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/*t*-BuOK	5.5	16(**3a**)
5	**2b**	THF/*t*-BuOK	5.5	53(**3a**)
6	**2b**	THF/*t*-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 70ºC 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.

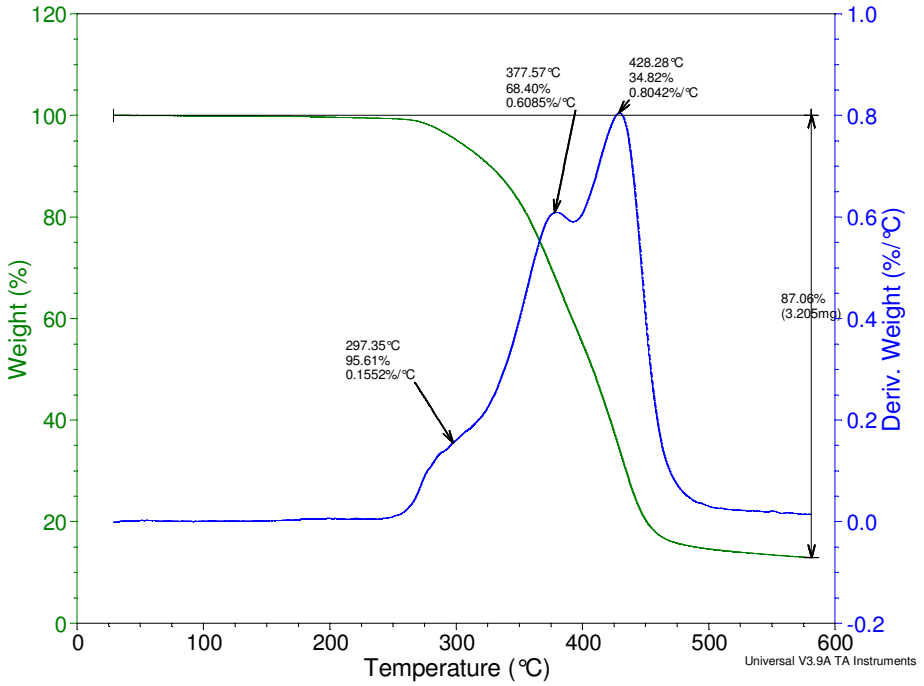

Figure S1. TGA profile and derivative weight loss (blue) for cyclopolymer **9**.

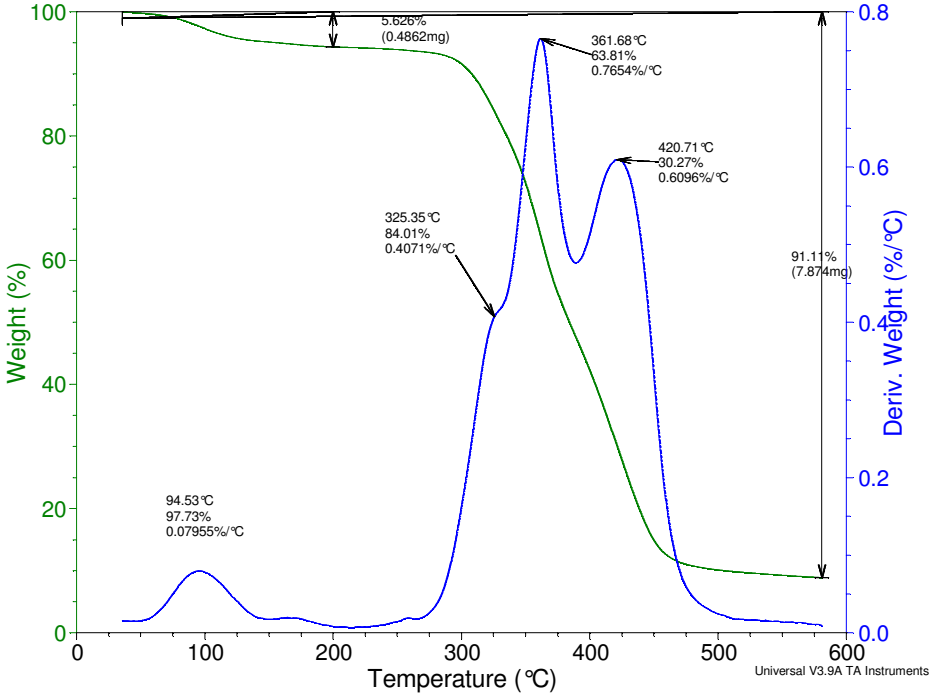

Figure S2. TGA profile and derivative weight loss (blue) for cyclopolymer **11**.

