Supporting Information

Electronic Supplementary Information (ESI)

Sulfur copolymer with a pyrrole compound for the crosslinking of unsaturated elastomers

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Characterization of *1,6-bis(2,5-dimethyl-1H-pyrrol-1-yl)hexane* (HMDP)

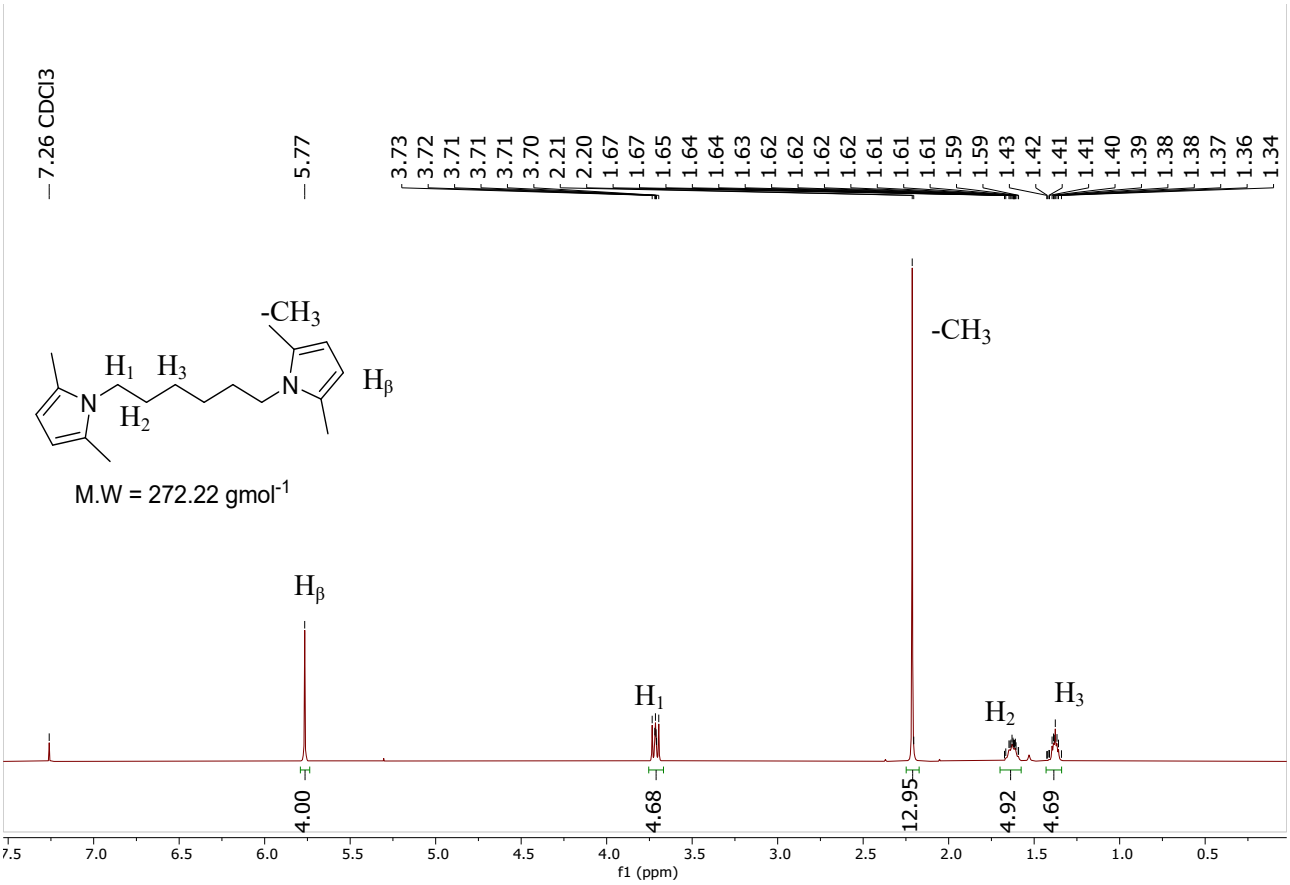

Figure S.1: ^{1}H-NMR spectrum (400 MHz, *$CDCl_3$*) of 1,6-bis(2,5-dimethyl-1*H*-pyrrol-1-yl)hexane (HMDP)

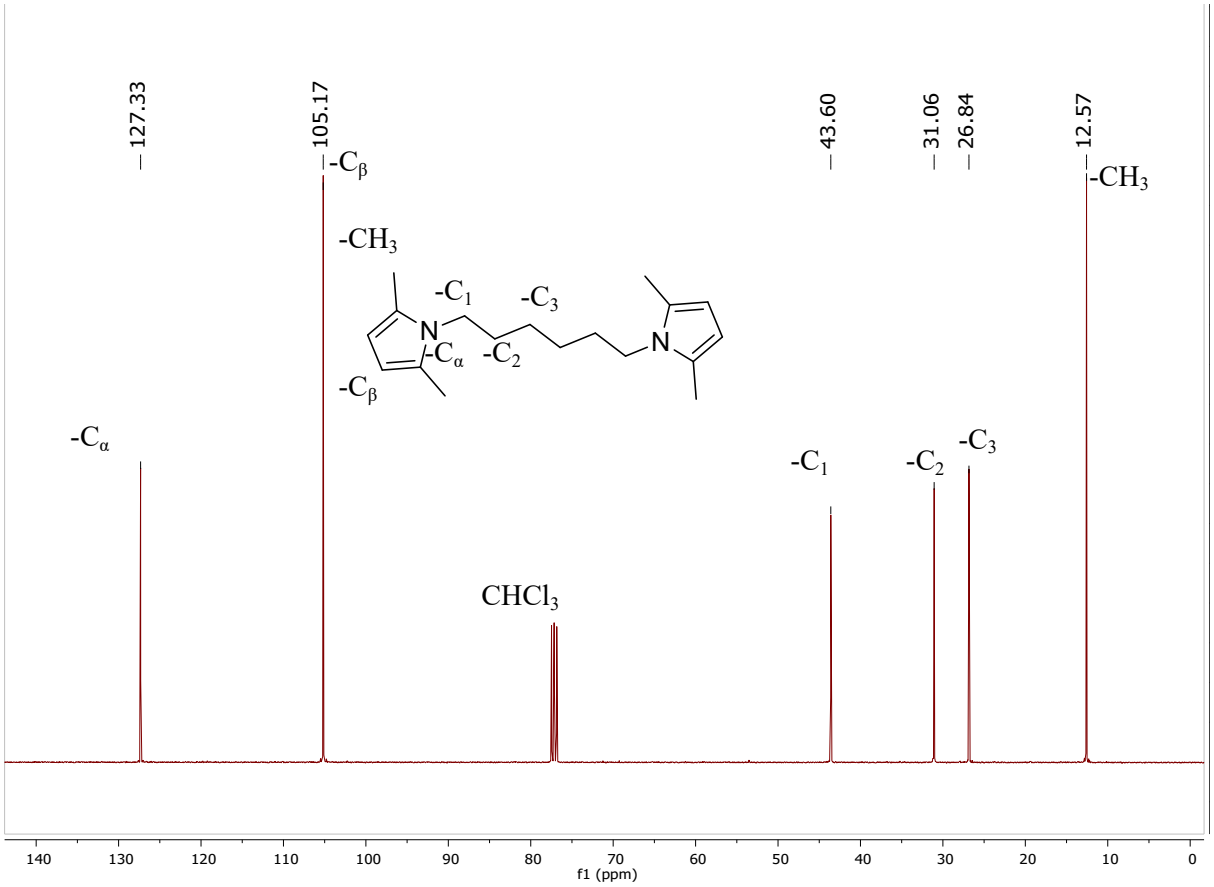

Figure S.2: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 1,6-bis(2,5-dimethyl-1*H*-pyrrol-1-yl)hexane (HMDP)

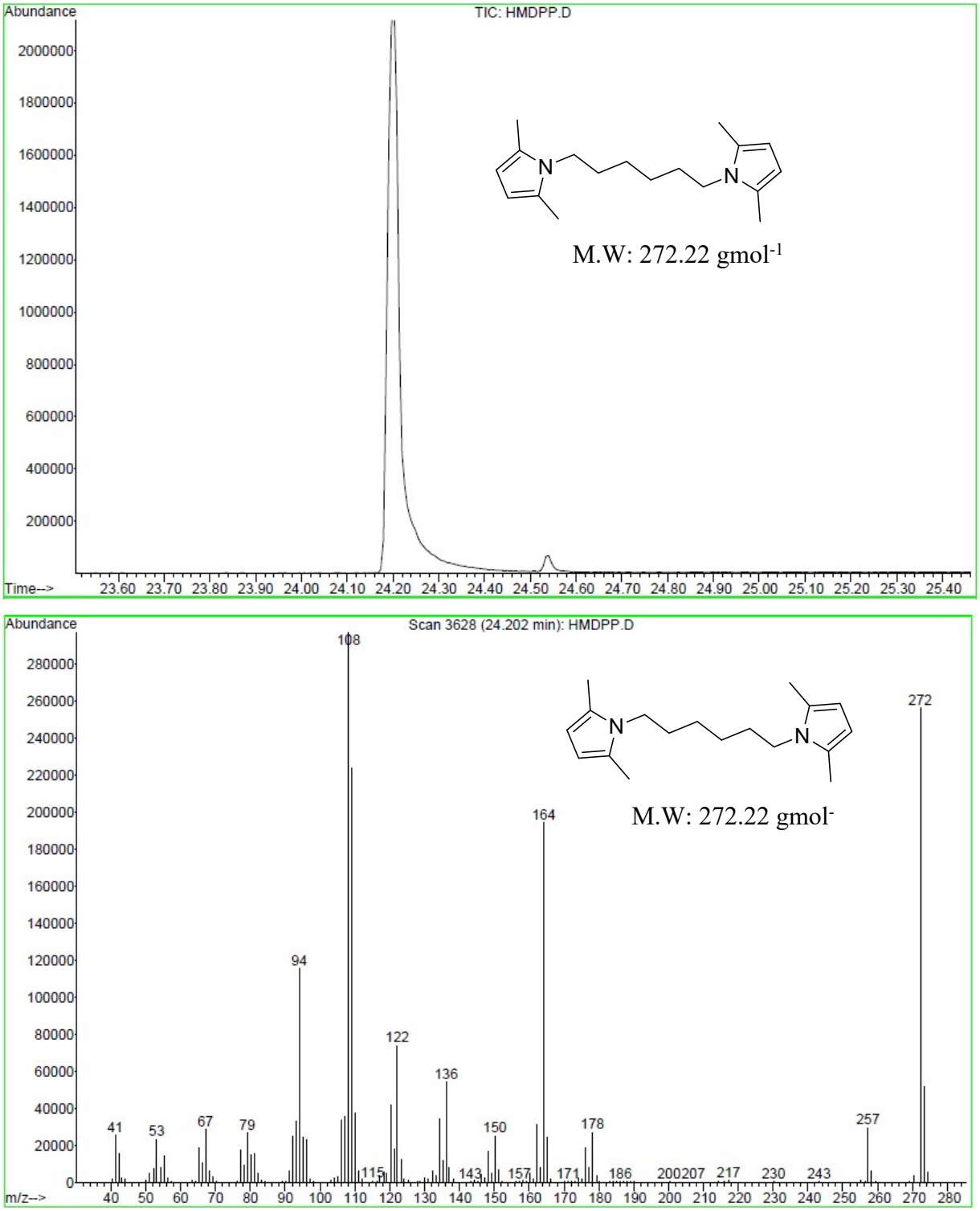

Figure S.3: GC-Mass spectrum of 1,6-bis(2,5-dimethyl-1*H*-pyrrol-1-yl)hexane (HMDP)

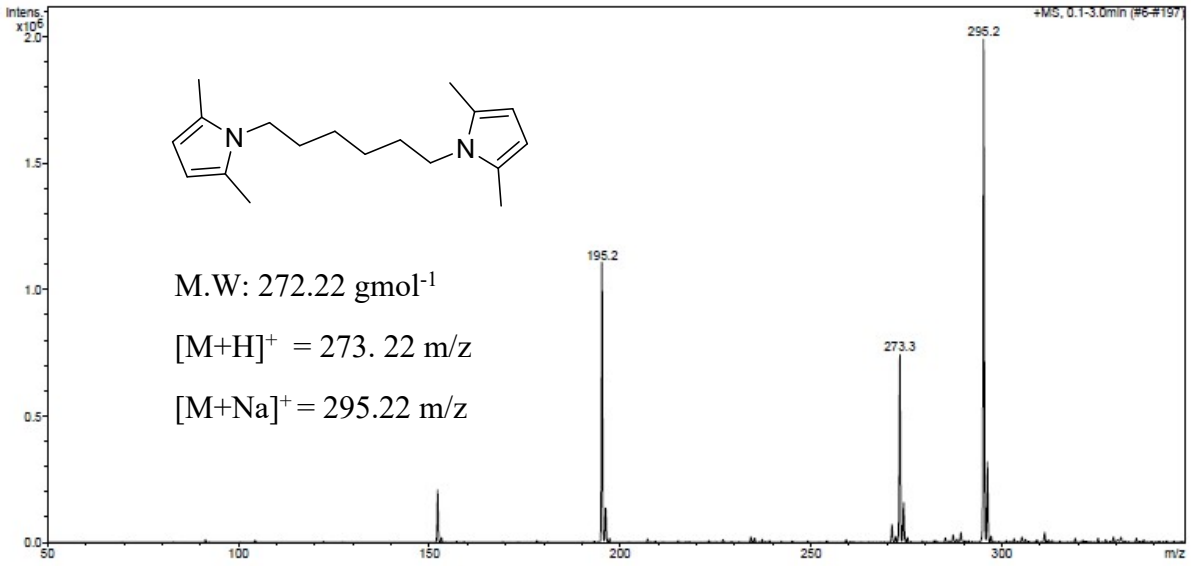

Figure S.4: ESI -Mass spectrum of 1,6-bis(2,5-dimethyl-1*H*-pyrrol-1-yl)hexane (HMDP)

