Supporting Information

High molecular weight acrylonitrile-butadiene architectures *via* a combination of RAFT polymerization and orthogonal copper mediated azide-alkyne cycloaddition

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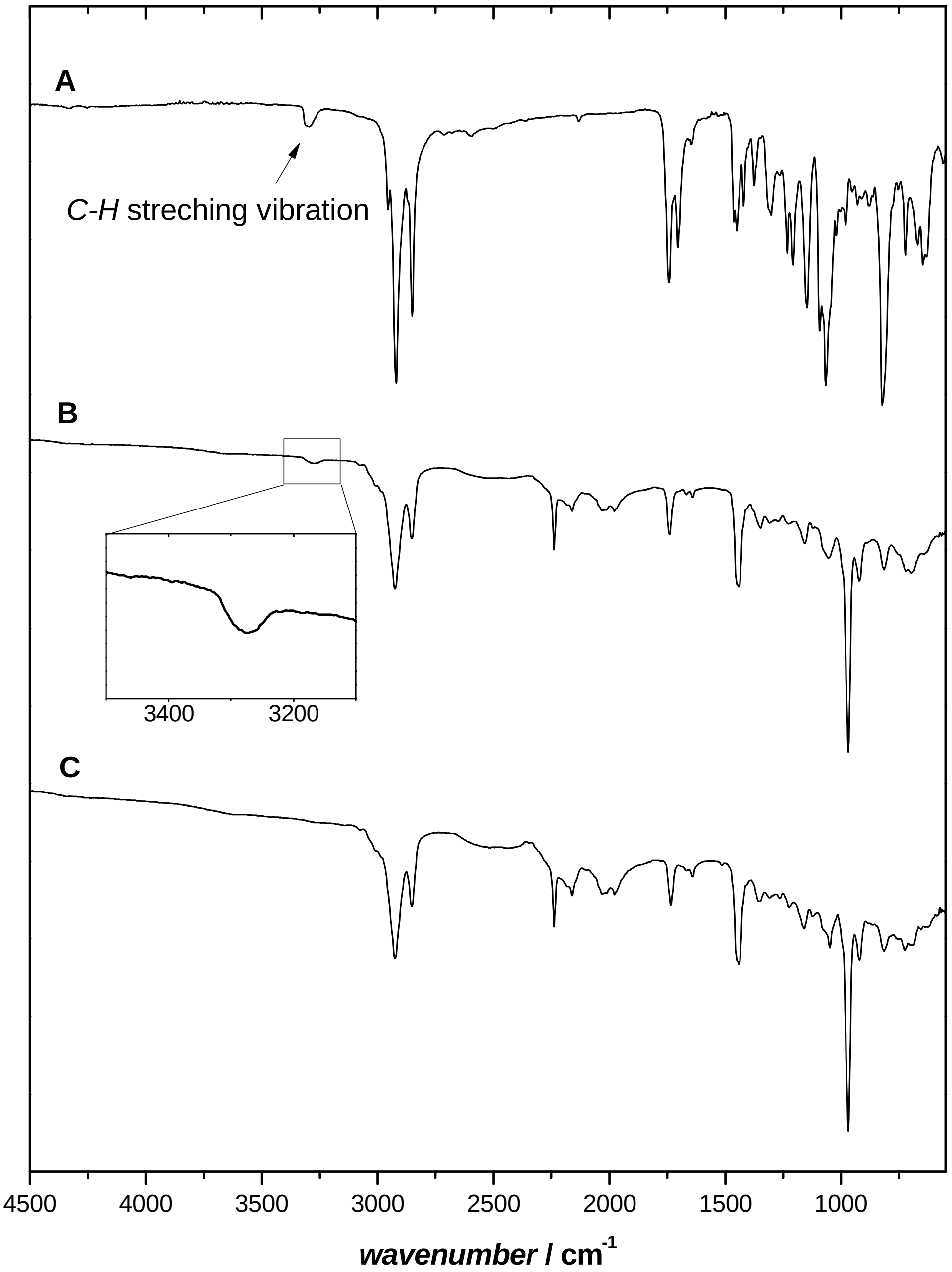


Figure S1. FT-IR spectra of **A**) alkyne functional RAFT agent **2**, **B**) alkyne capped acrylonitrile butadiene copolymer (**3)** and **C**) a comparative sample of a NBR synthesized from DoPAT.

