

Supporting Information

A Modular Route for the Synthesis of ABC Miktoarm Star Terpolymers via a New Alkyne-Substituted Diphenylethylene Derivative

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1. ADDITIONAL EXPERIMENTAL SECTION.

Materials. *sec*-Butyllithium (*sec*-BuLi, Acros, 1.3 M in cyclohexane/hexane: 92/8) and the phosphazene base *t*-BuP₄ (Fluka, 1 M in hexane) were used without further purification. Butadiene (Rießner-Gase, 2.5) was passed through columns filled with molecular sieves (4 Å) and basic aluminum oxide and stored over dibutylmagnesium (1 M solution in heptane, Aldrich). 2-Vinylpyridine (2VP, Aldrich) was degassed, stirred with triethylaluminium (1 M solution in hexanes, Aldrich) for 2 h and condensed on a high vacuum line into storage ampoules. *tert*-Butyl methacrylate (*t*BMA, BASF) and *N,N*-dimethylaminoethyl methacrylate (DMAEMA, Aldrich) were purified in a similar manner, except that DMAEMA was stirred with tri-*n*-octylaluminium (25 wt. % solution in hexanes, Aldrich) instead of triethylaluminium. Ethylene oxide (Linde, 3.0) was condensed onto CaH₂ and stirred at 0 °C for 3 h before being transferred into a glass ampoule for storage. Prior to use the ethylene oxide was additionally purified over *n*-BuLi and condensed into a sampling ampoule. THF (Sigma-Aldrich) was distilled from CaH₂ and K metal under dry nitrogen. 1,1-Diphenylethylene (Aldrich, 97%) was purified by stirring with *sec*-BuLi under N₂ followed by distillation. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (PMDETA) was purchased from Aldrich and distilled and degassed. CuBr (Aldrich) was treated with pure acetic acid and filtered. The monomers for ATRP and RAFT, which were *tert*-butyl methacrylate, styrene and *N,N*-dimethylaminoethyl methacrylate were destabilized by passing through a column filled with basic alumina. Azidoacetyl chloride was synthesized according to literature¹ and cryodistilled on a high vacuum line before use. The synthesis of 4-cyano-4-methyl-4-thiobenzoylsulfanyl-butyric acid 3-azidopropyl ester² and *N*-(1-heptyloctyl)-*N'*-(hexyl-6'-azido)-perylene-3,4,9,10-tetracarboxylic acid bisimide³ is described in literature. If not stated elsewhere, all other chemicals were purchased in analytical grade and used as received. The dialysis membranes used for purification were purchased from Roth (SpectraPor) with molecular weight cut-offs (MWCO) of 1,000 g/mol and 50,000 g/mol.

Polymerization. *Model-Reaction of click-DPE toward P2VP-Homopolymer.* To investigate the endcapping efficiency of click-DPE toward living poly(2-vinylpyridine) anions, a test polymerization was performed, similar to the previous reported procedures with the same setup. The monomer was directly initiated with *sec*-BuLi in THF at -70 °C and polymerized for 45 minutes. After withdrawing a precursor, the click-DPE was added in a two-fold excess regarding the living chain ends. Finally the polymerization was terminated with 1 mL of degassed methanol after 1 h. The polymer was isolated by precipitation in water.

Azido-functionalized Poly(ethylene oxide) (PEO-N₃) using Anionic Ring Opening Polymerization. The azido-functionalized poly(ethylene oxide) was synthesized via anionic ring opening polymerization in THF using the phosphazene base *t*-BuP₄ as additive and azidoacetyl chloride as functional termination agent.¹ First, the initiator diphenylhexyllithium was directly generated by reaction of *sec*-BuLi with 1.1 eq. of 1,1-diphenylethylene at -70 °C. Afterward, the purified ethylene oxide was added via ampoule and allowed to stir for 30 min. As ethylene oxide is not able to polymerize with lithium as counterion and only monoaddition takes place, the reaction mixture was warmed up to 10 °C and then the phosphazene base (2 eq. relative to the initiator) was added to the reaction mixture.^{4, 5} After polymerization at 50 °C for 15 h the temperature was lowered to 20 °C again and the freshly cryo-distilled azidoacetyl chloride (2 eq. with regard to the living anionic chain ends) was added. The reaction mixture was stirred for two additional hours. Finally, the product was isolated by precipitation in cold diethyl ether and subsequent drying in a vacuum oven.

Azido-end-functionalized Polymers via Atom Transfer Radical Polymerization (ATRP). All polymerizations were conducted according to standard polymerization procedures.⁶ To obtain azido-functionalized poly(*tert*-butyl methacrylate) (PtBMA-N₃) homopolymer, 2-bromo-isobutyric acid 3-azidopropylester was chosen as initiator. This was synthesized according to literature.⁷ The azido-functionalized initiator (205 mg, 0.82 mmol) and *t*BMA (5.95 g, 41.8 mmol) were mixed with 11 mL anisole in a screw cap glass, sealed with a rubber septum and purged with nitrogen for 10 minutes. Then, CuBr (118 mg, 0.82 mmol) was added and the solution was de-oxygenated with nitrogen for further 15 min. Degassed ligand PMDETA (42 mg, 0.82 mmol) was injected and the polymerization was conducted at 40 °C. Samples were withdrawn with time to follow the conversion via ¹H-NMR. The reaction solution was concentrated on a rotary evaporator and redissolved in cyclohexane. The cyclohexane solution was filtrated over a column filled with silica gel to remove copper. After precipitation in a mixture of water/methanol (40/60, v/v) it was filtrated and dried in a vacuum oven.