Characterization of *1,2-bis(2,5-dimethyl-1H-pyrrol-1-yl)ethane* (EDP)

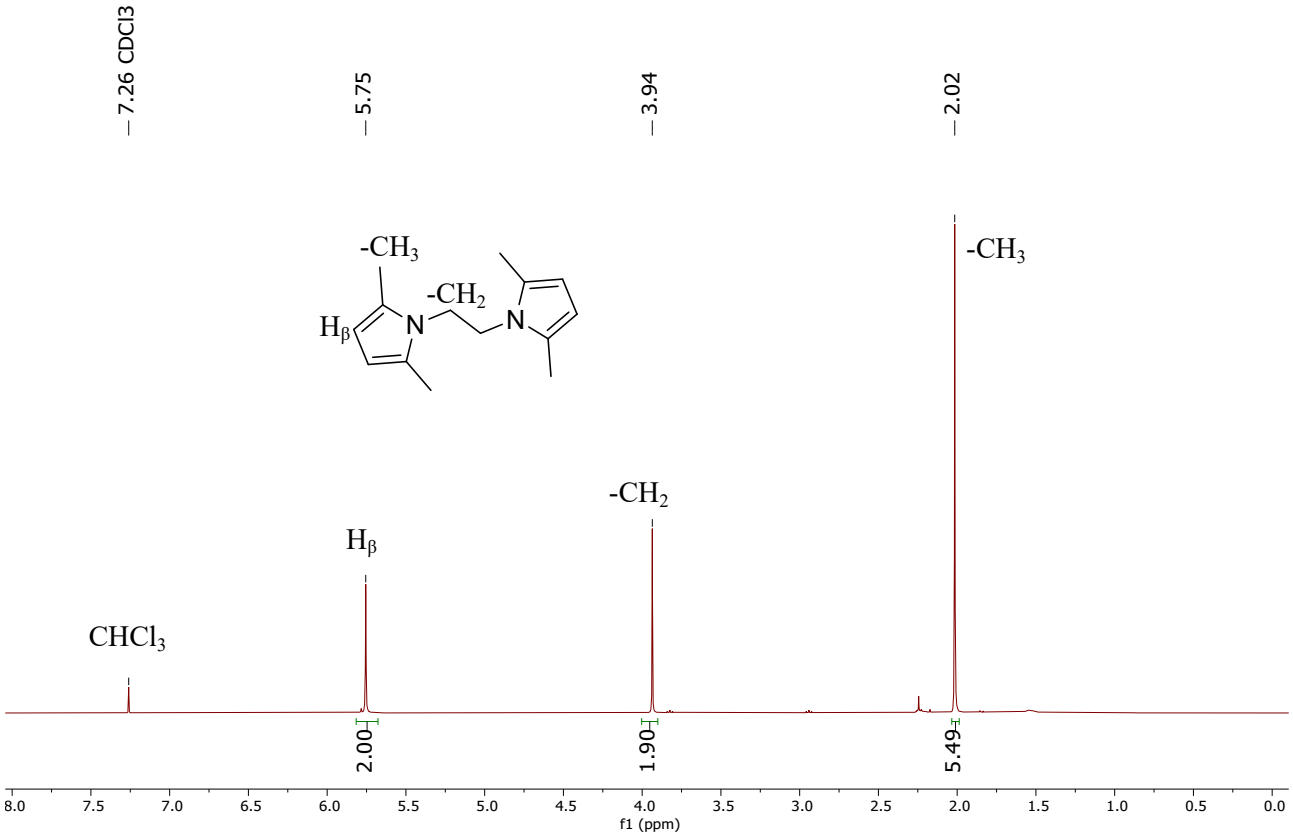

Figure S.5: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 1,2-bis(2,5-dimethyl-1*H*-pyrrol-1-yl)ethane (EDP)

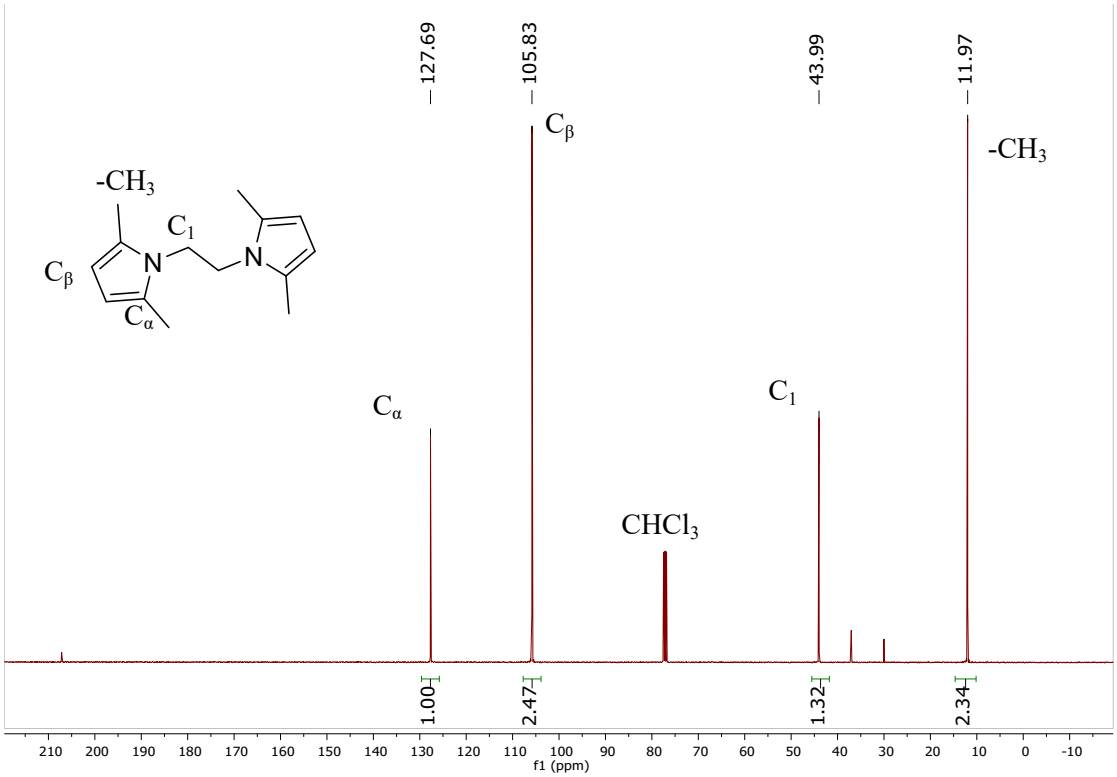

Figure S.6: ^{13}C-NMR spectrum of EDP (100 MHz, $CDCl_3$) of *1,2-bis(2,5-dimethyl-1H-pyrrol-1-yl)ethane* (EDP)

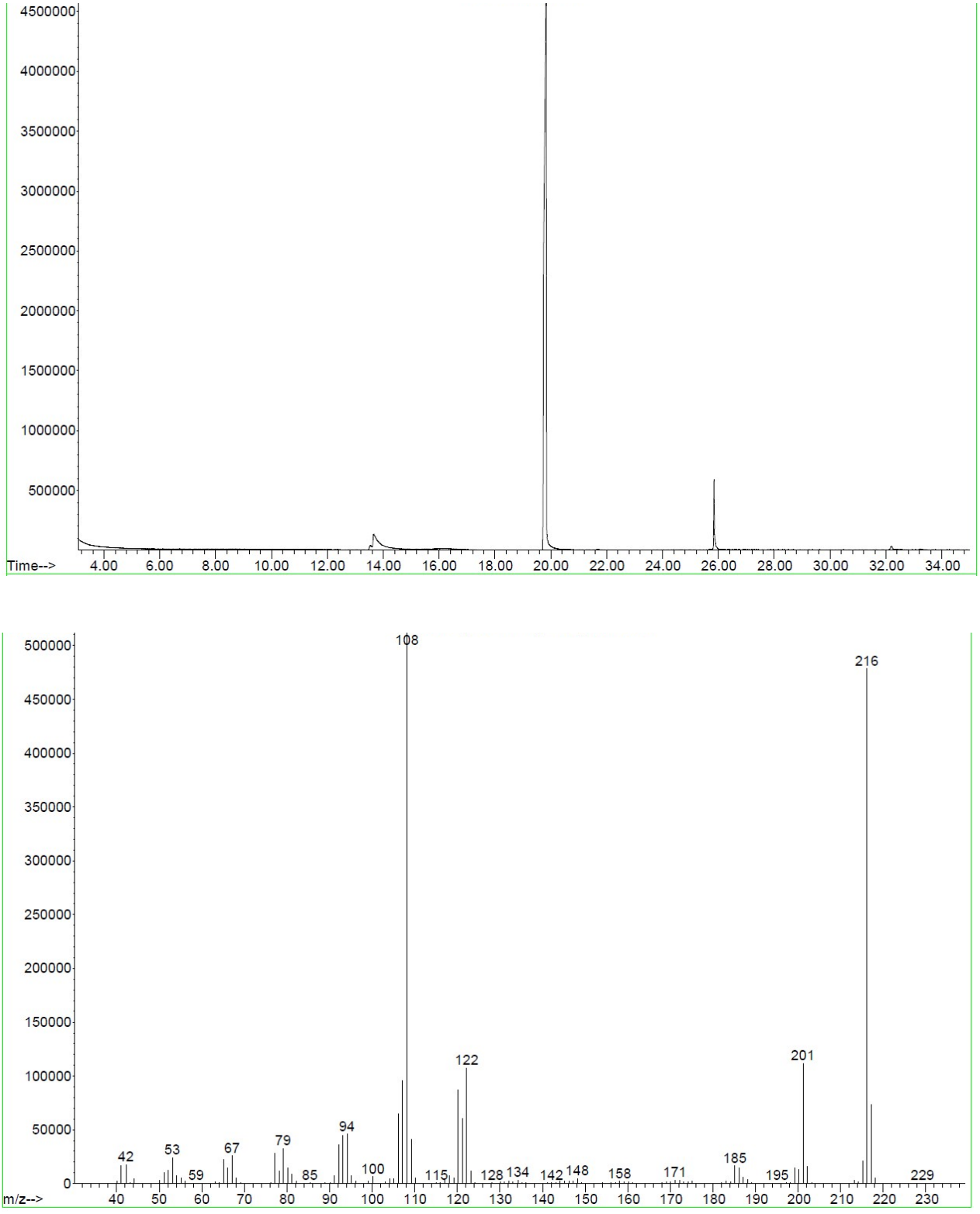

Figure S.7: GC-Mass spectrum of 1,2-bis(2,5-dimethyl-1*H*-pyrrol-1-yl)ethane

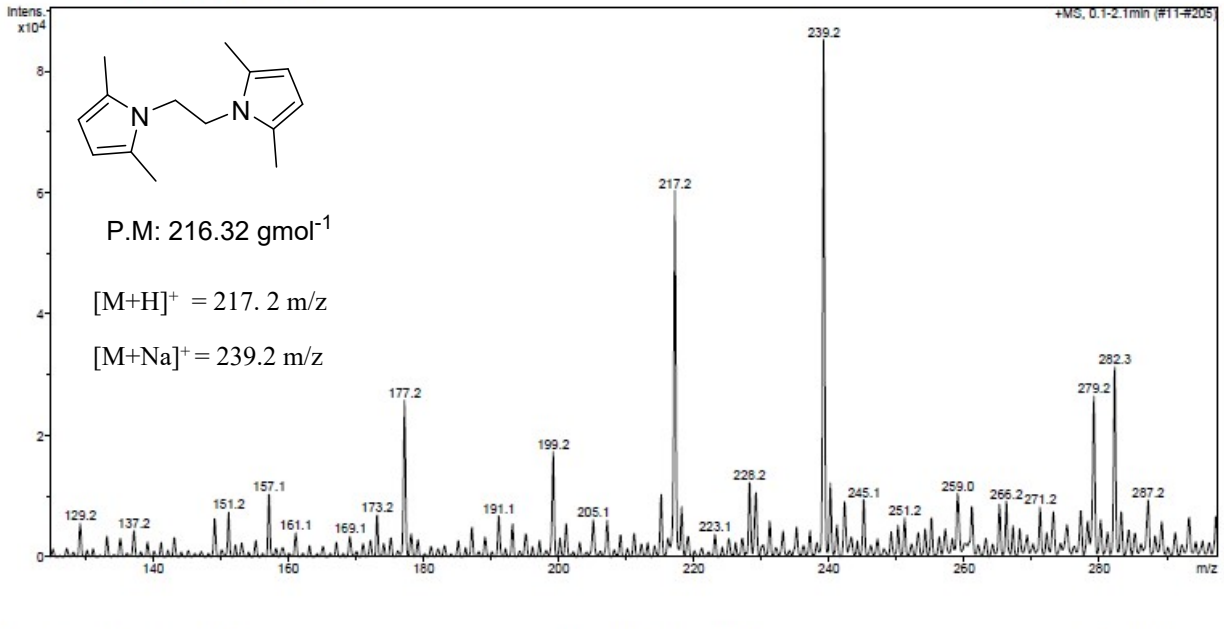

Figure S.8: ESI -Mass spectrum of 1,6-bis(2,5-dimethyl-1*H*-pyrrol-1-yl)hexane (EDP)