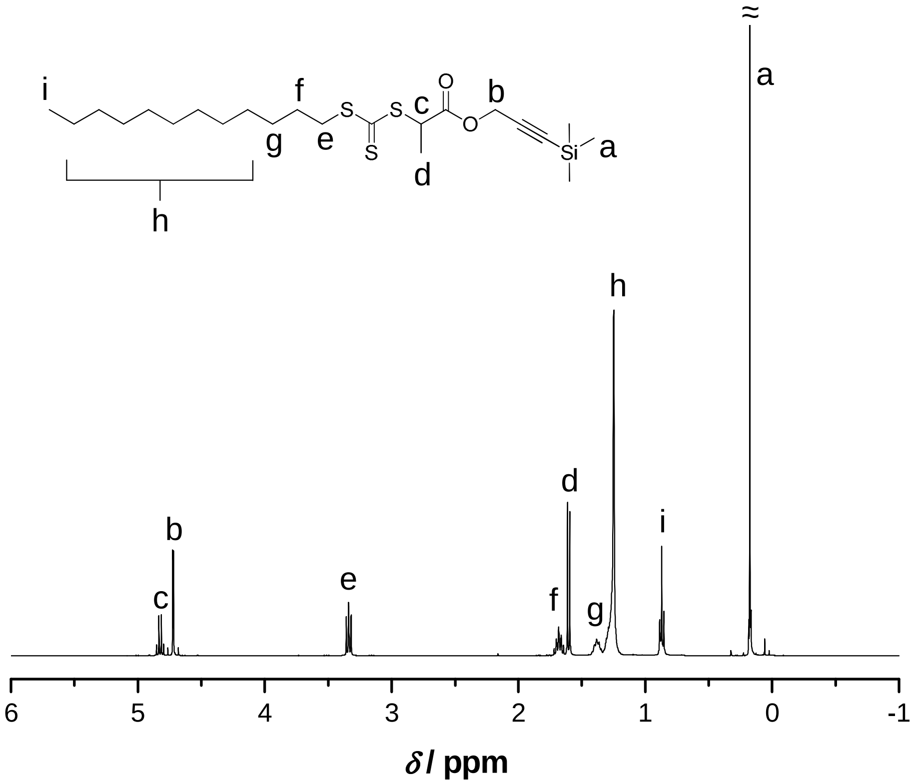


Figure S2. ^{1}H NMR characterization of TMS protected alkyne functional trithiocarbonate **2-TMS**.

Table S1. Experimental details of the 1,3-dipolar cycloaddition reactions of alkyne functional NBR building blocks **3** with 1,4-bis(azidomethyl)benzene (**4**).

Conj. Exp.	**$[3]_0$ ($mg\cdot mL^{-1}$)**	**$[4]_0$ ($mmol\cdot L^{-1}$)**	**[$CuSO_4$·$5H_2O$] ($mmol\cdot L^{-1}$)**	**Coupling product**	***M_n*** **($g\cdot mol^{-1}$)**	***PDI***
1[a]	167	111	29.4	**5a**	2 500	1.1
2[b]	98.0	13.2	31.4	**5b**	10 600	1.3
3[a]	106	8.80	34.7	**5c**	17 400	1.3
4[c]	214	4.05	158	**5d**	72 000	1.6
5	150	1.5	99.7	**5e**	97 000	1.6

Conditions: Reactions were stirred for 16 h in DMF at room temperature. Equimolar amounts of $CuSO_4\cdot 5H_2O$ and sodium ascorbate. [a] Total volume of 300 µL. [b] Total volume of 510 µL. [c] Total volume of 700 µL. [d] Total volume of 1000 µL.

Table S2. Experimental details for the cross-linking experiments of terpolymer **7**.

Cross-linking. Exp.	**n(4) (µmol)**	***r* = n(4):n(7)**	**V_{total} (mL)**	**M_n ($g \cdot mol^{-1}$)**	***PDI***
1	7.69	0.5	0.3	6 300	1.9
2	15.4	1	0.3	9 200	2.7
3	30.8	2	0.5	14 900	4.0
4	76.9	5	1.1	14 200	2.7

Conditions: 60 mg of terpolymer **7**. 3.2 mass-% of $CuSO_4 \cdot 5H_2O$. Addition of **4** from a 77 mM stock solution.