As the ATRP of styrene with the already mentioned azido-functionalized ATRP initiator was not successful, the polymers were synthesized in a two step reaction. First, styrene was polymerized in anisole with CuBr as catalyst, PMDETA as ligand and methyl-2-bromopropionate as initiator at 100 °C. After purification and precipitation in methanol the bromine endgroup was transformed into an azide function by treatment with 10 equivalents of sodium azide (relative to the bromine endgroups) in a 1/1 mixture of DMF/THF (v/v). The polymer was isolated by precipitation in methanol and extensively washed with water to remove residual NaN₃.⁸

Azido-end-functionalized Poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA- N_3) via RAFT. A mixture of 4-cyano-4-methyl-4-thiobenzoylsulfanyl-butyric acid 3-azidopropyl ester (67 mg, 0.186 mmol), DMAEMA (1.5 g, 9.54 mmol), AIBN (6 mg, 0.038 mmol) and 8.6 mL of anisole in a screw cap glass, sealed with a rubber septum, were purged with nitrogen for 30 minutes. Afterward, the polymerization flask was put in an oil bath at 65 °C. Samples were withdrawn to follow the conversion *via* $^1\text{H-NMR}$. For termination, the reaction mixture was cooled down and exposed to air. The polymer was purified by precipitation in cold *n*-hexane, dried in a vacuum oven and subsequently freeze-dried from dioxane solution.

Characterization. *Size Exclusion Chromatography (SEC).* SEC measurements were performed on a set of 30 cm SDV-gel columns of 5 μm particle size having a pore size of 10^5 , 10^4 , 10^3 , and 10^2 Å with refractive index and UV ($\lambda = 260$ nm) detection. THF was used as eluent at a flow rate of 1 mL/min using toluene as internal standard. The system was calibrated with PS, PtBMA, 1,4-PB and PEO standards. The characterization of the PDMAEMA homopolymer was conducted with a set of a PSS GRAM columns (7 μm particle size with pore sizes of 10^2 and 10^3 Å) with DMAc containing 0.5 M LiBr as mobile phase. The flow rate was 0.7 mL/min and the columns were thermostatted at 60 °C. The Agilent 1200 system was equipped with RI and UV ($\lambda = 260$ nm) detection. The diblock copolymers and miktoarm star terpolymers containing PDMAEMA were characterized with another system using THF with additional 0.25 wt% tetrabutylammonium bromide (TBAB) as eluent. This was necessary as the polybutadiene block of the miktoarm star terpolymers is insoluble in DMAc. The Waters instrument was equipped with PSS SDV gel columns (30 x 8 mm, 5 μm particle size) with 10^5 , 10^4 , 10^3 , 10^2 Å pore sizes, using RI and UV detection ($\lambda = 254$ nm). The flow rate was 0.5 mL/min and the obtained data were evaluated applying a PS calibration.

$^1\text{H-NMR}$ spectroscopy. $^1\text{H-NMR}$ spectra were recorded on a Bruker Ultrashield 300 spectrometer at an operating frequency of 300 MHz. CDCl_3 was used as solvent and tetramethylsilane as internal standard.

Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry (MALDI-ToF MS). MALDI-ToF MS analysis was performed on a Bruker Reflex III apparatus equipped with a N_2 laser ($\lambda = 337$ nm) at an acceleration voltage of 20 kV. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Fluka, 99.0%) was used as a matrix material and silver trifluoroacetate (AgTFA, Sigma-Aldrich, 99.99%) as ionization agent. Samples were prepared from THF solution by mixing matrix, polymer, and salt in a ratio of 20/5/1 (v/v).

Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were recorded using a Perkin Elmer Spectrum 100 FTIR spectrometer.

UV-Vis spectroscopy. UV-vis spectra were recorded on a Hitachi 3000 spectrophotometer. For the measurement of the living anions of 1-[(4-(*tert*-butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene a 5×10^{-4} M solution of the DPE compound in distilled THF was prepared under inert gas and 2 eq. of *sec*-BuLi were added. The solution was directly transferred into a specially designed cuvette, which can be evacuated and closed under nitrogen atmosphere. Upon injection into the cuvette the intensity of the color decreased, so that the actual concentration for the measurements is lower than 5×10^{-4} M. Nevertheless, the concentration was high enough to obtain the desired UV-vis spectra of the living anions.

2. ADDITIONAL FIGURES.

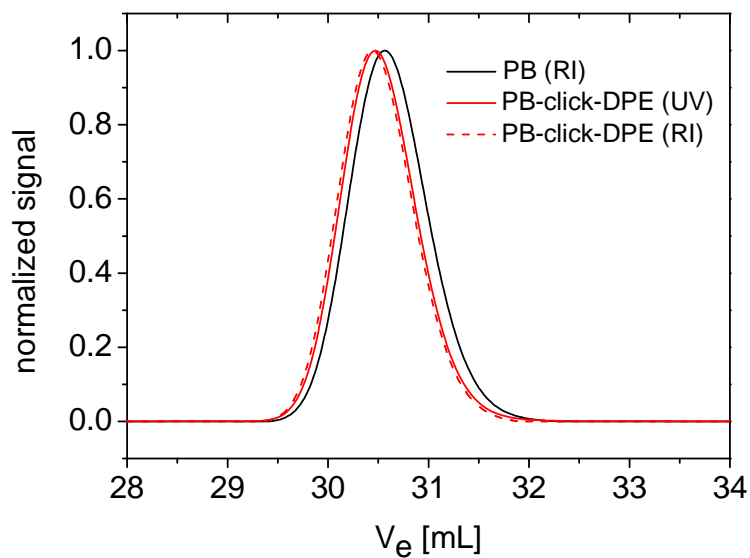


Figure S1. SEC traces of precursor samples from polybutadiene before (black) and after reaction with 1-[(4-(*tert*-butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene (red).