Characterization of poly(S-co-HMDP) from Entry 7. Weight amount of sulfur: 90%

^{1}H-NMR spectrum of poly(S-co-HMDP) from Entry 7

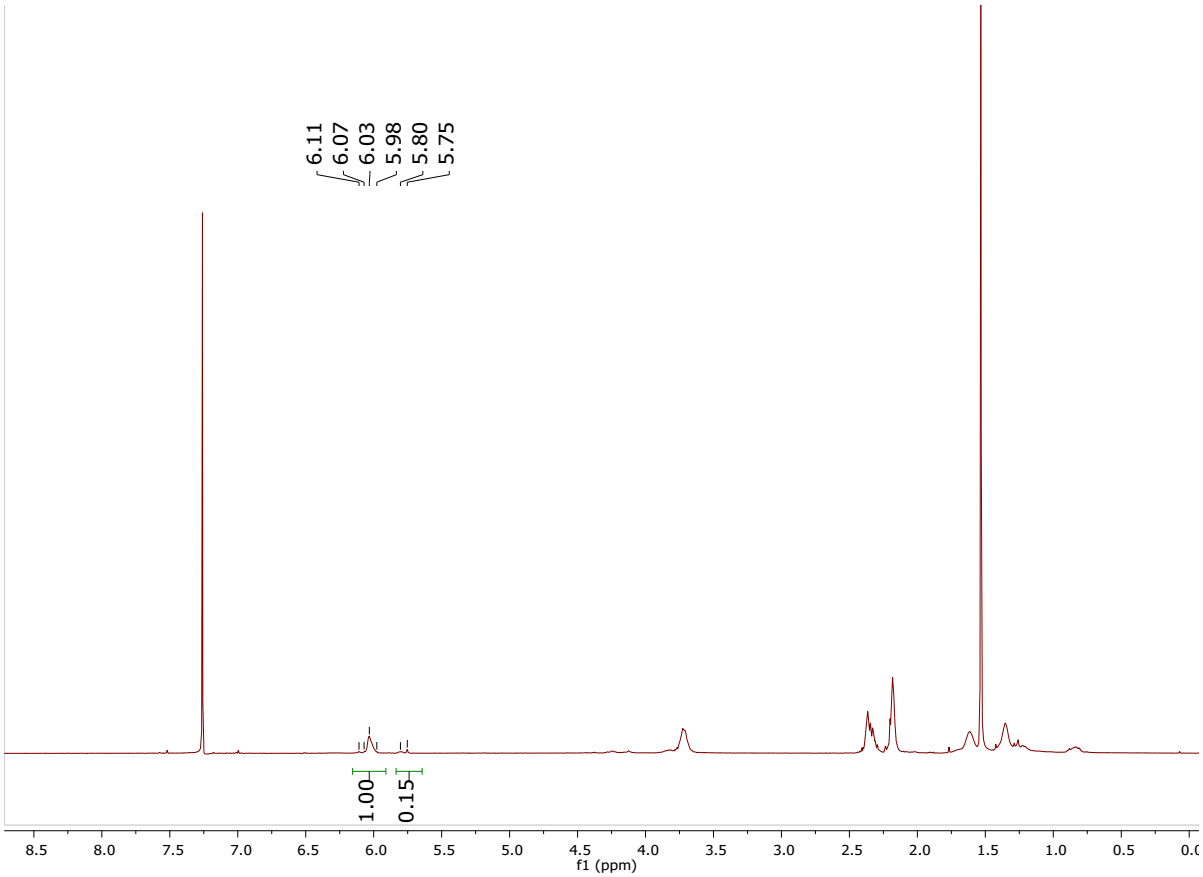

Figure S.9: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of Poly(S-co-HMDP); weight amount of sulfur 90%

^{13}C-NMR spectrum of poly(S-co-HMDP) from Entry 7

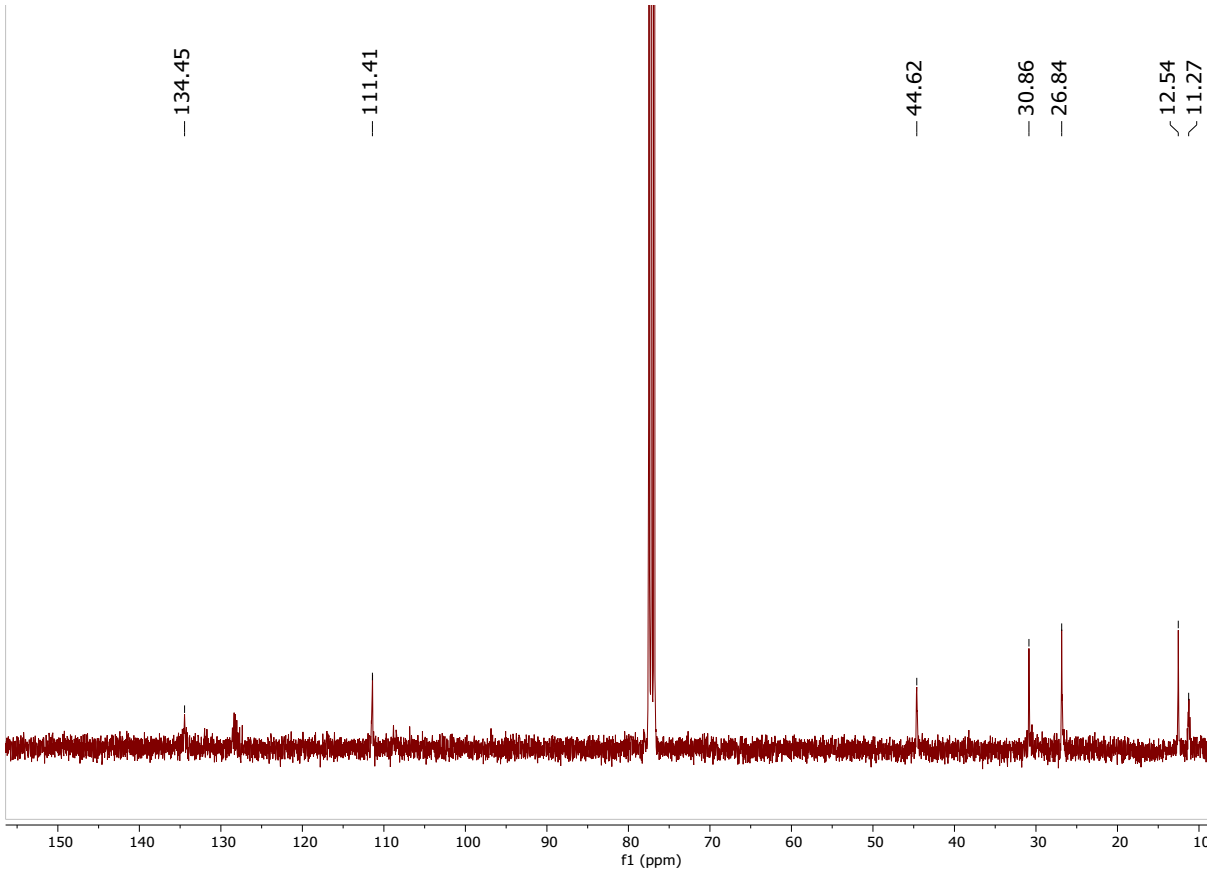

Figure S.10: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Poly(S-co-HMDP), weight amount of sulfur 90%

FT-IR spectra of HMDP and poly(S-co-HMDP) from Entry 7

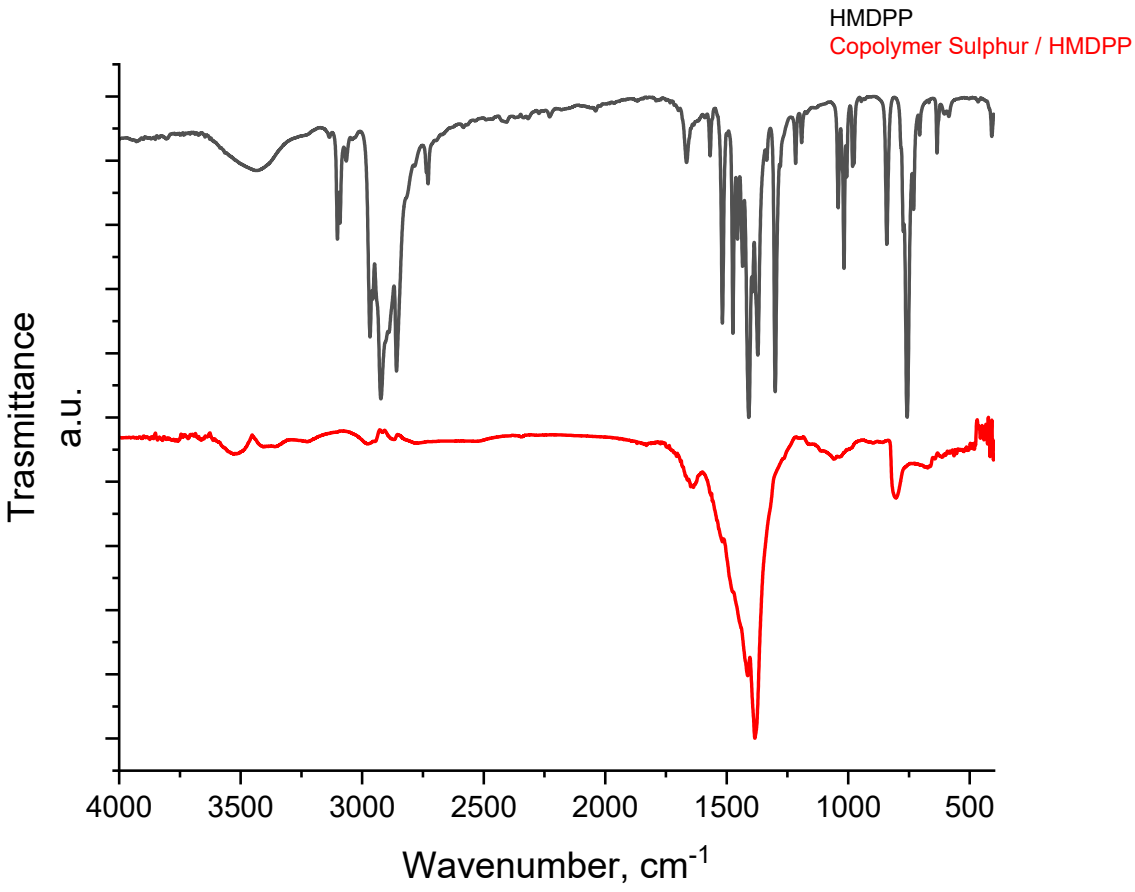

Figure S.11: FT-IR spectrum of Poly(S-co-HMDP); weight amount of sulfur 90%

DSC thermal analysis of sulfur, HMDP and poly(S-co-HMDP) from Entry 7

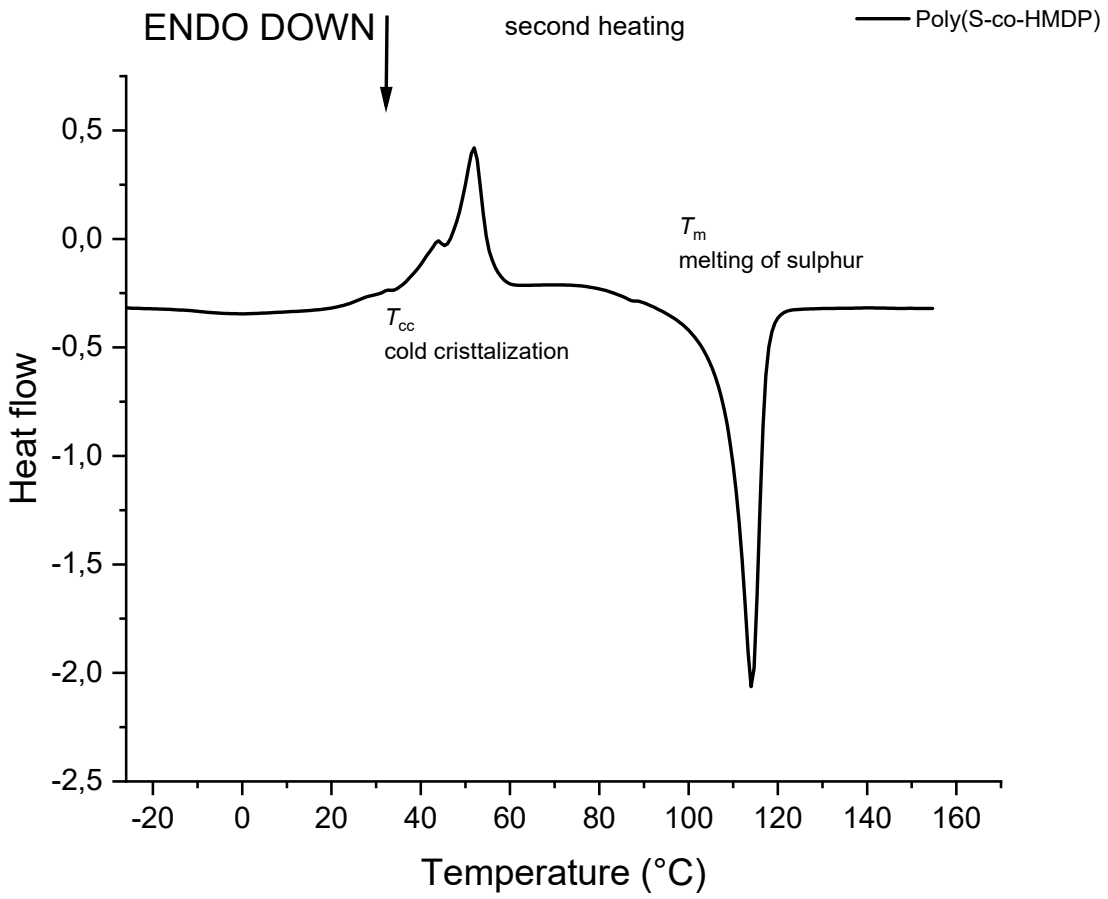

Figure S.12: DSC thermogram of Poly(S-co-HMDP); weight amount of sulfur of 90%

Cold crystallization phenomenon was observed during the second heating. Possible formation of polymeric sulfur.

