Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information for

Controlled radical polymerization of a styrenic sulfonium monomer and post-polymerization modifications

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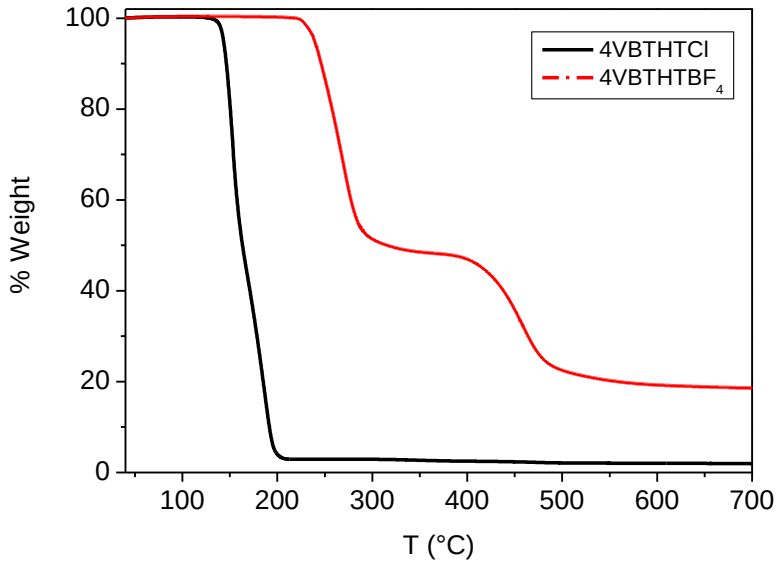

Figure S1 TGA of the monomers show an increased thermal stability of 4-VBThtBF$_4$ compared to 4-VBThtCl (scan from 40 to 700 °C at a constant heating rate of 10 °C min^{-1} under a flow of nitrogen).

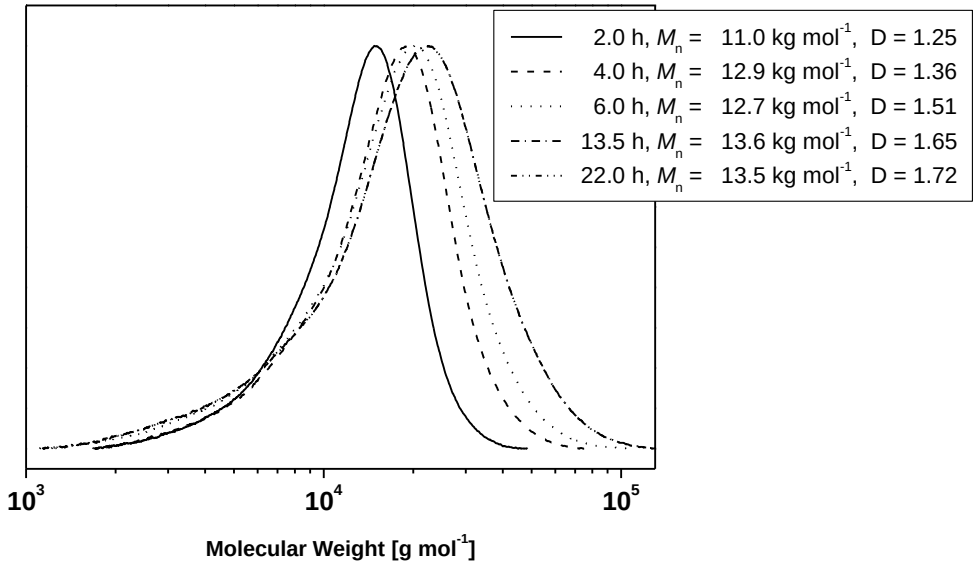

Figure S2 SEC traces of the ICAR ATRP of 4VBThtBF$_4$ using 3 mol% of $CuBr_2$ (resp. initiator) and a [Cu]:[TPMA] ratio of 1:2 in DMF at 70 °C. Progressive loss of control due to the permanent formation of dead polymer chains is evidenced by the increase in tailing with conversion.