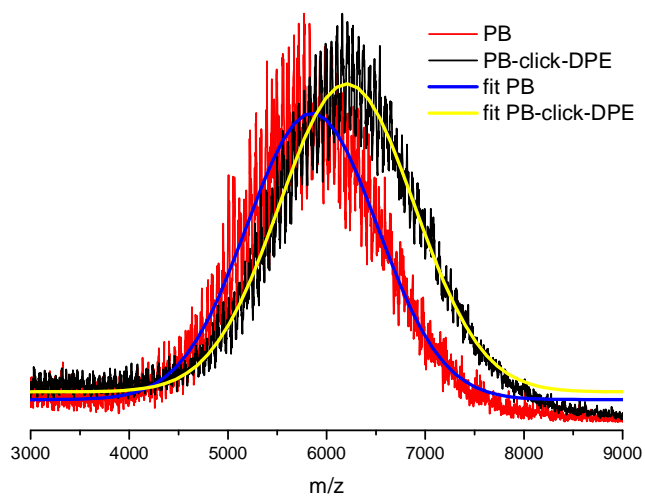


Figure S2. MALDI-ToF MS spectra of polybutadiene before (red) and after reaction with 1-[(4-(*tert*-butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene (black) and their corresponding fits.

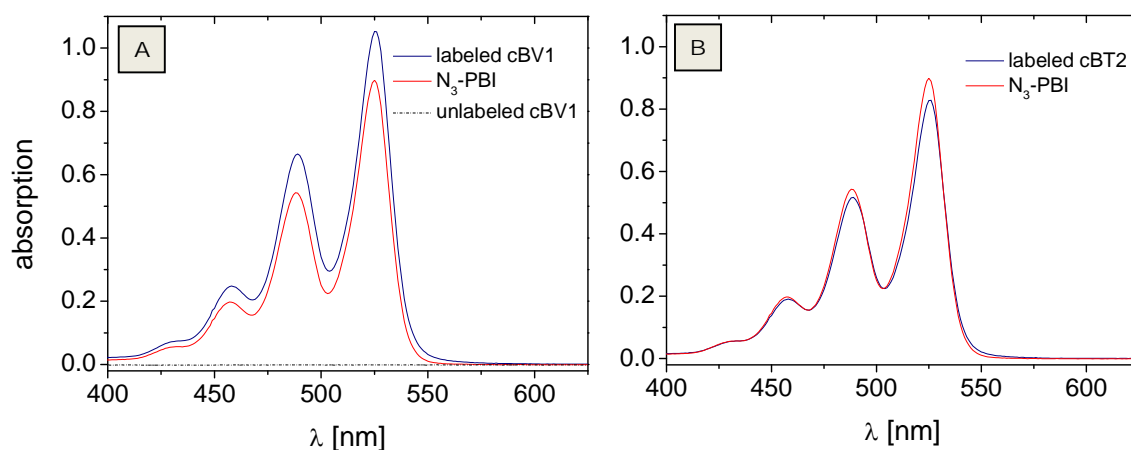


Figure S3. UV-vis spectra of 10^{-5} M CH_2Cl_2 solutions of *N*-(1-heptyloctyl)-*N'*-(hexyl-6'-azido)-perylene-3,4,9,10-tetracarboxylic acid bisimide (N_3 -PBI) and the respective perylene-labeled diblock copolymers (A) cBV1 and (B) cBT1.

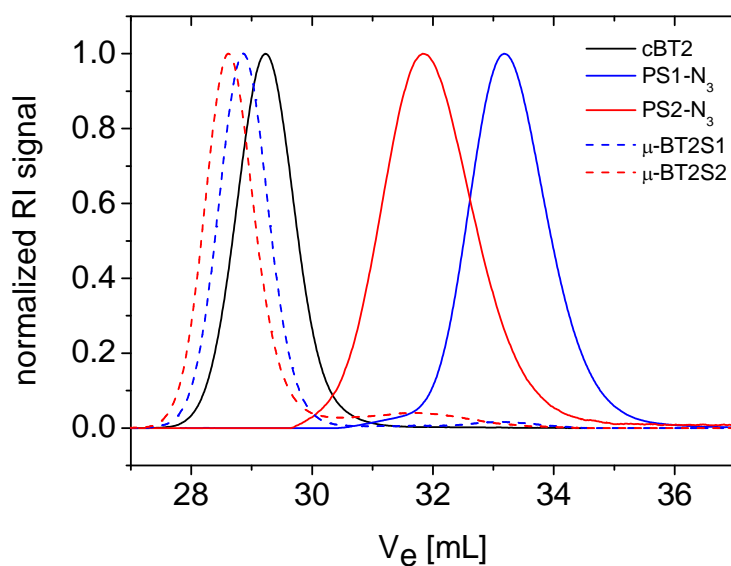


Figure S4. THF-SEC (RI signal) of alkyne-functionalized diblock cBT2, azido functionalized polystyrenes (PS1-N_3 , PS2-N_3) and the corresponding ABC miktoarm star terpolymers ($\mu\text{-BT2S1}$ and $\mu\text{-BT2S2}$) obtained after equimolar click reaction for 24 h.