GPC analysis

The low amount of HMDP in this copolymer did not allow the complete solubilization of copolymer in dichloromethane. It was not possible to perform the GPC analysis

Characterization of poly(S-co-HMDP) from Entry 1

^{1}H-NMR spectrum of poly(S-co-HMDP) from Entry 1

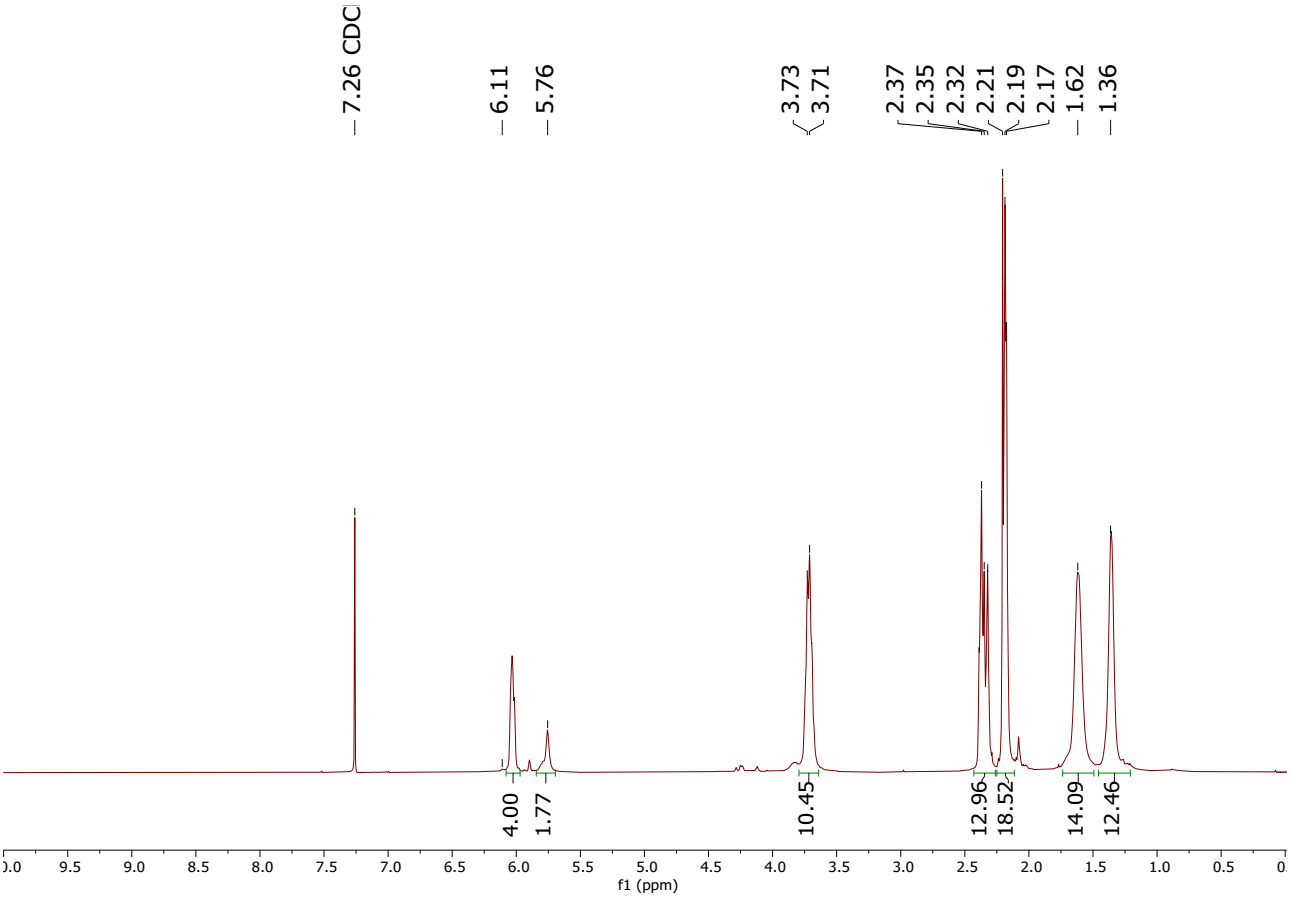

Figure S.13: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of poly(S-co-HMDP) with sulfur weight % of 41%

^{13}C-NMR spectrum of poly(S-co-HMDP) from Entry 1

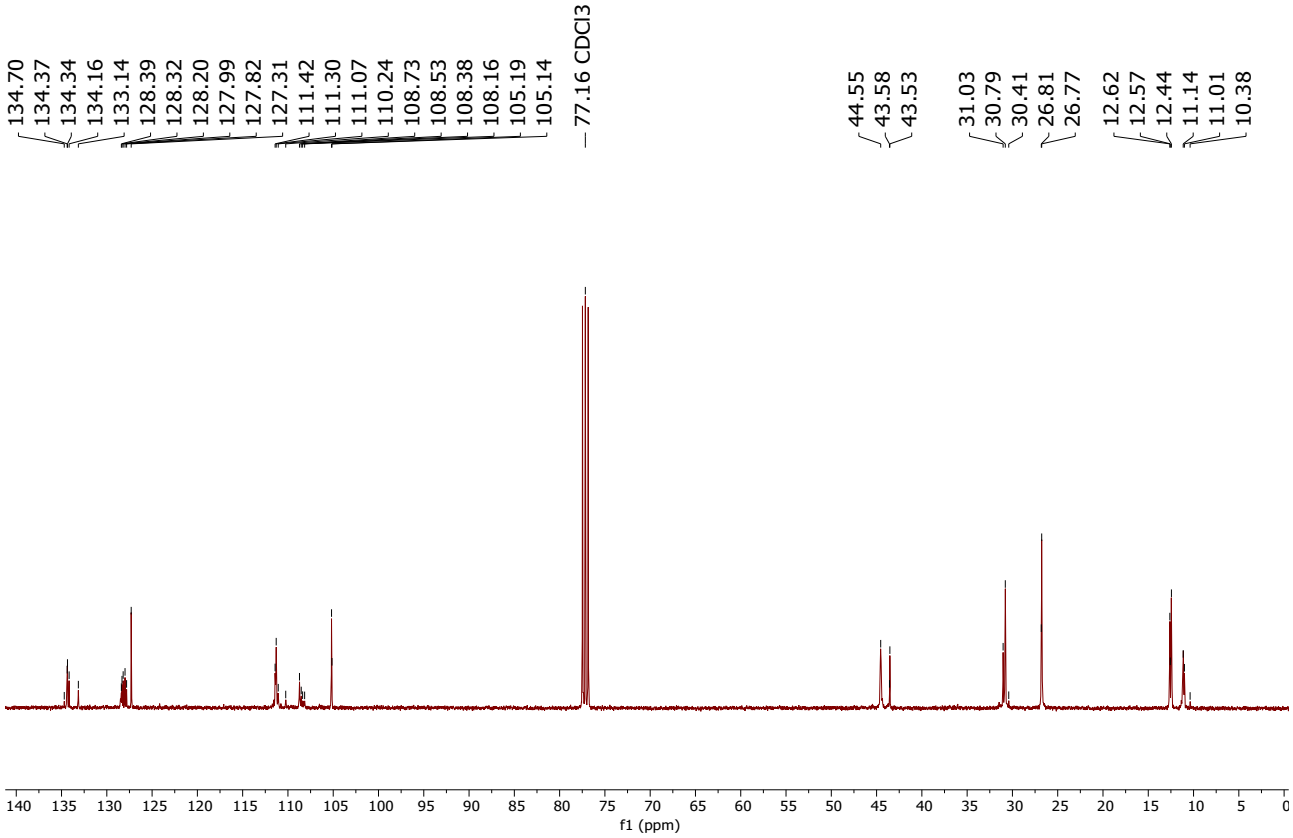

Figure S.14: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of poly(S-co-HMDP): molar ratio Sulfur/HMDP = 6

Characterization of poly(S-co-HMDP) from Entry 2

^{1}H-NMR spectrum of poly(S-co-HMDP) from Entry 2

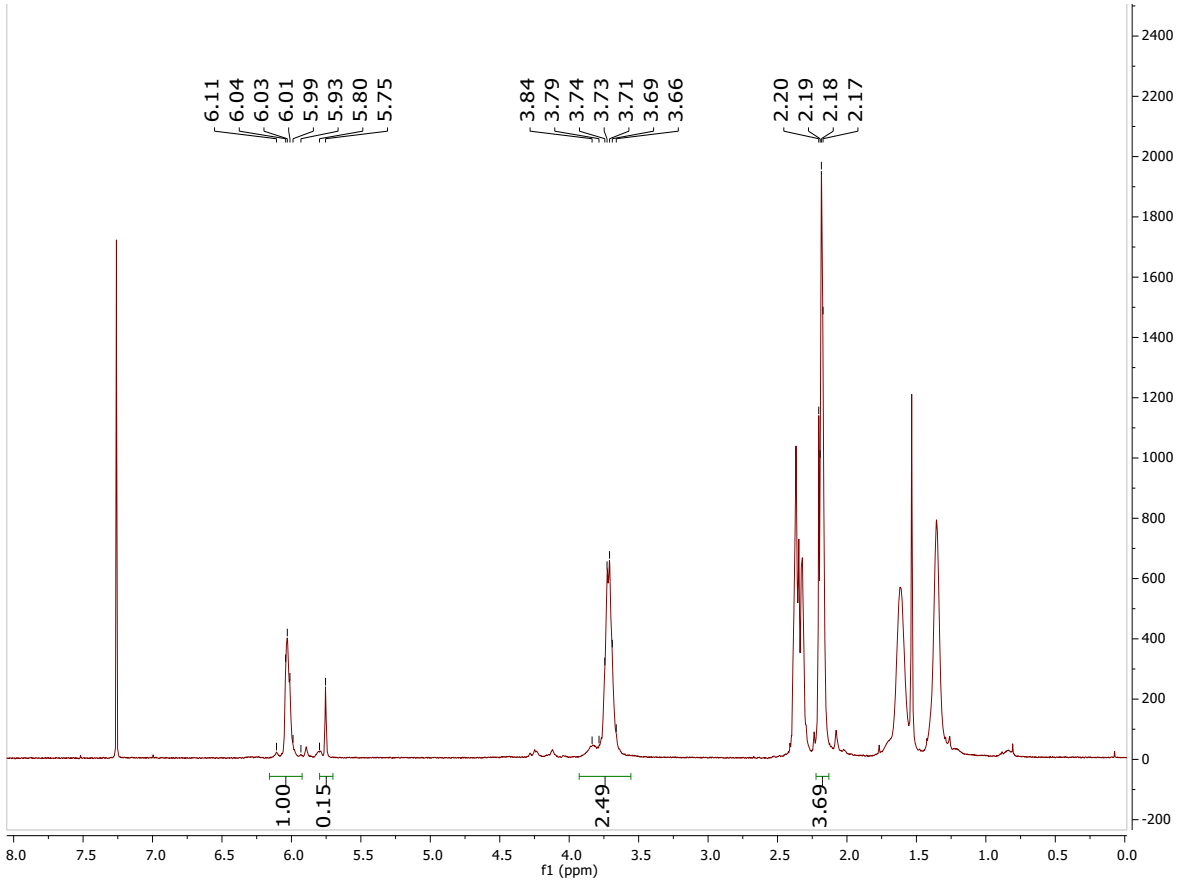

Figure S.15: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of poly(S-co-HMDP), weight amount of sulfur 50%

^{13}C-NMR spectrum of poly(S-co-HMDP) from Entry 2

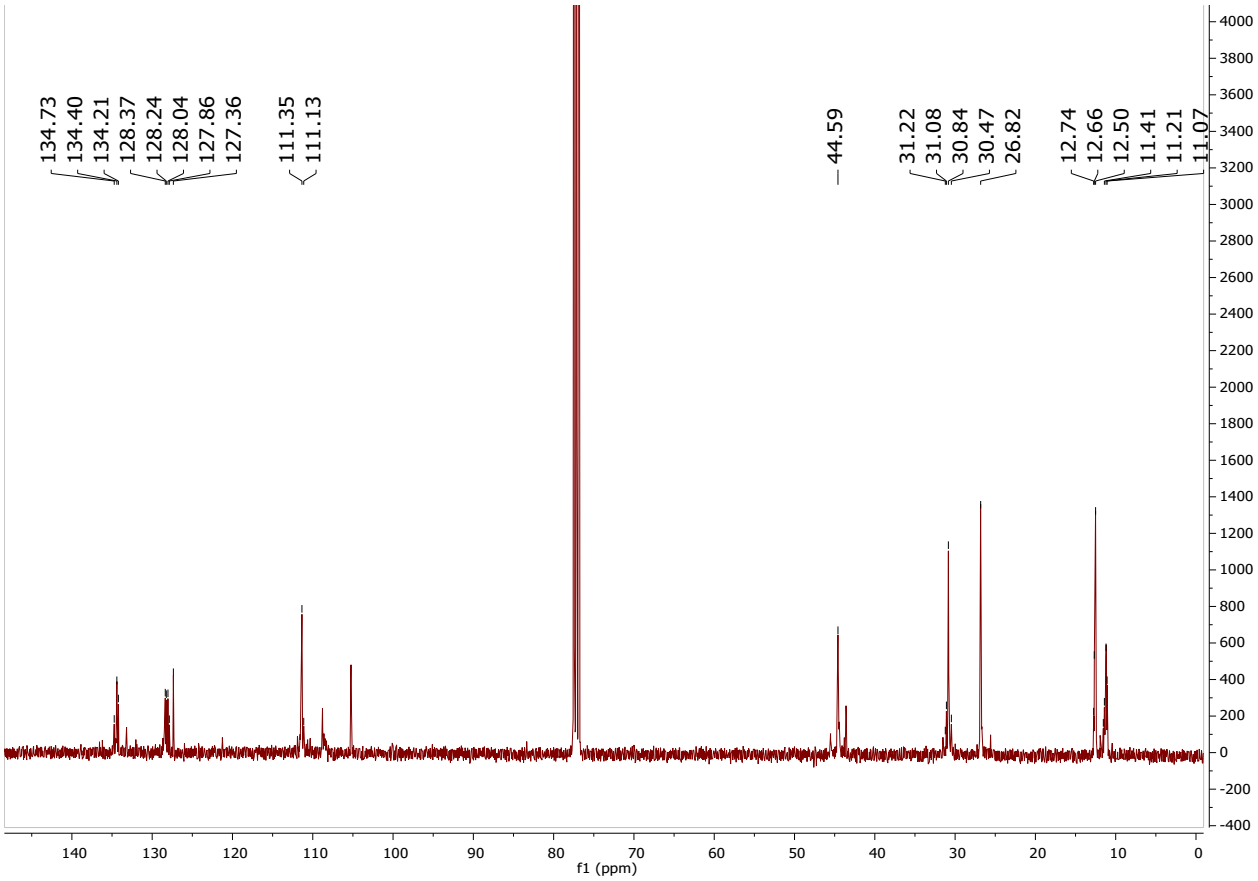

Figure S.16: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Poly(S-co-HMDP) weight amount of sulfur 50%

