C/min).

Figure S6. ^{13}C NMR monomer **5**

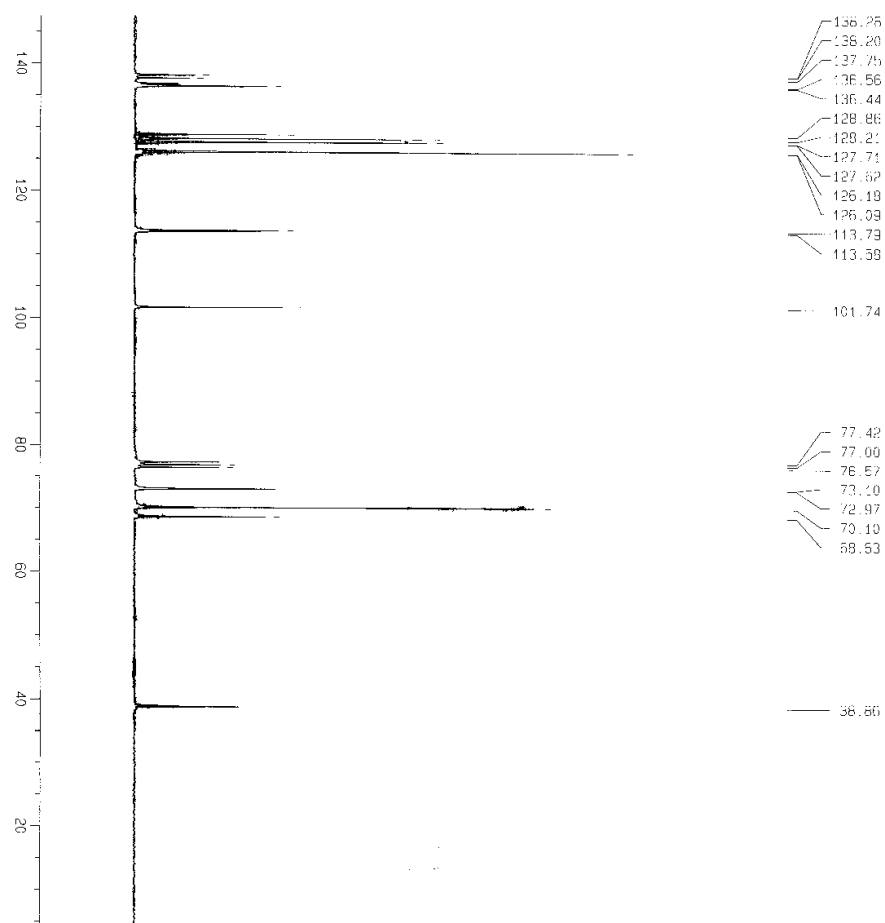
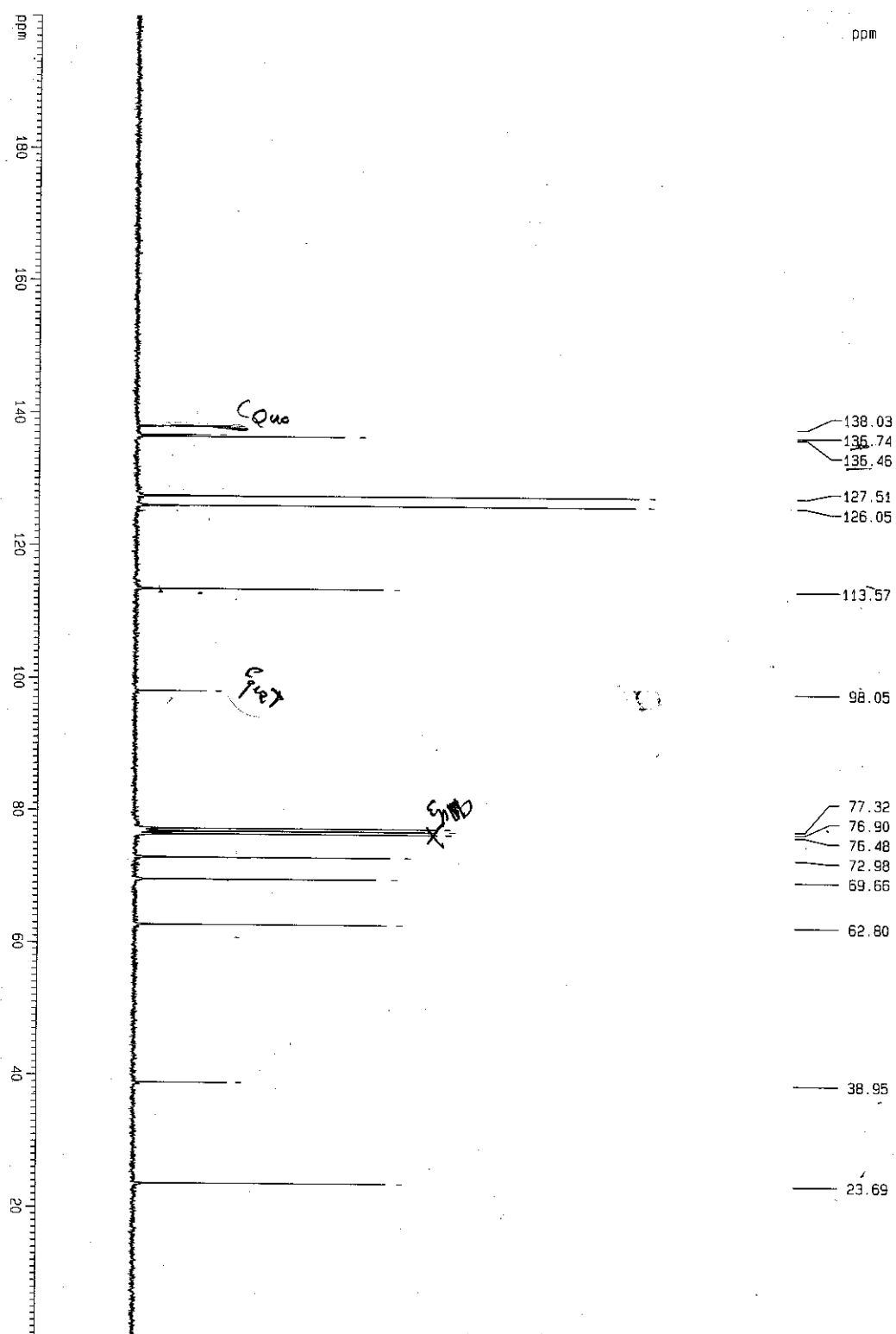