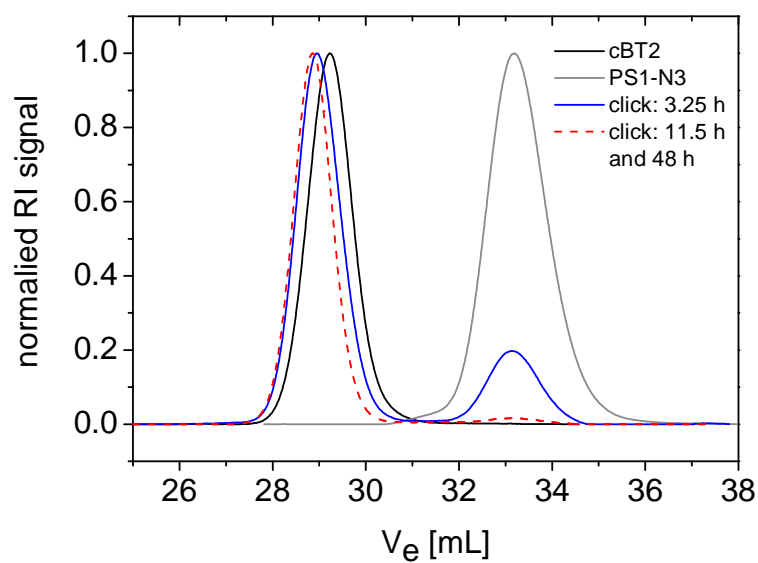


Figure S5. THF-SEC (RI-signal) of samples withdrawn during equimolar click reaction between cBT2 and PS1-N₃ after 3.25 h (-), 11.5 h and 48 h (· · ·).

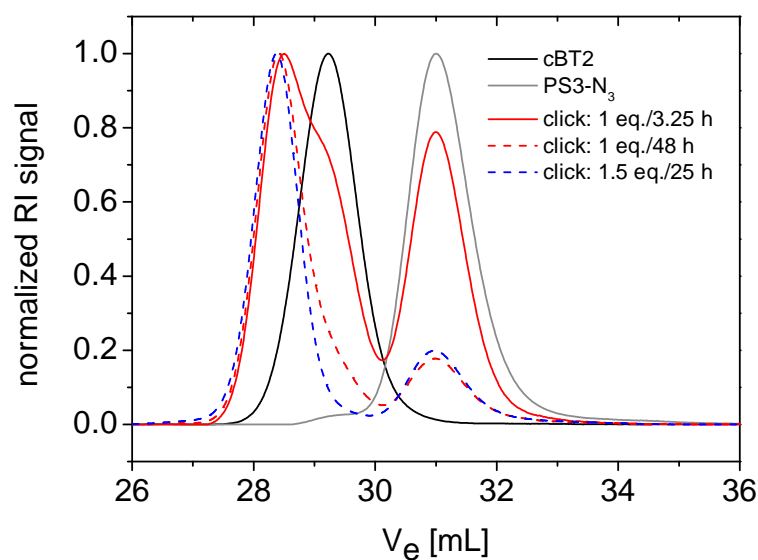


Figure S6. THF-SEC (RI signal) of click reaction between cBT2 and PS3-N₃ with further addition of 0.5 eq. PS3-N₃ 48 h after start of the click reaction. 25 h after addition of the second portion of PS3-N₃ a final sample was taken for SEC.