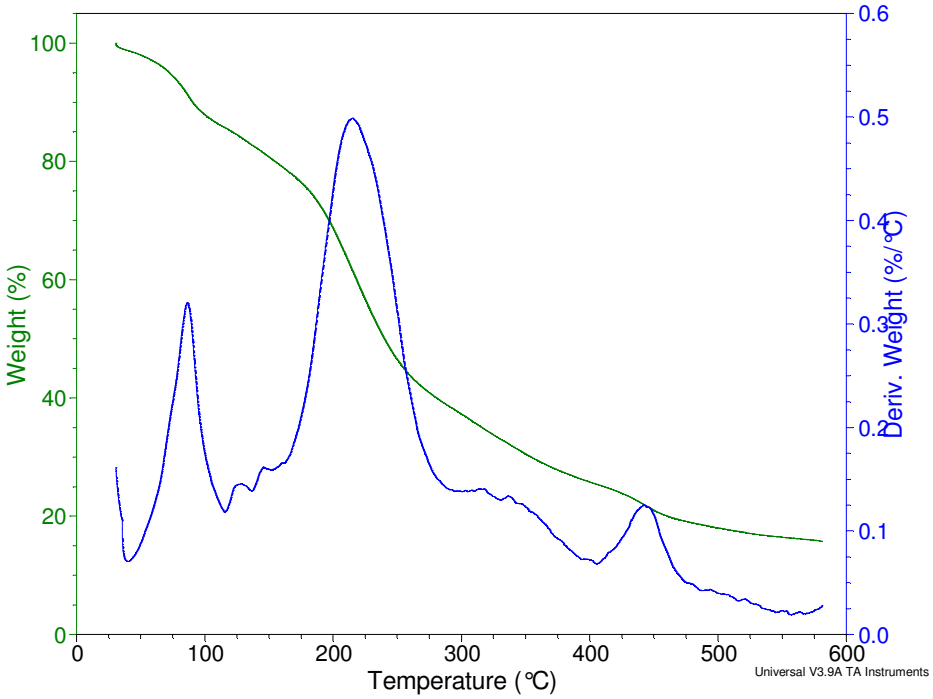

Figure S3. TGA profile and derivative weight loss (blue) for cyclopolymer **9** in the presence of a catalytic amount of solid *p*-toluenesulfonic acid.