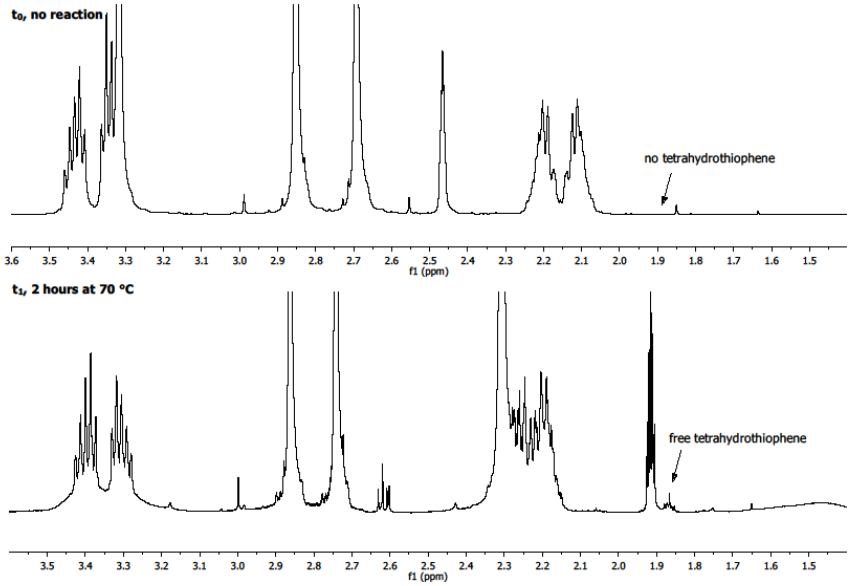

Figure S3 NMR spectra obtained before (top, DMSO-d_6) and after 2 hours (bottom, CD_3CN) of reaction during the ICAR ATRP of 4VBThtBF$_4$ at 70 °C showing the presence of tetrahydrothiophene.

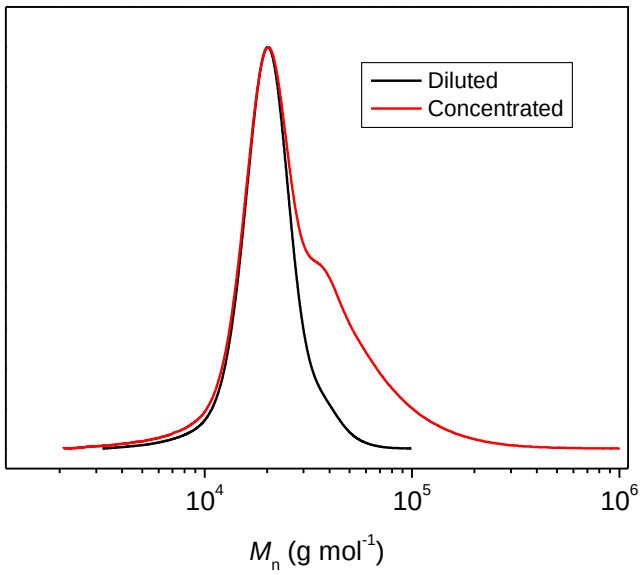

Figure S4 SEC traces for the polyVBSBn polymers obtained after reaction under dilute and concentrated conditions from samples of polyVBThtBF$_4$ obtained via RAFT polymerization. *Reaction conditions:* polyVBThtBF4 (5 mg) and BnSNa (10 mg) were reacted as described in the experimental section except for the total volume of solvent (DMF) being used (0.1 mL, red curve; 1.0 mL black curve).

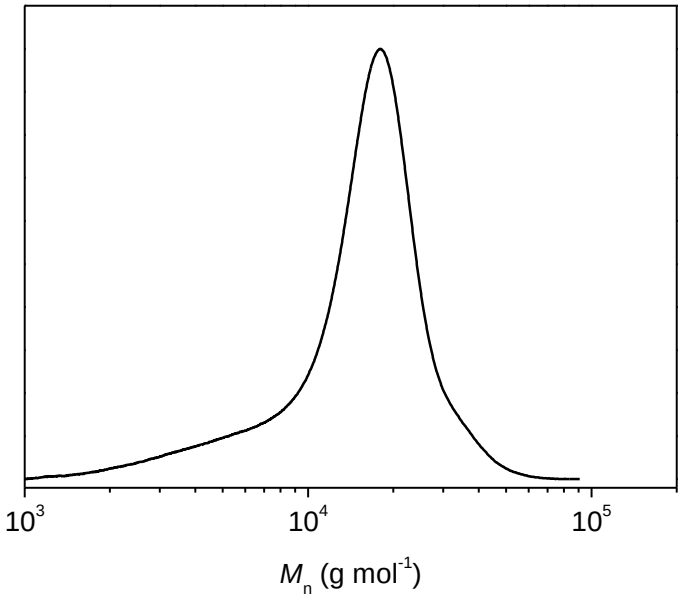

Figure S5 SEC trace for the poly4VBN_3 obtained by reaction between poly4VBThtBF_4 and NaN_3. Significant tailing of the curve towards the low M_n can be plausibly explained by the presence of residual charged monomer units along some polymer chain due to non-quantitative reaction with sodium azide.