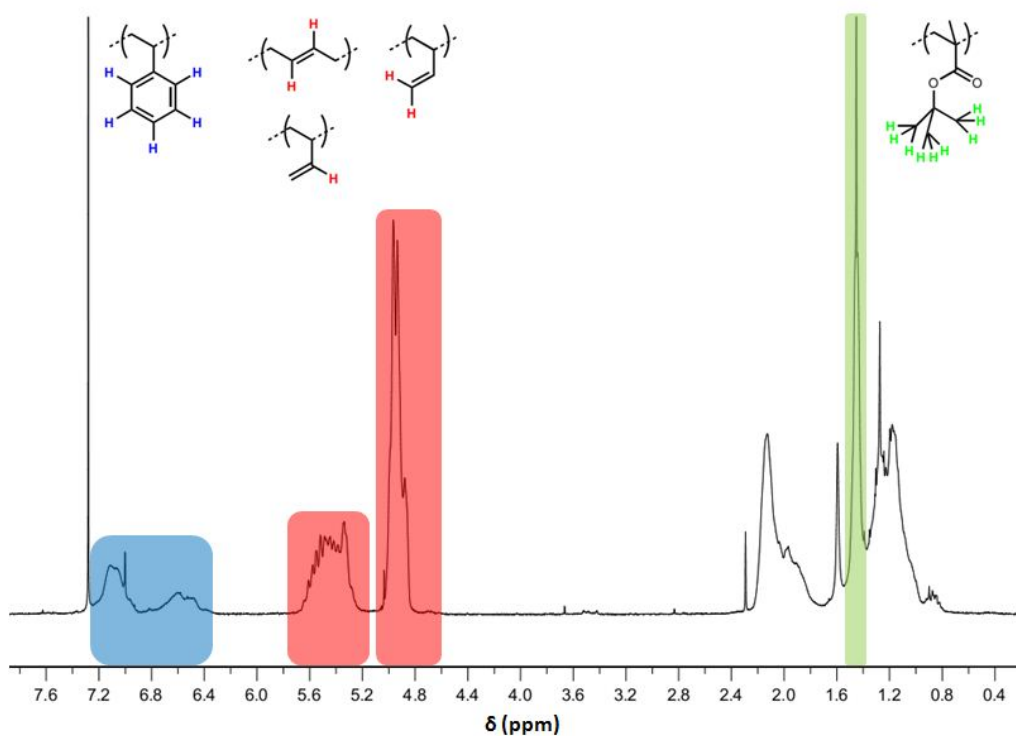


Figure S7. ^1H -NMR spectrum of μ -BT1S1 in CDCl_3 . The characteristic signals of the respective polymer blocks are highlighted.

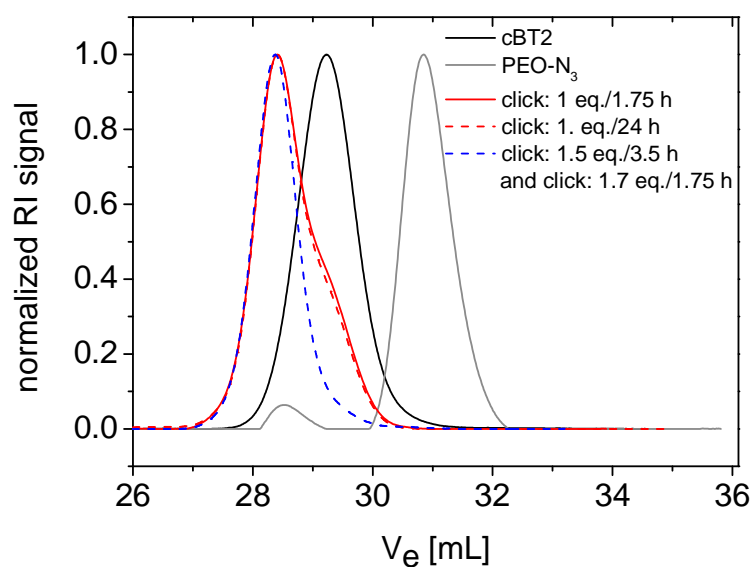


Figure S8. THF-SEC (RI signal) of click reaction between cBT2 and PEO-N_3 with stepwise addition of PEO-N_3 . Further 0.5 eq. PEO-N_3 were added 24 h after start of the click reaction and 3.5 h later further 0.2 eq. PEO-N_3 were added. The corresponding reaction times are relative to the point of addition of a further PEO-N_3 portion. The excess of PEO-N_3 is not visible as the PEO is adsorbed at the silica column used for removing copper catalyst.

3. TEST POLYMERIZATION WITH 2VP AND CLICK-DPE.

In contrast to polybutadienyl and polystyryl lithium, the living anion of poly(2-vinylpyridine) is less nucleophilic and hence, the initial assumption was that it is not able to attack excess click-DPE. This would lead to the desired diblock copolymers with only one click-DPE at the block junction. If the 2VP would incorporate more units of click-DPE the diblock would carry more than one alkyne function, which would result in star terpolymers with more than three arms. Hogen-Esch *et al.* reported that the endcapping of P2VPLi with unsubstituted DPE is an equilibrium reaction⁹ and that even the addition of a large excess of 1,1-diphenylethylene to living poly(2-vinylpyridine) does not lead to a significant endcapping of the anion.¹⁰ Hirao *et al.* showed that silyl-protected hydroxyl-functionalized DPE, 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-phenylethylene did not undergo copolymerization with living poly(2-vinylpyridine) anions.¹¹ Also, in previous tests on the endcapping of poly(2-vinylpyridine) with DPE functionalized polybutadiene macromonomers, we found no significant coupling between the two polymeric chains. Therefore, a test reaction was conducted to verify whether the alkyne-substituted click-DPE can be attacked by a living P2VPLi as a result of the altered electronic configuration of the DPE derivative. For this purpose, 2-vinylpyridine was polymerized in THF at -70 °C with *sec*-BuLi as initiator, yielding a molecular weight of 5,000 g/mol. Then, a 2-fold excess of the alkyne-functionalized click-DPE was added at the same temperature. Directly after injection, the color of the P2VPLi anion changed from red to violet giving a first qualitative indication for the addition of the click-DPE. ¹H-NMR determined the degree of alkyne functionalization as around 98%.

MALDI-ToF MS supported a quantitative end-functionalization (Figure S9 A). Before addition the M_n of the P2VP was 4,750 g/mol. After 1 h reaction with click-DPE the M_n increased to 5,230 g/mol. These values indicate that click-DPE addition took place quantitatively, considering the accuracy of the determination method. Moreover, the molecular weight distribution shifted completely and in the case of the reflectron mode a distinct shift of the individual peaks was noticeable (Figure S9 B). This proved the presence of only one species after addition of click-DPE. The shift of the peaks with a difference of around 4.5 g/mol is in good agreement with the expected 3 g/mol difference ($M(2VP) = 105.14$ g/mol, $M(\text{click-DPE}) = 318.53$ g/mol; $\Delta = 318.53$ g/mol - 3 x 105.14 g/mol = 3.11 g/mol). For example, the peak at $m/z = 4791.6$ in the P2VP precursor, i.e. before addition of click-DPE, corresponds to 44 repeating units of 2VP with a *sec*-butyl residue and Ag^+ as counter-ion. This is in accordance with the theoretical m/z value of 4792.0. In the spectrum

after click-DPE addition, the modified P2VP with the same number of repeating units and an additional click-DPE was detected at $m/z = 5111.1$. Also here, this value is consistent with the expected $5110.5 (= 4792.0 + 318.5)$. Hence, click-DPE adds to living poly(2-vinylpyridine) anions quantitatively, in contrast to other DPE derivatives reported in literature.