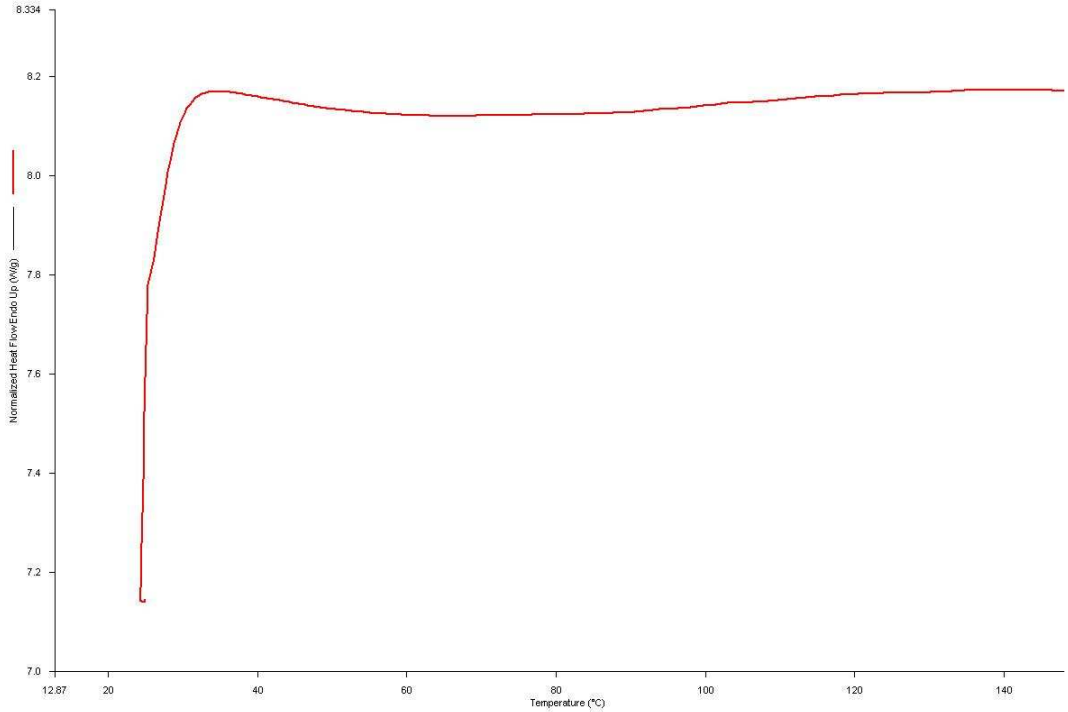

Figure S4. DSC thermogram for polymer **9** (second scan: from 25 to 150°C, 25°C/min).

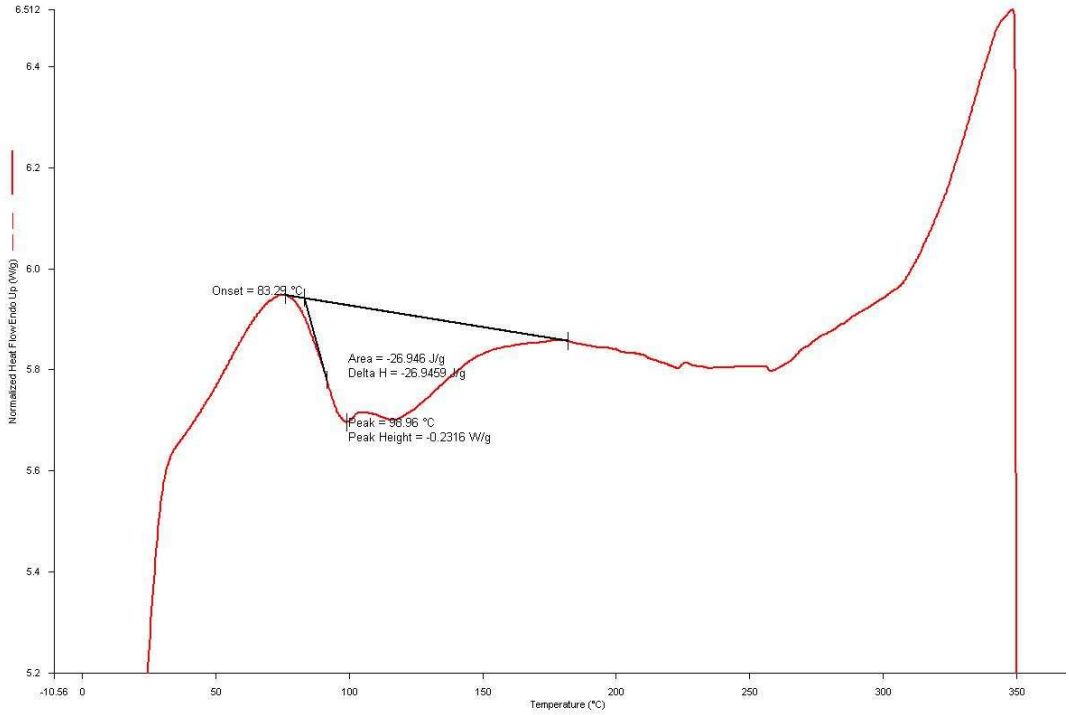

Figure S5. DSC thermogram for polymer **11** (first scan: from 25 to 350°C, 25°C/min)**.**

