Supporting Information

Synthesis of megadalton stereoregular ring-substituted poly(phenylacetylene)s by a rhodium(I) catalyst with a *N*-functionalized hemilabile phosphine ligand

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1.- NMR spectra of poly(phenylacetylene)s.

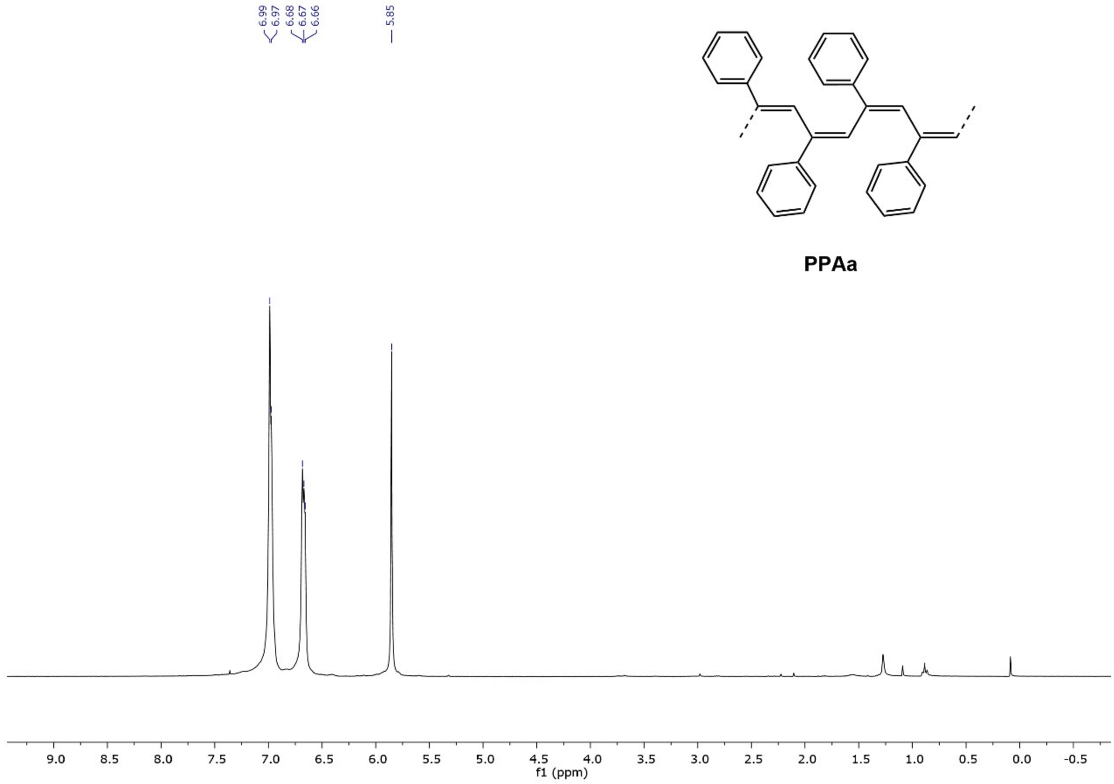


Figure S1. ^{1}H NMR (300 MHz) spectrum of polymer **PPAa** in CD_2Cl_2.

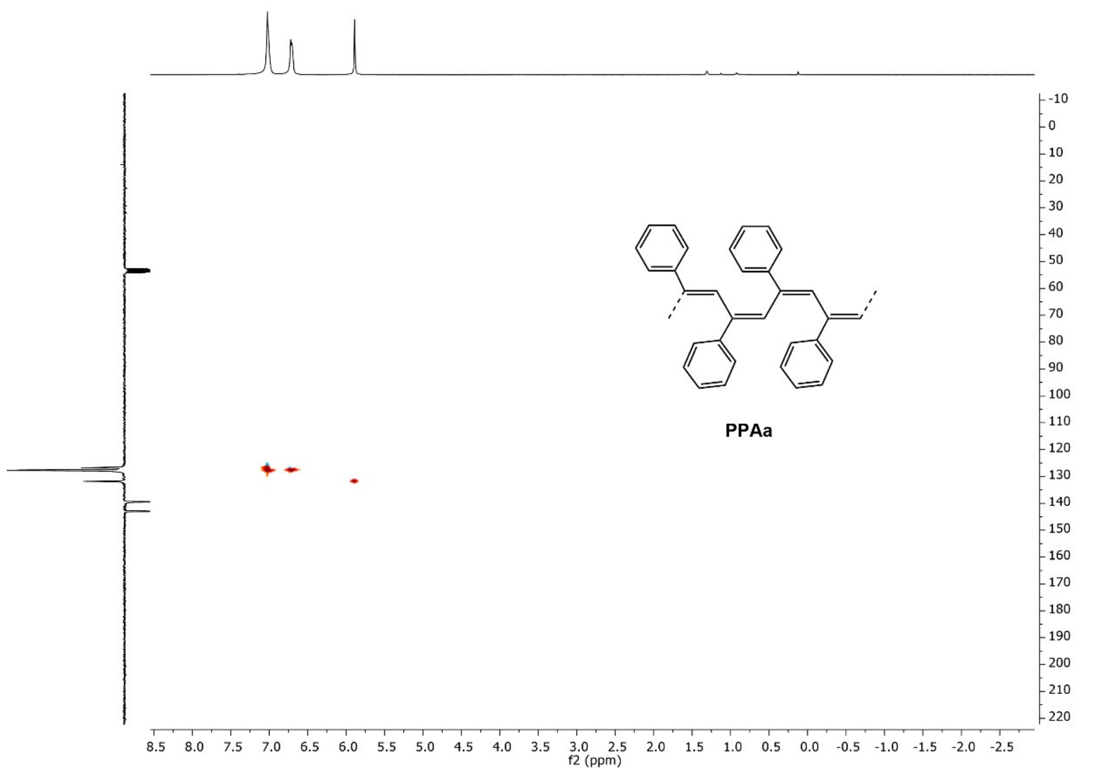


Figure S2. ^{1}H-^{13}C-HSQC (300 MHz) spectrum of polymer **PPAa** in CD_2Cl_2.

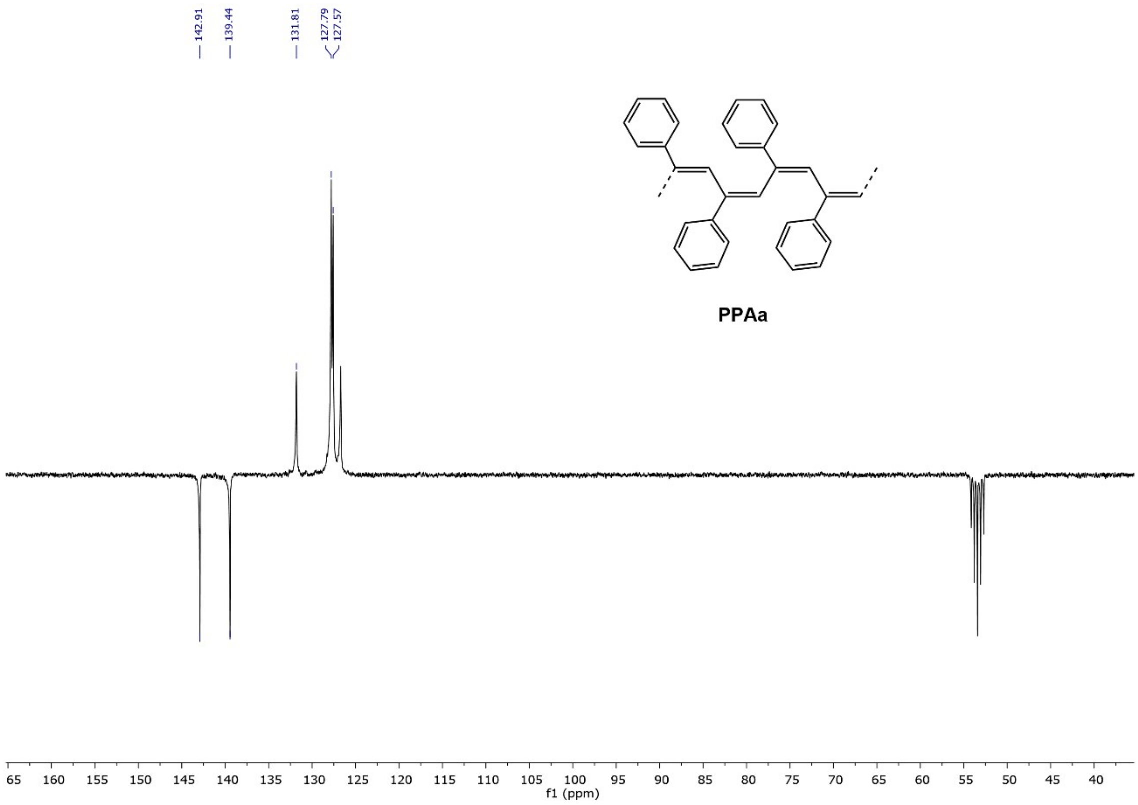


Figure S3. $^{13}C\{^1H\}$-APT NMR (300 MHz) spectrum of polymer **PPAa** in CD_2Cl_2.

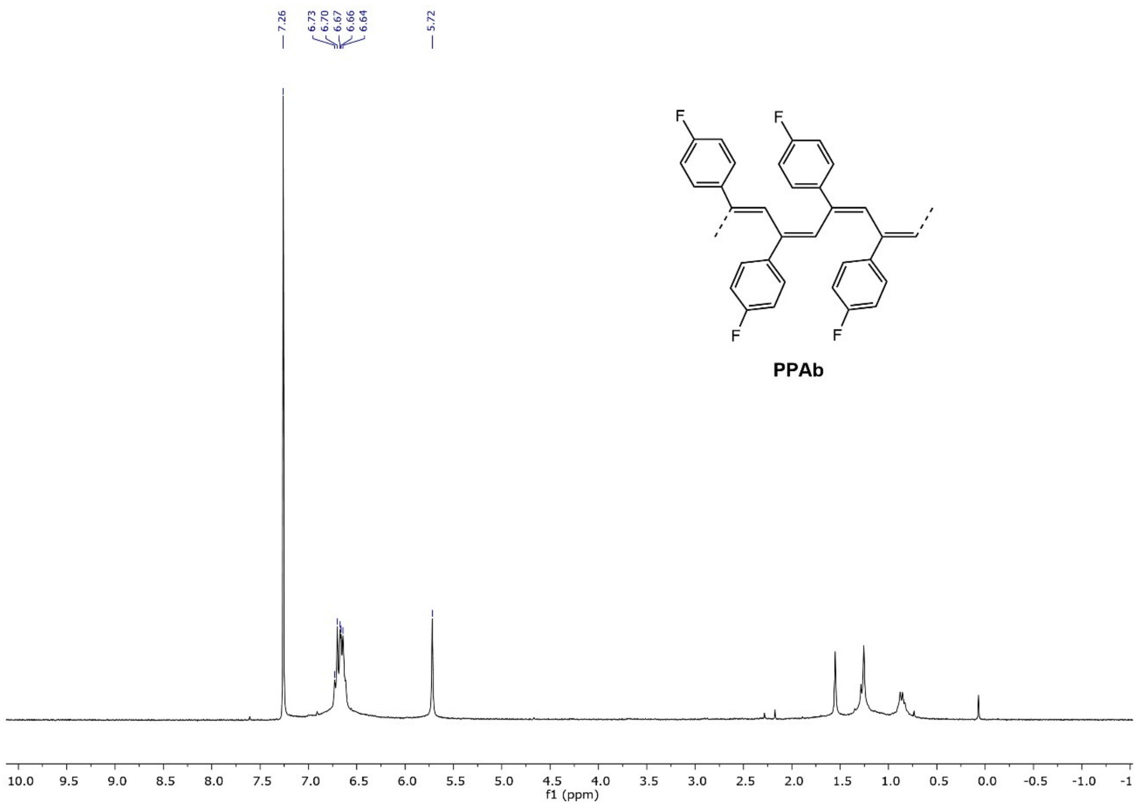


Figure S4. ^1H NMR (300 MHz) spectrum of polymer **PPAb** in $CDCl_3$.