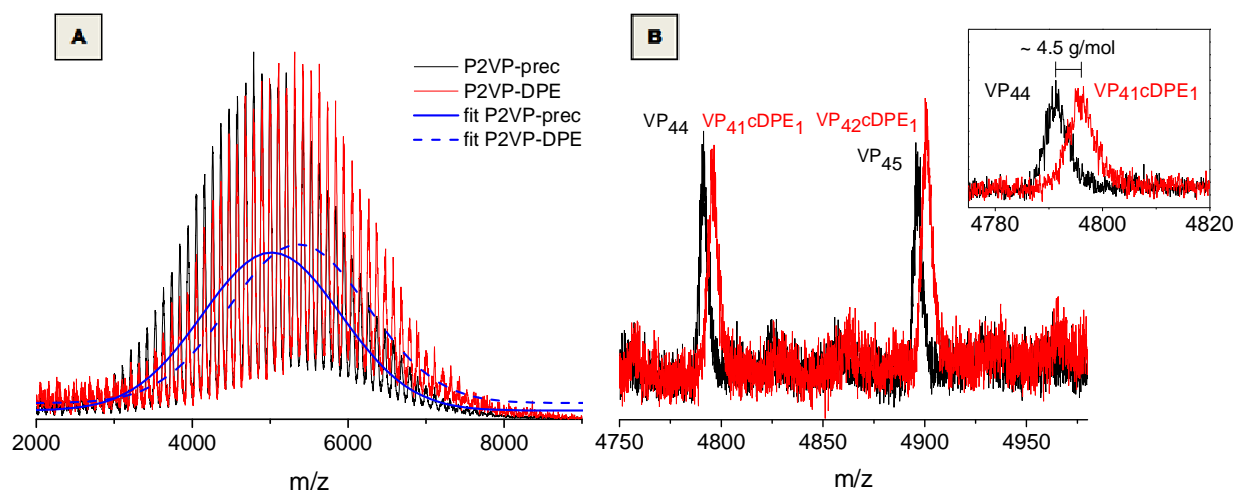


Figure S9. MALDI-ToF MS spectra of poly(2-vinylpyridine) before (black line) and after addition of click-DPE (cDPE, red line), recorded in linear (A) and reflectron mode (B) with AgTFA as ionization agent.

In summary, the anion of the alkyne-functionalized DPE has a nucleophilicity comparable to P2VPLi, whereas the anion of unsubstituted DPE is more nucleophilic than P2VPLi. One reason for this might be the electron withdrawing effect of the *tert*-butyldimethylsilyl group which leads to a reduction of the electron density in the double bond and thus decreases the nucleophilicity of the click-DPE as compared to the unsubstituted DPE.¹² As the living anion of the click-DPE is able to start the polymerization of P2VP and click-DPE also adds to P2VPLi, it is possible to copolymerize P2VP and click-DPE. Therefore, if the click-DPE is used in a slight excess and not under equimolar conditions, the DPE derivative might also be incorporated in or most probably after consumption of all 2VP monomer at the end of the P2VP block for the aimed PB-*b*-P2VP diblock copolymers. In contrast to butadiene and styrene, methacrylates are known to be not nucleophilic enough to attack diphenylethylene and its derivatives.^{13, 14} Consequently, monomers like *t*BMA and DMAEMA can be polymerized as second block to obtain well-defined diblock copolymers with exactly one alkyne function at the block junction.

Due to the altered reactivity of the click-DPE toward living P2VP-Li compared to other DPE derivatives both α - and ω -alkyne modified P2VP homopolymers are accessible. In

addition, alkyne mid-functionalized diblock copolymers with poly(2-vinylpyridine) as first and a methacrylate-type monomer as second block can be synthesized.

4. CHARACTERIZATION OF ω -AZIDO HOMOPOLYMERS.

Besides the qualitative proof of the presence of an azido function *via* IR (Figure S10) the degree of azide-functionalization was additionally tried to be quantified by MALDI-ToF MS or $^1\text{H-NMR}$.

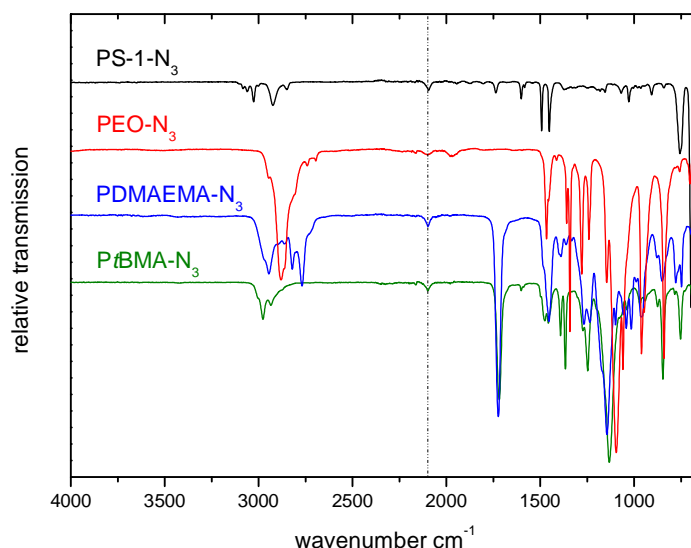


Figure S10. IR spectra of the corresponding homopolymers show the characteristic stretching vibration of the azido group at $\sim 2098\text{ cm}^{-1}$.