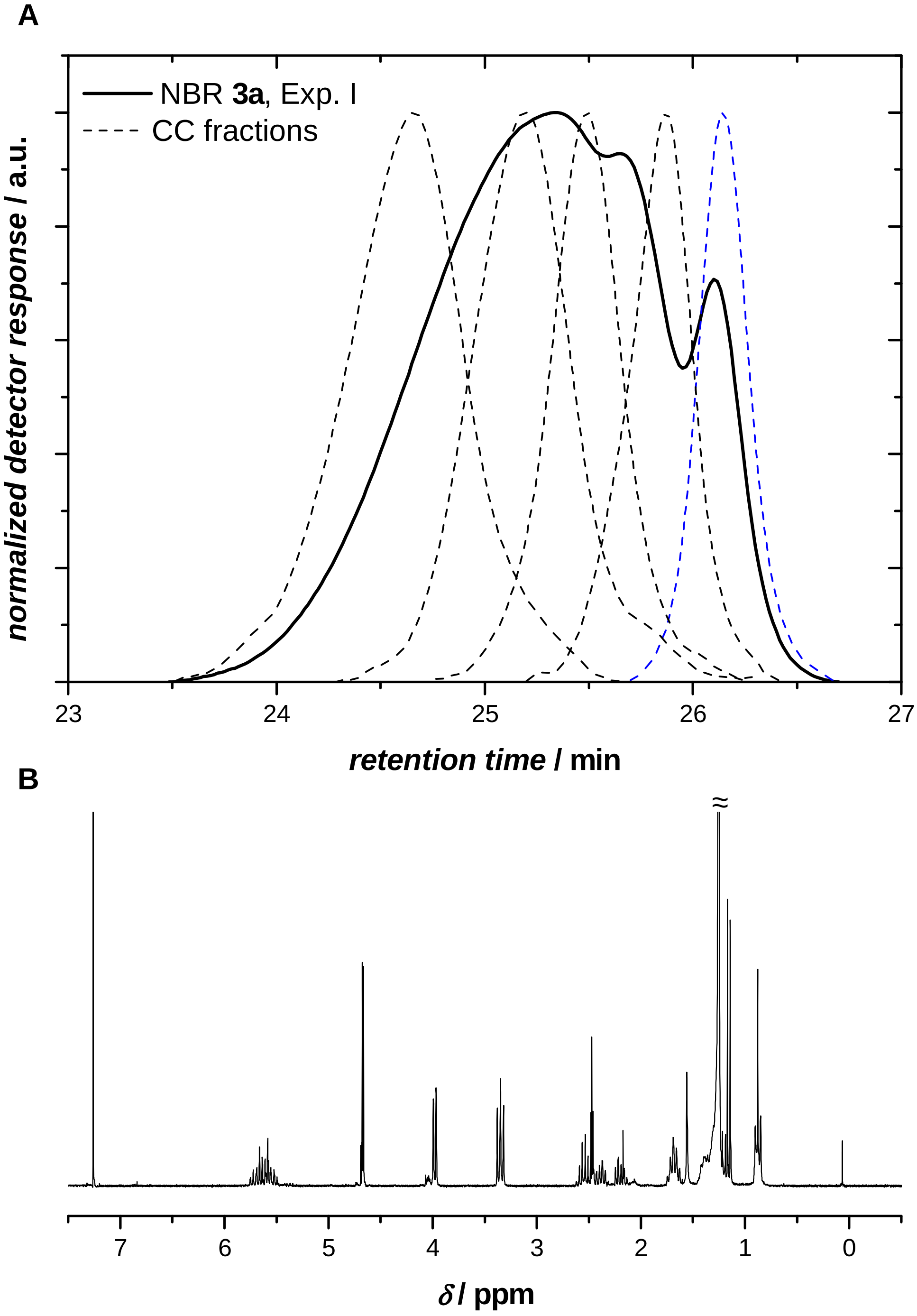