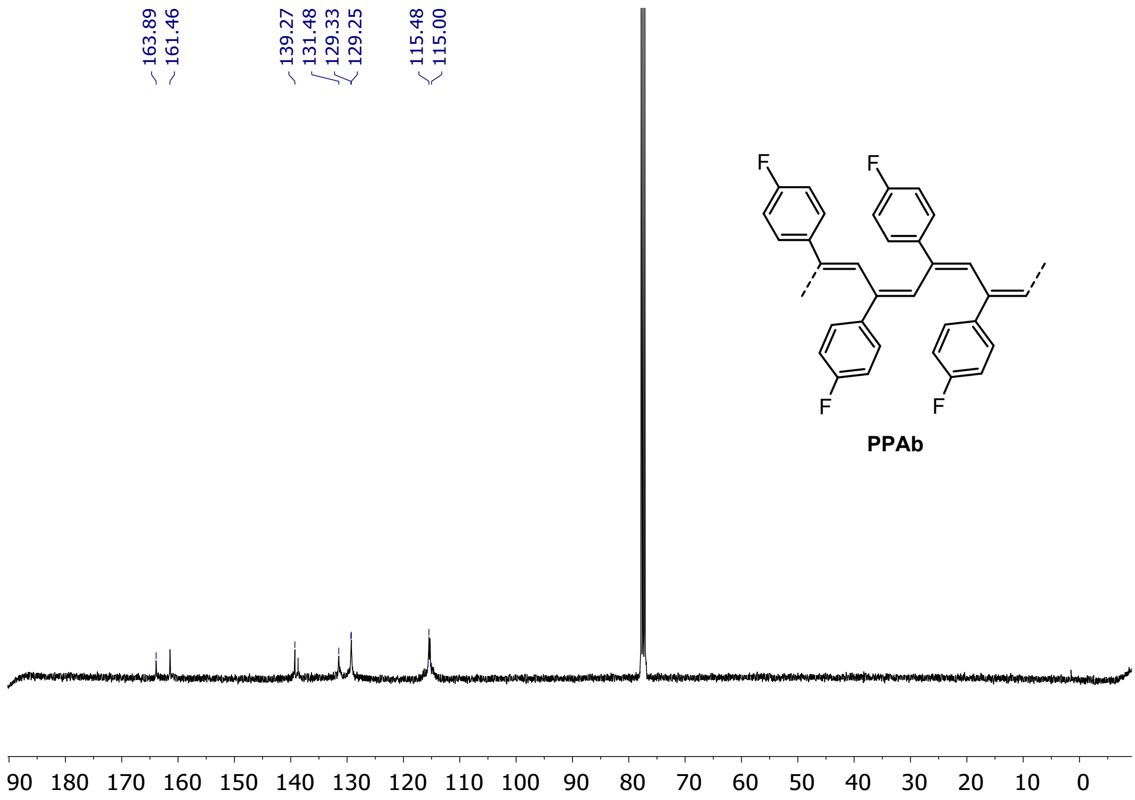


Figure S5. $^{13}C\{^{1}H\}$ NMR (400 MHz) spectrum of polymer **PPAb** in $CDCl_3$.

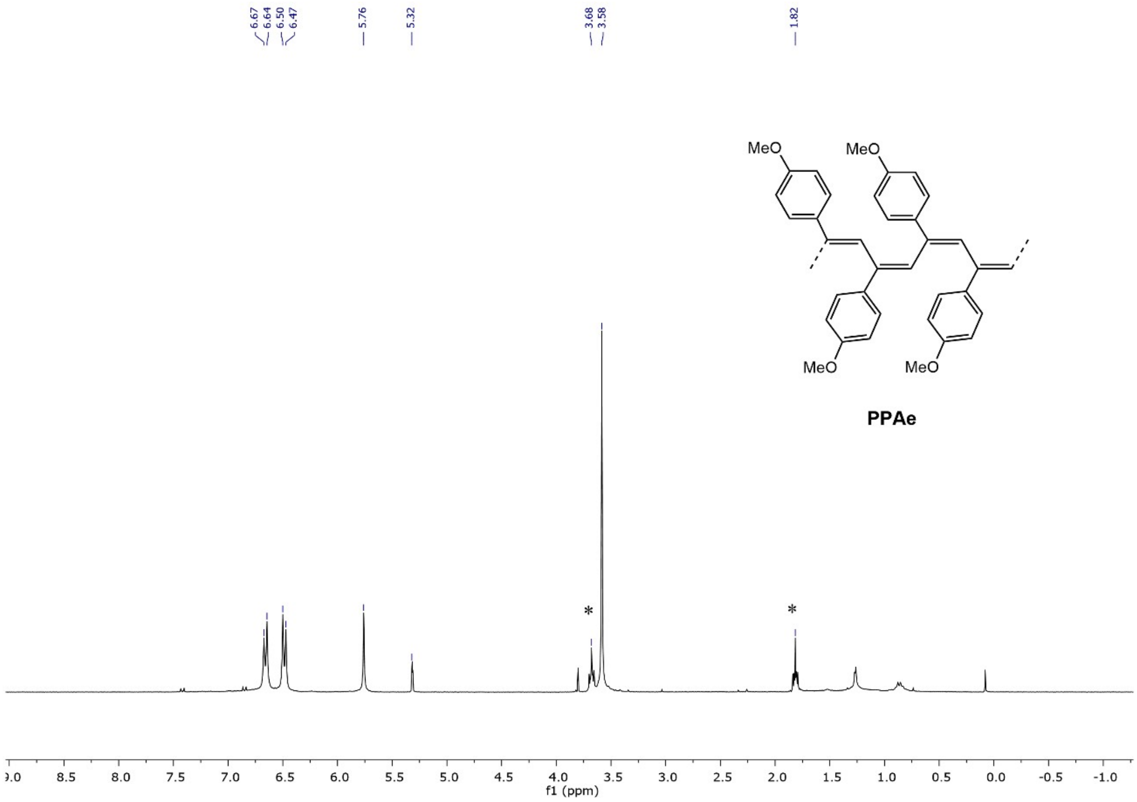


Figure S6. ^{1}H NMR (400 MHz) spectrum of polymer **PPAe** in CD_2Cl_2 (* THF).

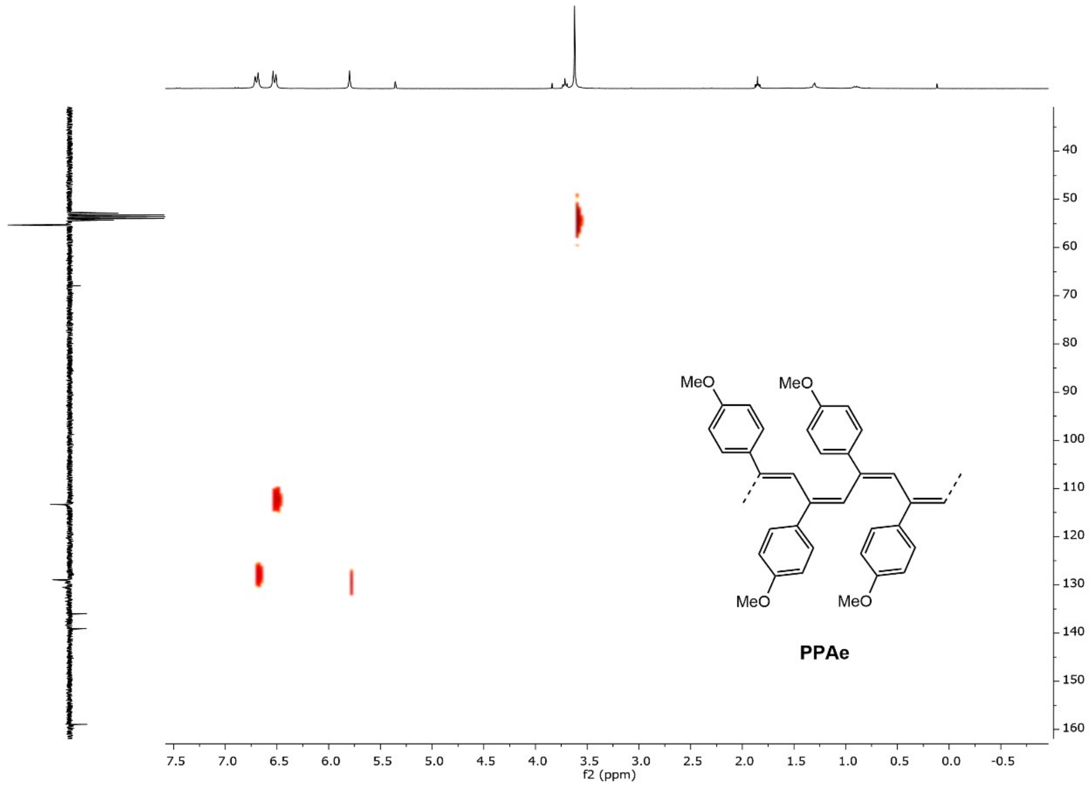


Figure S7. ^{1}H-^{13}C-HSQC (400 MHz) spectrum of polymer **PPAe** in CD_2Cl_2.

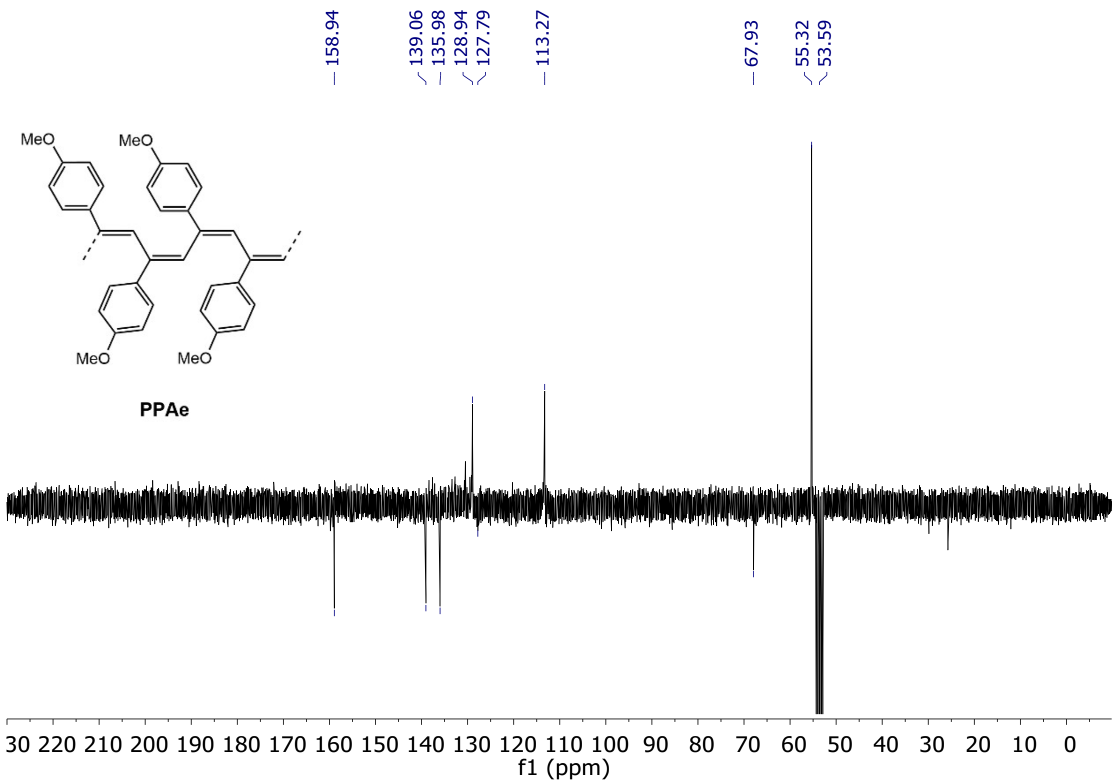


Figure S8. $^{13}C\{^{1}H\}$-APT NMR (400 MHz) spectrum of polymer **PPAe** in CD_2Cl_2.

