Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Efficient click-addition sequence for polymer-polymer couplings

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NMR spectra of polymerization solutions

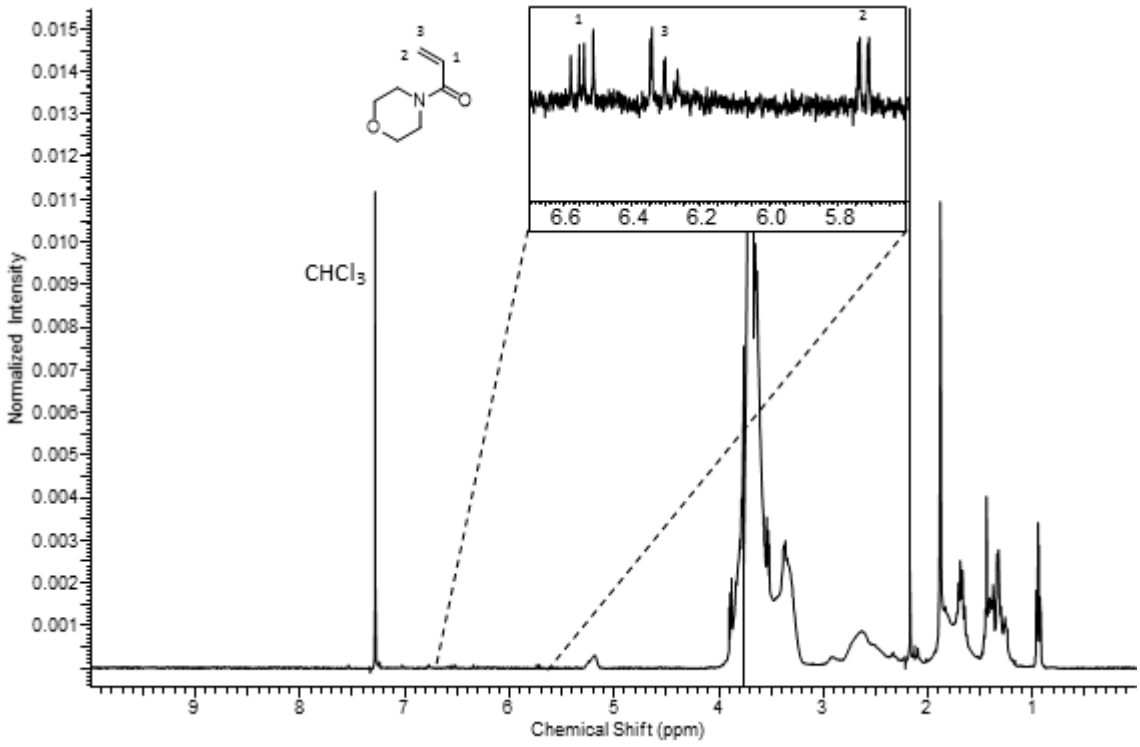


Figure S 1. NMR sample taken out of polymerization mixture for sample $pNAM_{10}$.

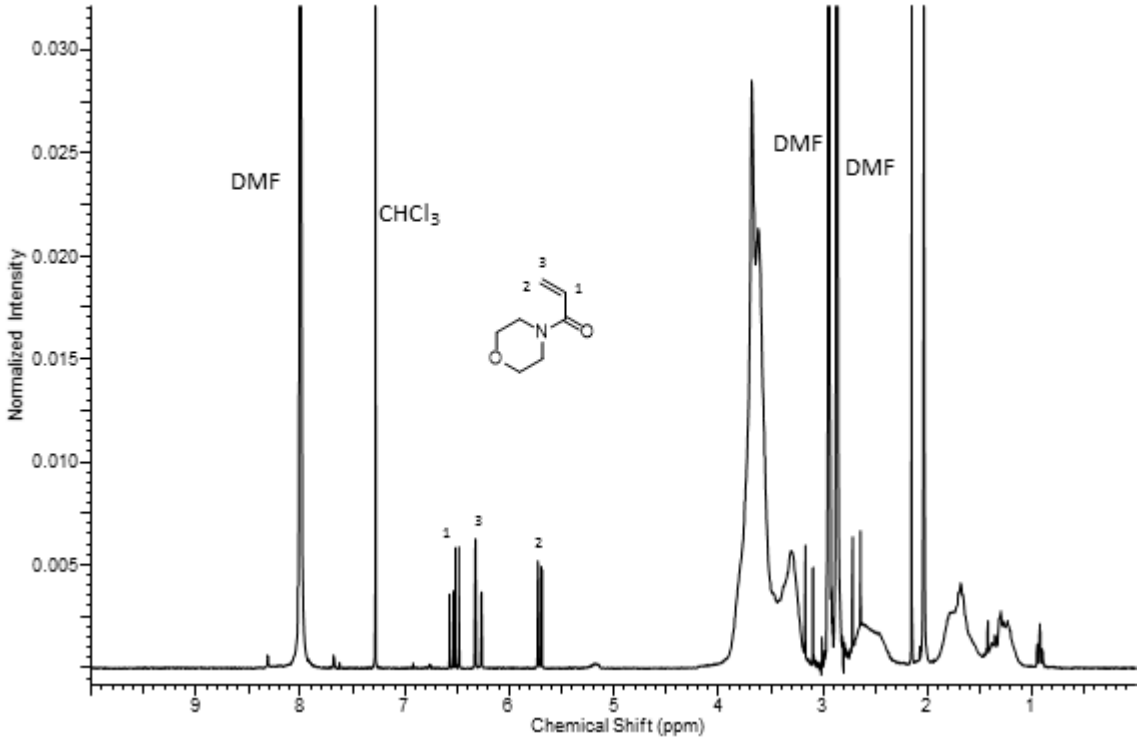


Figure S 2. NMR sample taken out of polymerization mixture for sample $pNAM_{37}$.

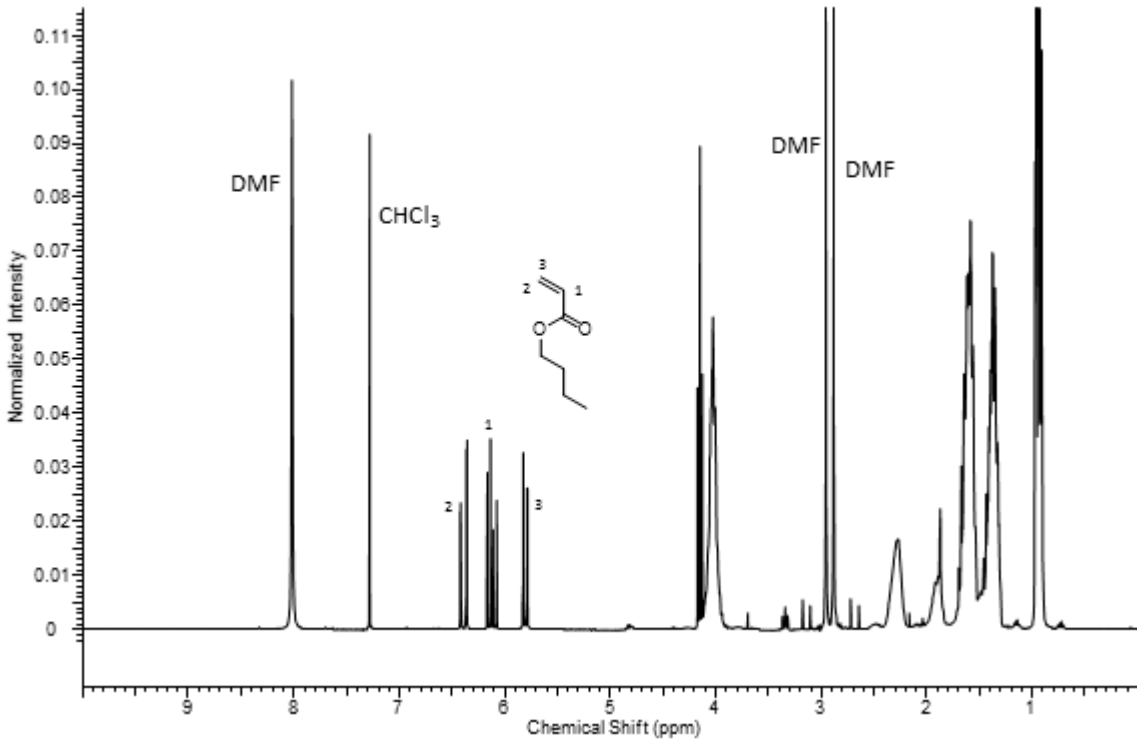


Figure S 3. NMR sample taken out of polymerization mixture for sample pBA_{42}.