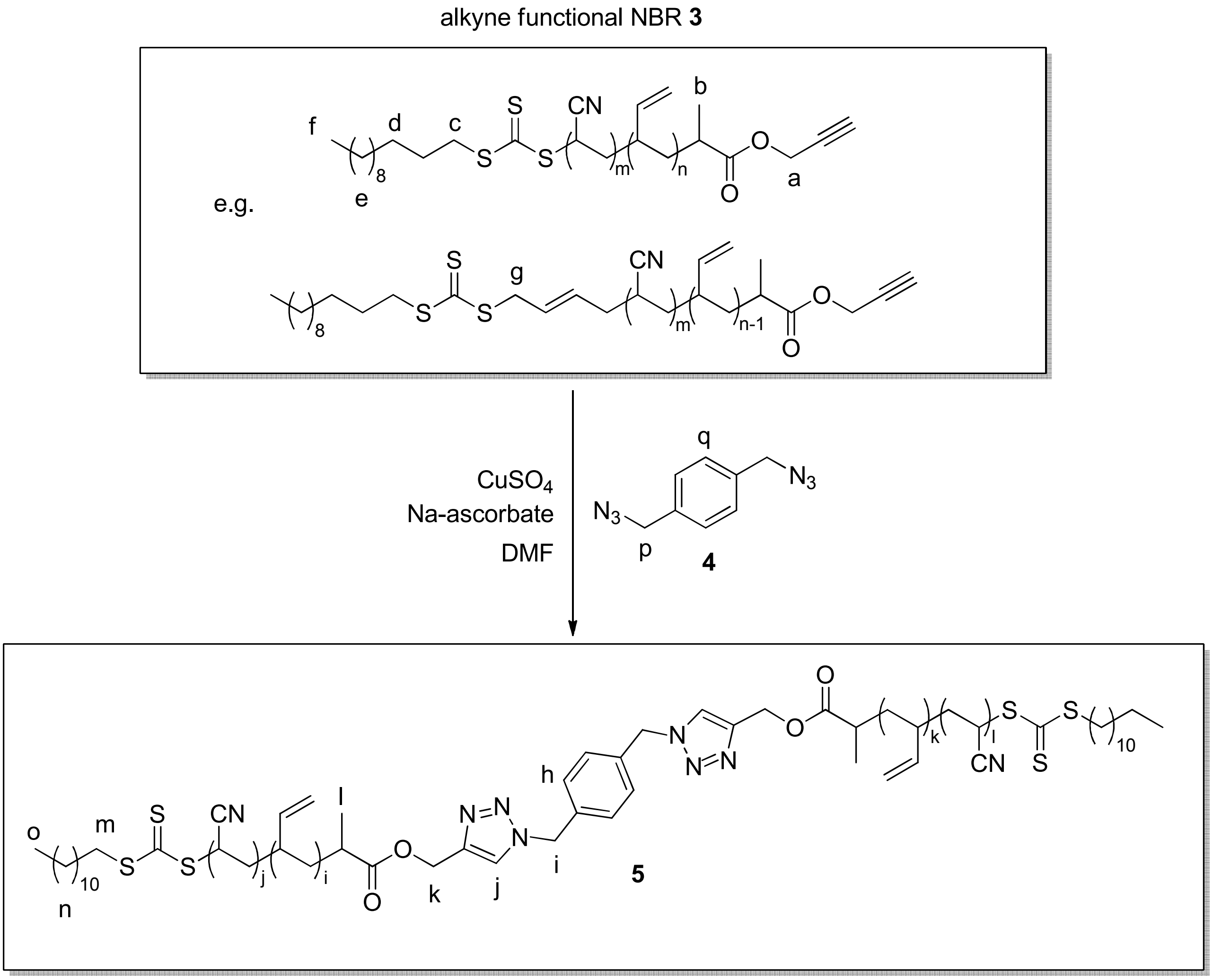