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

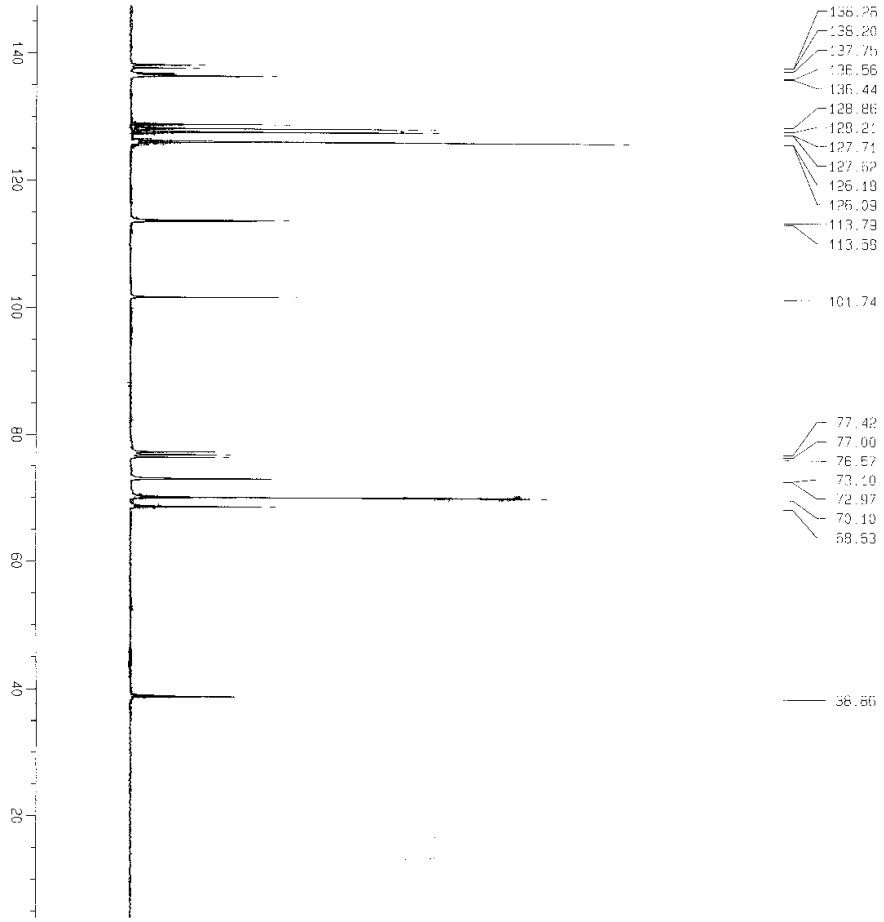