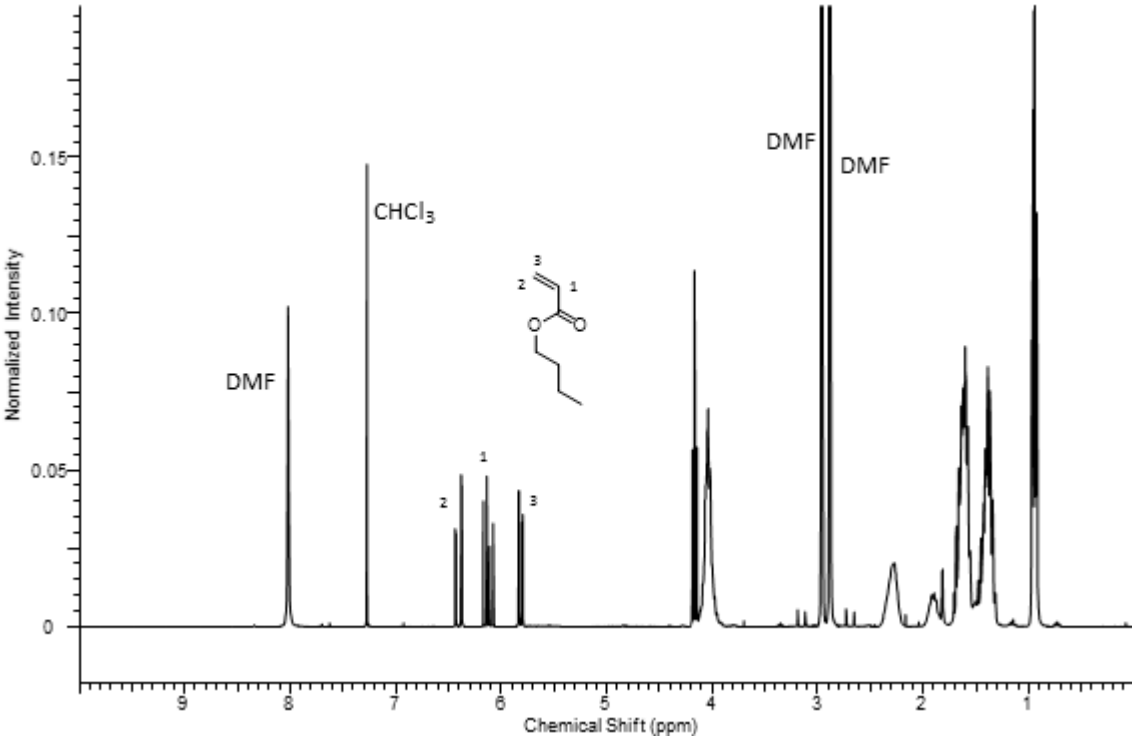


Figure S 4. NMR sample taken out of polymerization mixture for sample pBA_{206}.

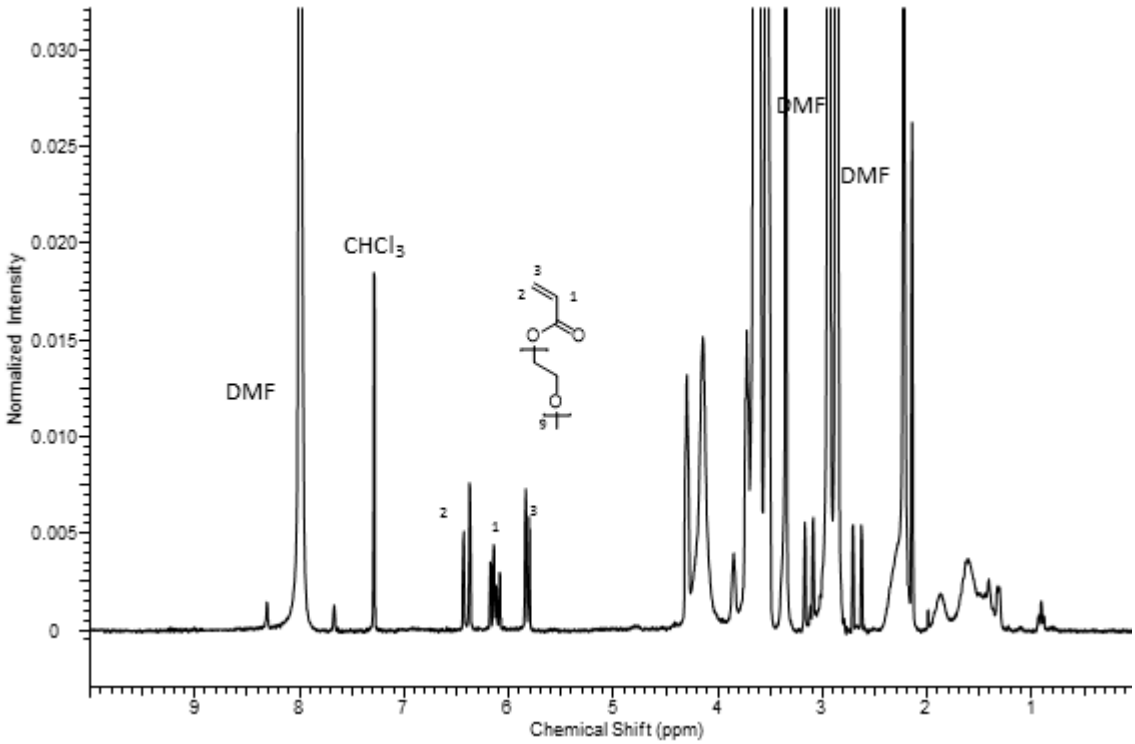


Figure S 5. NMR sample taken out of polymerization mixture for sample $pPEGA_{38}$.