Figure S3. Separation of components of alkyne functional NBR **3a** of 1 000 g·mol^{-1} (Exp. I) by column chromatography (CC) on silica gel in hexane/methylene chloride (1:1). **A**) SEC traces of the polymer as obtained from polymerization (solid line) and several fractions (dashed lines) after separation. **B**) ^{1}H NMR spectrum of the first fraction eluting from the column (blue curve), M_n 500 g·mol^{-1} and *PDI* 1.02.



Scheme S1. Coupling of two alkyne functional NBR building blocks *via* CuAAC upon addition of 1,4-bis(azidomethyl)benzene (**4**). Lower case letters are provided for the facile assignment of ^{1}H NMR resonances (see **Figure S4**) to the respective protons.

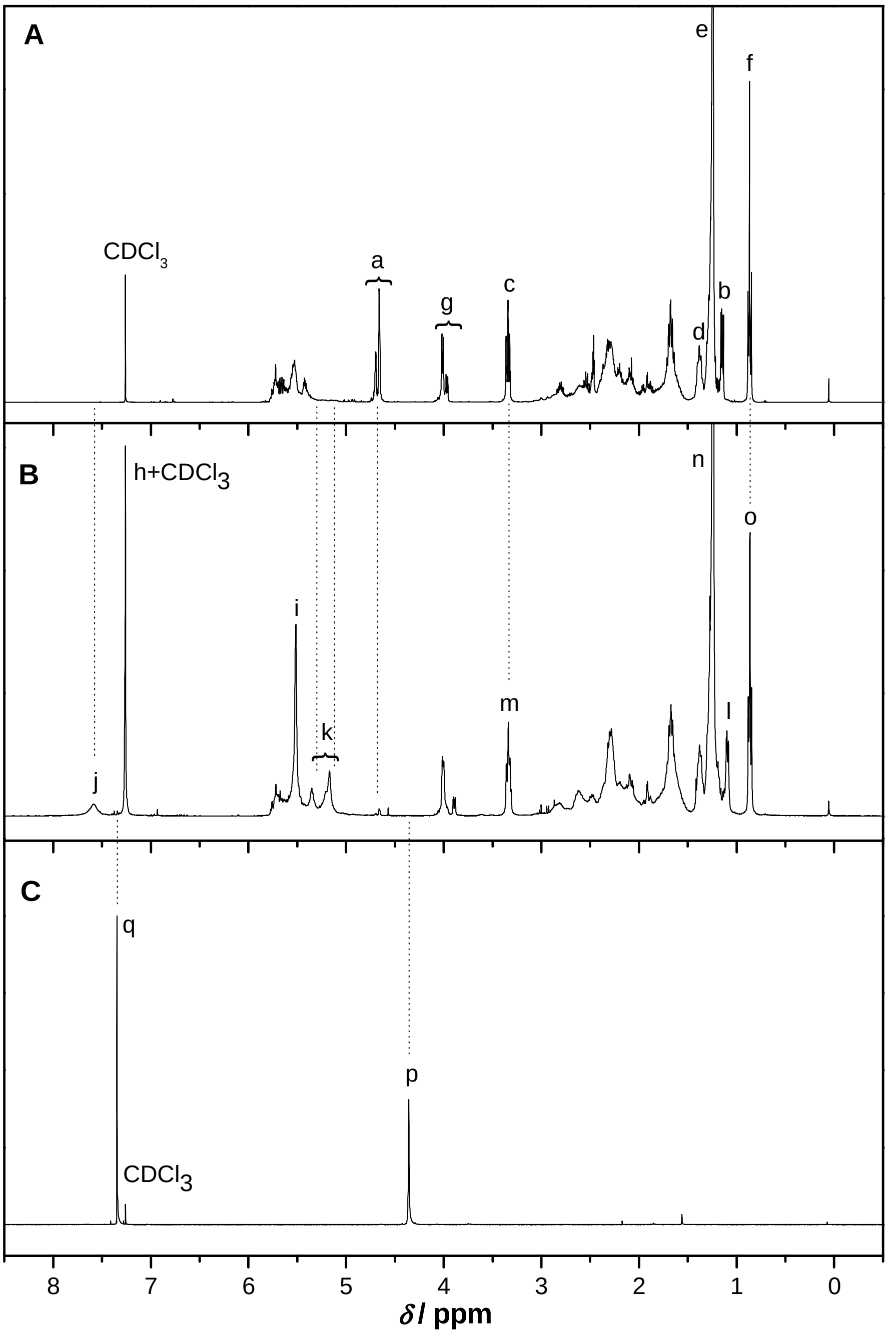


Figure S4. Molecular verification of the triazole moiety as the linking structure within the coupled polymer building blocks *via* ambient temperature ^{1}H NMR spectroscopic analysis in $CDCl_3$. For comparison, ^{1}H NMR spectra of **A**) a linear alkyne functional NBR **3a** of 1 000 g·mol^{-1}, **B**) long-chain polymer **5a** (M_n 2 500 g·mol^{-1}) obtained from coupling these *via* addition of 1,4-bis(azidomethyl)benzene (**4**) in presence of copper sulfate and sodium ascorbate and **C**) the linking agent 1,4-bis(azidomethyl)benzene (**4**) are depicted. Lower-case letters are provided for peak assignments and can be found in **Scheme S1**.