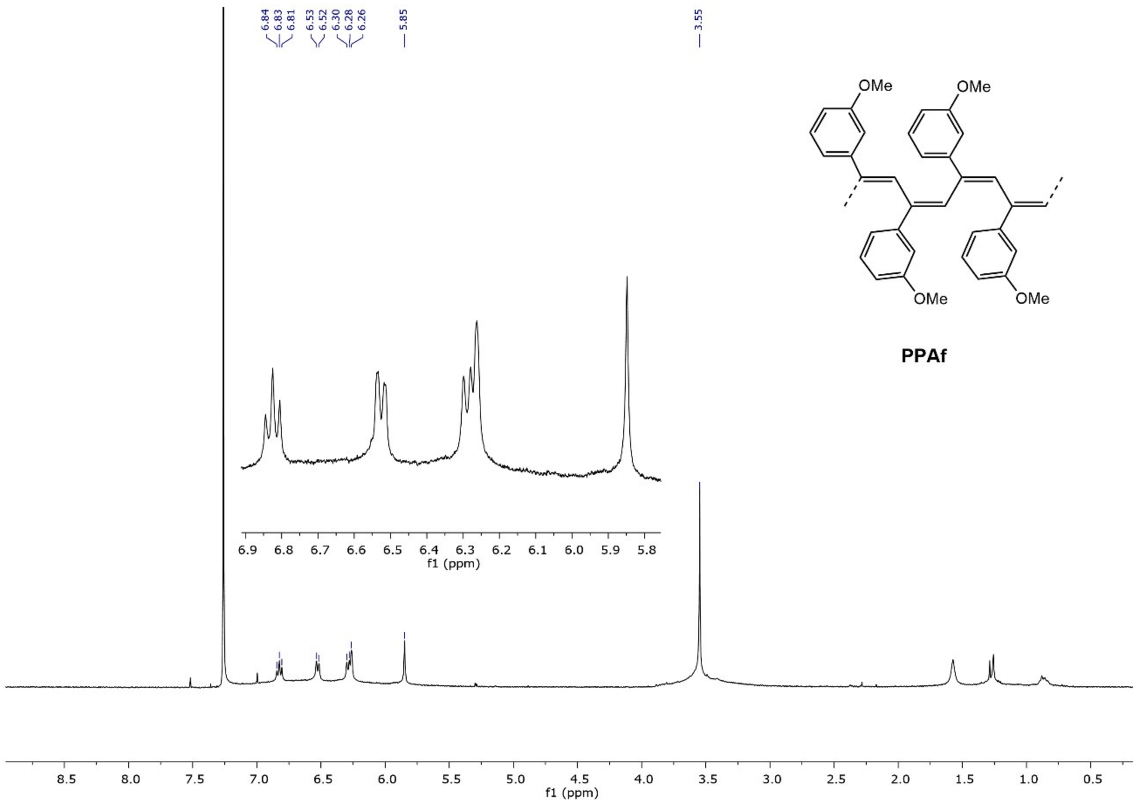


Figure S9. ^{1}H NMR (300 MHz) spectrum of polymer **PPAf** in $CDCl_3$.

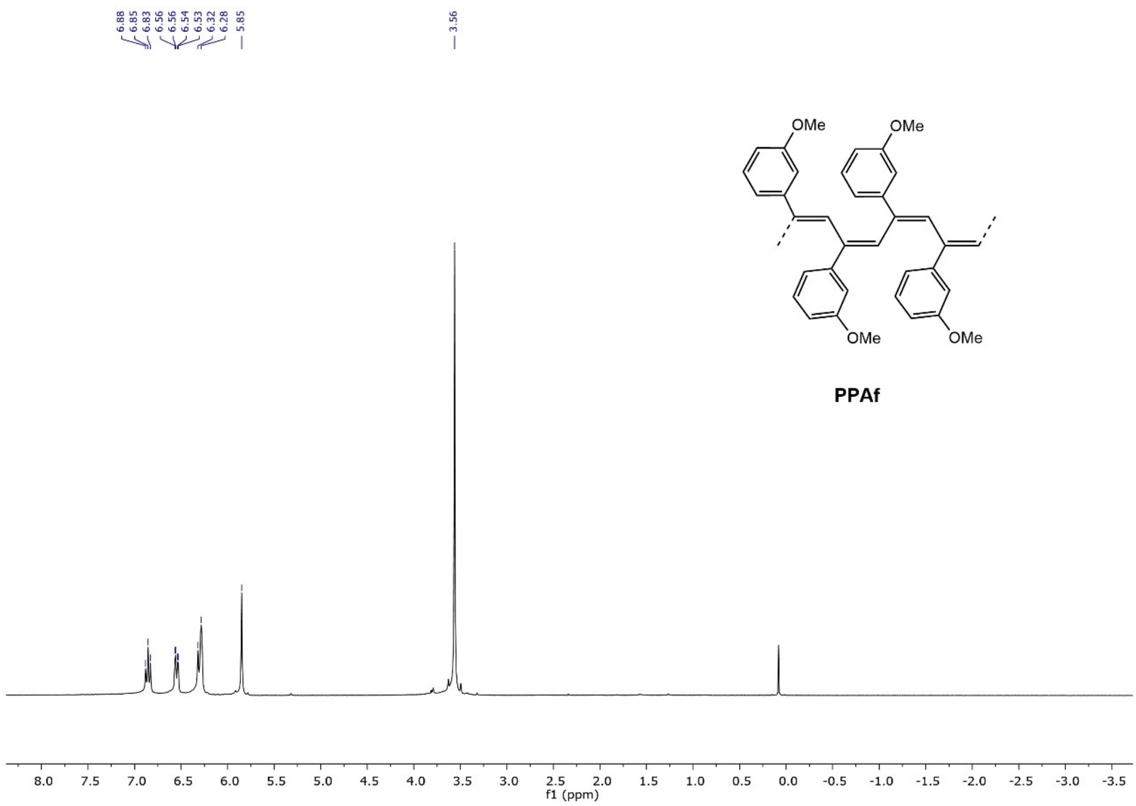


Figure S10. ^{1}H NMR (300 MHz) spectrum of polymer **PPAf** in CD_2Cl_2.

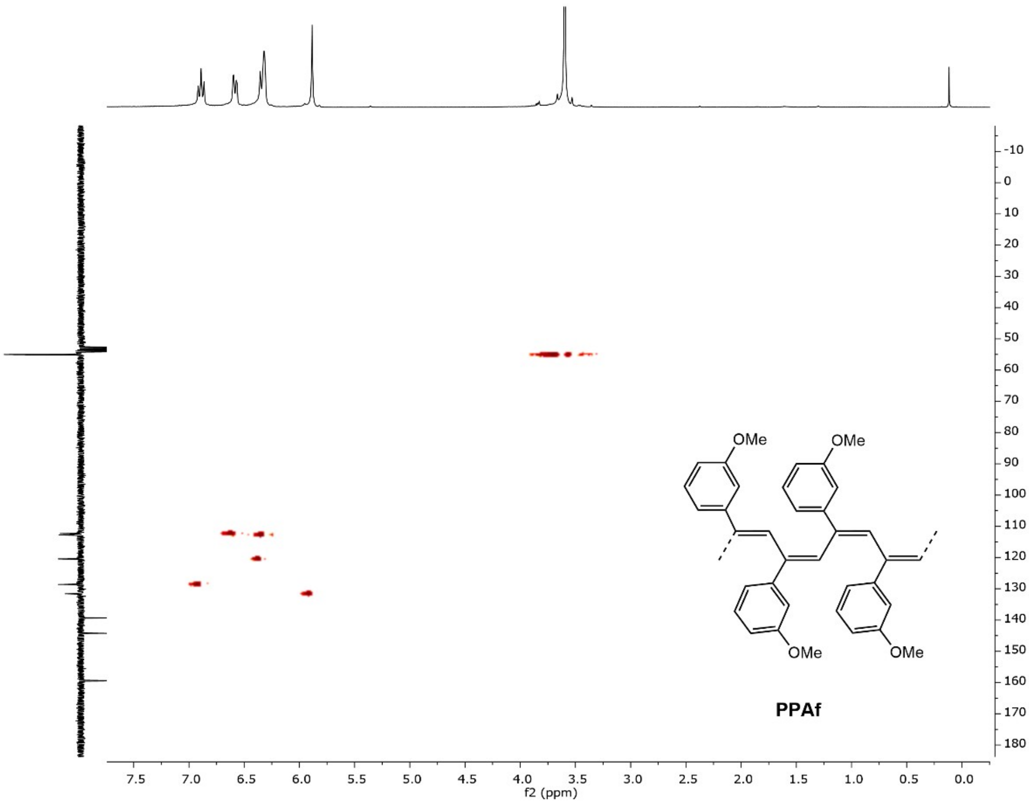


Figure S11. ^{1}H-^{13}C-HSQC (300 MHz) spectrum of polymer **PPAf** in CD_2Cl_2.

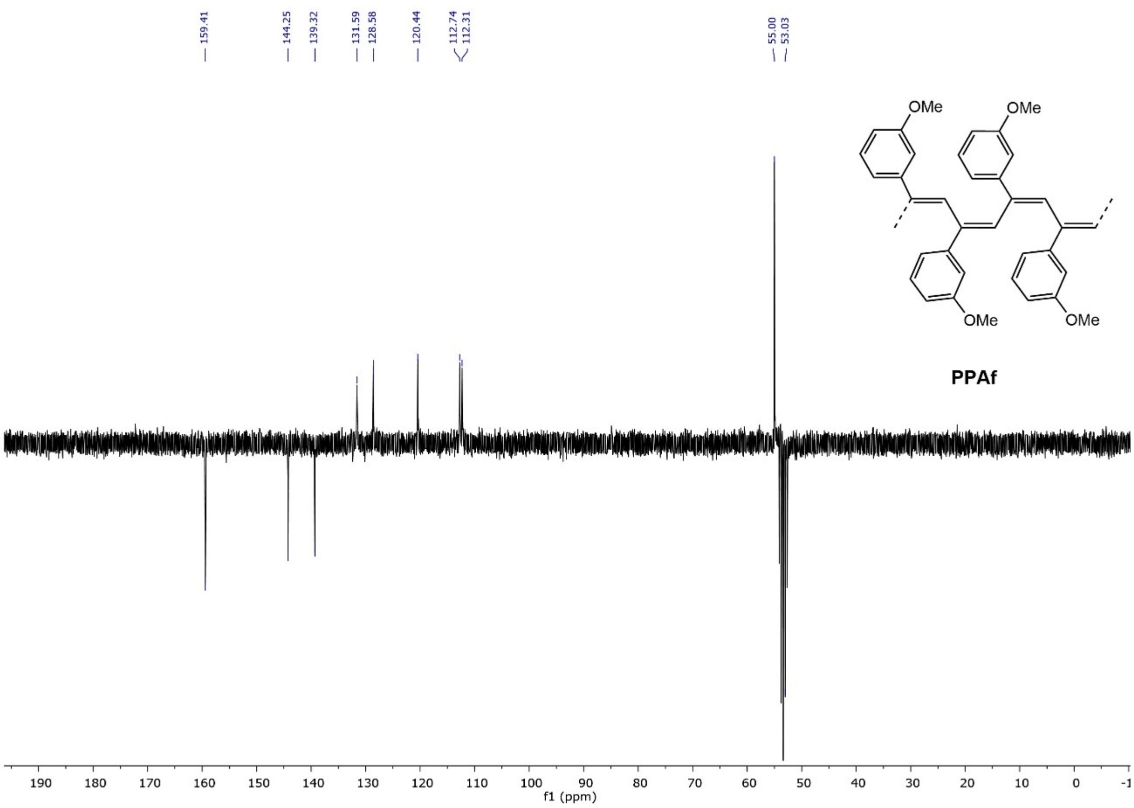


Figure S12. $^{13}C\{^{1}H\}$-APT NMR (300 MHz) spectrum of polymer **PPAf** in CD_2Cl_2.