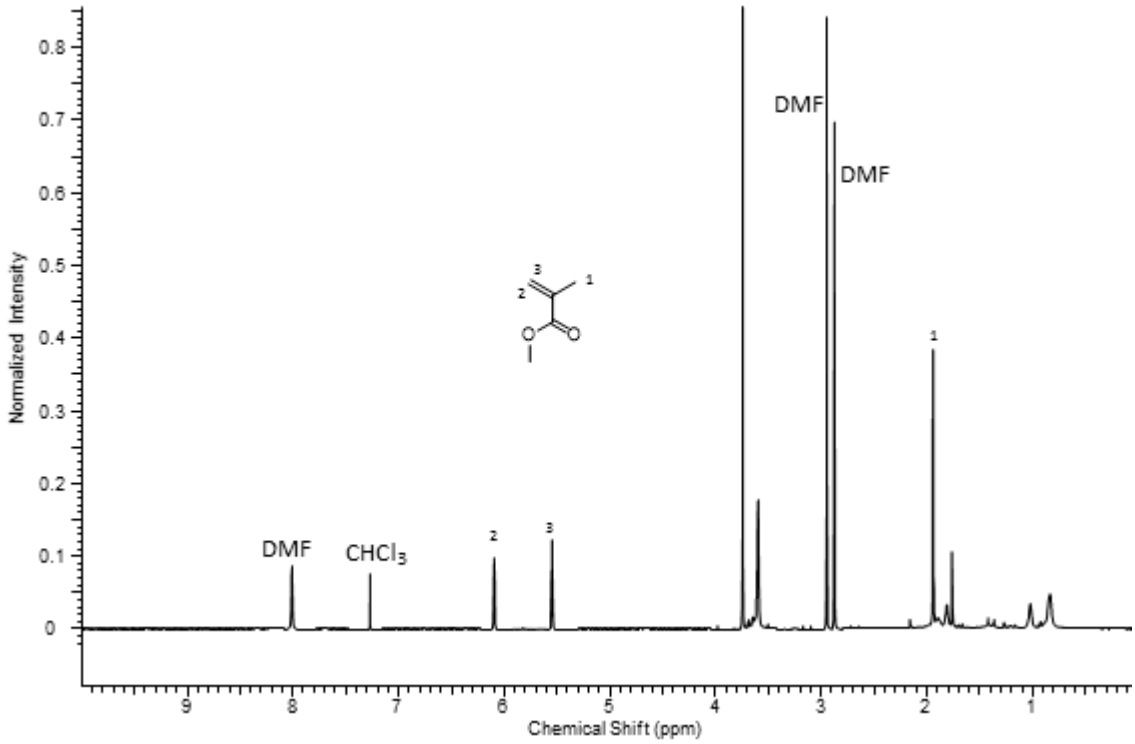


Figure S 6. NMR sample taken out of polymerization mixture for sample $pMMA_{27}$.

Electron spray ionisation-time of flight (ESI-ToF) measurements

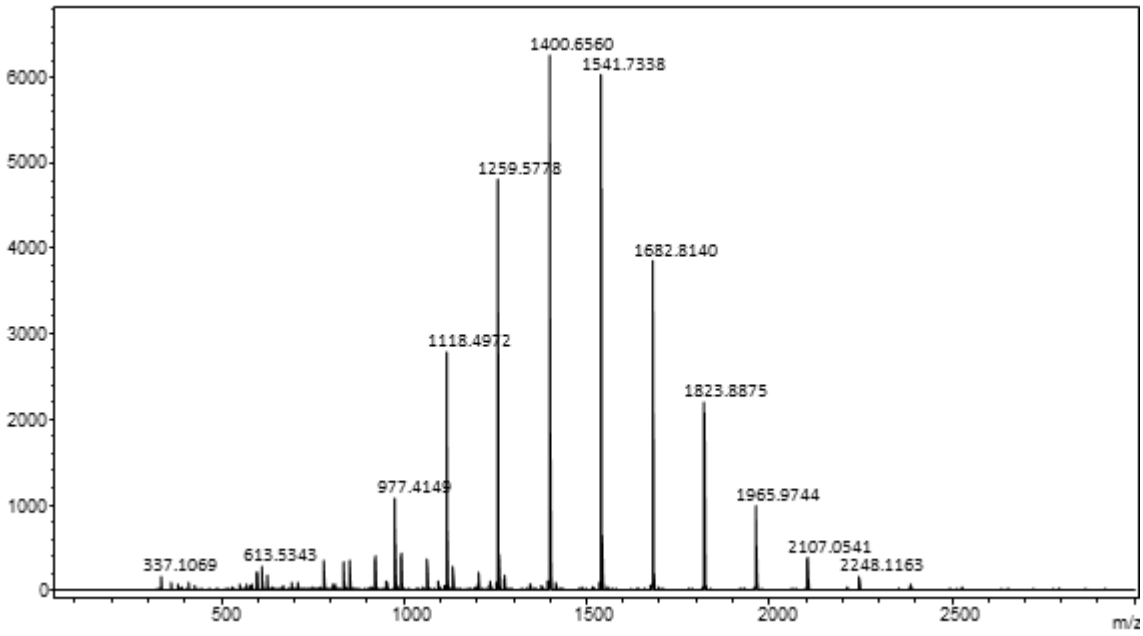


Figure S 7. Full ESI-ToF spectrum of the initial isocyanate modified polymer ($pNAM_{10}$-NCO).

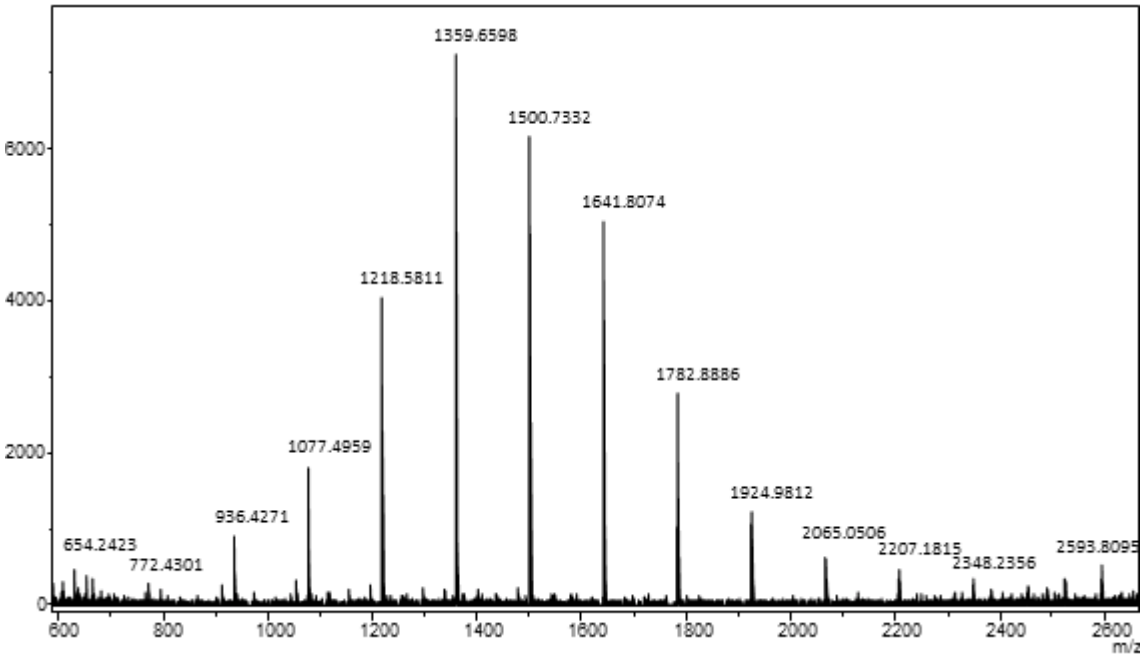


Figure S 8. Full ESI-ToF spectrum of the azido modified polymer ($pNAM_{10}$-N_3).

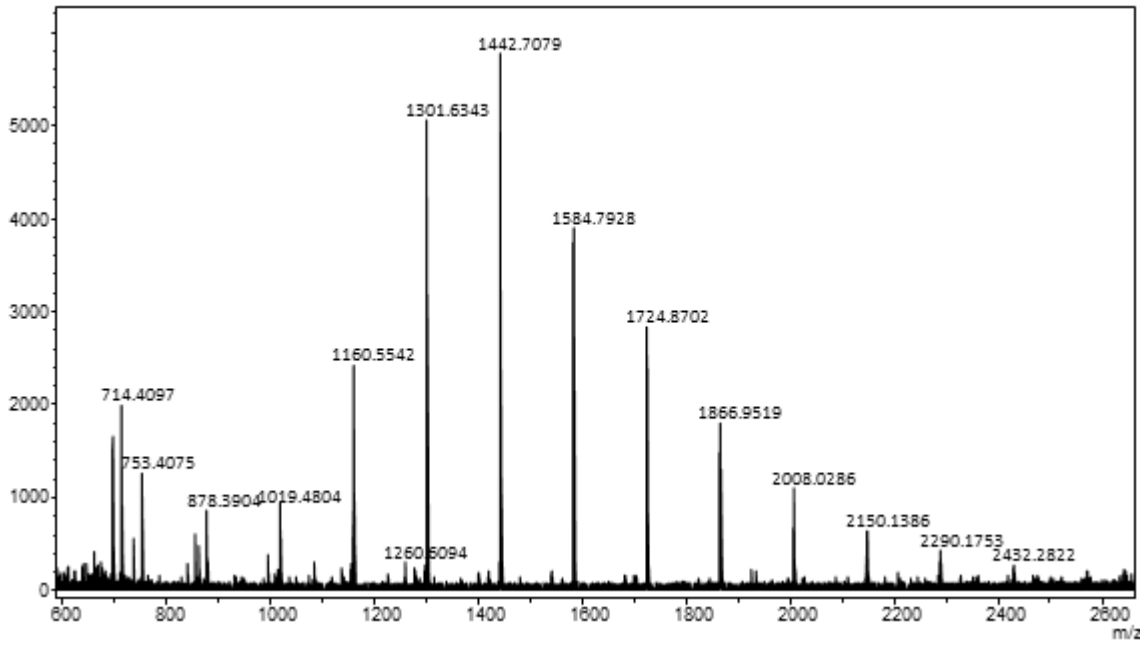


Figure S 9. Full ESI-ToF spectrum of the BCN modified polymer ($pNAM_{10}$-BCN).