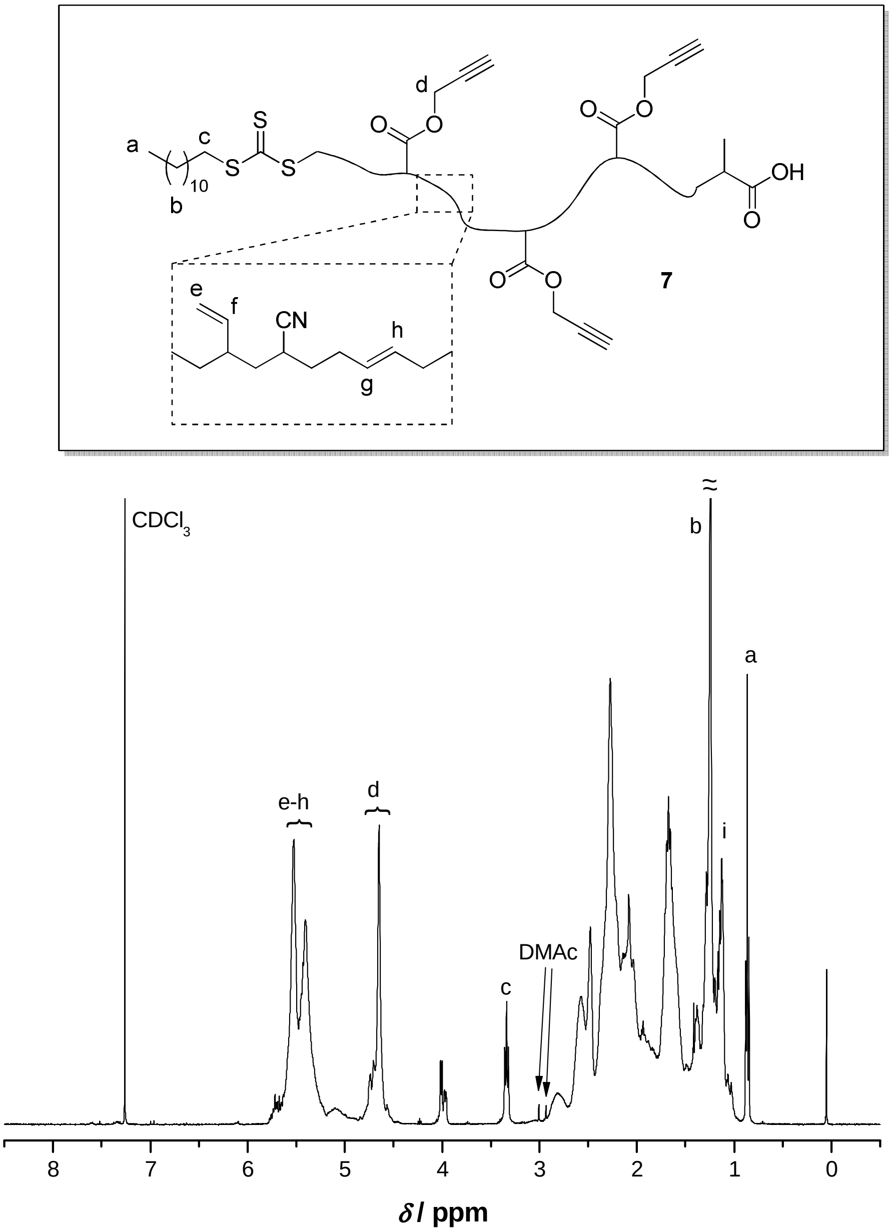


Figure S5. ^{1}H NMR characterization (CDCl$_3$) of a 3 900 g·mol^{-1} terpolymer **7** synthesized in a DoPAT (**1**)-mediated polymerization of acrylonitrile, 1,3-butadiene and prop-2-ynyl methacrylate within 5 h at 100 °C, using 1,1'-azobis(cyclohexane-1-carbonitrile) as the initiator and *N*,*N*-dimethylacetamide (DMAc) as the solvent.