Figure S7. ^{13}C NMR Monomer 8



Chemical structure of compound 10b is shown above the spectrum. The structure is a substituted benzene ring with a methoxy group (-OCH₃) at position 1, a methyl group (-CH₃) at position 2, and a vinyl group (-CH=CH₂) at position 3. The protons are labeled: H_a (methoxy), H_b (methyl), H_c (vinyl CH), H_d (vinyl CH₂), and H_e (aromatic).

The ¹H NMR spectrum (CDCl₃) shows the following peaks and integrations:

Chemical Shift (ppm)	Integration
7.844	25.844
5.970	5.970
6.128	6.128
5.802	5.802
4.295	12.295
4.079	-0.079
3.999	25.999
1.7444	17.4444

Chemical structure of the monomer is shown below the spectrum:

C=CC1=CC=C(C=C1)COC(=O)C(COC(=O)C2=CC=C(C=C2)C=C)O

The spectrum displays chemical shifts (ppm) on the x-axis, ranging from 0 to 140. Key peaks are labeled with their corresponding chemical shift values:

- 138.00
- 136.71
- 136.43
- 136.29
- 127.72
- 127.51
- 126.21
- 126.04
- 113.90
- 113.58
- 77.32
- 77.10
- 76.90
- 76.47
- 73.33
- 72.95
- 69.51
- 62.79
- 38.90
- 0.90