Characterization of poly(S-co-HMDP) from Entry 3

^{1}H-NMR spectrum of poly(S-co-HMDP) from Entry 3

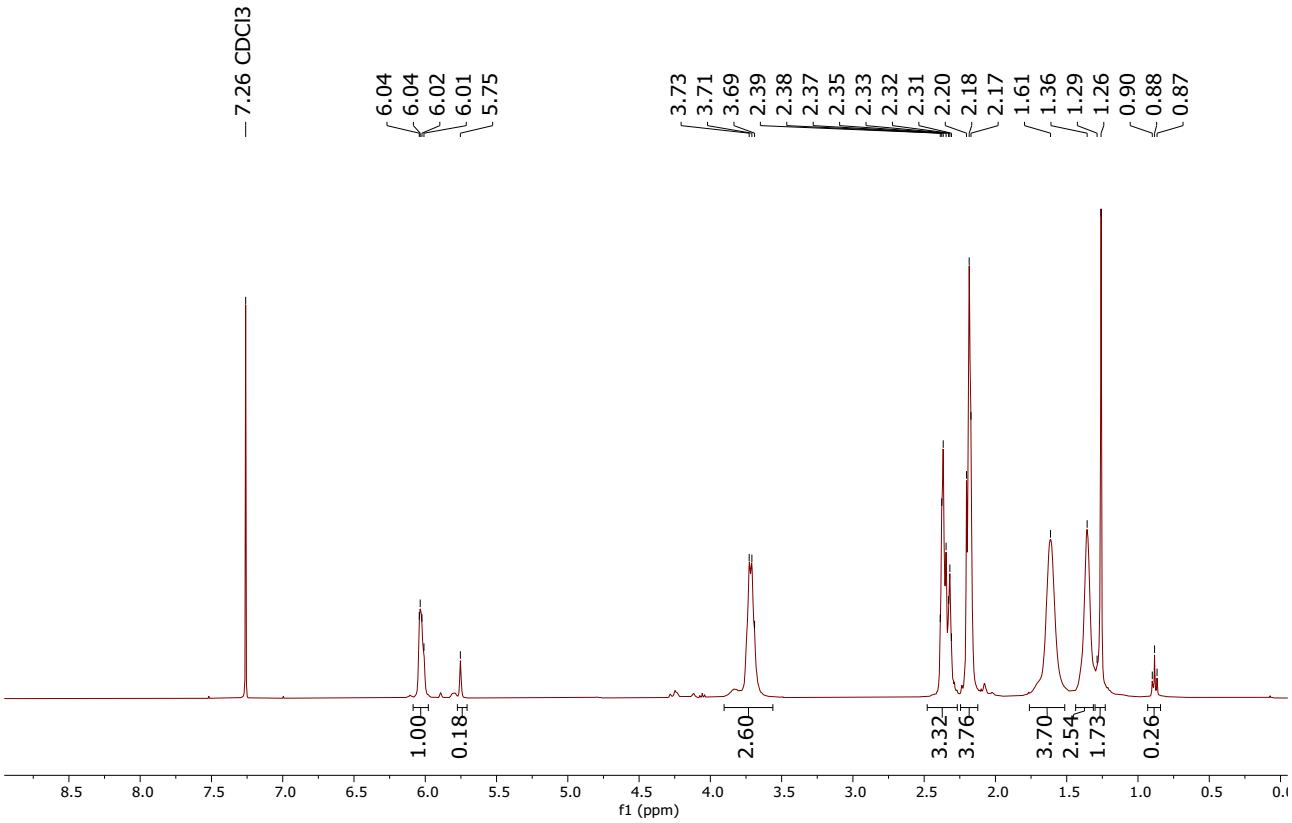

Figure S.17: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of Poly(S-co-HMDP) weight amount of sulfur 52%

^{13}C-NMR spectrum of poly(S-co-HMDP) from Entry 3

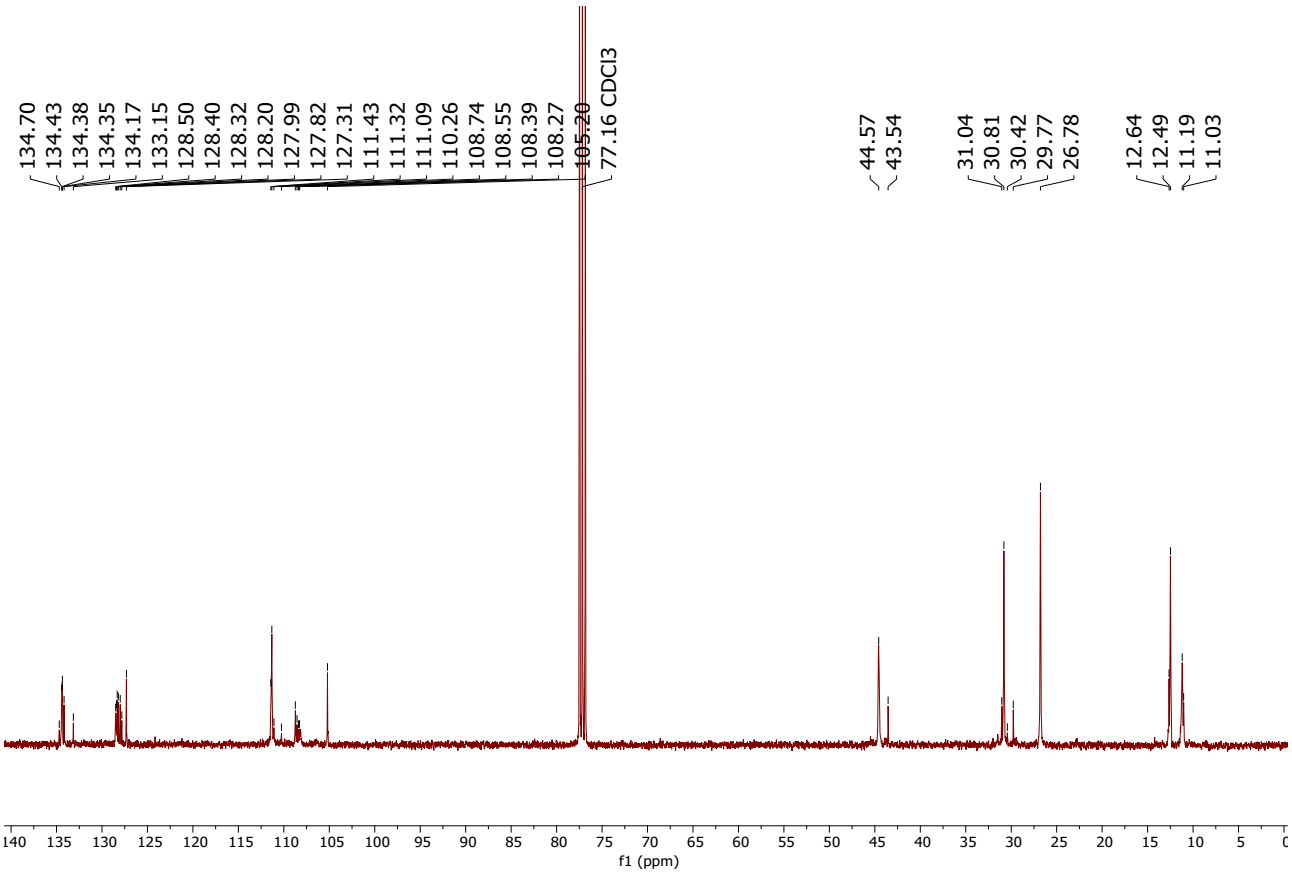

Figure S.18: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Poly(S-co-HMDP) with weight amount of sulfur 52%

Characterization of poly(S-co-HMDP) from Entry 4

^{1}H-NMR spectrum of poly(S-co-HMDP) from Entry 4

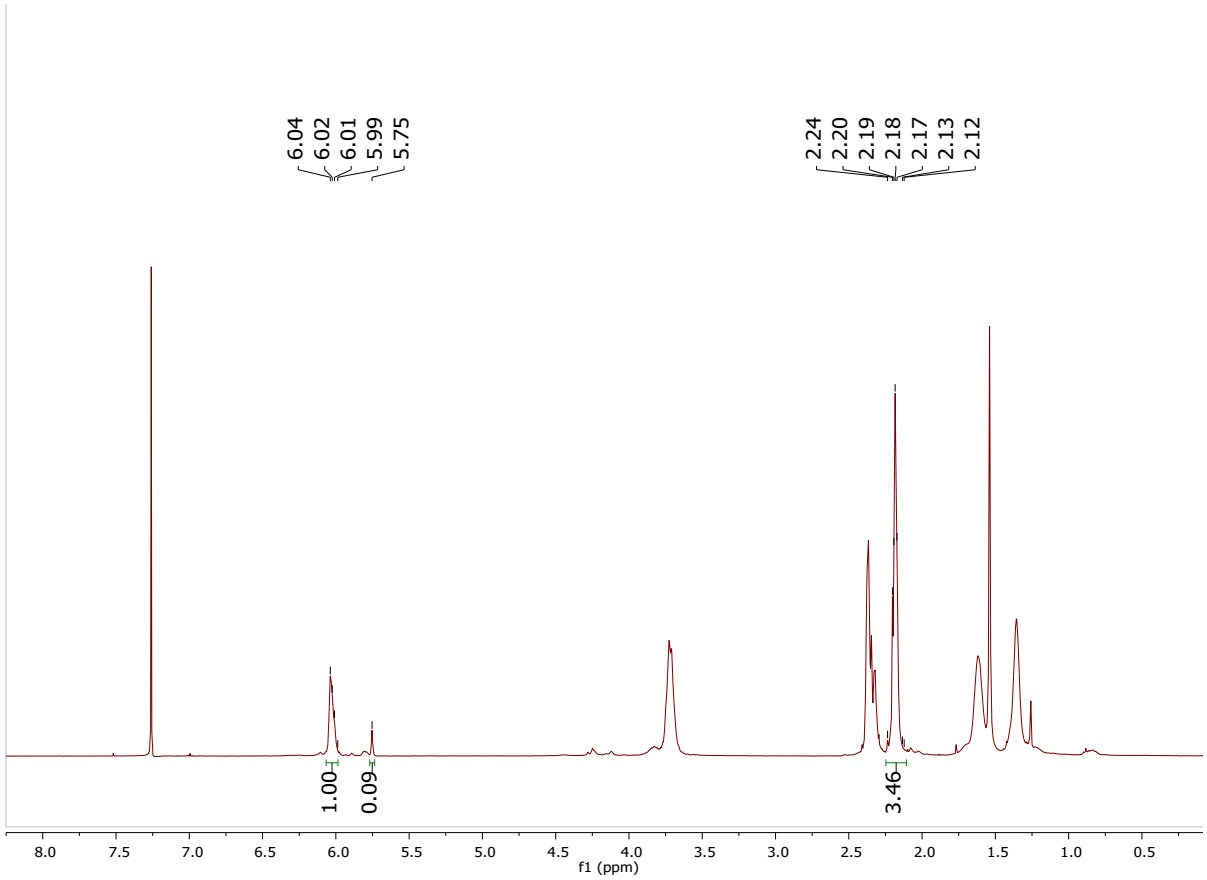

Figure S.19: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of Poly(S-co-HMDP), weight amount of Sulfur 60% (entry 4)