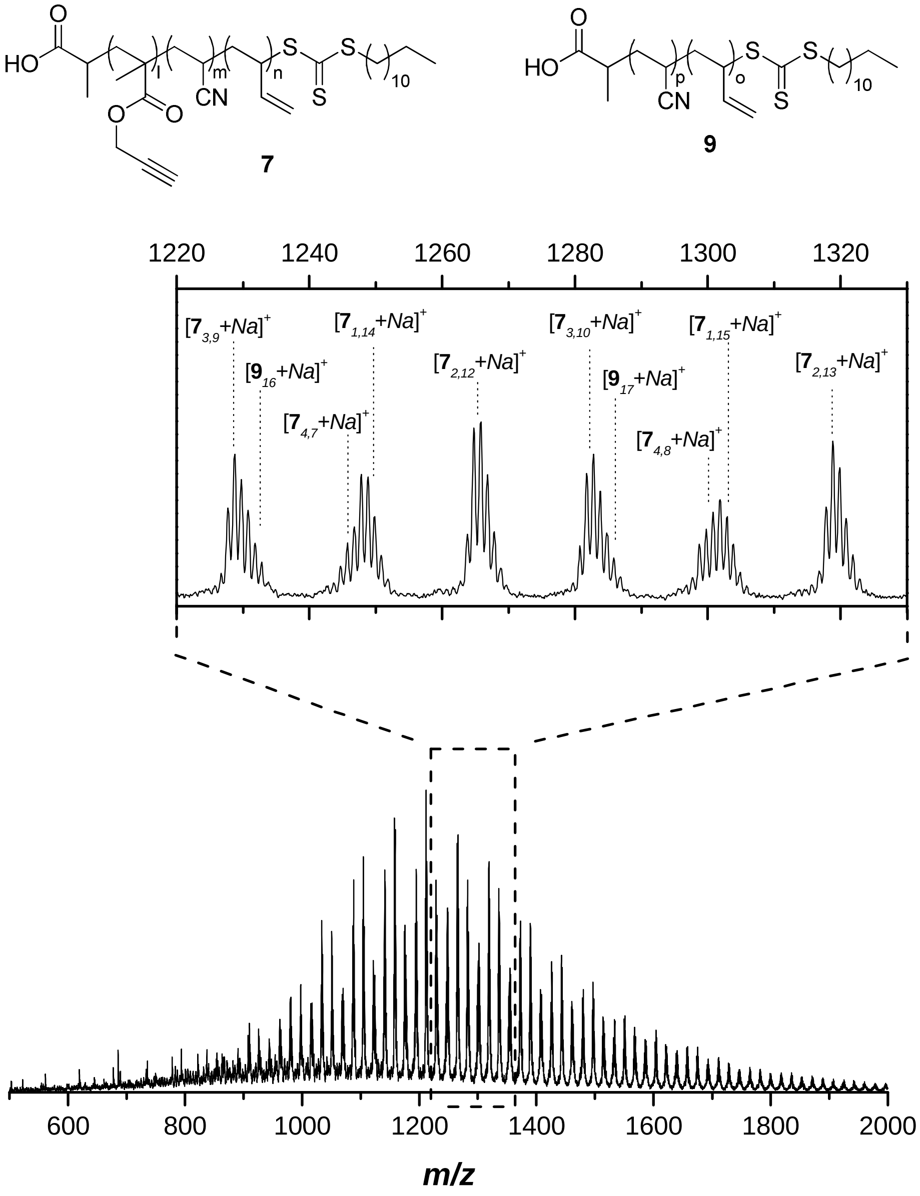


Figure S6. SEC-ESI-MS characterization of terpolymer **7**. An integral over a section of single charged species is provided, showing the typical NBR signal structure resulting from the superposition of the isotopic pattern of macromolecules with similar overall amount of acrylonitrile/butadiene repeating units yet different acrylonitrile/butadiene ratios. The main signals are assigned to the sodium adducts of the terpolymer $[\mathbf{7}_{(l,m+n)}+Na]^{+}$. For statistical reason, a distinct amount of sodium adducts of polymer strands without propargyl methacrylate incorporation $[\mathbf{9}_{(o+p)}+Na]^{+}$ is observed.

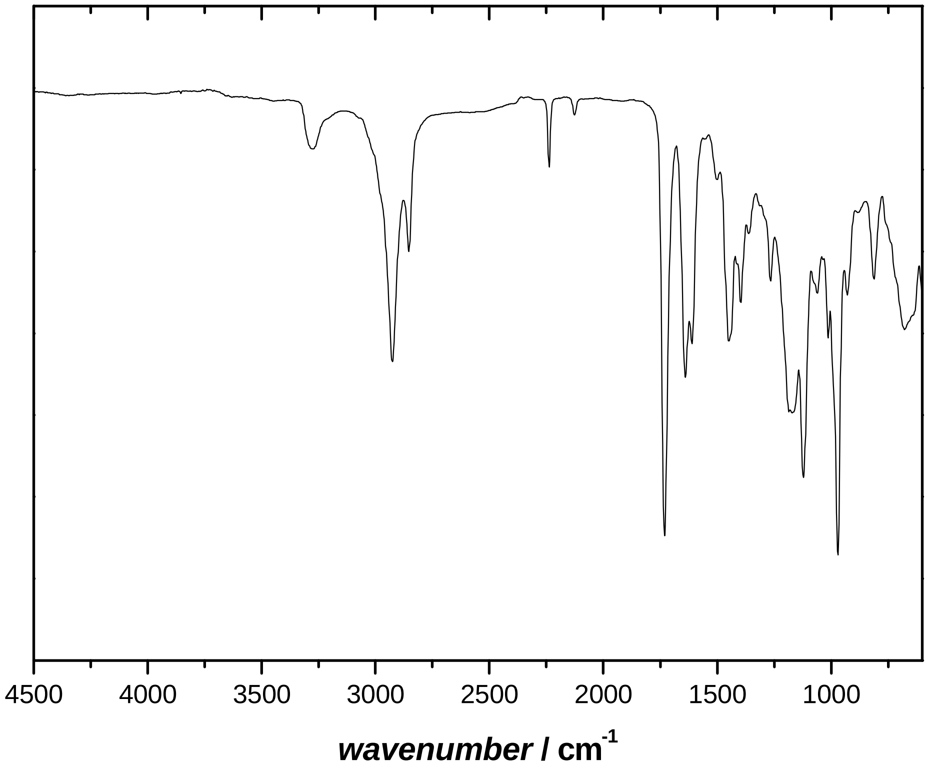


Figure S7. FT-IR spectrum of a 3 900 g·mol^{-1} terpolymer **7** synthesized in a DoPAT (**1**)-mediated polymerization of acrylonitrile, 1,3-butadiene and prop-2-ynyl methacrylate within 5 h at 100 °C, using 1,1'-azobis(cyclohexane-1-carbonitrile) as the initiator and *N*,*N*-dimethylacetamide (DMAc) as the solvent.