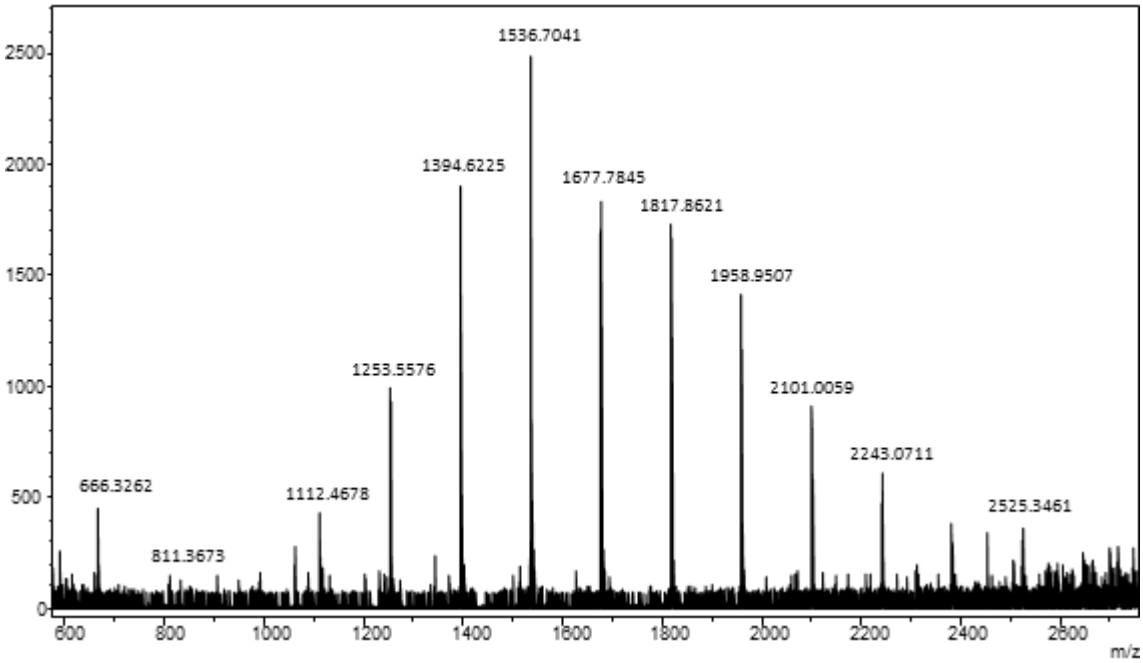


Figure S 10. Full ESI-ToF spectrum of the DBCO modified polymer ($pNAM_{10}$-DBCO).

NMR spectra of the amine-isocyanate reaction on $pNAM_{10}$

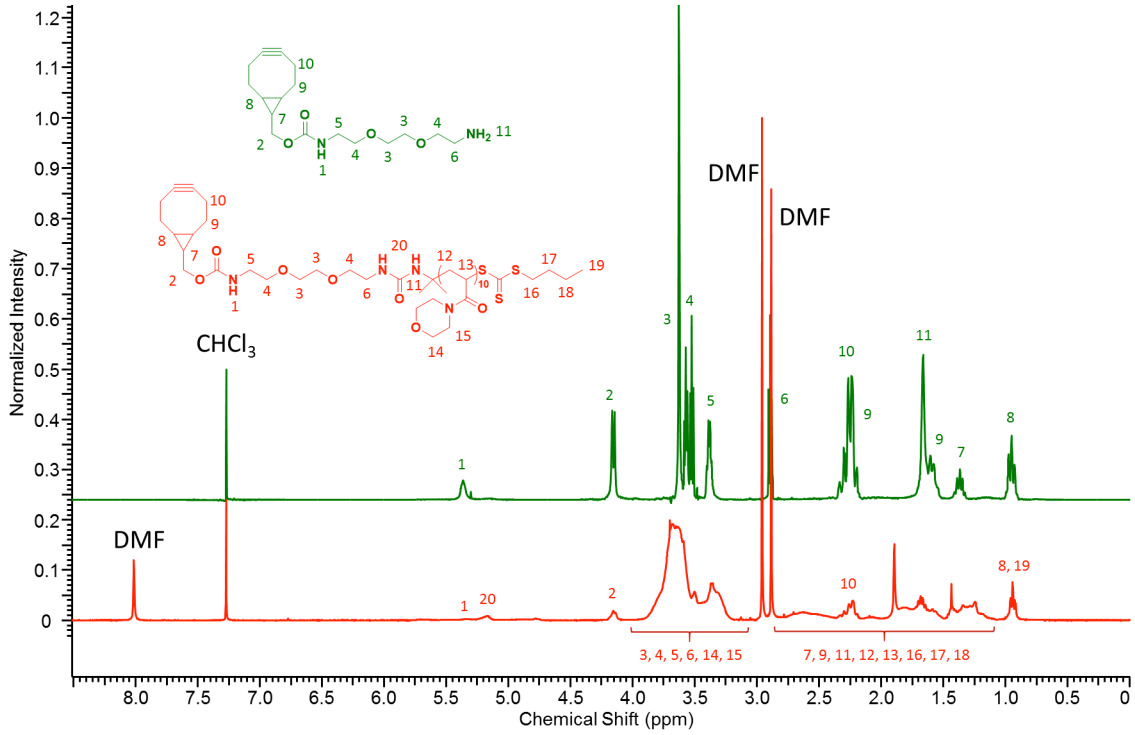


Figure S 11. NMR spectrum of a sample taken out of the reaction mixture (red) with $pNAM_{10}$-NCO and the amine BCN-NH_2 after 4h. The NMR spectrum of the pure BCN-NH_2 (green) is given as a reference.