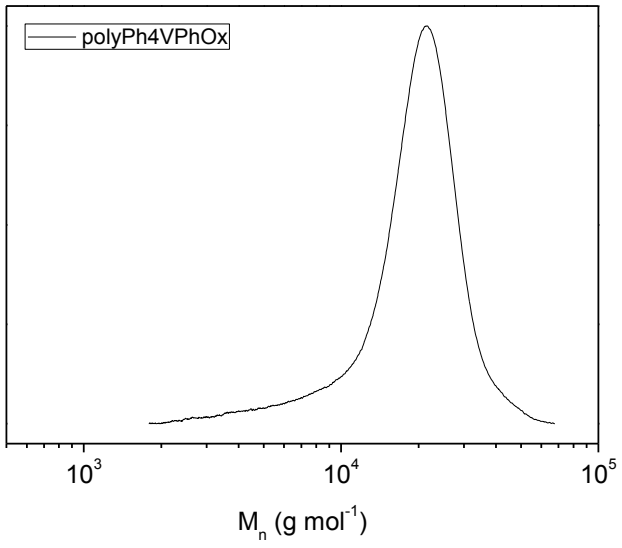

Figure S6 SEC trace for the polyPh4VPhOx obtained after reaction of poly4VBThtBF_4 with DBU and benzaldehyde.