Figure S7. ^{13}C NMR Monomer **8**

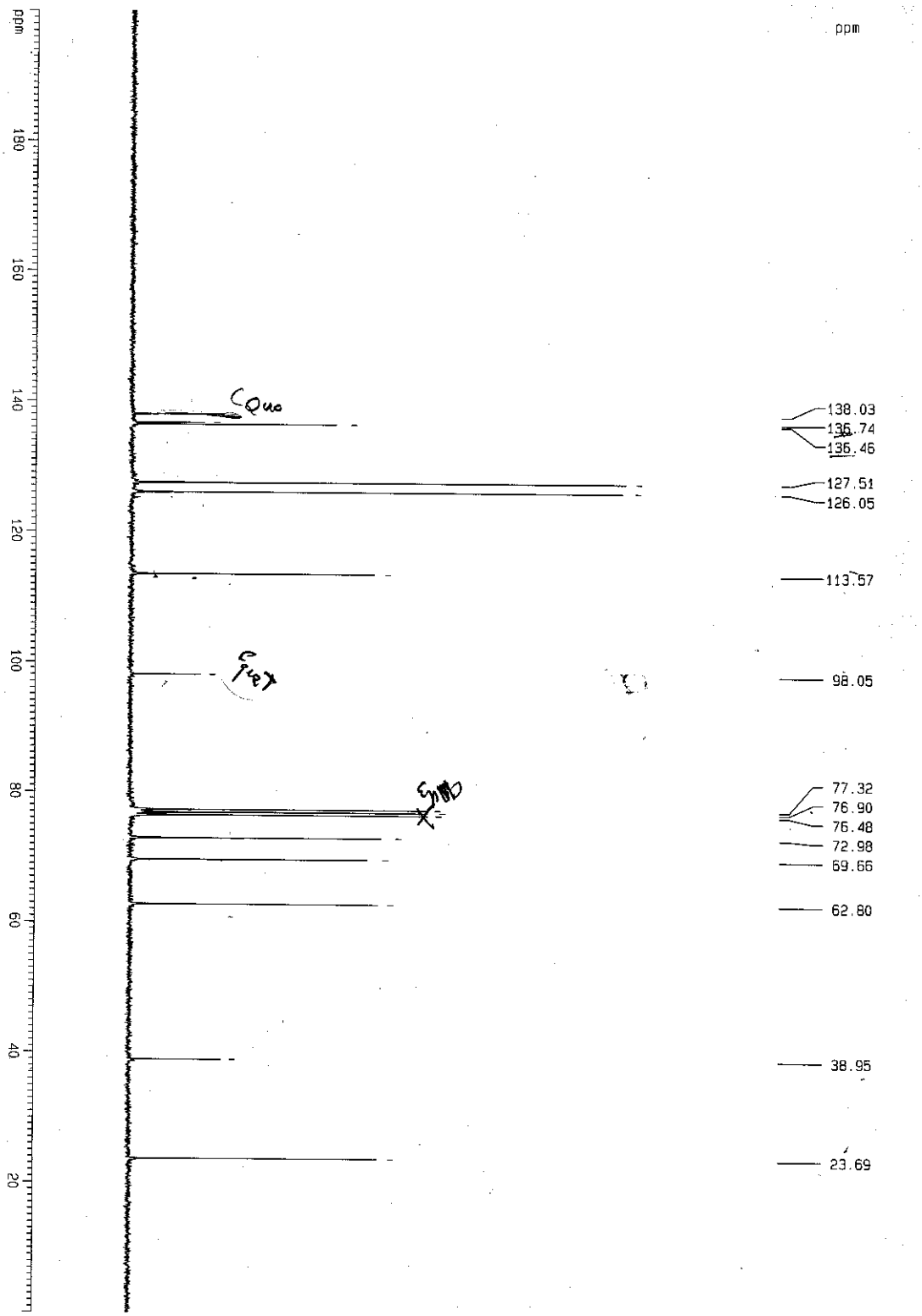

Figure S8. ^{1}H NMR Monomer **10**