In case of PS1-N₃ and PEO-N₃ mass spectrometry in reflectron mode was possible. The respective spectra are shown in Figure S11 and S12. In the case of the azido-terminated PS1-N₃ only a small peak resembling the desired functional species is present. As already reported in literature formation of postsource metastable ions from azido-functionalized polymers is possible under high laser powers in reflectron mode.¹⁵ Therefore, by comparing the relative intensities of the azido-functionalized species and the corresponding metastable ion with the intensity of the unfunctionalized species, as main population the azido-terminated polystyrene is clearly concluded. We have to mention here that the peak at the left side of the proton-terminated polystyrene could not be assigned clearly.

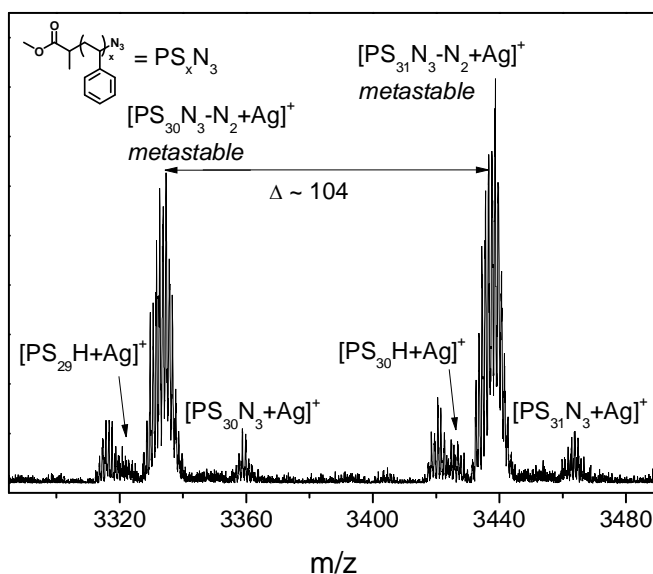


Figure S11. MALDI-ToF MS spectrum of PS1-N₃ recorded in reflectron mode with AgTFA as ionization agent.

In the MALDI spectrum of PEO-N₃ (Figure S12) two series of peaks were present. Here, the main population resembles the azido-terminated PEO. The second population could be attributed to azido-terminated PEO with a proton as counter ion. Another possible explanation could be deduced from SEC measurements, where a small second peak at lower elution volume was detected (around 6 wt. %, see Figure S13). This originates from minimal residual amounts of thionyl chloride which was used for the synthesis of the azidoacetyl chloride and is hard to remove completely despite thorough purification.¹ This population cannot take part in the click reaction. For the molecular characterization, only the major peak was taken into consideration. The molecular weight determined by MALDI-ToF MS was consistent with the values from SEC. Therefore, the second population in MALDI can be interpreted as the lower molecular weight side of the coupling product with thionyl chloride. Even though the main peak corresponds to the desired functionalized PEO, one has to notice that chains where HN₃ was eliminated ($\Delta \sim 43$ g/mol) and chains which were terminated with a proton instead of the acid chloride ($\Delta \sim 5$ g/mol) would not be distinguishable and could possibly be present.

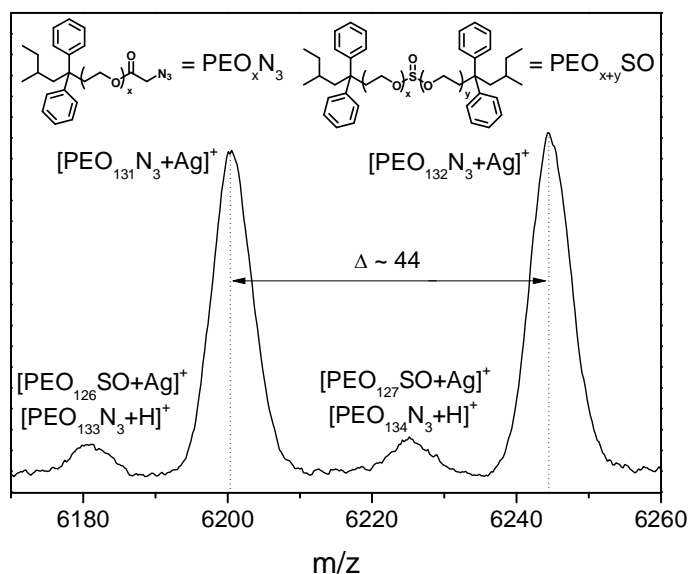


Figure S12. MALDI-ToF MS spectrum of PEO- N_3 recorded in reflectron mode with AgTFA as ionization agent.