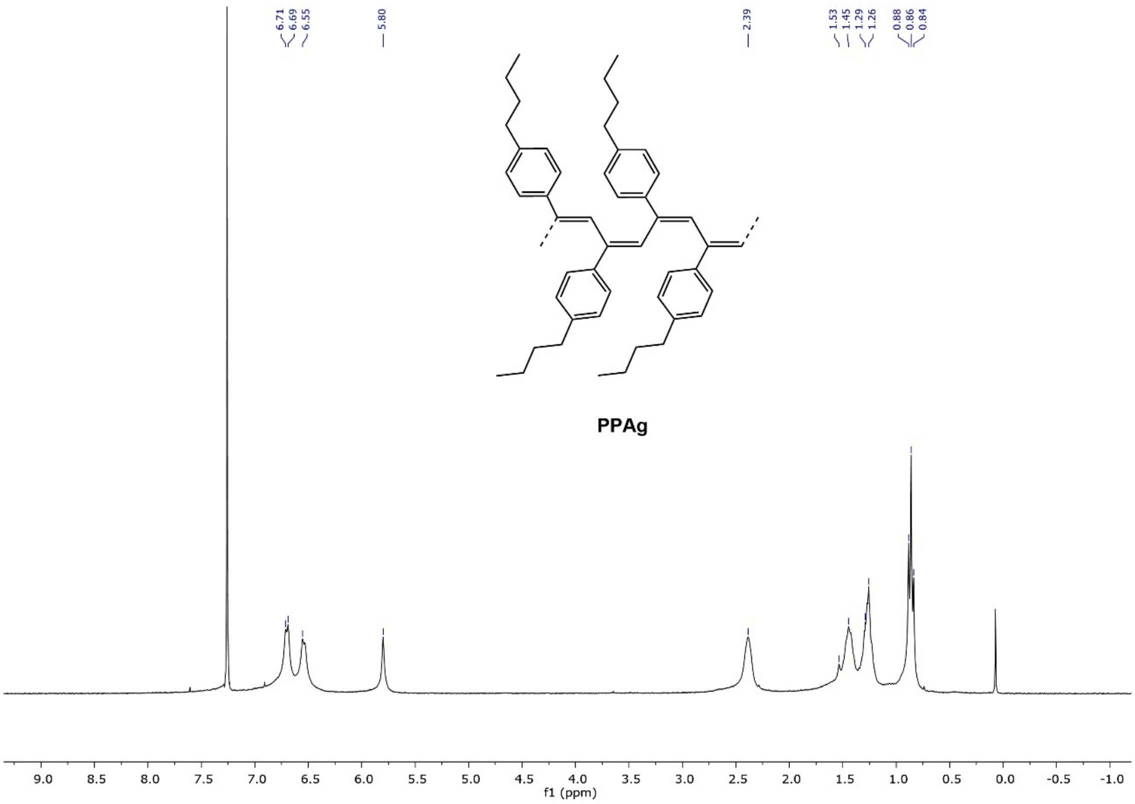


Figure S13. ^{1}H NMR (300 MHz) spectrum of polymer **PPAg** in $CDCl_3$.

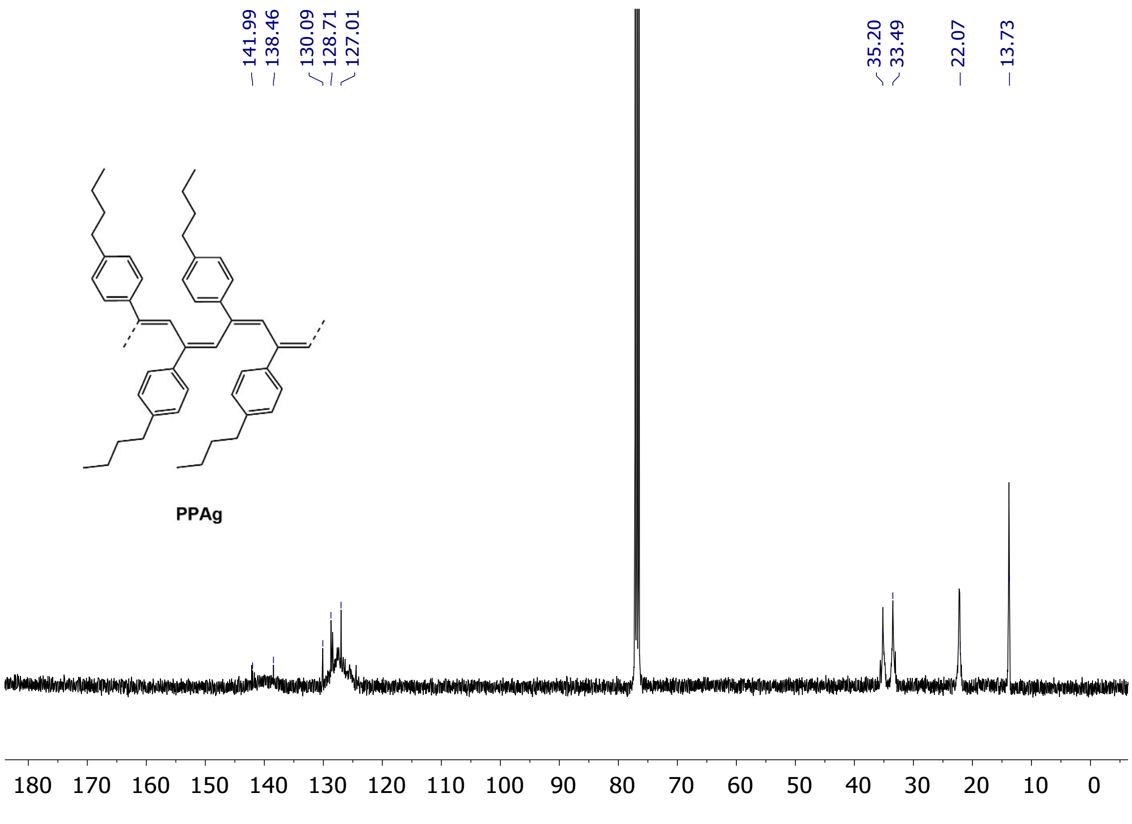


Figure S14. $^{13}C\{^{1}H\}$ NMR (400 MHz) spectrum of polymer **PPAg** in $CDCl_3$.

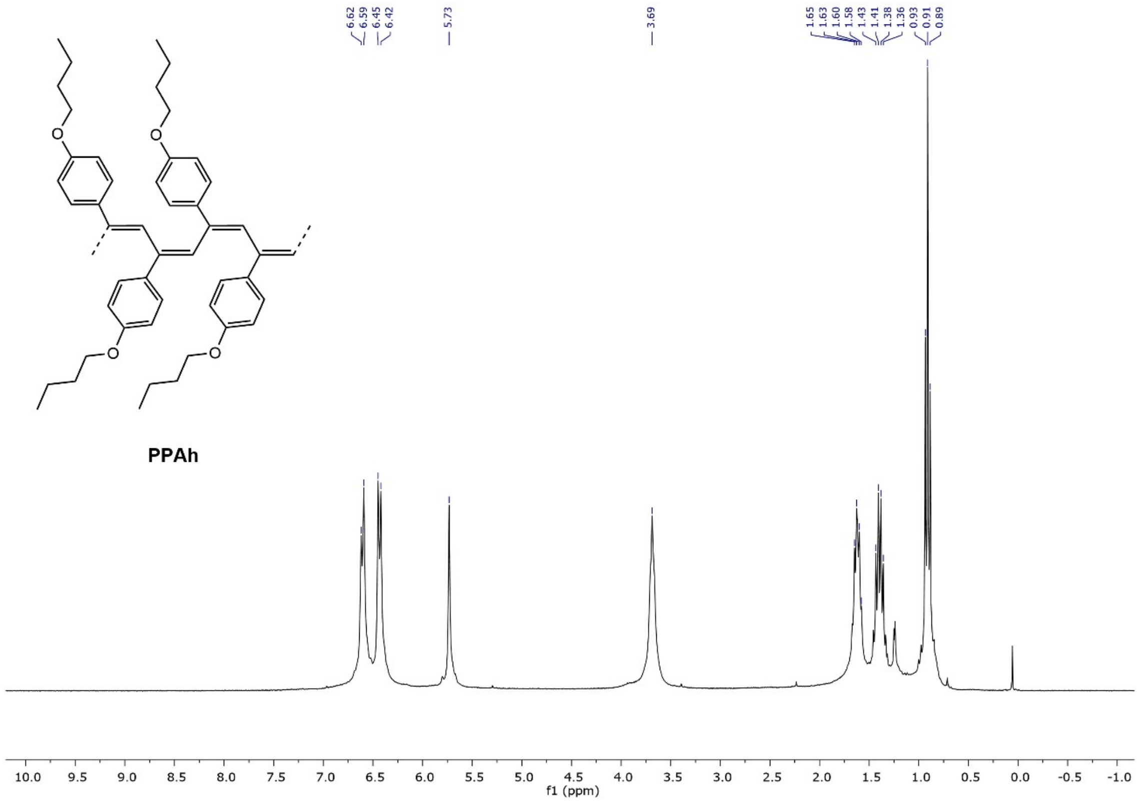


Figure S15. ^{1}H NMR (300 MHz) spectrum of polymer **PPAh** in CD_2Cl_2.

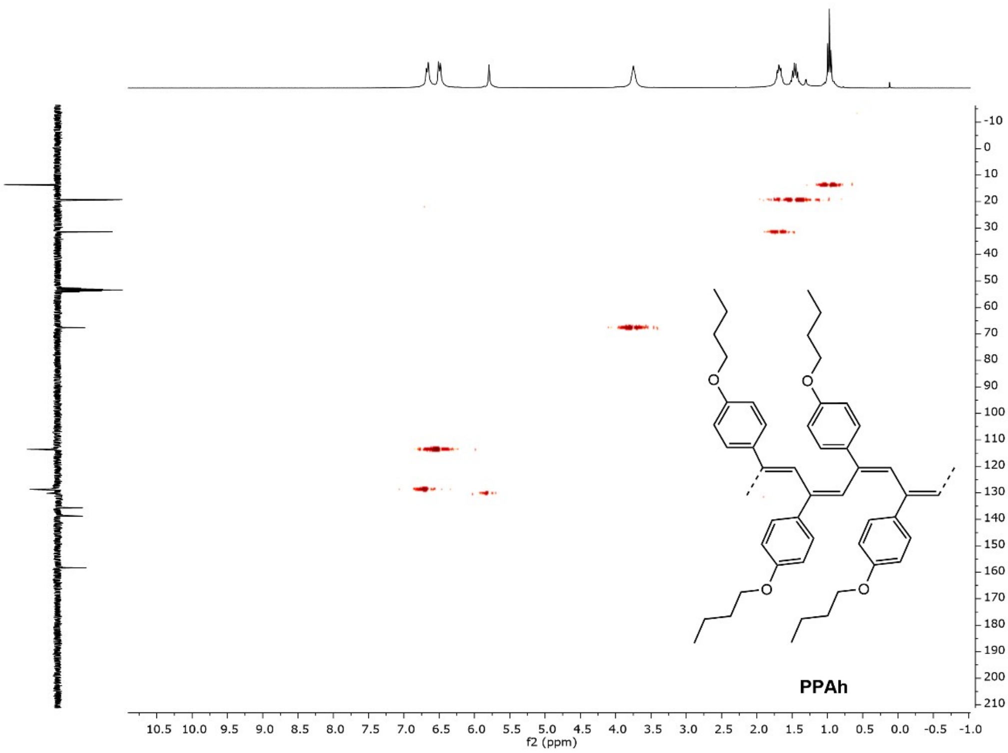


Figure S16. ^{1}H-^{13}C-HSQC (300 MHz) spectrum of polymer **PPAh** in CD_2Cl_2.