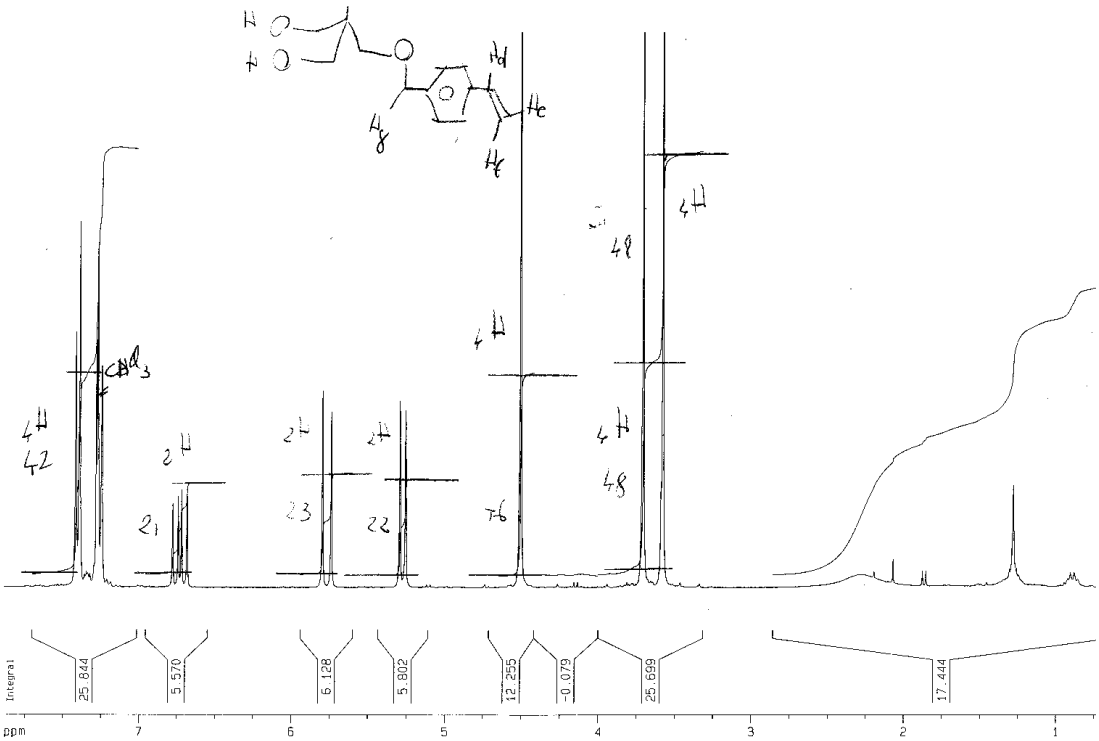

Figure S9. ^{13}C NMR Monomer **10**

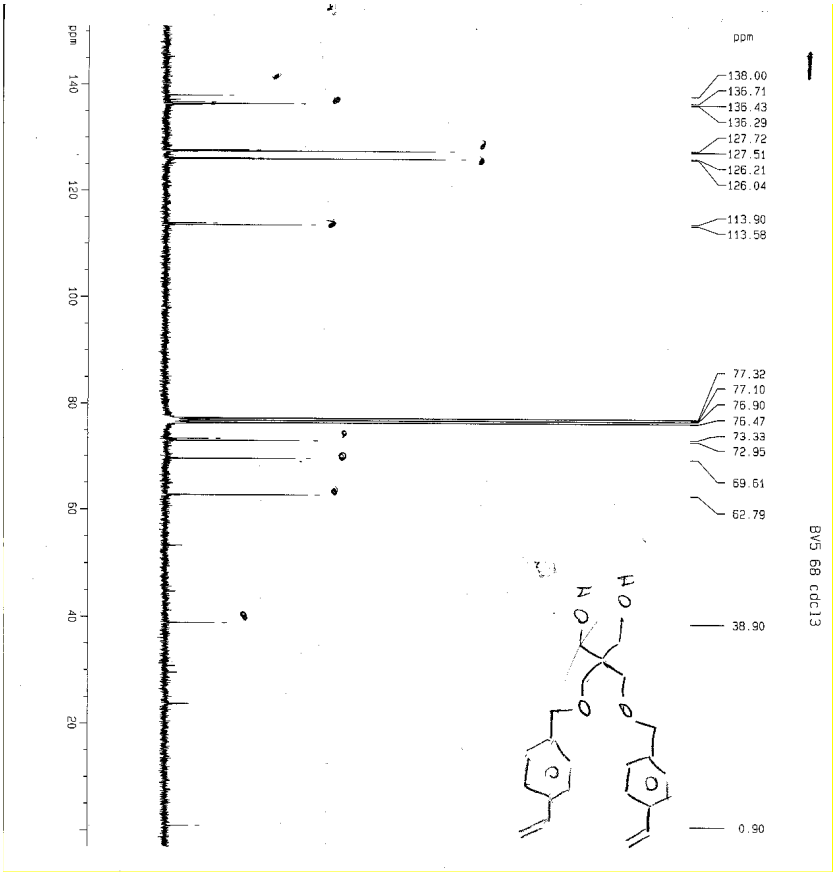

