

Electronic Supporting Information

Diels-Alder cycloaddition and RAFT chain end functionality: an elegant route to fullerene end-capped polymers with control over molecular mass and architecture

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1. ¹³C NMR spectra

The ¹³C NMR PENDANT (Polarization Enhancement During Attached Nucleus Testing) technique allows one to detect quaternary carbons in addition to other types of carbon atoms, similar to DEPT experiments. In our routinely used PENDANT experiment, the C* and CH₂ carbons are positive and CH₃ and CH are negative.

Thus, ¹³C spectra of PDMS-FUL (Figure S1) show the quaternary peaks in the region typically attributed to the fullerene carbons (135 – 139 ppm). The observed pattern is more structured than that in various other reports¹⁻³ but agrees with a monosubstituted fullerene polymer^{4,5}. Two peaks at 57 and 67 ppm also originate from the quaternary carbon from the C-C bond in the cycloadduct.

The numerous peaks in the alkyl region are attributed to the alkyl tail of the DDMAT agent. The prominent broad peaks at 56 ppm (methoxy carbons), at 110 ppm and 120 ppm (tertiary carbons of the benzene ring) and 150 and 148 ppm (quaternary carbons of the benzene ring) belong to the PDMS part of the conjugate material.

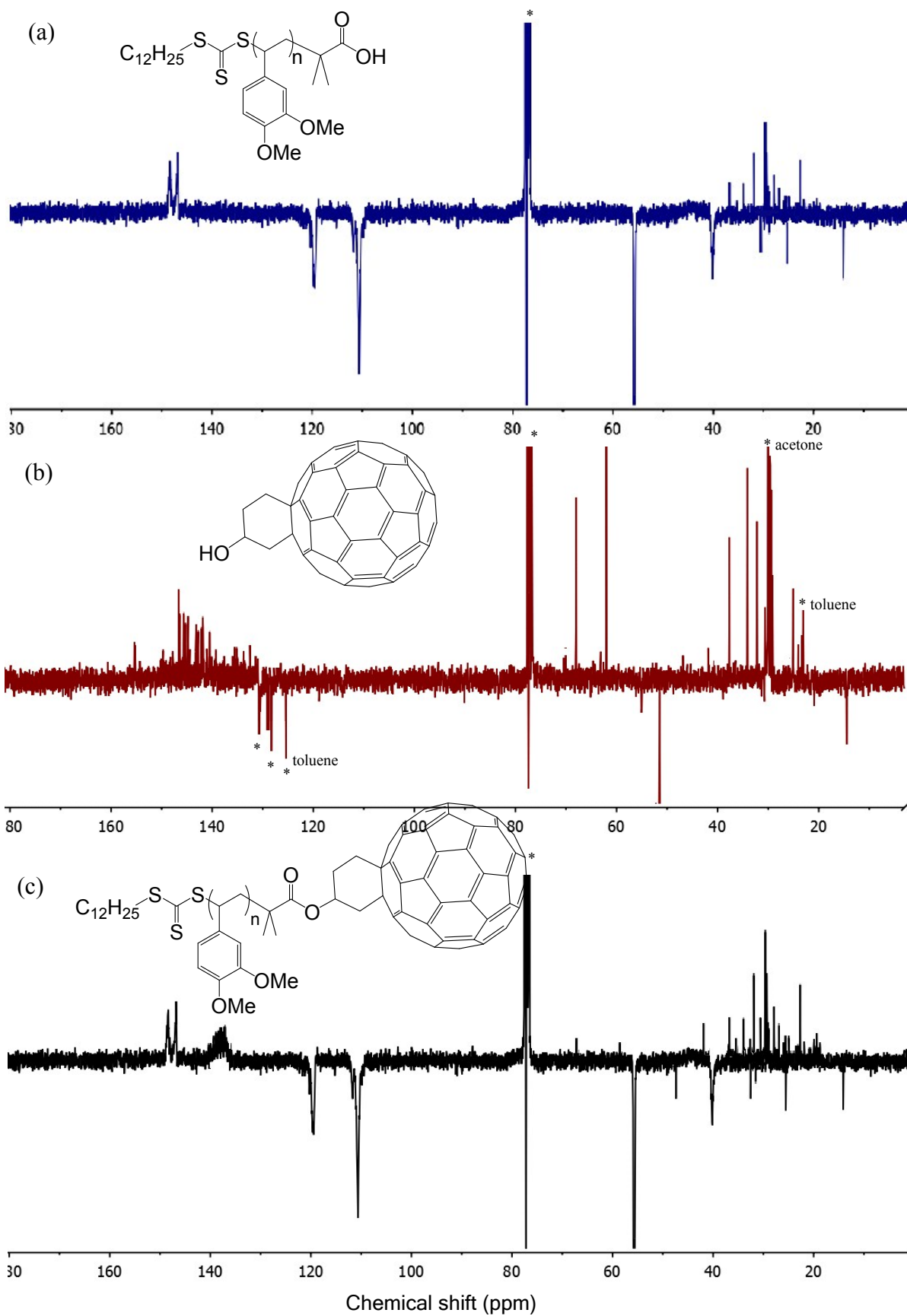


Figure S1. ^{13}C NMR spectra of (a) PDMS (in CDCl_3); (b) FUL-OH (in acetone- d_6 : CDCl_3) and (c) PDMS-FUL (in CDCl_3).

The ^{13}C spectrum of PDMS-FULP (Figure S2) is essentially a combination of spectra of PDMS and FULP-OH derivative. Spectrum of PDMS-FULP shows the quaternary peaks in the region typically attributed to the fullerene carbons (135 – 150 ppm) are less structured than in FULP-OH spectrum (Fig.S2b) and partially overlay the peaks for PDMS at 145 and 148 ppm. Two peaks at 65 and 66 ppm are attributed to the pyrrolidine carbons in the FULP-OH derivative and are observed in the spectra of FULP-OH and PDMS-FULP.⁶ Another peak at 37 ppm is attributed to the methyl group on the pyrrolidine nitrogen. The peaks at 125-130 ppm originate from benzene ring carbons of the pyrrolidine substituent. The numerous peaks in the alkyl region are attributed to the alkyl tail of the DDMAT agent.