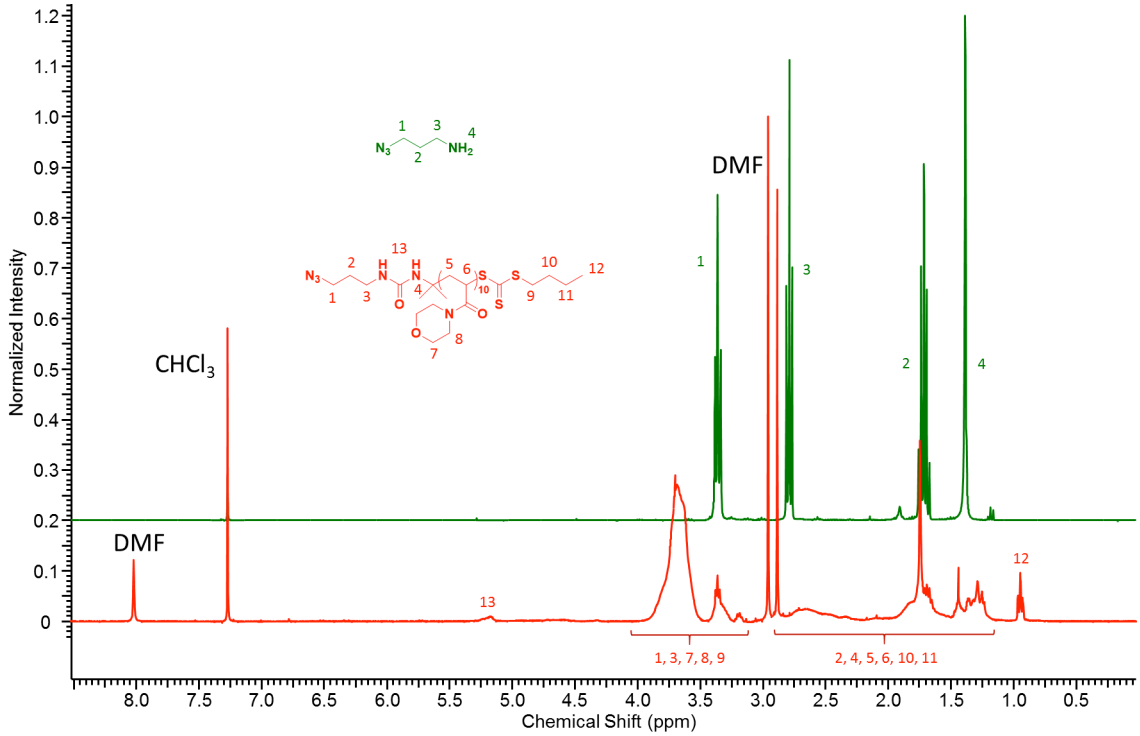


Figure S 12. NMR spectrum of a sample taken out of the reaction mixture (red) with $pNAM_{10}$-NCO and azidopropylamine after 4h. The NMR spectrum of the pure azidopropylamine (green) is given as a reference.

FT-IR spectra of amine-isocyanate reaction on $pNAM_{10}$ and the homocoupling

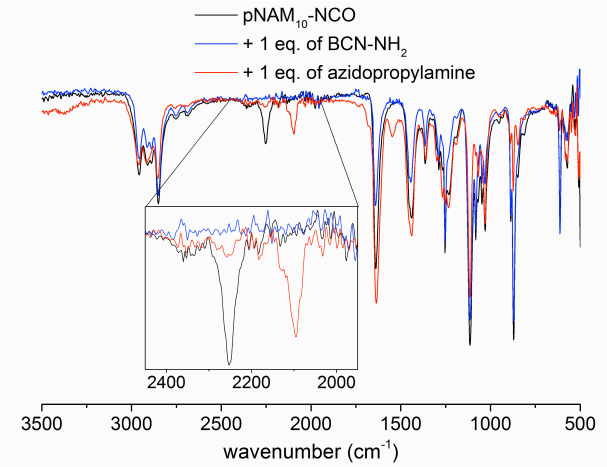


Figure S 13. FT-IR spectra of the starting material $pNAM_{10}$-NCO (black), the product after addition of 1 equivalent of BCN-NH_2 (blue), and the product after addition of 1 equivalent of azidopropylamine (red). In both cases the characteristic signal for the isocyanate at 2250 cm^{-1} disappears and for the product with azidopropylamine a new signal at 2095 cm^{-1} is detected which is characteristic for azide groups.

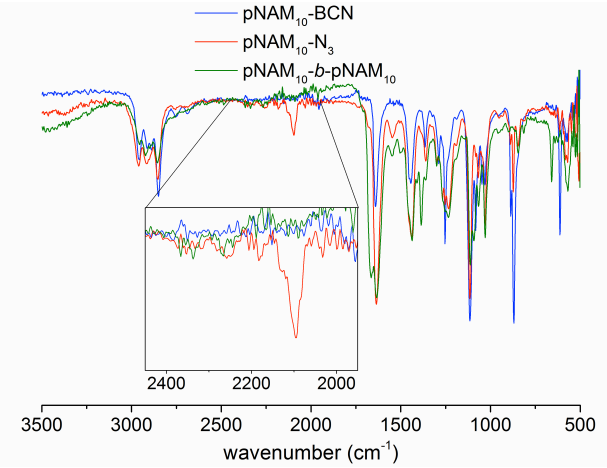


Figure S 14. FT-IR spectra of the SPAAC between $pNAM_{10}$-BCN (blue) and $pNAM_{10}$-N_3 (red). The characteristic signal for the azide at 2095 cm^{-1} disappears after 4h of reaction (green).

Raw RI signals and number distribution plots of homocouplings

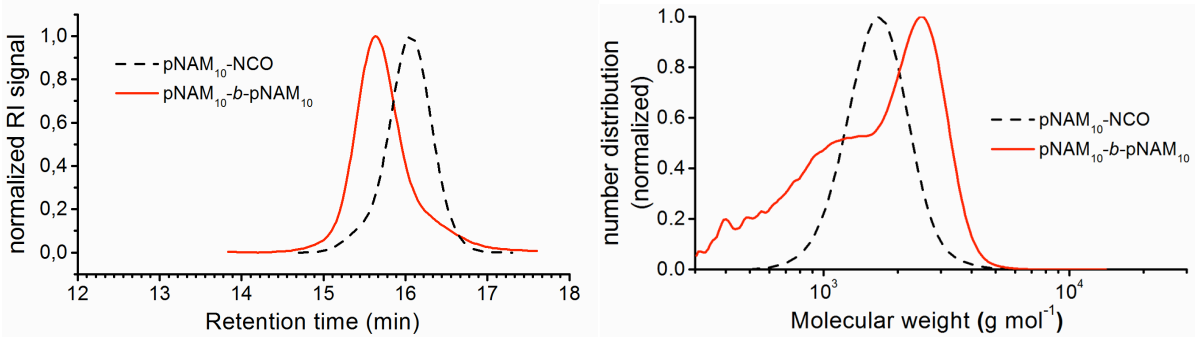


Figure S 15. Normalized RI traces (left) and number distribution plot (right) of the initial precursors (dashed line) and the homocoupling (solid line) of $pNAM_{10}$-NCO combining equal amounts of the polymers modified with exactly one equivalent of azidopropylamine or DBCO-NH_2, respectively.

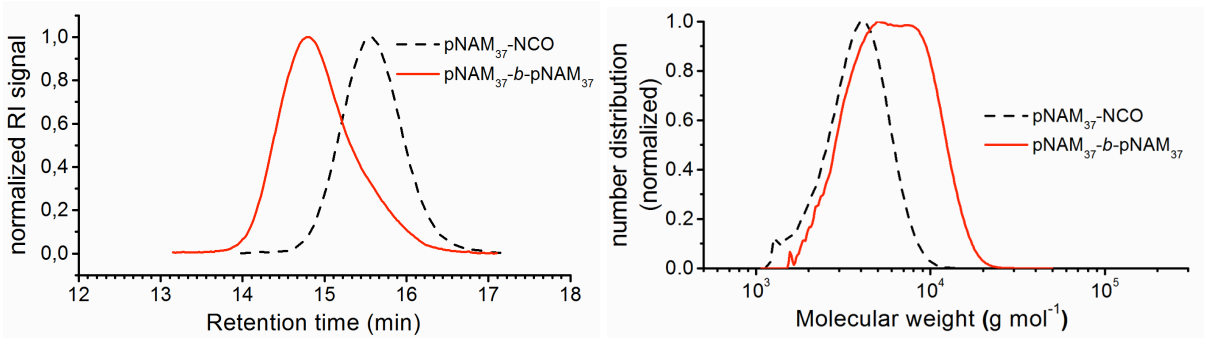


Figure S 16. Number distribution plot of the initial precursors (dashed line) and the homocoupling (solid line) of $pNAM_{37}$-NCO combining equal amounts of the polymers modified with exactly one equivalent of azidopropylamine or DBCO-NH_2, respectively.