Figure S10. ^{13}C NMR Polymer **6**

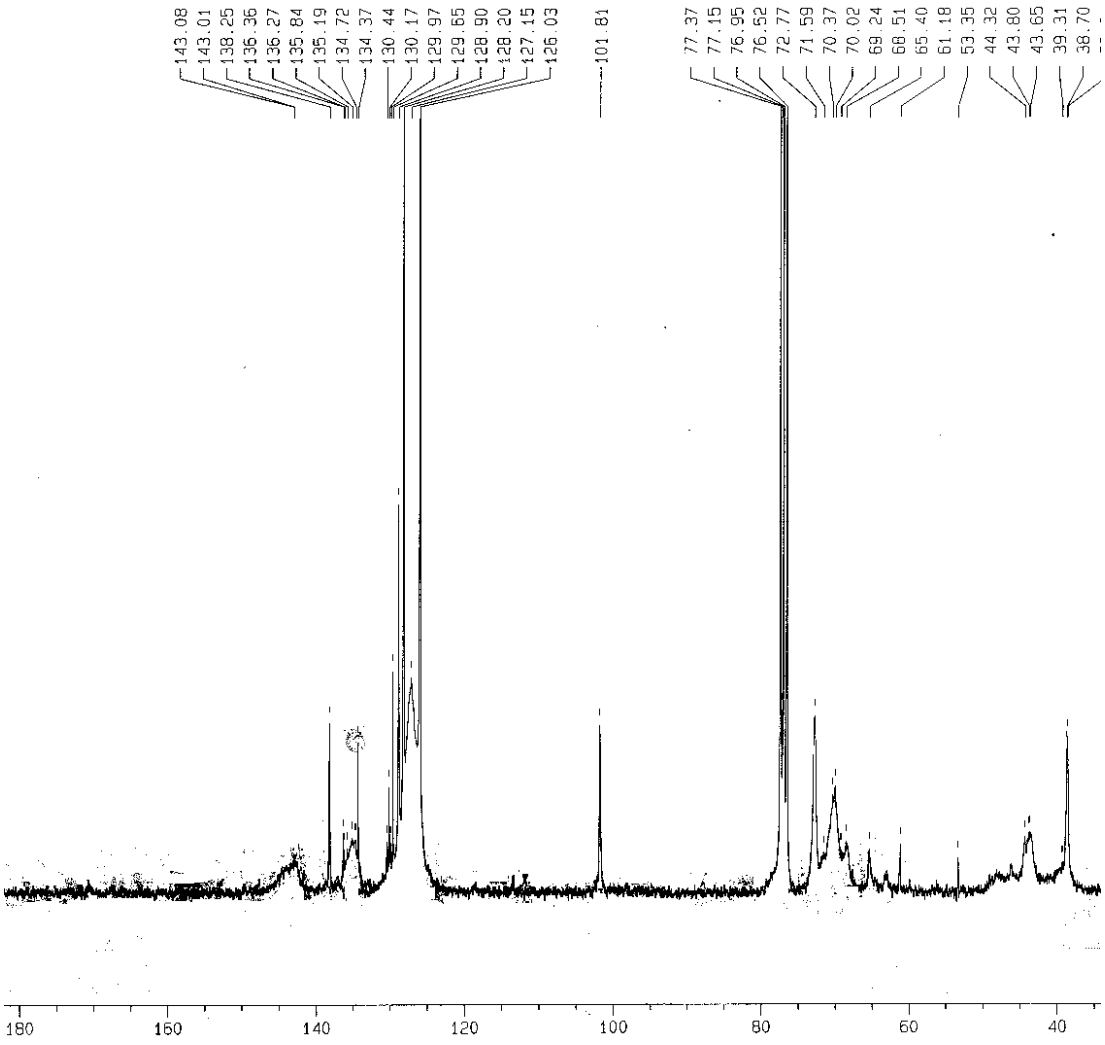