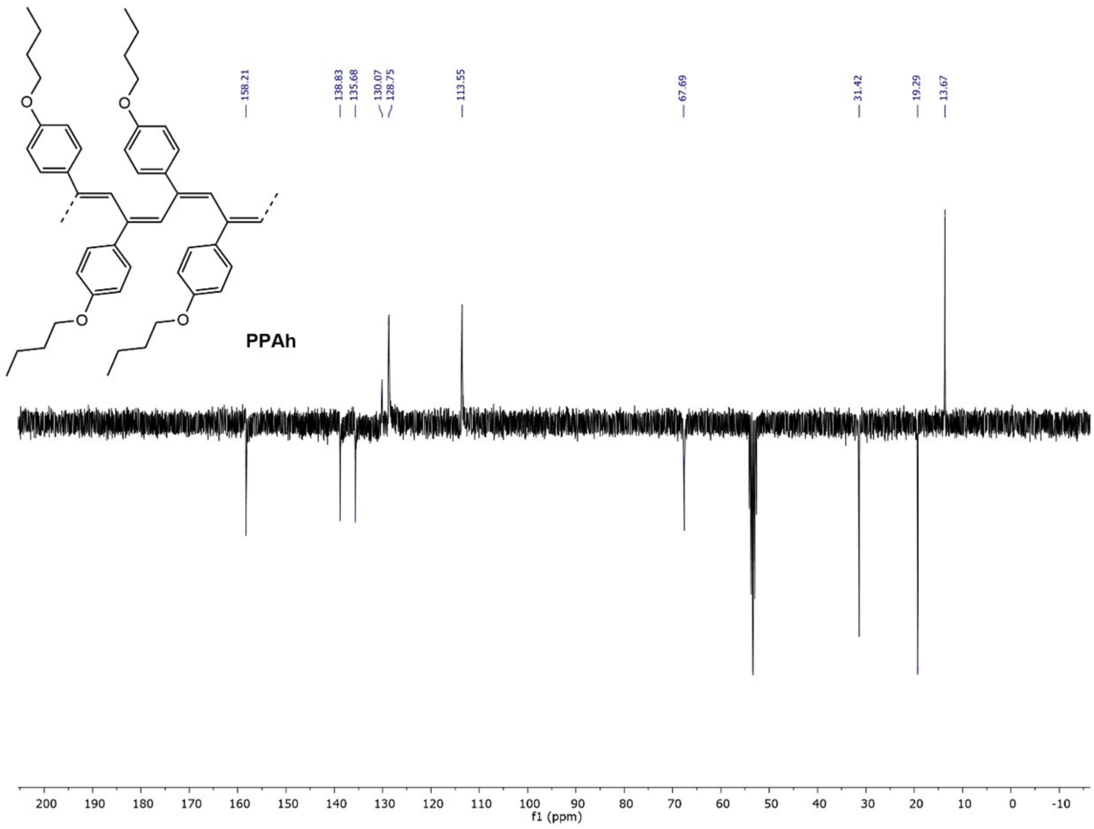


Figure S17. $^{13}C\{^{1}H\}$-APT NMR (300 MHz) spectrum of polymer **PPAh** in CD_2Cl_2.

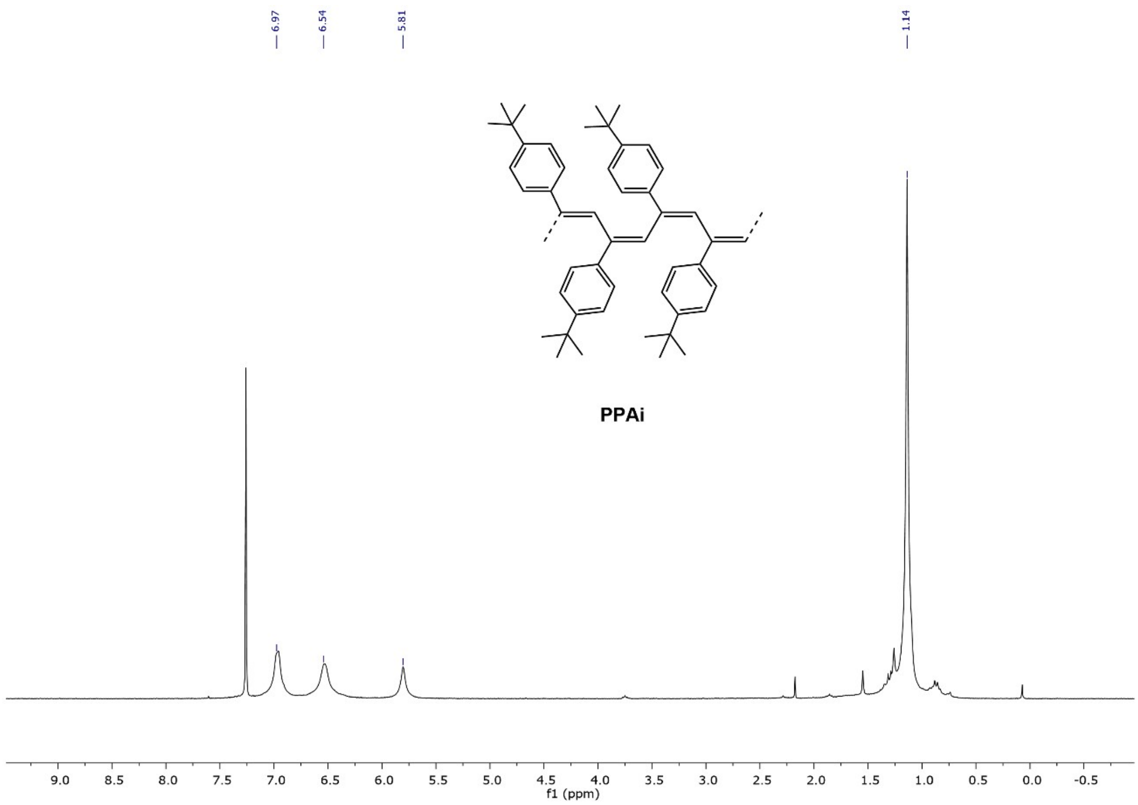


Figure S18. ^{1}H NMR (300 MHz) spectrum of polymer **PPAi** in $CDCl_3$.

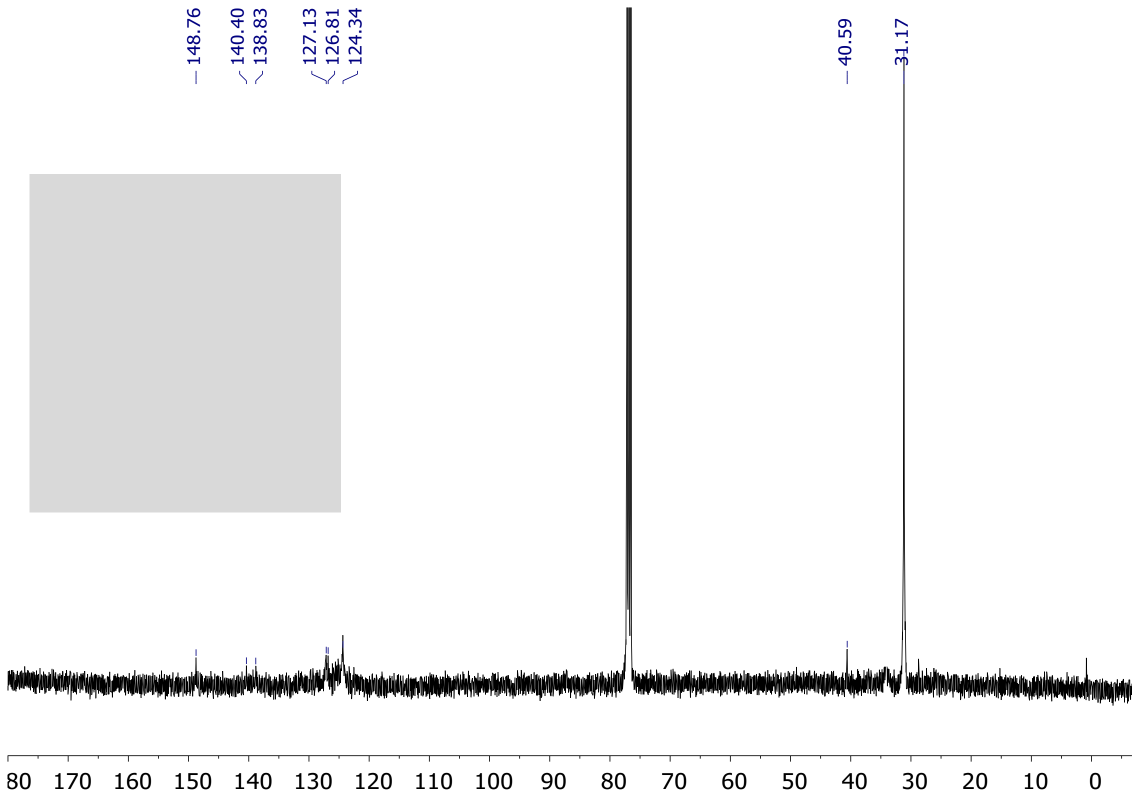


Figure S19. $^{13}C\{^{1}H\}$ NMR (400 MHz) spectrum of polymer **PPAi** in $CDCl_3$.

2.- SEC-MALS chromatograms.

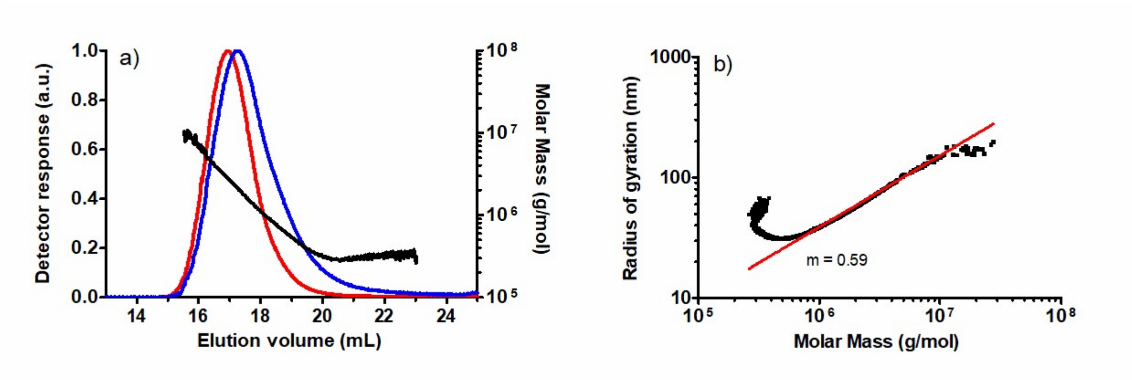


Figure S20. (a) SEC chromatograms: light scattering detector response (90 degrees) (red) and differential refractometer response (blue), MM (molar mass) vs. elution volume plot for a **PPAa** sample prepared from **PAa** (R = H). (b) Log-log plot of the radius of gyration (r_g) vs MM.