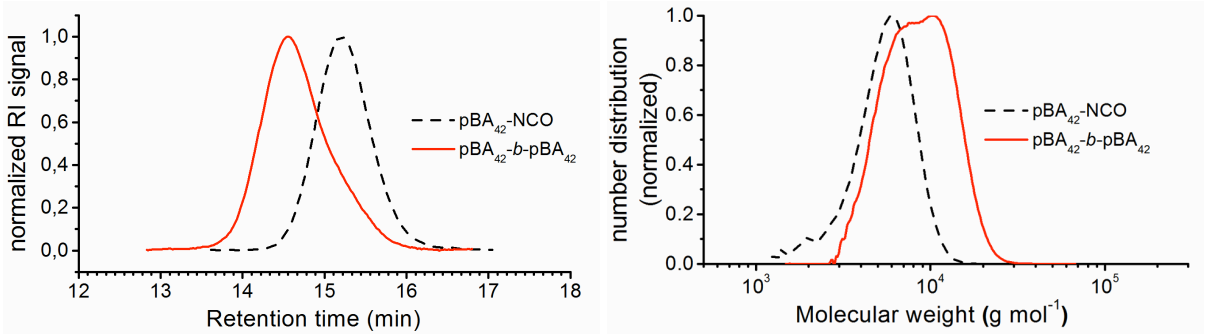


Figure S 17. Normalized RI traces (left) and number distribution plot (right) of the initial precursors (dashed line) and the homocoupling (solid line) of pBA_{42}-NCO combining equal amounts of the polymers modified with exactly one equivalent of azidopropylamine or DBCO-NH_2, respectively.

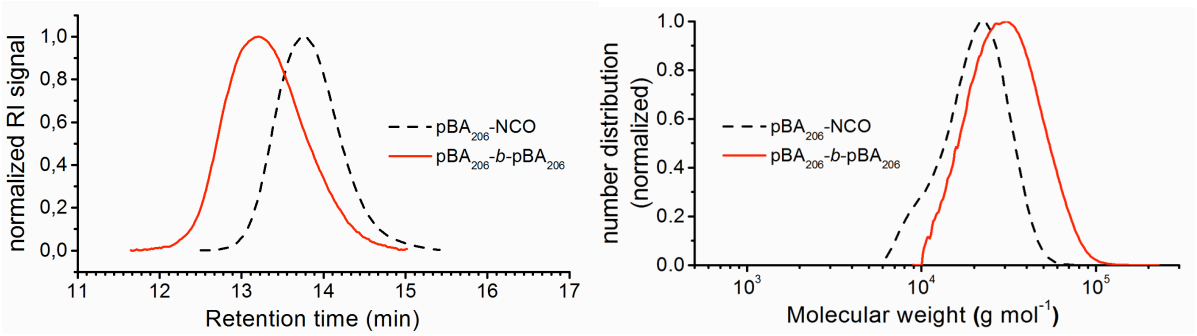


Figure S 18. Normalized RI traces (left) and number distribution plot (right) of the initial precursors (dashed line) and the homocoupling (solid line) of pBA_{206}-NCO combining equal amounts of the polymers modified with exactly one equivalent of azidopropylamine or DBCO-NH_2, respectively.

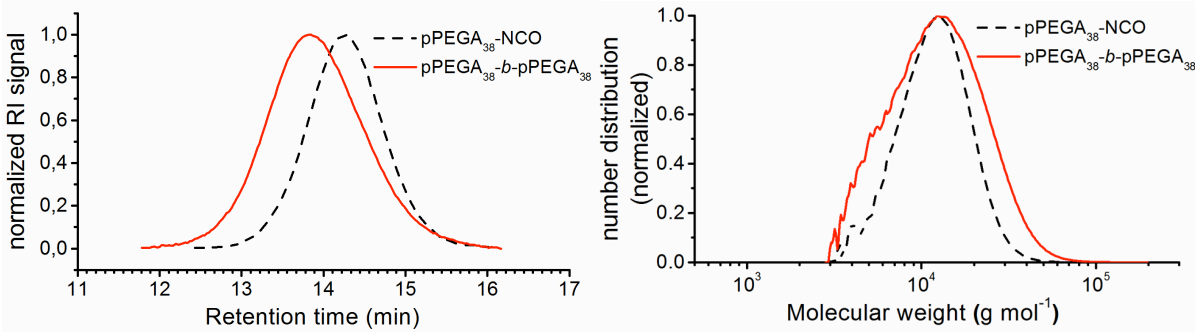


Figure S 19. Normalized RI traces (left) and number distribution plot (right) of the initial precursors (dashed line) and the homocoupling (solid line) of $pPEGA_{38}$-NCO combining equal amounts of the polymers modified with exactly one equivalent of azidopropylamine or DBCO-NH_2, respectively.

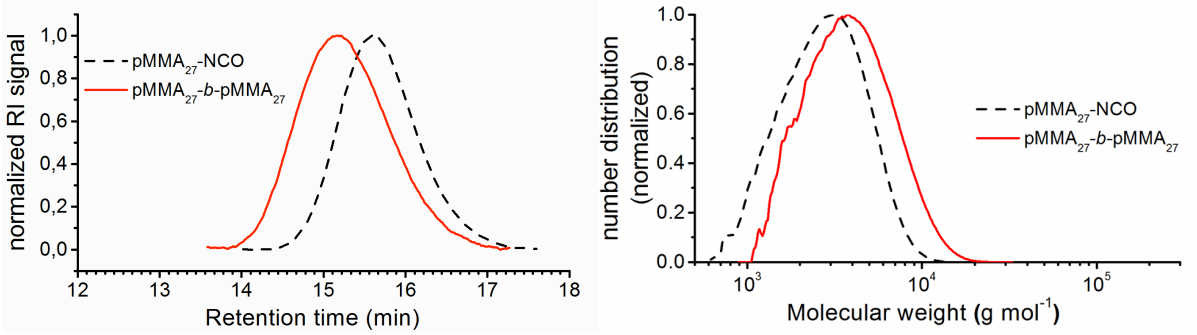


Figure S 20. Normalized RI traces (left) and number distribution plot (right) of the initial precursors (dashed line) and the homocoupling (solid line) of $pMMA_{27}$-NCO combining equal amounts of the polymers modified with exactly one equivalent of azidopropylamine or DBCO-NH_2, respectively.

Deconvolutions of homocouplings

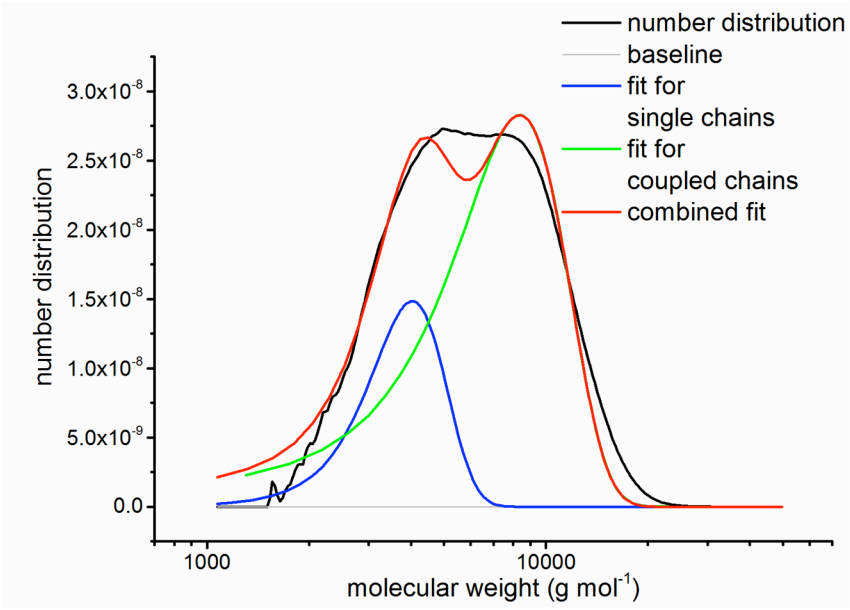
Although Poisson distributions are accepted models of molecular weight distributions (number distribution) obtained by living polymerization, they are typically limited excellently controlled polymerizations and the resulting very narrow dispersities ($Đ$ < 1.05). For controlled radical polymerization techniques, Gaussian distributions are a good approximation which takes into account the broadening of the molecular weight due to side reaction of irreversible transfer and termination. In order to quantify the efficiency of the coupling reactions, the number distribution obtained by SEC was deconvoluted using Gaussian curves. The position of the initial starting material (single chains) was determined from the number distribution plots of the SEC traces of the polymerization solutions.