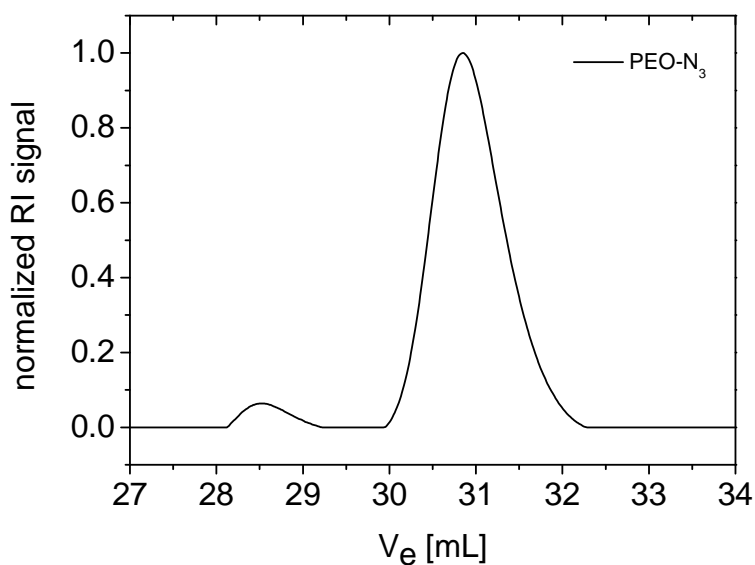


Figure S13. THF-SEC (RI signal) of azido functionalized poly(ethylene oxide).

Both in case of PtBMA- N_3 and PDMAEMA- N_3 endgroup determination was not possible *via* MALDI-ToF MS. In contrast to PtBMA- N_3 for the DMAEMA homopolymer calculation of the degree of azido-functionalization was possible from the characteristic signals in the ^1H -NMR spectrum (Figure S14). According to the calculated value of approximately 96%, quantitative azido-functionalization of the polymer was assumed.

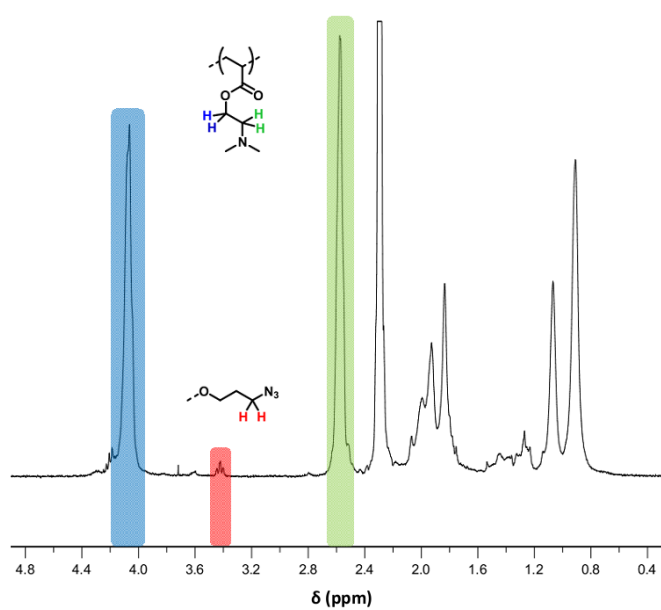


Figure S14. ^1H -NMR spectrum of PDMAEMA- N_3 in CDCl_3 . The characteristic signals of the monomer unit and chain transfer agent are highlighted.

5. CLICK REACTION WITH ω -AZIDO-FUNCTIONALIZED POLY(*TERT*-BUTYL METHACRYLATE).

Since we also synthesized an alkyne-functionalized diblock with DMAEMA as second block (cBD), a μ -BDT miktoarm star terpolymer was achievable by click reaction with the azido-terminated *Pt*BMA. Similar to the click reactions with PDMAEMA- N_3 , the reaction conditions were not optimized. The ligation was conducted for 3 days with 1.3 eq. of azido-functionalized homopolymer to guarantee 100 % conjugation of the diblock. The SEC of the click-product after dialysis in methanol/isopropanol (2/1 v/v) is shown in Figure S15 and a complete shift of the molecular weight distribution of the miktoarm star terpolymer compared to the diblock terpolymer was detected. This demonstrates the efficiency of our approach. Even though we were not able to remove all excess homopolymer, we showed that formation of a μ -BDT miktoarm star terpolymer is possible starting from two different diblock copolymers. The molecular parameters of the obtained ABC miktoarm star terpolymer are summarized in Table 3.

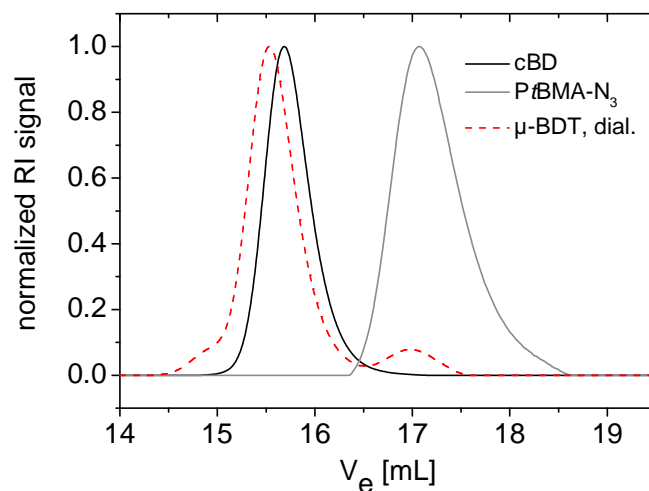


Figure S15. Salt-THF-SEC (RI-signal) of the μ -BDT miktoarm star terpolymers obtained after click reaction of alkyne-functionalized diblock cBD with the azido functionalized *Pt*BMA- N_3 .

4. REFERENCES.

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