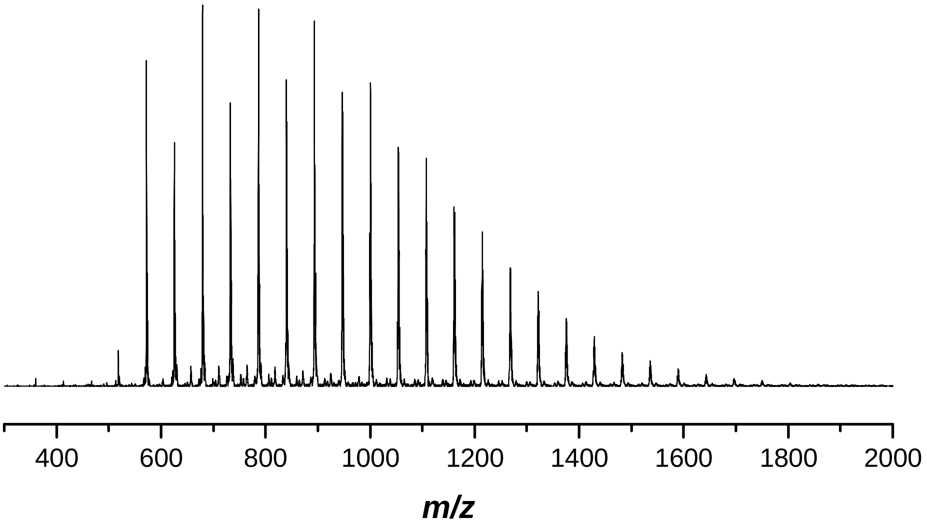


Figure S8. Full ESI mass spectrum of 1 000 g·mol^{-1} alkyne-functional acrylonitrile-butadiene copolymer **3a**.

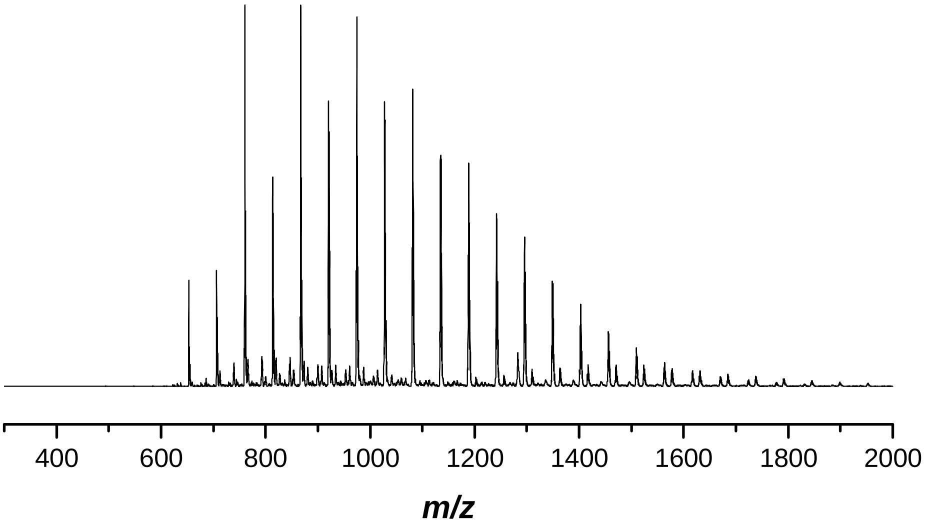


Figure S9. Full ESI mass spectrum of alkyne functional NBR **3a** after reacting with an excess of **4**, resulting in on-sided cycloaddtion product (**3a+4**). M_n 1 400 g·mol^{-1}, *PDI* 1.2.

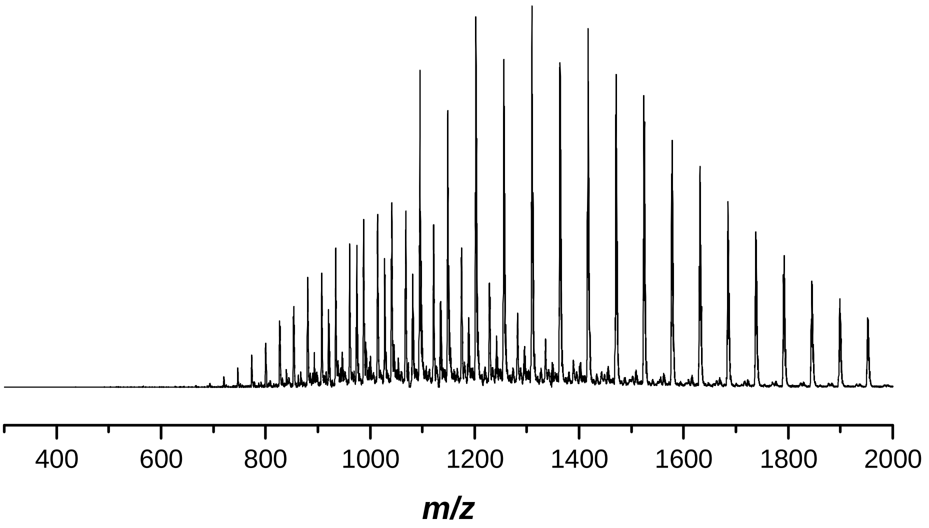


Figure S10 Full ESI mass spectrum of 2 500 g·mol^{-1} coupled acrylonitrile-butadiene rubber **5a**.