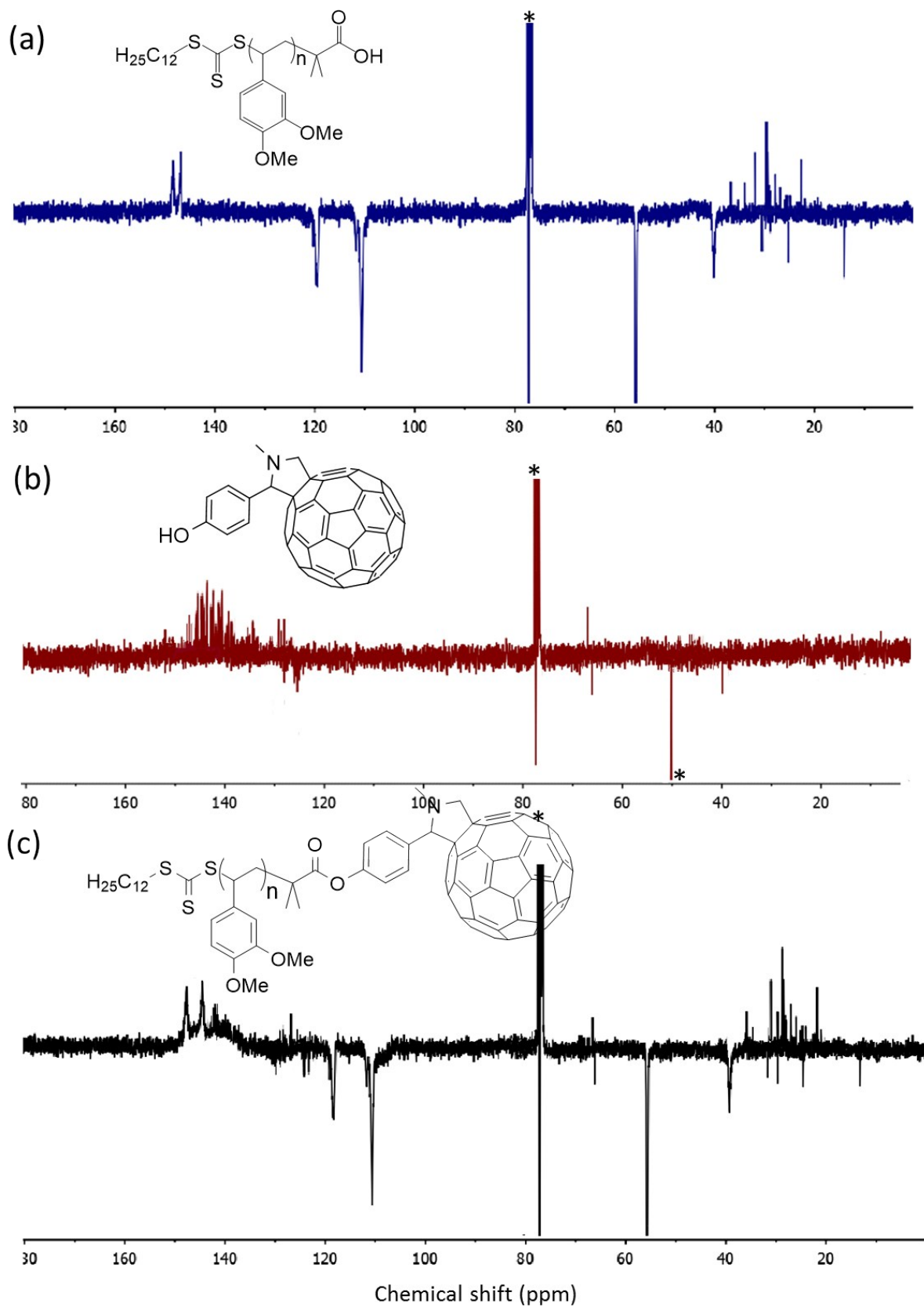


Figure S2. ^{13}C NMR spectra of (a) PDMS (in CDCl_3); (b) FULP-OH (in $\text{MeOD-d}_6:\text{CDCl}_3$) and (c) PDMS-FULP (in CDCl_3). Residual solvent peaks are labelled with asterisks.

2. Elemental analysis

Theoretical calculations are based on the average degree of polymerisation (D_P) equal to 28 (M_n 5,000 g/mol), as approximated from GPC. The actual results suggest that the average D_P of PDMS is higher than 28, based on the slightly higher content of the carbon (originating from the monomer) and slightly lower content of sulfur (originating from the CTA). Furthermore, the addition of the fullerene derivative on the chain end increases the content of the carbon in the polymer, however, not as much as the theoretical calculations would predict, indicating that the average D_P of PDMS is higher than predicted from GPC (Table S1).

Table S1. Elemental analysis of PDMS and PDMS-FUL.

Sample ID PDMS

Formula $C_{297}H_{366}O_{56}S_3$

ELEMENT	C	H	N	S	O
% Theory	71.89	7.47	-	1.94	18.70
% Found	72.11	7.46	-	1.85	18.58

Sample ID PDMS-FUL

Formula $C_{361}H_{374}O_{58}S_3$

ELEMENT	C	H	N	S	O
% Theory	75.58	6.57	-	1.68	16.18
% Found	75.45	6.65	-	1.63	16.27

Sample ID PDMS-FULP

Formula $C_{368}H_{377}O_{58}N_1S_3$

ELEMENT	C	H	N	S	O
% Theory	75.63	6.49	0.24	1.65	15.99
% Found	74.84	6.54	0.26	1.84	16.52