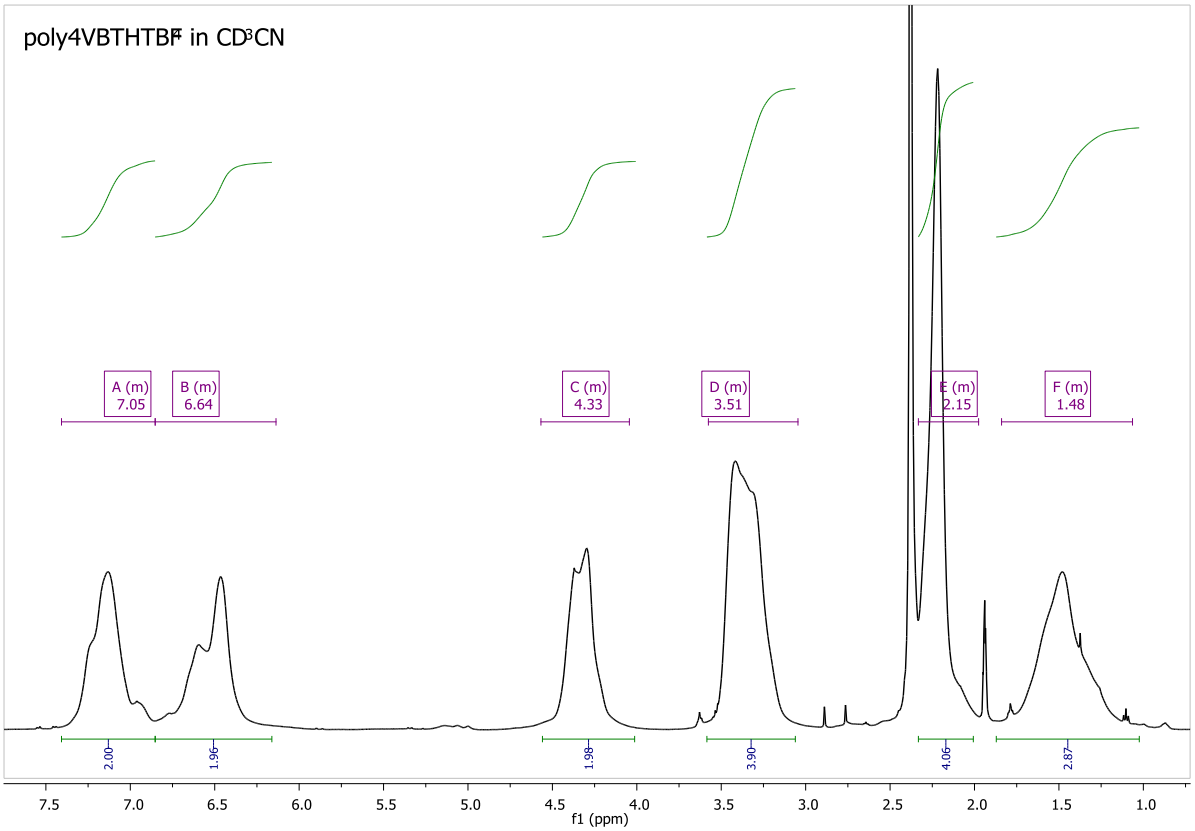

Figure S7 ^{1}H NMR spectrum of poly4VBThtBF$_4$ in CD$_3$CN.

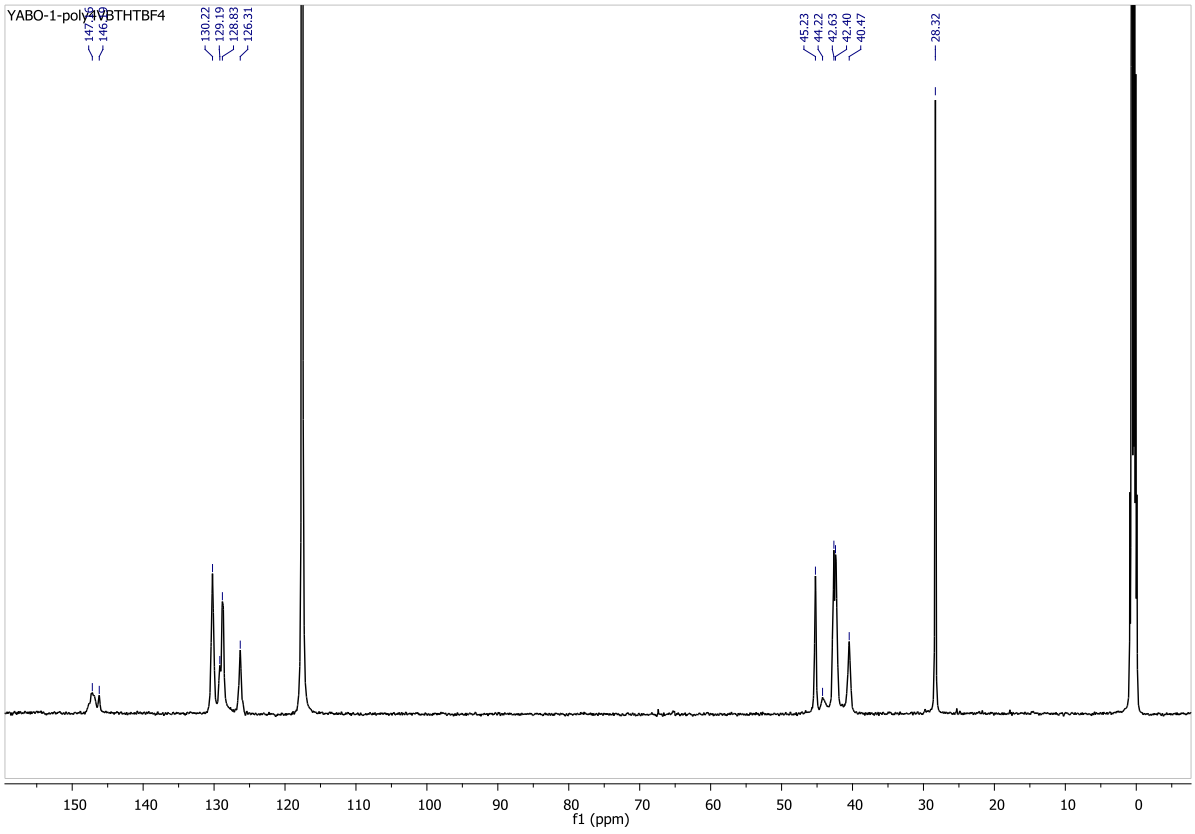

Figure S8 ^{13}C NMR spectrum of poly4VBThtBF$_4$ in CD$_3$CN.