The percentage of coupled chains or the efficiency of the coupling was determined using equation 1:

$$\%\ coupled\ polymer\ chains = \frac{\%\ Area\ coupled\ chains * 2}{\%\ Area\ coupled\ chains * 2 + \%\ Area\ single\ chains} \times 100 \qquad (1)$$

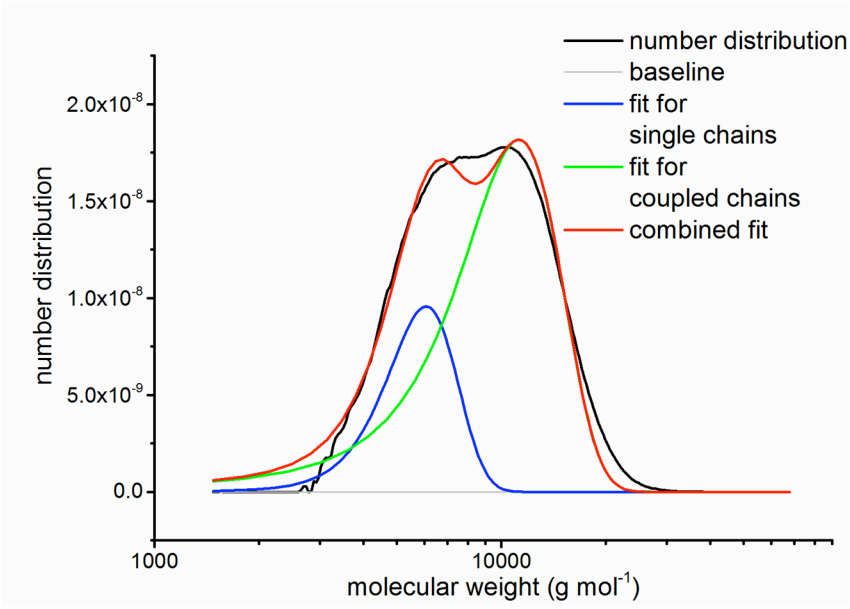
Table S 1. Fitted percentage peak areas for single and coupled chains and the resulting coupling efficiencies for the homocoupling reactions.

sample	area (%) single chains	area (%) coupled chains	coupling efficiency
$pNAM_{37}$	85	15	92%
pBA_{42}	83	17	91%
pBA_{206}	83	17	91%
$pPEGA_{38}$	49	51	68%
$pMMA_{27}$	81	19	90%



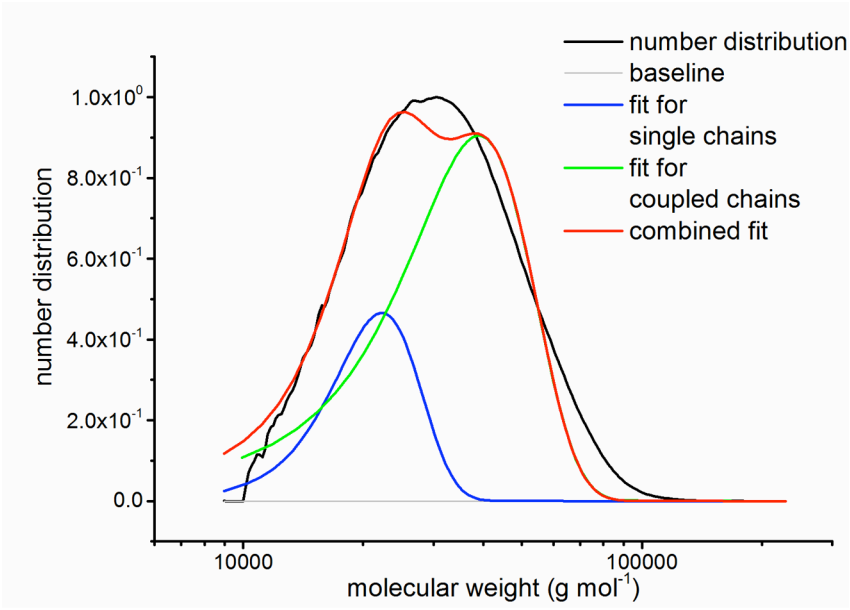
Peak	Fit for	FWHM	Centre (g mol^{-1})	Area (%)
1	Single chains	2402	4033	14.63
2	Coupled chains	7415	8368	85.37

Figure S 21. Deconvolution of the SEC number distribution for the homocoupling of $pNAM_{37}$.



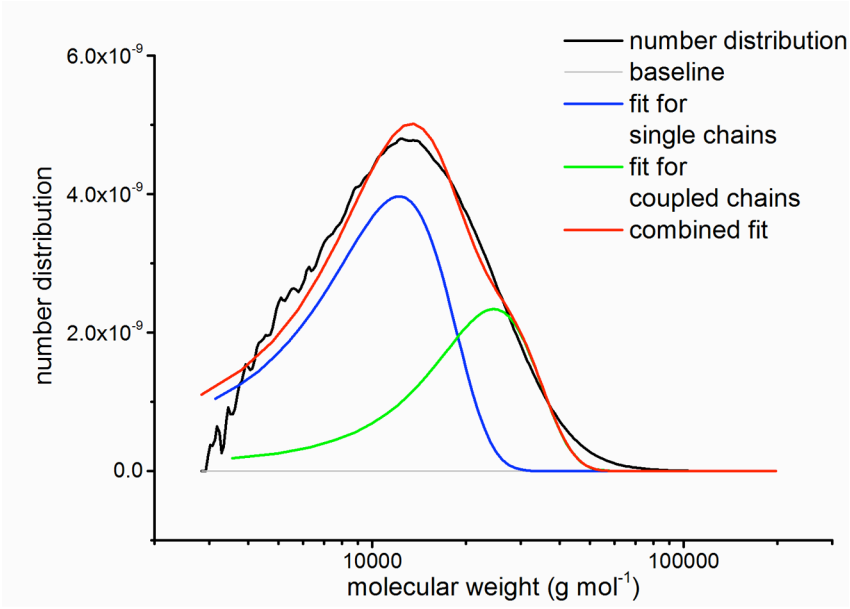
Peak	Fit for	FWHM	Centre (g mol^{-1})	Area (%)
1	Single chains	3279	6065	16.65
2	Coupled chains	8673	11222	83.35

Figure S 22. Deconvolution of the SEC number distribution for the homocoupling of pBA_{42}.



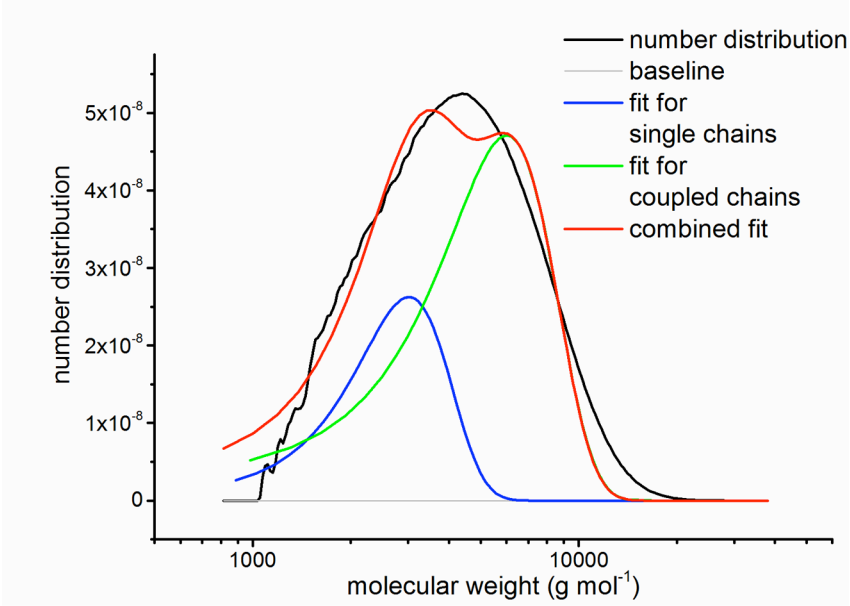
Peak	Fit for	FWHM	Centre (g mol^{-1})	Area (%)
1	Single chains	12989	22268	16.90
2	Coupled chains	33131	38992	83.10

Figure S 23. Deconvolution of the SEC number distribution for the homocoupling of pBA_{206}.