Figure S10. ^{13}C NMR Polymer 6

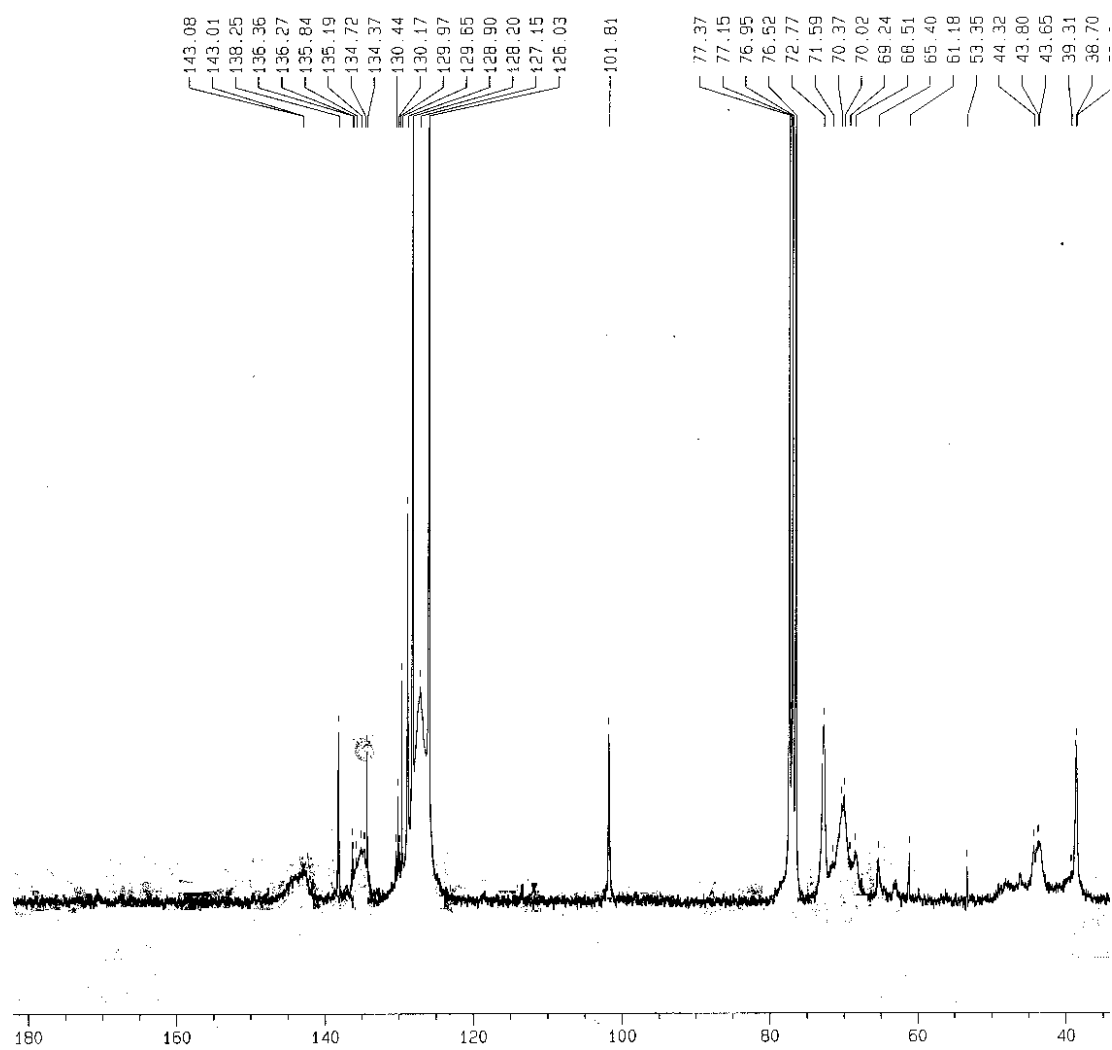


Figure S11. ^{13}C