^{13}C-NMR spectrum of poly(S-co-HMDP) from Entry 4

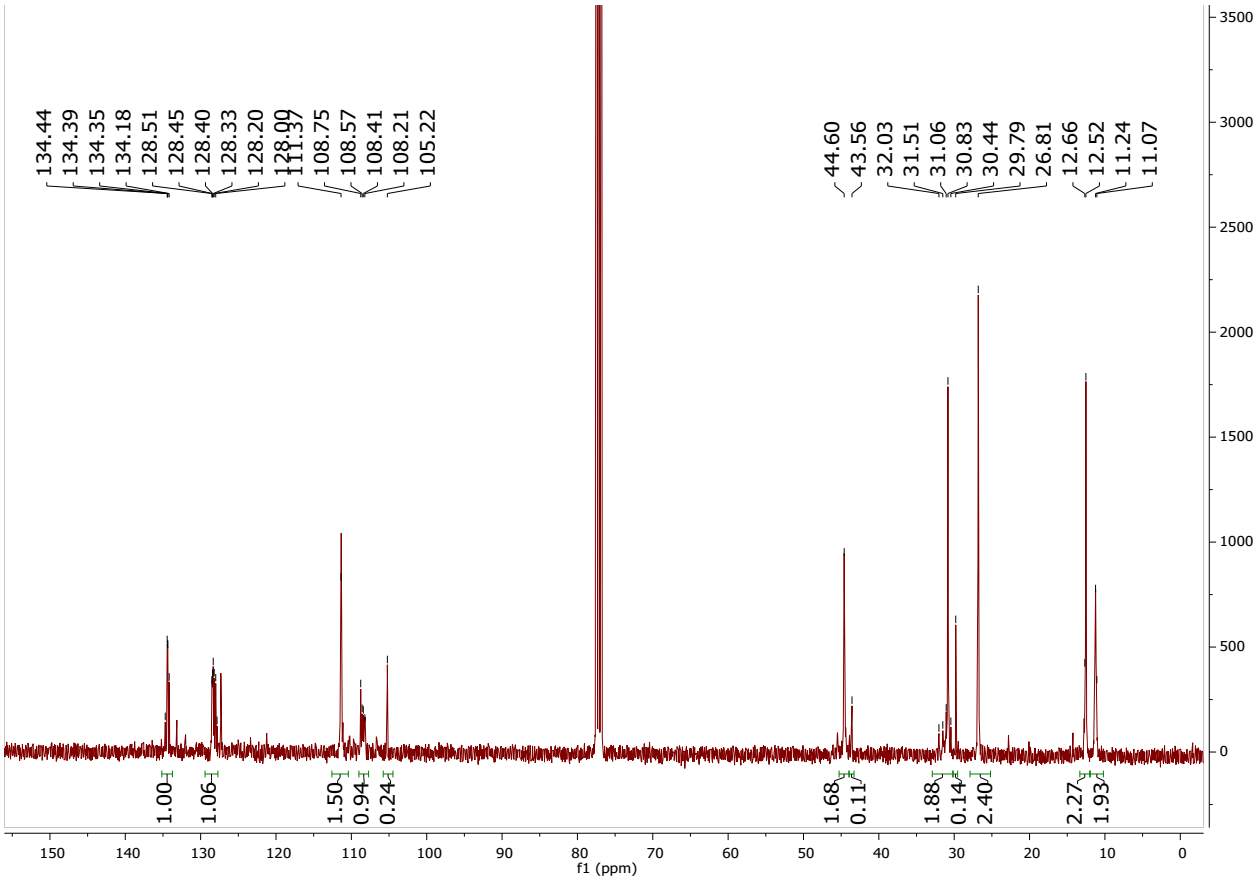

Figure S.20: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Poly(S-co-HMDP), weight amount of Sulfur 60%

Characterization of poly(S-co-HMDP) from Entry 5

^{1}H-NMR spectrum of poly(S-co-HMDP) from Entry 5

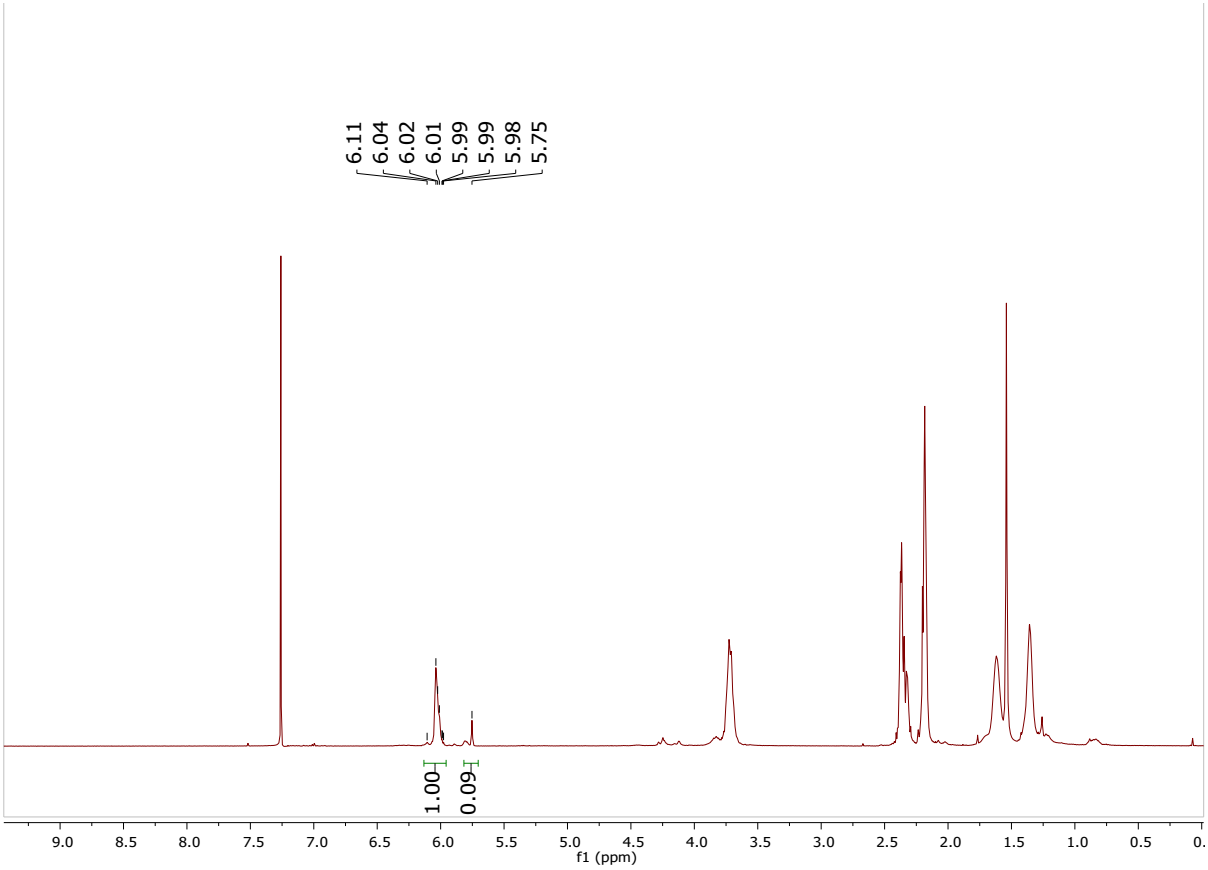

Figure S.21: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of Poly(S-co-HMDP), weight amount of sulfur 70%

^{13}C-NMR spectrum of poly(S-co-HMDP) from Entry 5

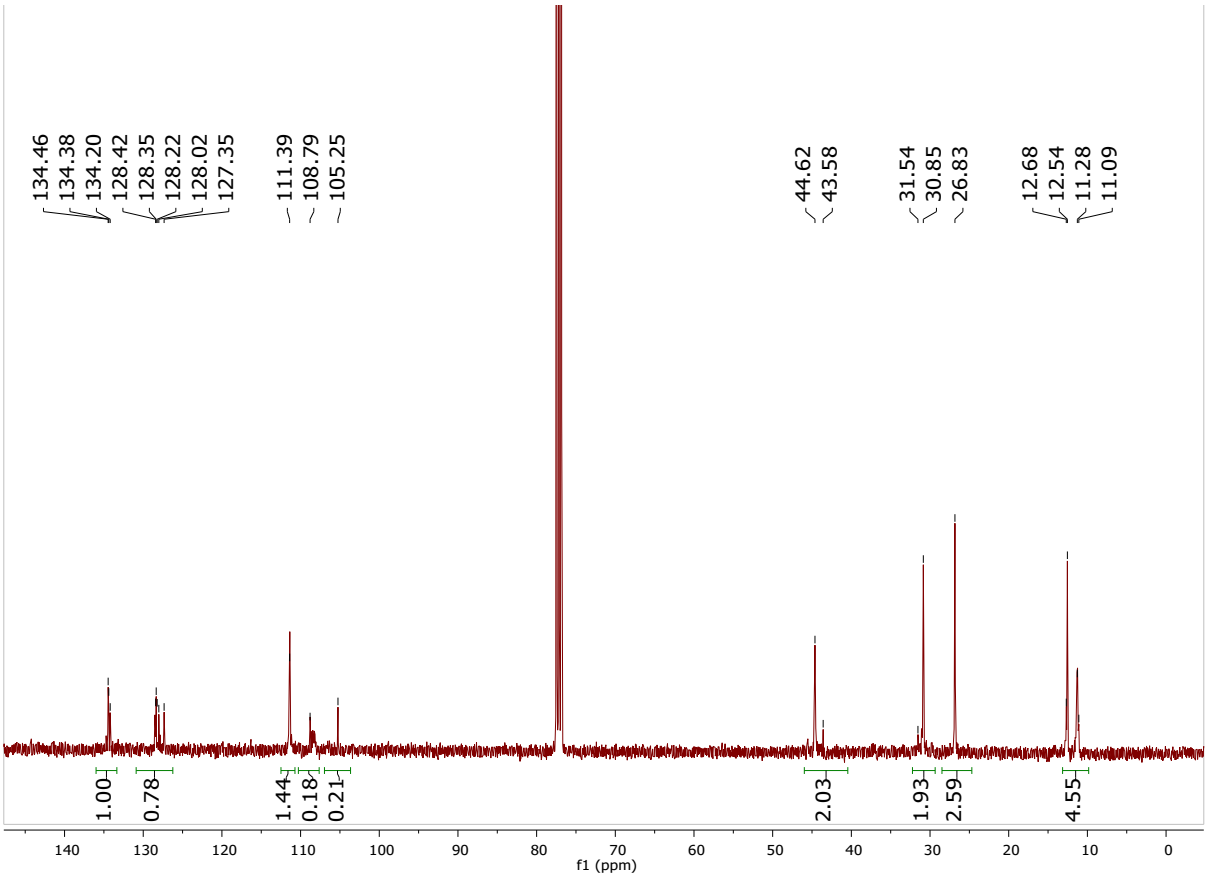

Figure S.22: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Poly(S-co-HMDP), weight amount of sulfur 70%

Characterization of poly(S-co-HMDP) from Entry 6

^{1}H-NMR spectrum of poly(S-co-HMDP) from Entry 6

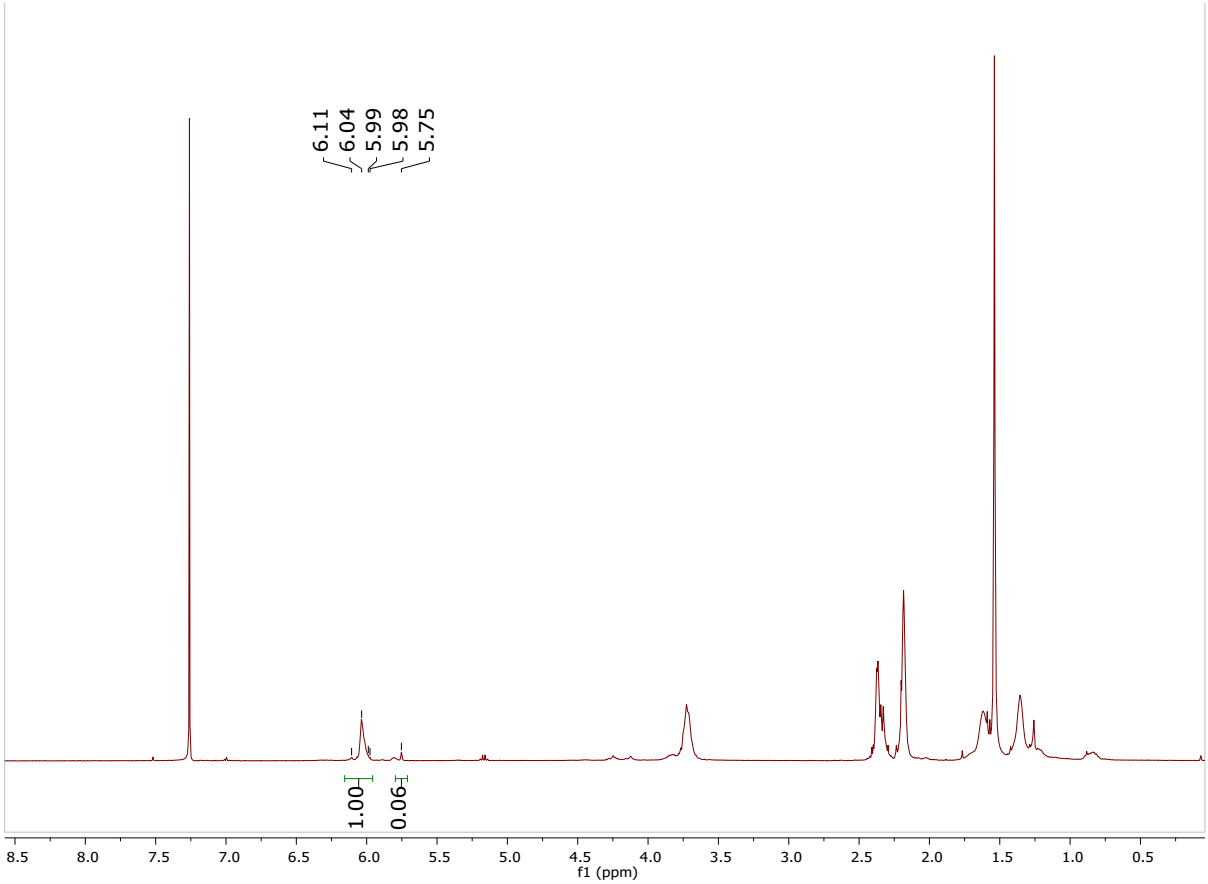

Figure S.23: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of Poly(S-co-HMDP), weight ratio of sulfur 80%