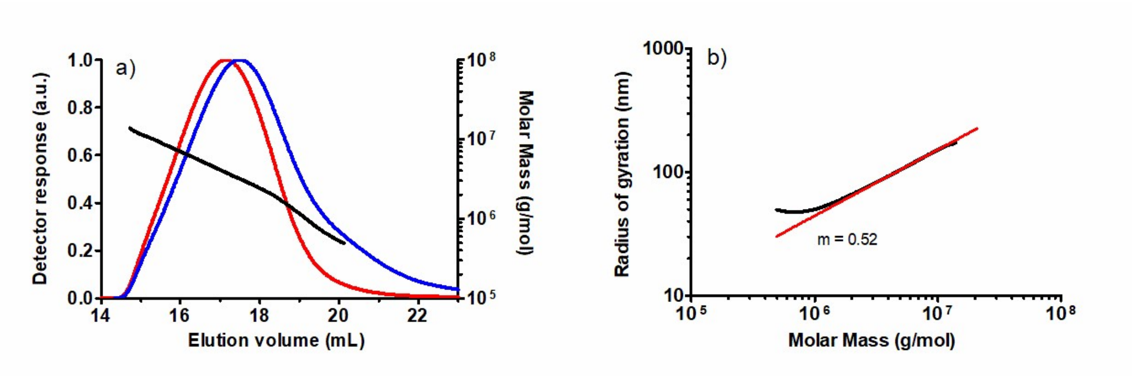


Figure S21. (a) SEC chromatograms: light scattering detector response (90 degrees) (red) and differential refractometer response (blue), MM (molar mass) vs. elution volume plot for a **PPAb** sample prepared from **PAb** (R = *p*-F). (b) Log-log plot of the radius of gyration (r_g) vs MM.

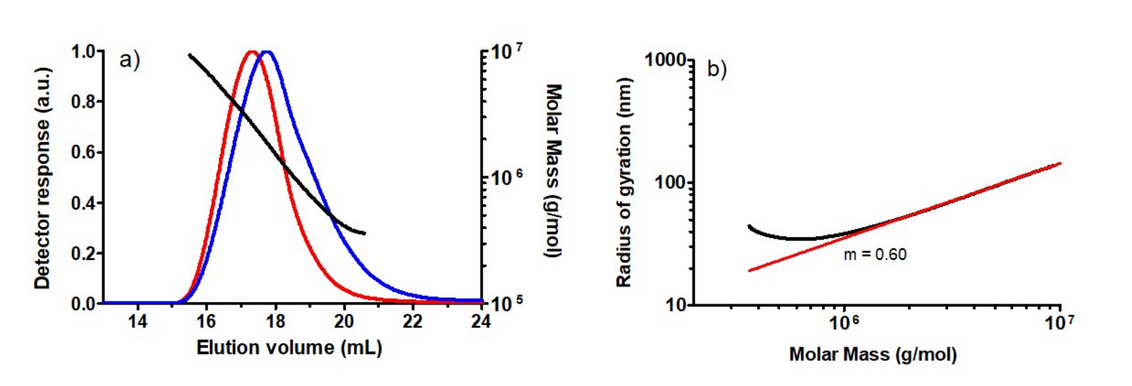


Figure S22. (a) SEC chromatograms: light scattering detector response (90 degrees) (red) and differential refractometer response (blue), MM (molar mass) vs. elution volume plot for a **PPAf** sample prepared from **PAf** (R = *m*-OMe). (b) Log-log plot of the radius of gyration (r_g) vs MM.

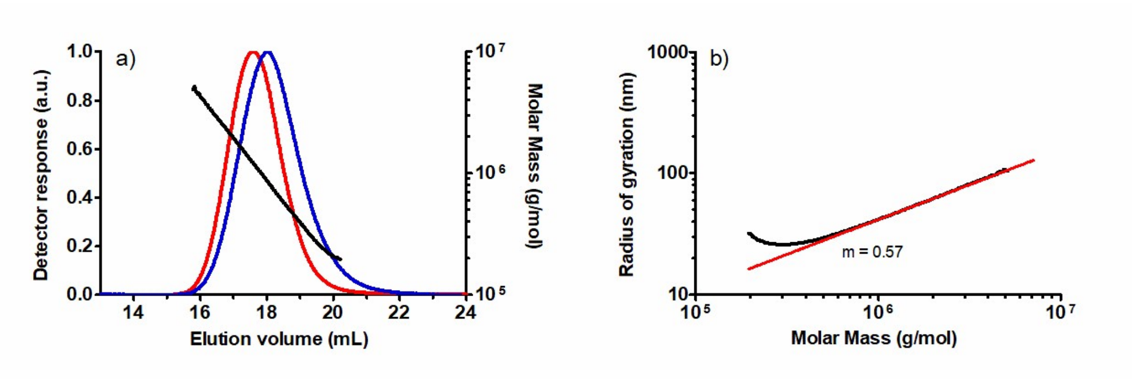


Figure S23. (a) SEC chromatograms: light scattering detector response (90 degrees) (red) and differential refractometer response (blue), MM (molar mass) vs. elution volume plot for a **PPAg** sample prepared from **PAg** (R = *p*-Bu). (b) Log-log plot of the radius of gyration (r_g) vs MM.

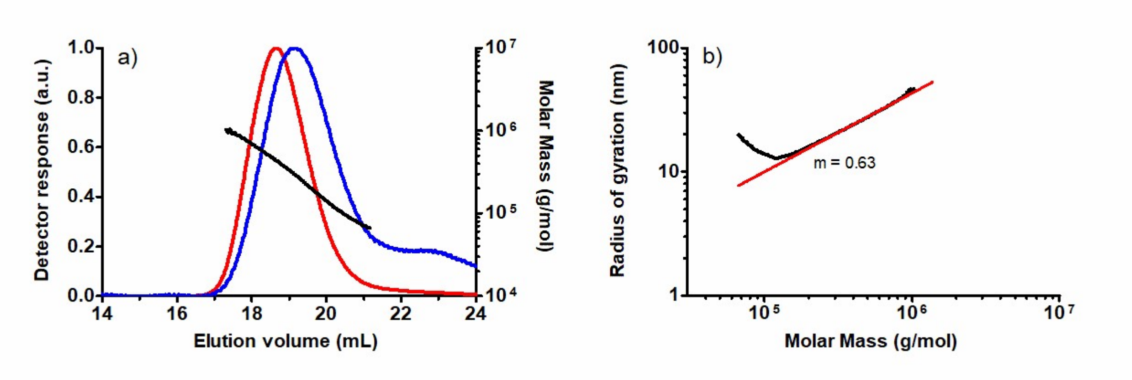


Figure S24. (a) SEC chromatograms: light scattering detector response (90 degrees) (red) and differential refractometer response (blue), MM (molar mass) vs. elution volume plot for a **PPAh** sample prepared from **PAh** (R = *p*-OBu). (b) Log-log plot of the radius of gyration (r_g) vs MM.

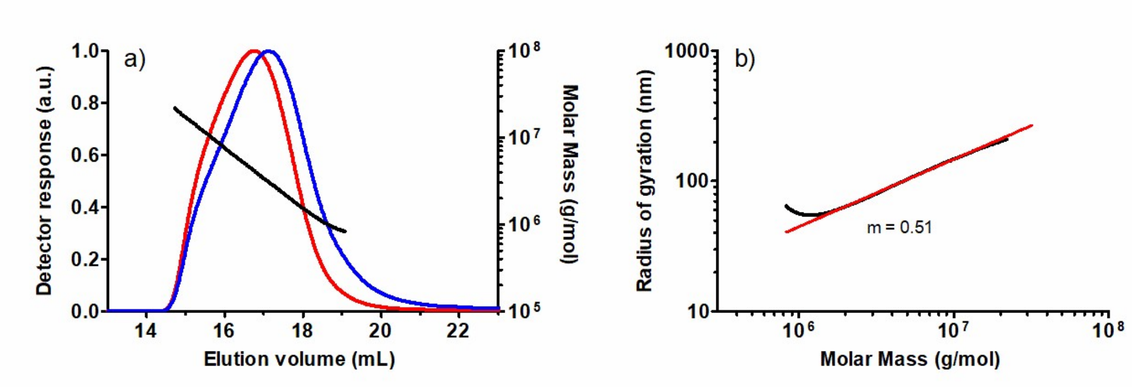


Figure S25. (a) SEC chromatograms: light scattering detector response (90 degrees) (red) and differential refractometer response (blue), MM (molar mass) vs. elution volume plot for a **PPAi** sample prepared from **PAi** (R = *p*-tBu). (b) Log-log plot of the radius of gyration (r_g) vs MM.

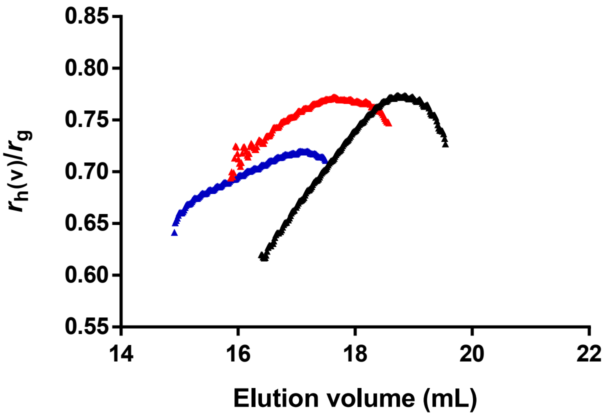
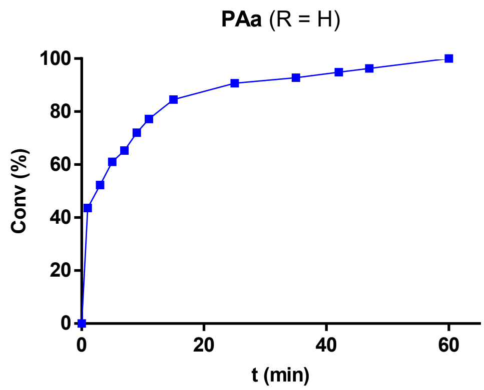


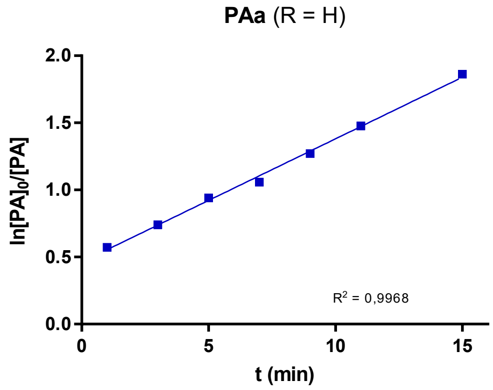
Figure S26. Compactness plot, $r_h(v)/r_g$ ratio vs elution volume, for polymers **PPAa** (R = H, black), **PPAg** (R = *p*-Bu, red) and **PPAi** (R = *p*-^{t}Bu, blue).

3.- Kinetic data.