Figure S11. ^{13}C NMR Polymer **9**

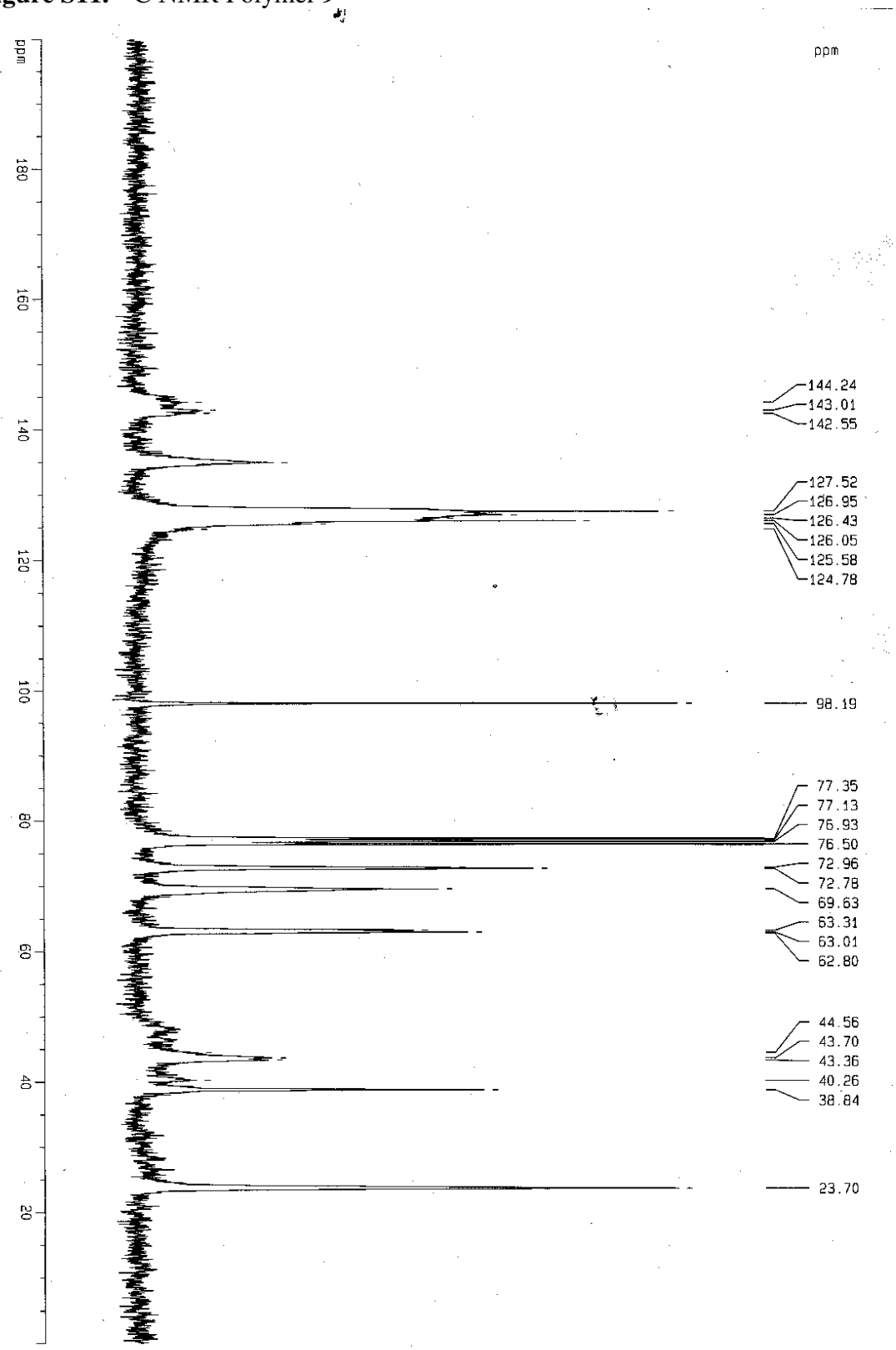

Figure S12. ^{13}C NMR Polymer **11**