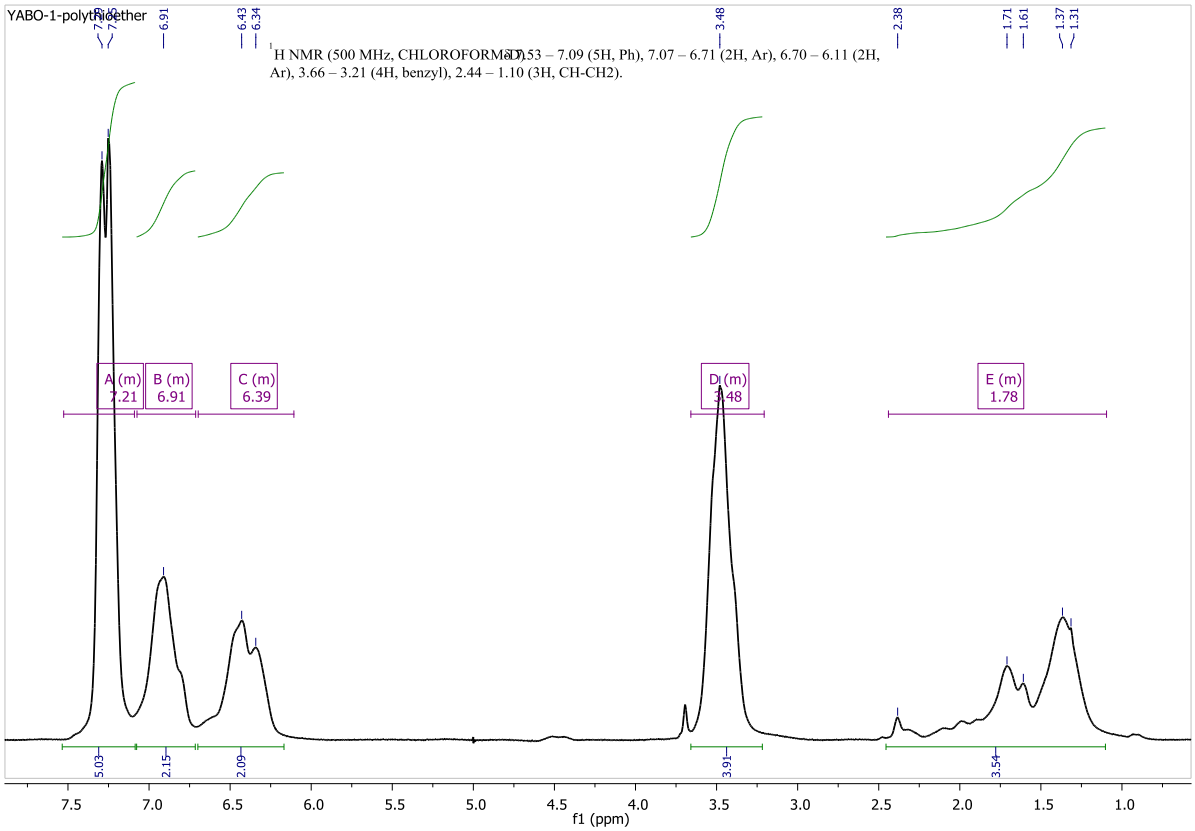

Figure S9 ^{1}H NMR spectrum of poly4VBSBn in $CDCl_3$.