NMR Polymer 9

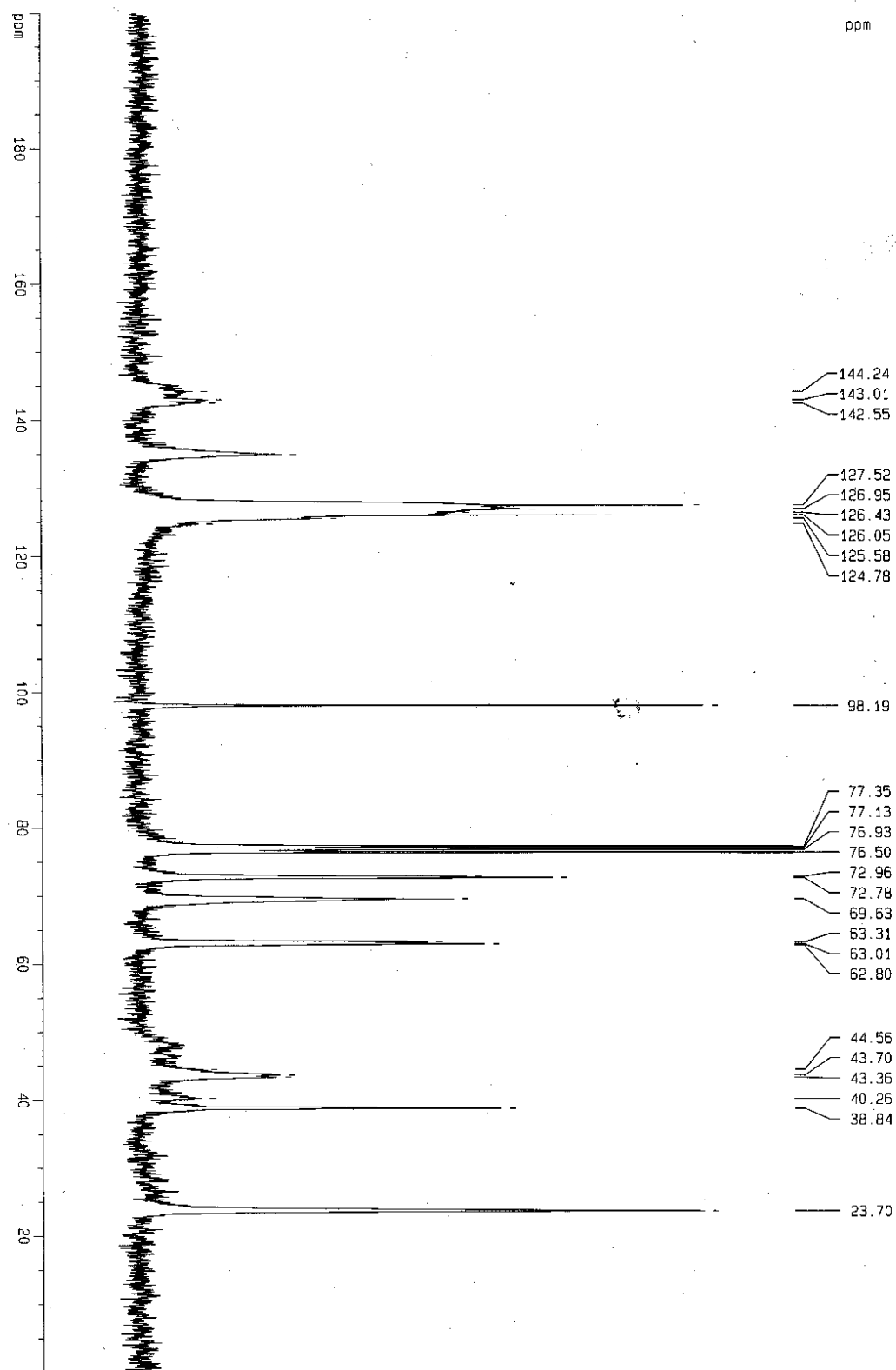


Figure S12. ^{13}C NMR Polymer 11