PAa (R = H)

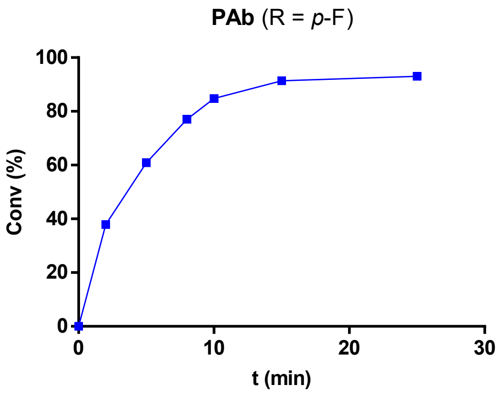
t (min)	Conv (%)		t (min)	[PA]	[PA]o/[PA]	Ln([PA]o/[PA])
0	0,0		0	0,250	1,000	0,000
1	43,6		1	0,141	1,774	0,573
3	52,3		3	0,119	2,096	0,740
5	61,0		5	0,098	2,563	0,941
7	65,3		7	0,087	2,882	1,058
9	72,0		9	0,070	3,565	1,271
11	77,2		11	0,057	4,380	1,477
15	84,5		15	0,039	6,439	1,862
25	90,7					
35	92,8					
42	94,9					
47	96,3					
60	100,0					

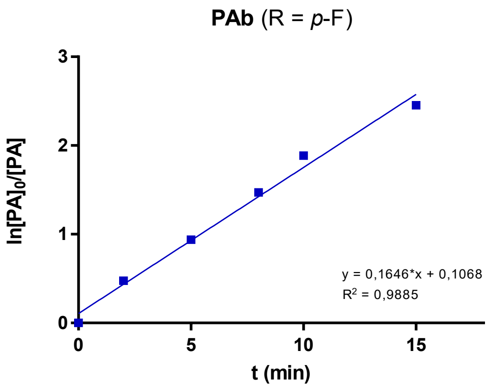




PAb (R = p-F)

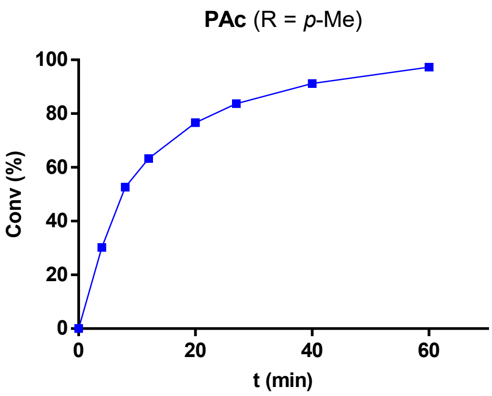
t (min)	Conv (%)		t (min)	[PA]	[PA]o/[PA]	Ln([PA]o/[PA])
0	0,0		0	0,250	1,000	0,000
3	37,9		3	0,155	1,611	0,477
5	60,9		5	0,098	2,557	0,939
8	77,0		8	0,057	4,349	1,470
10	84,8		10	0,038	6,593	1,886
15	91,4		15	0,021	11,647	2,455
25	93,0					

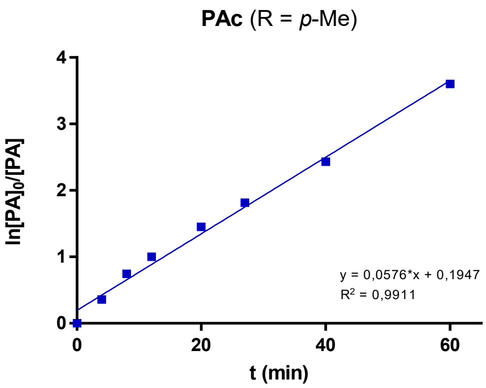




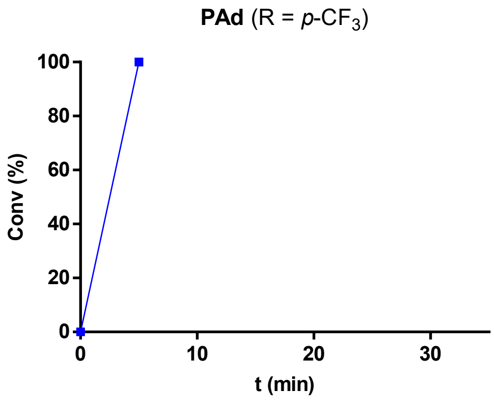
PAc (R = *p*-Me)

t (min)	Conv (%)		t (min)	[PA]	[PA]o/[PA]	Ln([PA]o/[PA])
0	0,0		0	0,250	1,000	0,000
4	33,2		4	0,174	1,433	0,360
8	55,6		8	0,119	2,109	0,746
12	66,3		12	0,092	2,724	1,002
20	76,6		20	0,058	4,276	1,453
27	83,7		27	0,041	6,145	1,816
40	91,2		40	0,022	11,389	2,433
60	97,3		60	0,007	36,610	3,600



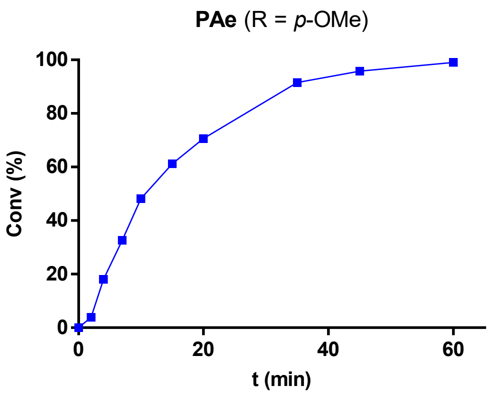


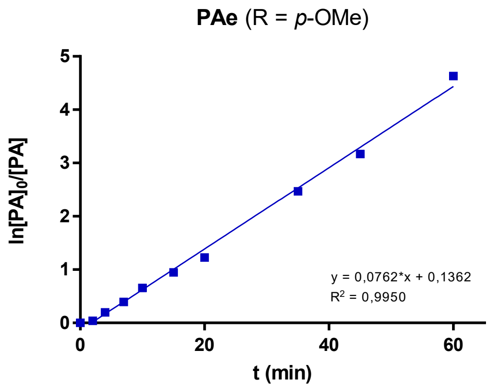
PAd (R = *p*-CF_3)



PAe (R = *p*-OMe)

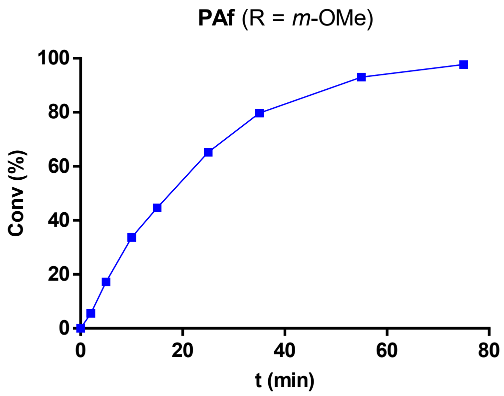
t (min)	Conv (%)		t (min)	[PA]	[PA]o/[PA]	Ln([PA]o/[PA])
0	0,0		0	0,250	1,000	0,000
2	3,9		2	0,245	1,020	0,040
4	18,0		4	0,240	1,042	0,198
7	32,6		7	0,233	1,075	0,395
10	48,2		10	0,225	1,111	0,658
15	61,2		15	0,213	1,176	0,947
20	70,6		20	0,200	1,250	1,226
35	91,5		35	0,163	1,538	2,470
45	95,8		45	0,138	1,818	3,167
60	99,0		60	0,100	2,500	4,629

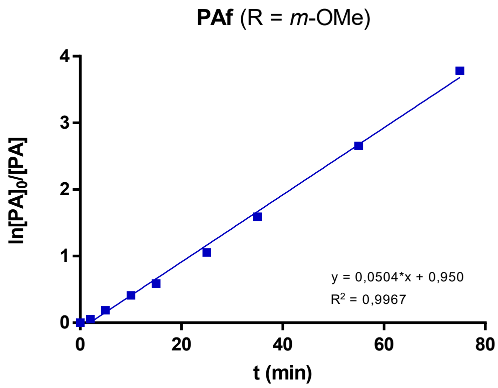




PAf (R = *m*-OMe)

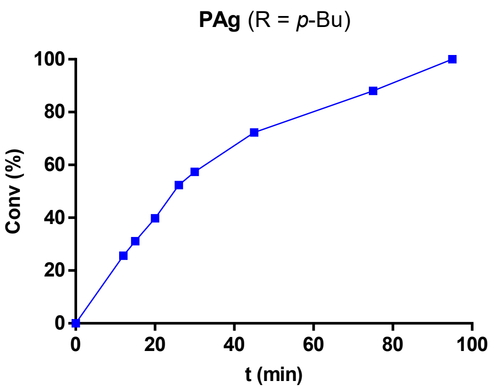
t (min)	Conv (%)		t (min)	[PA]	[PA]o/[PA]	Ln([PA]o/[PA])
0	0,0		0	0,250	1,000	0,000
2	5,5		2	0,236	1,058	0,056
5	17,2		5	0,207	1,208	0,189
10	33,7		10	0,166	1,508	0,411
15	44,6		15	0,139	1,804	0,590
25	65,2		25	0,087	2,871	1,055
35	79,7		35	0,051	4,915	1,592
55	93,0		55	0,018	14,228	2,655
75	97,7		75	0,006	43,842	3,781

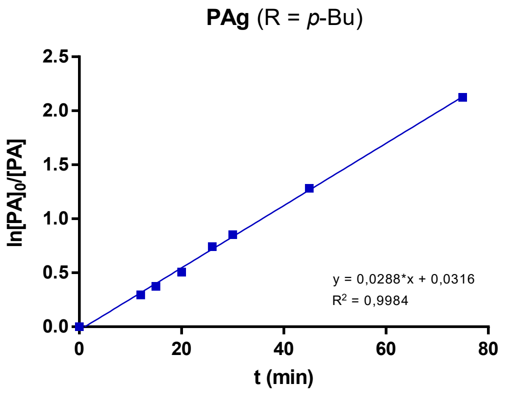




PAg (R = *p*-Bu)

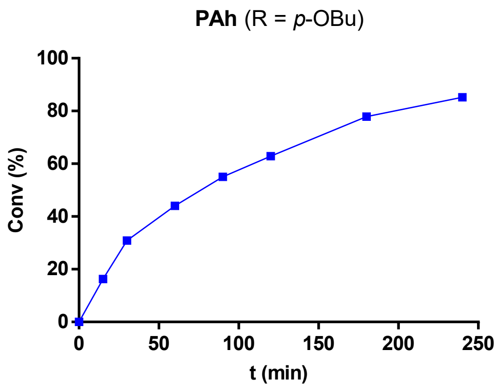
t (min)	Conv (%)		t (min)	[PA]	[PA]o/[PA]	Ln([PA]o/[PA])
0	0,0		0	0,250	1,000	0,000
12	25,6		12	0,186	1,343	0,295
15	31,1		15	0,172	1,452	0,373
20	39,8		20	0,150	1,661	0,508
26	52,4		26	0,119	2,102	0,743
30	57,4		30	0,107	2,347	0,853
45	72,3		45	0,069	3,605	1,282
75	88,0		75	0,030	8,357	2,123
95	100,0					

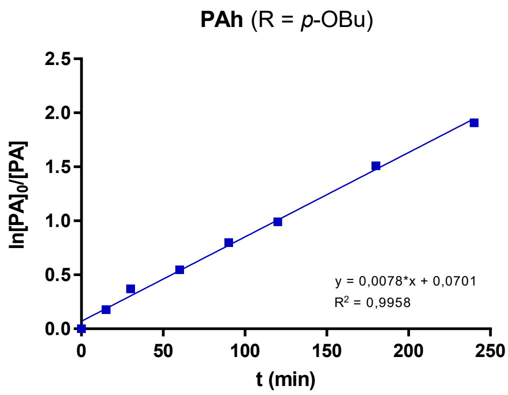




PAh (R = *p*-OBu)