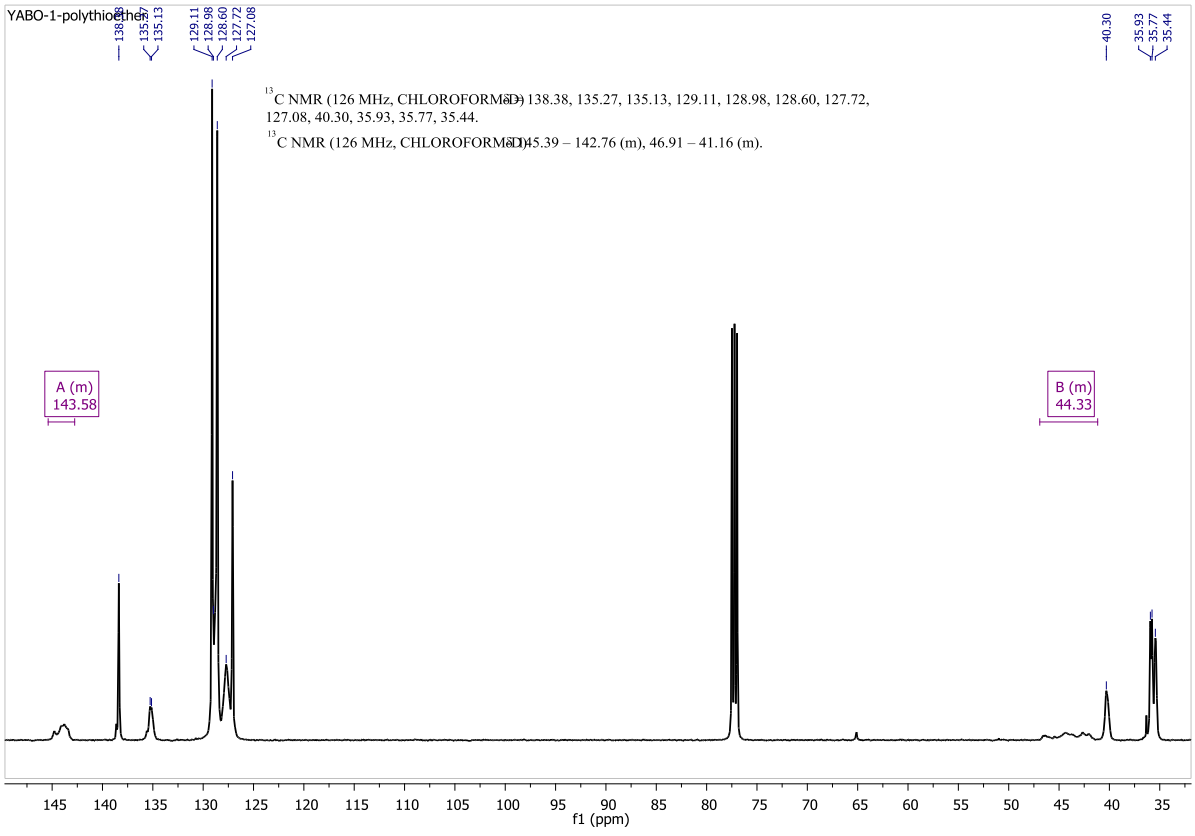

Figure S10 ^{13}C NMR spectrum of poly4VBSBn in $CDCl_3$.