Peak	Fit for	FWHM	Centre (g mol^{-1})	Area (%)
1	Single chains	13071	12200	49.33
2	Coupled chains	21932	24540	50.67

Figure S 24. Deconvolution of the SEC number distribution for the homocoupling of $pPEGA_{38}$.



Peak	Fit for	FWHM	Centre (g mol^{-1})	Area (%)
1	Single chains	2335	3014	18.77
2	Coupled chains	5642	6015	80.23

Figure S 25. Deconvolution of the SEC number distribution for the homocoupling of $pMMA_{27}$.

Stability of strained alkynes in solution

To test the stability of the reagents in solution, homocoupling reactions of pBA_{42} (see Figure 5 in the publication) were repeated after storing DBCO-NH_2 and BCN-NH_2 in DMF at -18°C for 4 months.

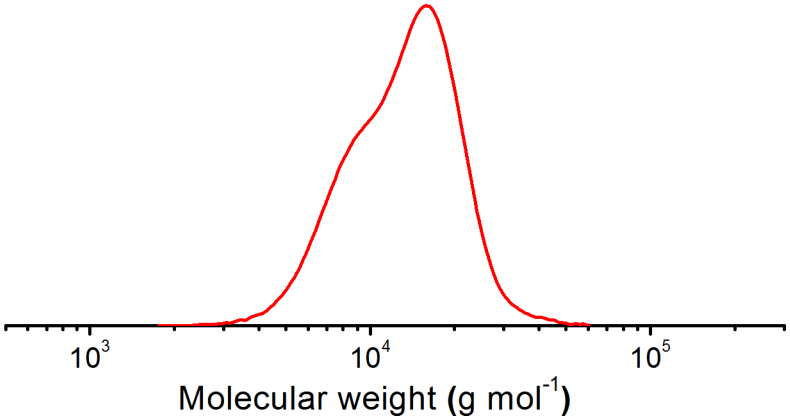


Figure S 26. SEC traces for the homocoupling of pBA_{42} with BCN-NH_2 after storing the stock solution for 4 months.

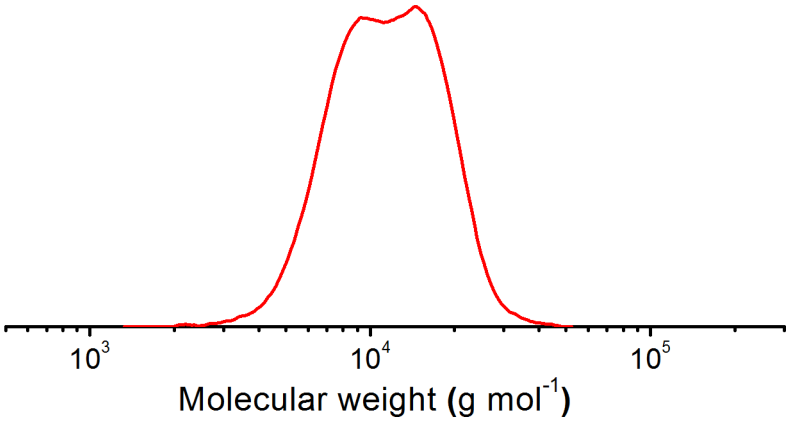


Figure S 27. SEC traces for the homocoupling of pBA_{42} with DBCO-NH_2 after storing the stock solution for 4 months.

Number distribution plots of combinations

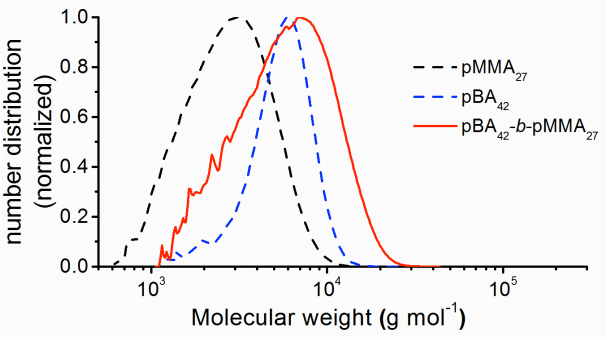


Figure S 28. Number distribution plots of the initial precursors (dashed lines) $pMMA_{27}$ (black), pBA_{42} (blue) and the coupled block copolymer (solid red line) $pMMA_{27}$-*b*-pBA_{42}.

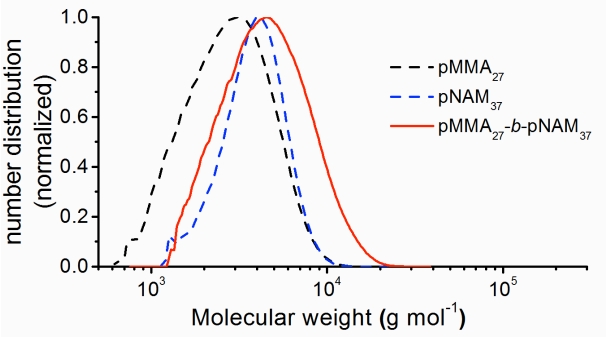


Figure S 29. Number distribution plots of the initial precursors (dashed lines) $pMMA_{27}$ (black), $pNAM_{37}$ (blue) and the coupled block copolymer (solid red line) $pMMA_{27}$-*b*-$pNAM_{37}$.

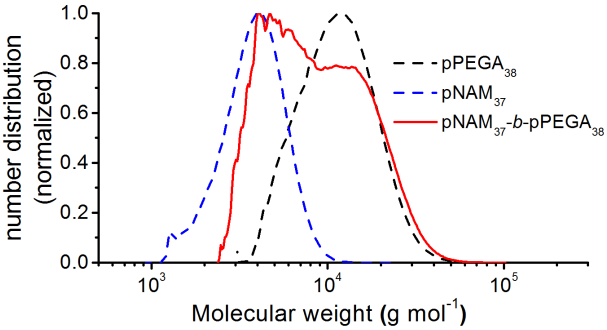


Figure S 30. Number distribution plots of the initial precursors (dashed lines) $pPEGA_{38}$ (black), $pNAM_{37}$ (blue) and the coupled block copolymer (solid red line) $pNAM_{37}$-*b*-$pPEGA_{38}$.

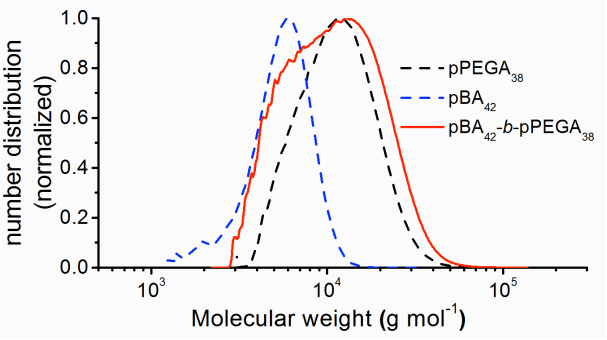


Figure S 31. Number distribution plots of the initial precursors (dashed lines) pPEGA$_{38}$ (black), pBA$_{42}$ (blue) and the coupled block copolymer (solid red line) pBA$_{42}$-*b*-pPEGA$_{38}$.