3. UV spectroscopy of PDMS-FUL

The UV-Vis spectra of the materials are shown in Figure S3. In agreement with An *et al.* and Zhang *et al.*, a characteristic absorption peak for a functionalised fullerene is observed at 435 nm.^{7,8} The peak at 705 nm is attributed to the absorption of the fullerene conjugated system (intrinsic to pure C₆₀), which is seen to be somewhat diluted by the presence of the covalently bound polymer chain PDMS-FUL. PDMS absorbs in the UV part of the spectrum, where the aromatic system of the fullerene also strongly absorbs. Consequently, the spectrum of PDMS-FUL resembles that of pristine FUL-OH in this region albeit with a marginal decrease in absorption.

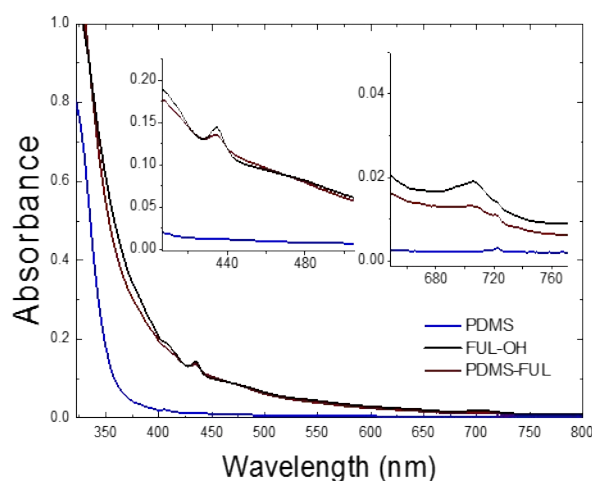


Figure S3. UV-Vis spectra of PDMS (blue), FUL-OH (black) and resulting PDMS-FUL (red).

4. GPC traces

GPC traces of the different molecular weights are shown in Figure S4. The molecular weight of the polymers are presented in the Table S1:

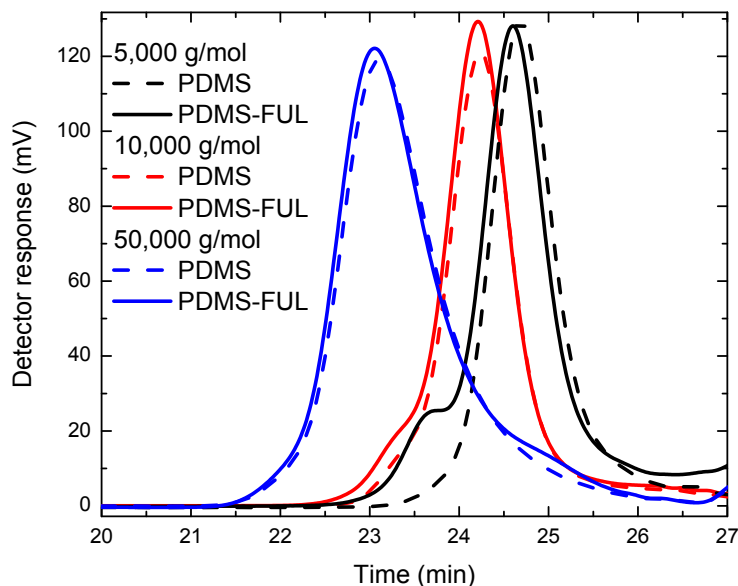


Figure S4. GPC traces of pristine PDMS (dotted line) and fullerene-functionalised (dashed lines) PDMS-FUL polymers of different targeted molecular masses, 5,000 g/mol, 10,000 g/mol and 50,000 g/mol.

Table S2. Molecular mass data of pristine PDMS and PDMS-FUL after coupling with fullerene, in g/mol.

M_n PDMS (g/mol) target	M_n PDMS (g/mol)	M_n PDMS-FUL (g/mol)
5,000	5,000	5,400
10,000	10,400	10,500 (g/mol)
50,000	46,700	46,800

References

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