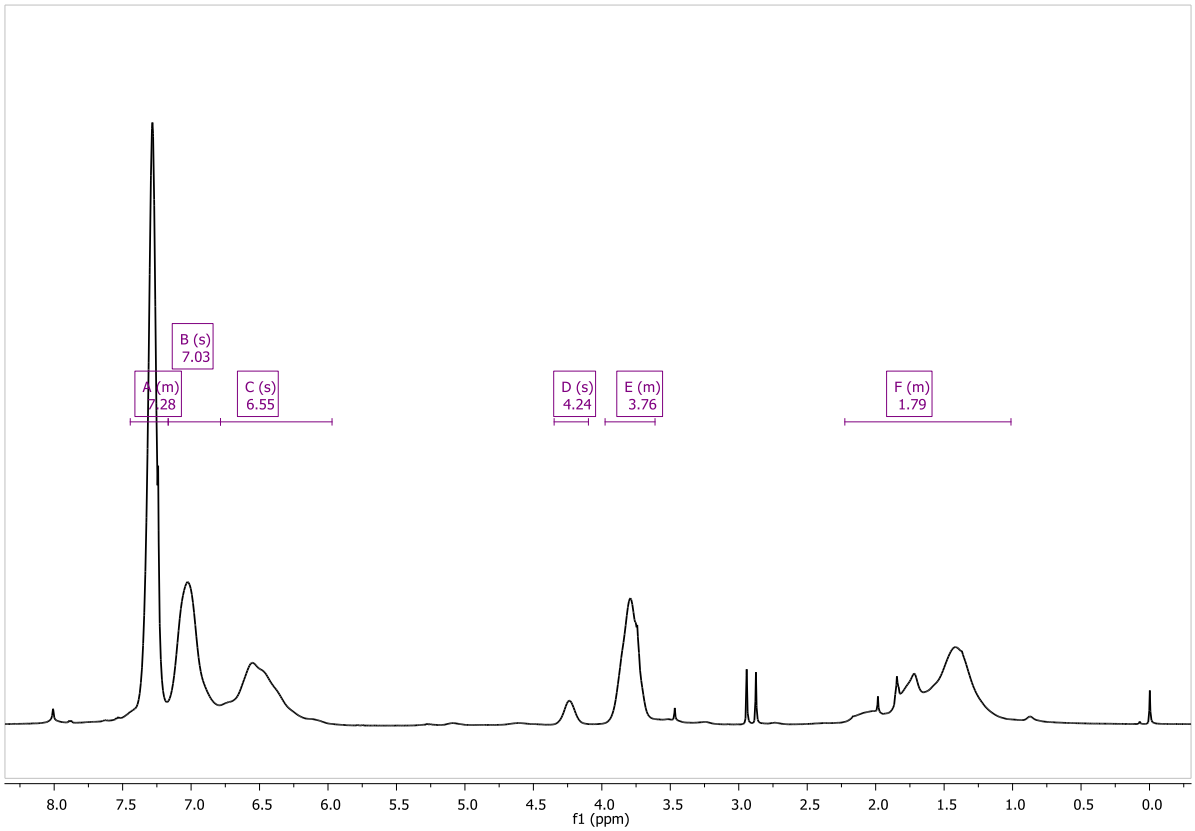

Figure S11 ^{1}H NMR spectrum of polyPh4VPhOx in $CDCl_3$.

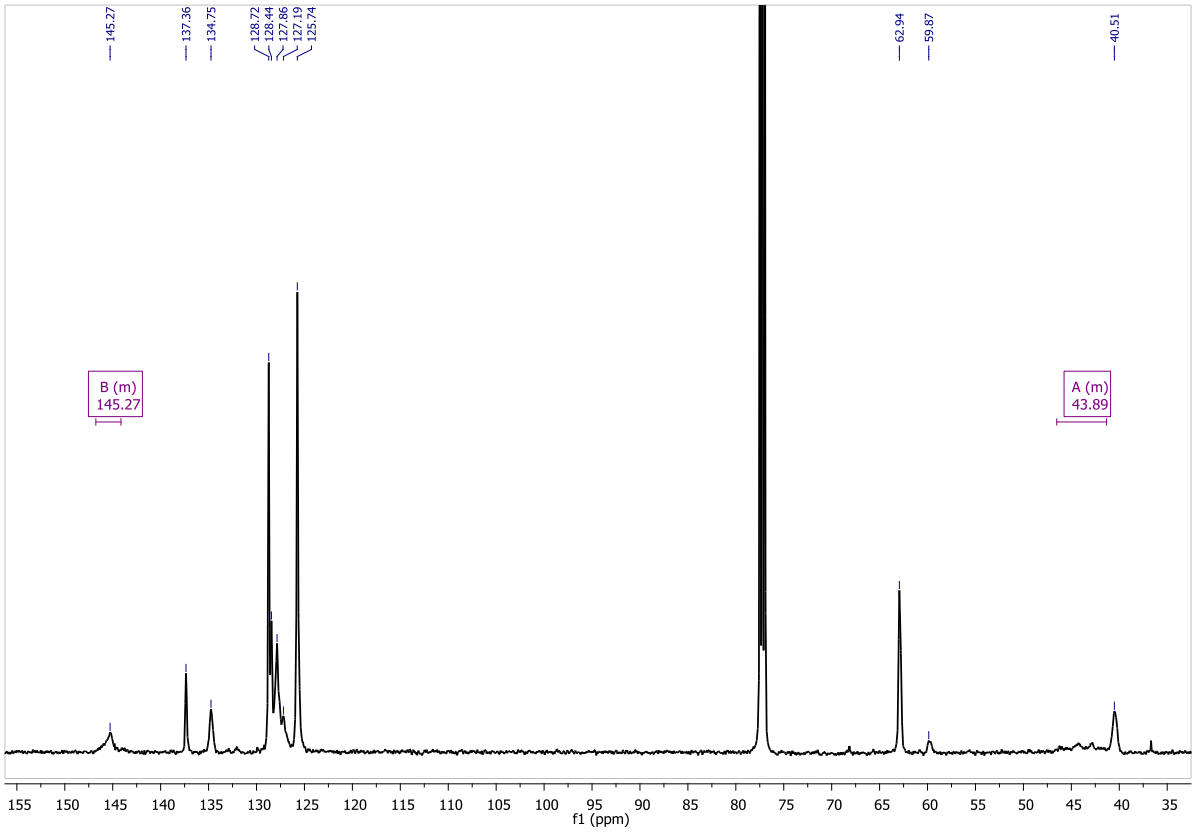

Figure S12 ^{13}C NMR spectrum of polyPh4VPhOx in $CDCl_3$.