^{13}C-NMR spectrum of poly(S-co-HMDP) from Entry 6

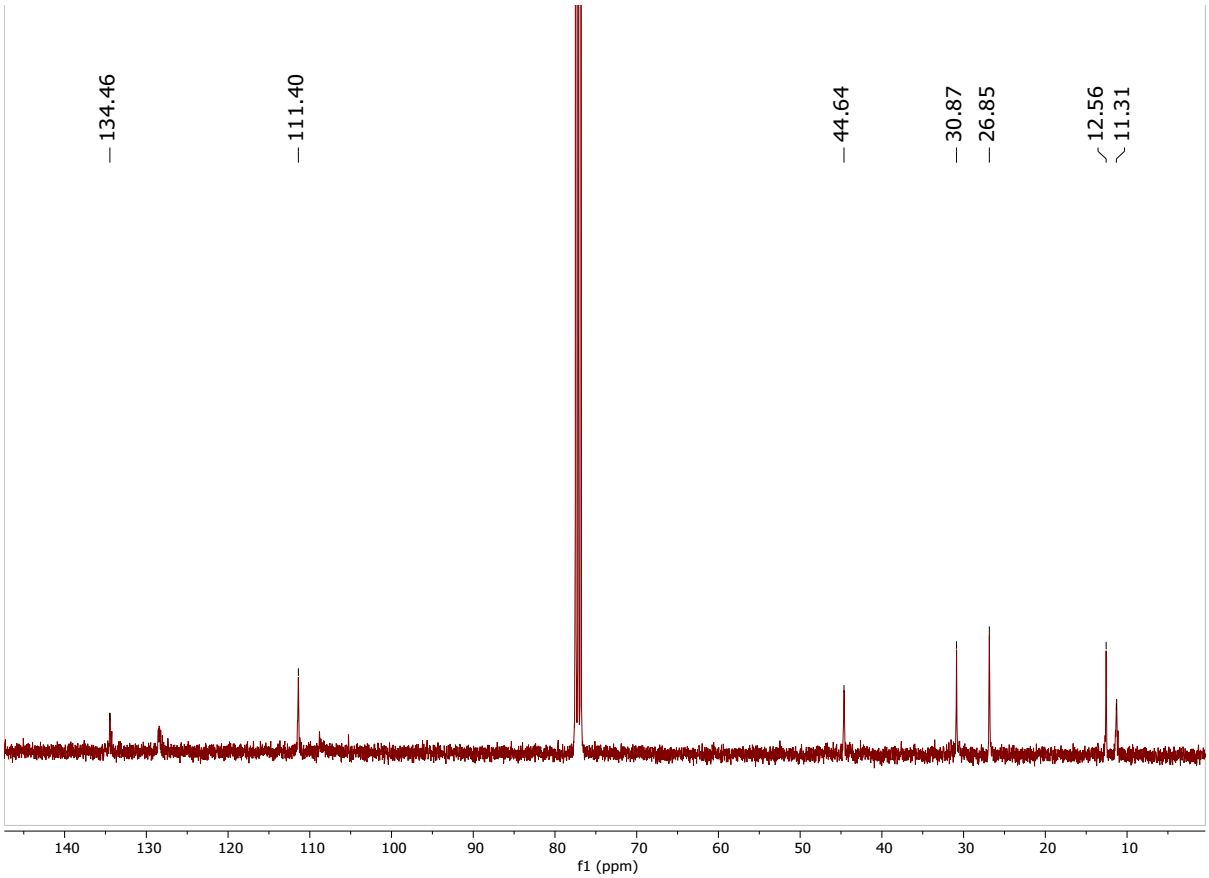

Figure S.24: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) Poly(S-co-HMDP); weight ratio of sulfur 80%

Table S.1: Hansen and Hildebrand solubility parameters of solvents used for the solubility tests of poly(S-co-PyC)[a]

Solvent	**δ_D**	**δ_P**	**δ_H**	**δ_T** [b]
Hexane	14.9	0.0	0.0	14.9
Toluene	18.0	1.4	2.0	18.2
Chloroform	17.8	3.1	5.7	18.9
Tetrahydrofuran	16.8	5.7	8.0	19.5
Acetone	15.5	10.4	7.0	19.9
Dichloromethane	18.2	6.3	6.1	20.2
Dimethyl Sulfoxide	18.4	16.4	10.2	26.7
Water	18.1	17.1	16.9	30.1

[a] values taken from Supplementary materials of reference [52] of the manuscript

[b] δ_T (Hildebrand solubility parameter) $= \sqrt{\delta_d^2 + \delta_p^2 + \delta_H^2}$

Table S.2: Solubility of sulfur, HMDP, and poly(S-co-PyC). PyC = HMDP or EDP

Sample	**Solvent**							
	Hexane	**Toluene**	**THF**	**DCM**	**$CHCl_3$**	**Acetone**	**DMSO**	**H_2O**
Sulfur	No	Yes	No	Yes	Yes	No	Partially	No
HMDP	No	Yes	Yes	Yes	Yes	Yes	Yes	No
Poly(S-co-HMDP)								
Entry 1	No	No	Yes	Yes	Yes	Partially[a]	Partially[a]	No
Entry 2	No	No	Yes	Yes	Yes	Partially[a]	Partially[a]	No
Entry 3	No	No	Yes	Yes	Yes	Partially[a]	Partially[a]	No
Entry 4	No	No	Yes	Yes	Yes	Partially[a]	Partially[a]	No
Entry 5	No	No	Yes	Yes	Yes	Partially[a]	Partially[a]	No
Entry 6	No	No	Yes	Yes	Yes	Partially[a]	Partially[a]	No
Poly(S-co-EDP)								
Entry 8	No	No	Yes	Yes	Yes	Partially[a]	Partially[a]	No

N.B: the solvents in which the poly(S-co-PyC) were partially soluble were considered good solvents for the calculation of Hansen solubility parameters

Table S.3: Solubility parameters of common rubbers involved for the preparation of elastomer composites and of poly(S-co-HMDP) of entry 1

Substrate	δ_d $(MPa)^{1/2}$	δ_p $(MPa)^{1/2}$	δ_H $(MPa)^{1/2}$	δ_T $(MPa)^{1/2}$	Reference
EPDM	17.2	2.0	2.6	17.5	1
NR	17.5	3.2	1.4	17.8	2
SBR	18.0	2.9	2.3	18.4	3
NBR	18.4	6.0	4.5	19.9	4
Entry 1	18.0	7.7	6.7	20.7	this work

1) Hansen, C. M., "*Hansen solubility parameters: a user's handbook*", **2007**, CRC press;

2) Jing, Y., Cui, Z., Zou, H., Tu, J., Jiang, X., Shi, X., ... & Liu, G., "Three-dimensional solubility parameters of natural rubber and its predictive power in diffusion coefficients", *Journal of Applied Polymer Science*, **2022**, 139(2), 51473;

3) Liu, S. S., Li, X. P., Qi, P. J., Song, Z. J., Zhang, Z., Wang, K., ... & Liu, G. Y., "Determination of three-dimensional solubility parameters of styrene butadiene rubber and the potential application in tire tread formula design", *Polymer Testing*, **2020**, *81*, 106170;

4) Liu, G., Hoch, M., Wrana, C., Kulbaba, K., & Qiu, G., "A new way to determine the three-dimensional solubility parameters of hydrogenated nitrile rubber and the predictive power", *Polymer testing*, **2013**, *32(6)*, 1128-1134;

Table S.4 E-Factor for the synthesis of poly(sulfur-co-EMDP) copolymers, step 1 and step 2, evaluated for the organic compounds

Step	Chemical substances	E-factor [a]
pyrrole compound = HMDP [b]		
Step 1: synthesis of HMDP	2,5-hexanedione; hexamethylenediamine	0.97 g (waste) [c] / 9.0 g (product) = 0.11
Step 2: synthesis of poly(S-co-HMDP)	HMDP; Sulfur	0 [d]
pyrrole compound = EDP		
Step 1: synthesis of EDP	2,5-hexanedione; ethylenediamine	0.28 g (waste) [c]/ 4.32 g (product) = 0.07
Step 2: synthesis of poly(S-co-HMDP)	EDP; Sulfur	0 [e]

[a] E Factor = (g waste / g product); [b] evaluation of E Factor was done for Entries 1-5 [c] the waste was calculated on the basis of the yield; [d] for Entries 1 – 5, unreacted sulfur or HMDP were not detected at the end of the reaction; [e] for entry 8, unreacted sulfur or EDP were not detected at the end of the reaction

Table S.5: Weight average molecular weight (M_w), number average molecular weight (M_n), Dispersity (M_w,/M_n)[a]

Entry[b]	PyC (wt%)	M_w x 10^{-3}	M_n x 10^{-3}	M_w /M_n
1	59	7.6	6.0	1.3
2	51	6.1	5.1	1.2
3	50	6.4	5.0	1.3
4	40	13.7	9.9	1.4
5	30	12.9	7.8	1.7
6	20	2.7	1.5	1.7
8	45	3.7	2.7	1.4

[a] from GPC analysis [b] Entry 1-6: HMDP as the comonomer; Entry 8: EDP as the comonomer

Table S.6: Number average molecular weight (M_n) and Dispersity (Đ) of the sulfur-based copolymers reported in the scientific literature and of the new poly(S-co-PyC).

Comonomer	M_n ($gmol^{-1}$)	Đ	Ref. (see manuscript)
D-limonene	210	1.16	[14]
mixture of dipentene	< 1000	Not reported	[24]
Limonene, di-isopropenyl benzene, myrcene, farnesene, farnesol	401 - 1197	from 1.81 to 8.47	[19]
1,3-diisopropenylbenzene	1260	2.86	[11]
styrene	1275	1,85	[9]
styrene	2680 - 2760	from 1.12 to 1.75	[15]
Poly(ionic-liquids)	2000 - 3800	from 1.4 to 2.4	[58]
Benzoxazine	$2.8 \times 10^5 – 3.1 \times 10^5$	from 2.5 to 2.9	[18]
Cardanol	$1,64 \times 10^4$ - $1,81 \times 10^6$	from 3.7 to 4.1	[20]
Pyrrole compounds	1500 - 9000	from 1.2 to 1.7	this work

Characterization of poly(S-co-EDP) from entry 8

^{1}H-NMR of Poly(S-co-EDP) from Entry 8

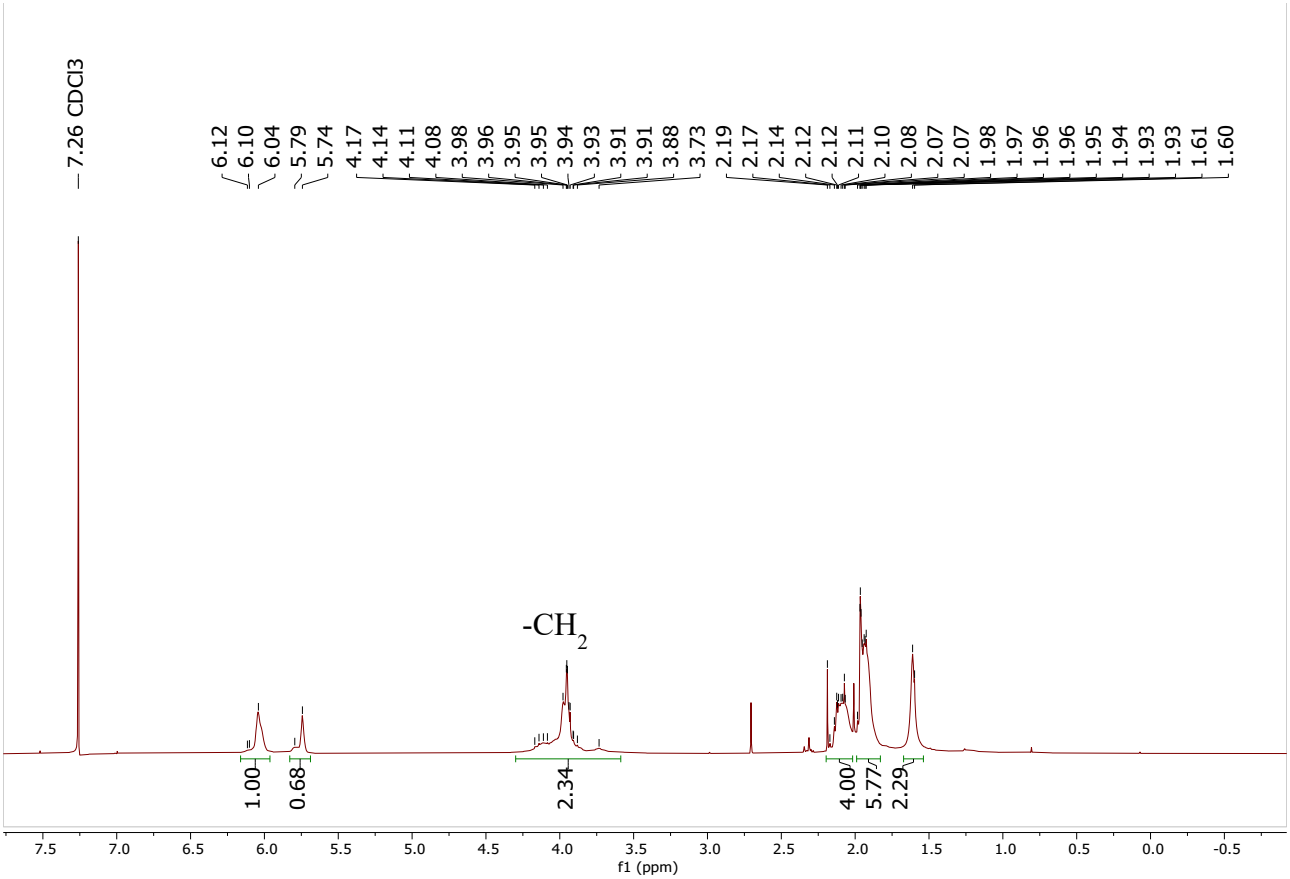

Figure S.25: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of poly(S-co-EDP) with weight amount of sulfur of 54%