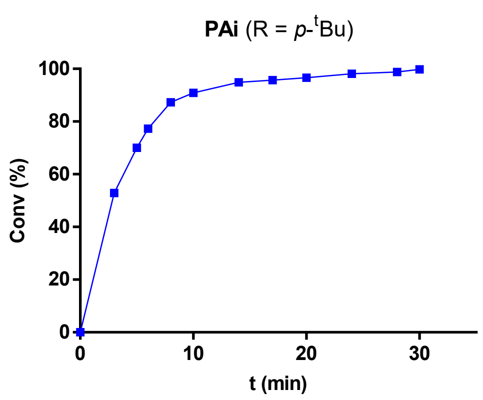
t (min)	Conv (%)		t (min)	[PA]	[PA]o/[PA]	Ln([PA]o/[PA])
0	0,0		0	0,250	1,000	0,000
15	16,3		15	0,209	1,195	0,178
30	30,9		30	0,173	1,447	0,369
60	44,0		60	0,140	1,787	0,581
90	55,0		90	0,112	2,224	0,799
120	62,9		120	0,093	2,694	0,991
180	77,9		180	0,055	4,523	1,509
240	85,2		240	0,037	6,736	1,908

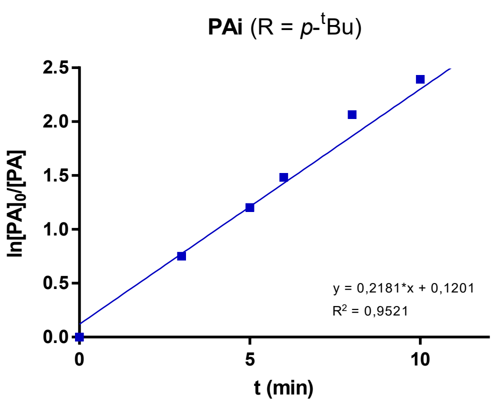




PAi (R = *p*-^{t}Bu)

t (min)	Conv (%)		t (min)	[PA]	[PA]o/[PA]	Ln([PA]o/[PA])
0	0,0		0	0,250	1,000	0,000
3	52,9		3	0,118	2,121	0,752
5	70,0		5	0,075	3,333	1,204
6	77,3		6	0,057	4,400	1,482
8	87,3		8	0,032	7,888	2,065
10	90,9		10	0,023	10,937	2,392
14	94,9		14	0,013	19,663	2,979
17	95,7					
20	96,6					
24	98,1					
28	98,8					
30	99,8					





4.- Selected DSC thermograms.

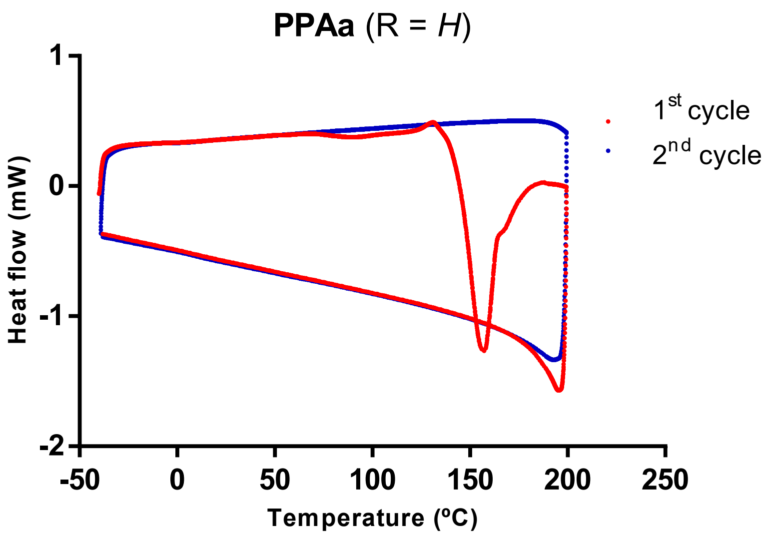


Figure S27. DSC thermogram of polymer **PPAa**.

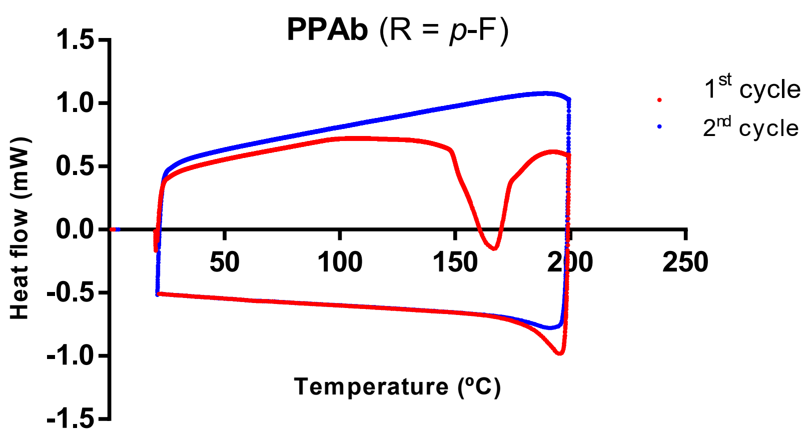


Figure S28. DSC thermogram of polymer **PPAb**.

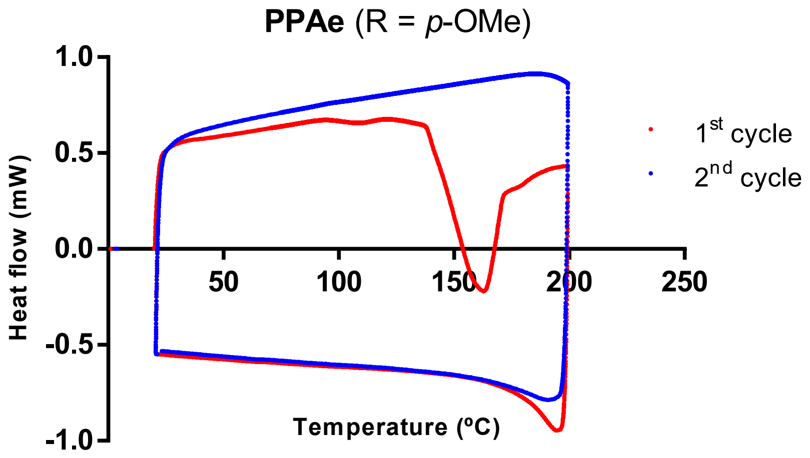


Figure S29. DSC thermogram of polymer **PPAe**.

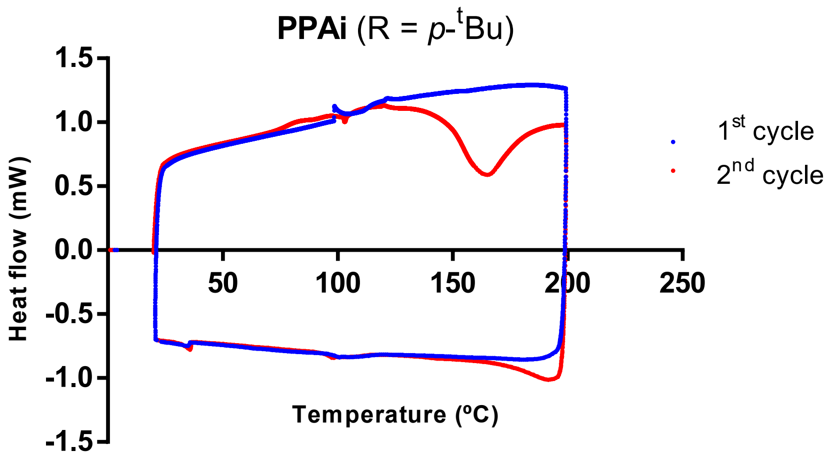


Figure S30. DSC thermogram of polymer **PPAi**.

5.- Thermal degradation of polymer PPAe (R = *p*-OMe).

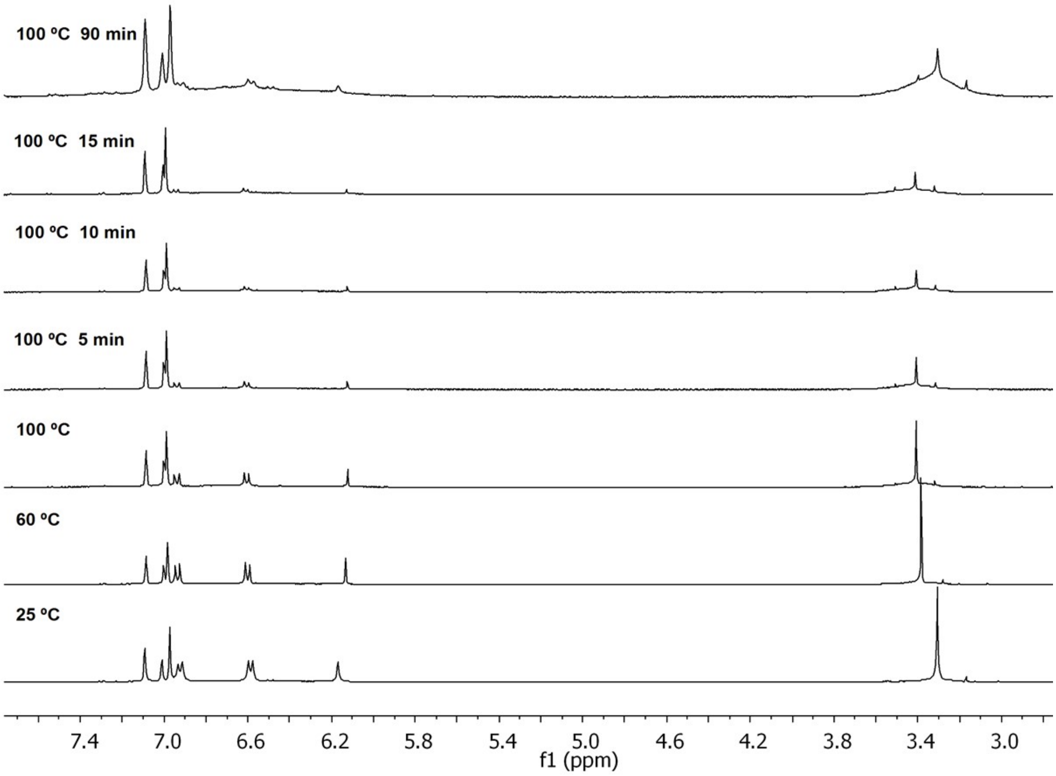


Figure S31. ^{1}H NMR monitoring of a solution of **PPAe** (R = *p*-OMe) in toluene-d_8 at different temperatures.

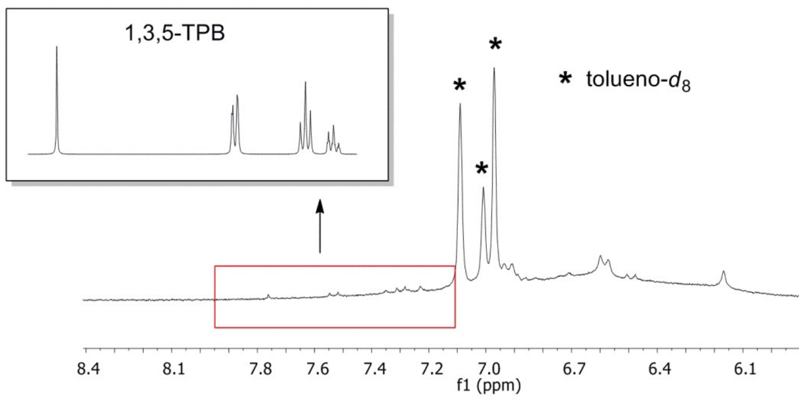


Figure 32. Aromatic region of the ^{1}H NMR spectrum of a solution of **PPAe** (R = *p*-OMe) in toluene-d_8 after heating at 100 °C for 90 min showing the formation of 1,3,5-triphenylbenzene (1,3,5-TPB).