Comparison of ^{1}H-NMR spectra of EDP and poly(S-co-EDP) from entry 8

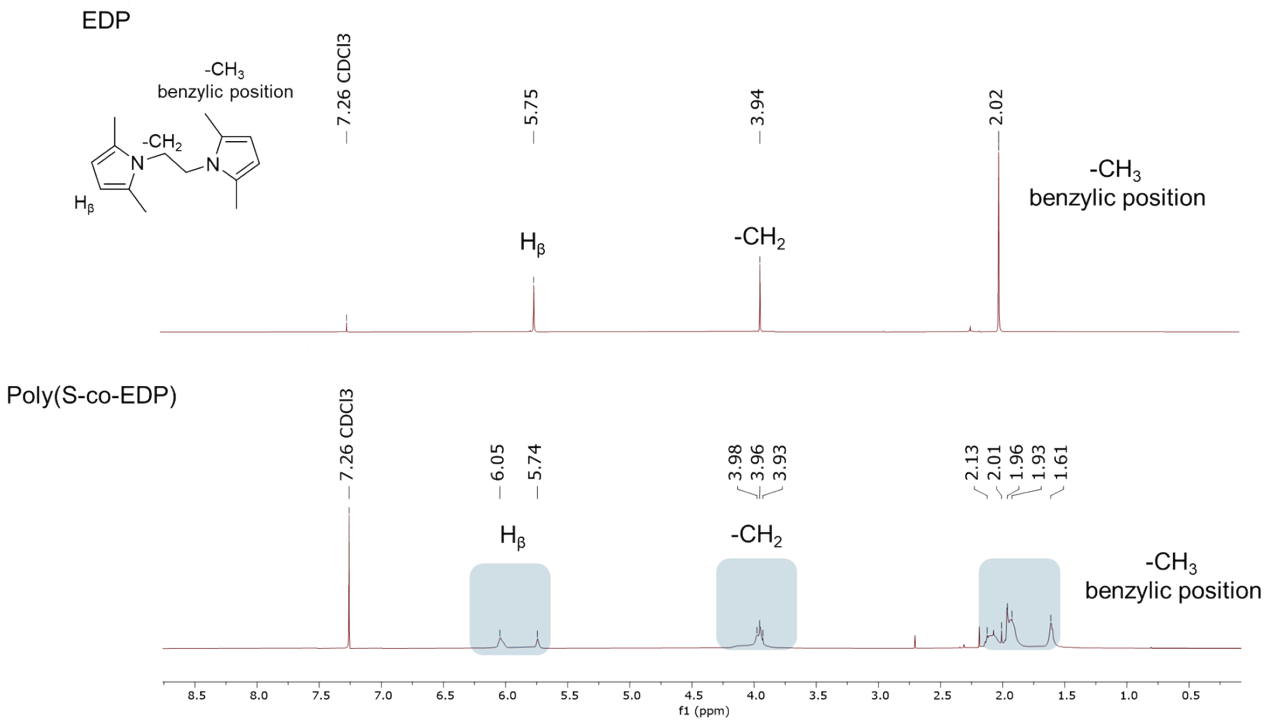

Figure S.26: ^{1}H-NMR spectra (400 MHz, $CDCl_3$) of EDP and poly(S-co-EDP) weight amount of sulfur of 54%

^{13}C-NMR of Poly(S-co-EDP) from Entry 8

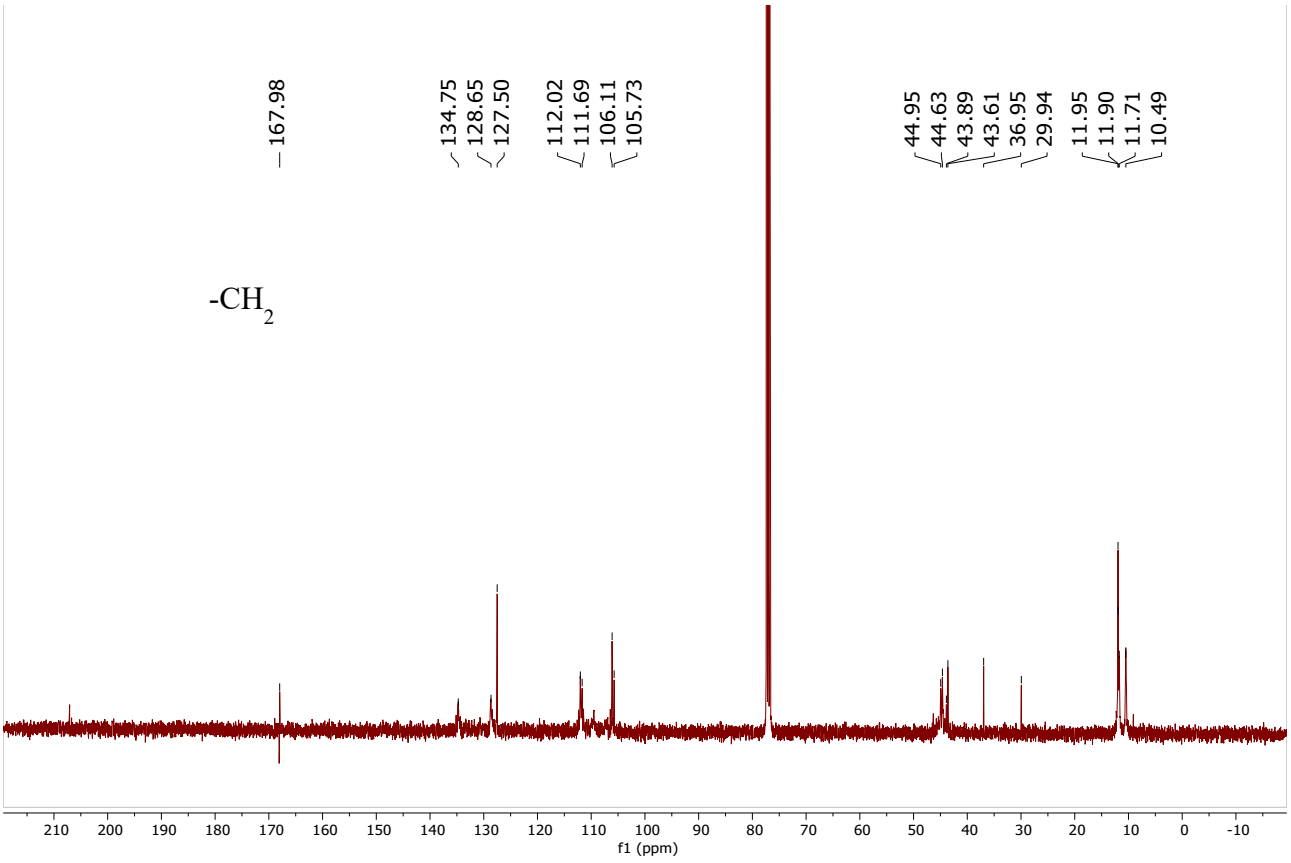

Figure S.27: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Poly(S-co-EDP) copolymer with weight amount of sulfur of 54%

Comparison of ^{13}C-NMR spectra of EDP and poly(S-co-EDP) from Entry 8

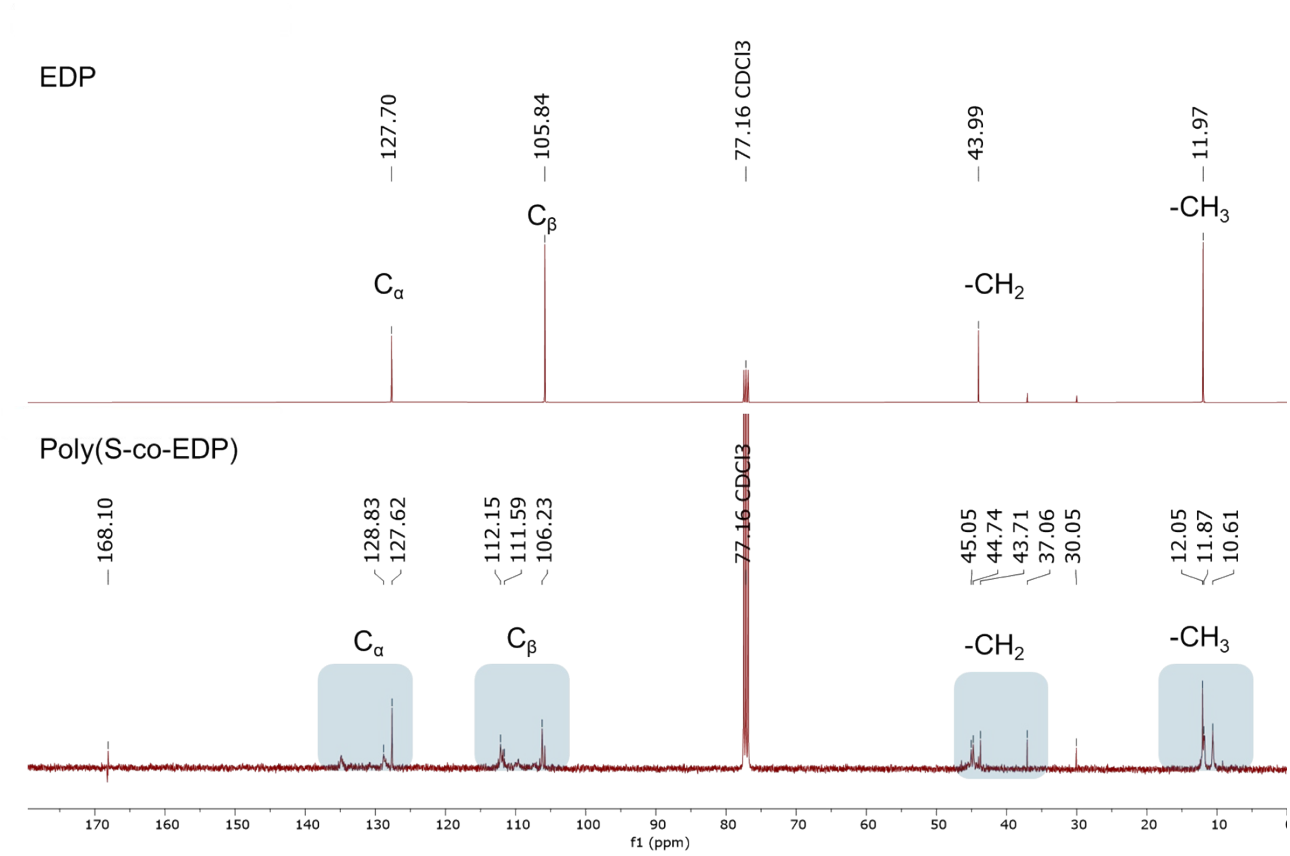

Figure S.28: Comparison of ^{13}C-NMR spectra (100 MHz, $CDCl_3$) of EDP and poly(S-co-EDP) with weight amount of sulfur of 54%

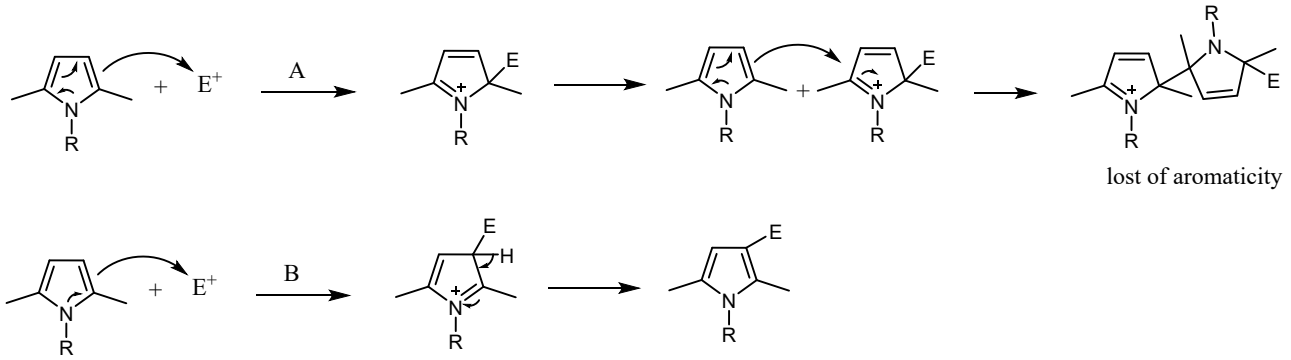

Figure S.29. Possible pathways for the reaction of an alfa-substituted pyrrole ring with an electrophile

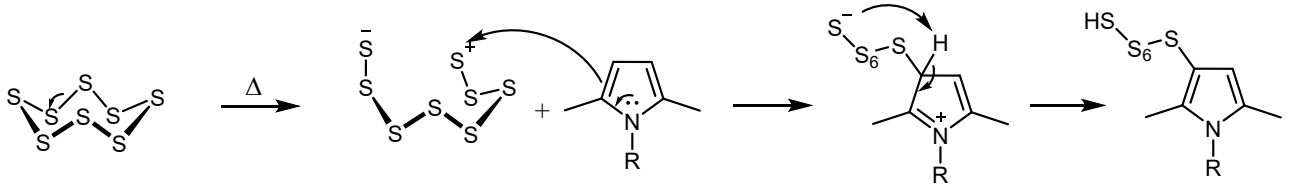

Figure S.30. Hypothesis for the ionic reaction of elemental sulfur with an alfa substituted pyrrole ring

Table S.7: Properties from curing reaction of elastomer composites

	Poly(S-co-HMDP)	Poly(sulfur-co-HMDP) + DBU
M_L	1.9	1.8
M_H	3.6	5.0
M_H-M_L	1.7	3.2
t_{s1}	2.7	2.7
t_{90}	16.7	15.4
t_{90}-t_{s1}	14.1	12.7
Vulcanization rate	0.12	0.25
Increase % of M_H with respect to the reference compounds	0	+39%

Table S.8: G', G'', ΔG', ΔG'/G', G'' $_{(max)}$ and tan δ $_{(max)}$ of the elastomer composites of Table 2

	Poly(S-co-HMDP)	Poly(sulfur-co-HMDP) + DBU
$G'_{(\delta=0.28\%)}$	1.42	1.18
$G'_{(\delta=25\%)}$	0.48	0.49
ΔG'	0.94	0.69
ΔG' / $G'_{(\delta=0.28)}$	0.66	0.58
$G''_{(max)}$	0.28	0.23
tan δ $_{(max)}$	0.30	0.27