Supporting Information

# Mild and Efficient Modular Synthesis of 

# Poly(Acrylonitrile-co-Butadiene) Block and 

# Miktoarm Star-Copolymer Architectures 

Christoph J. Dürr, ${ }^{\dagger}$ Lebohang Hlalele, ${ }^{\dagger}$ Andreas Kaiser, ${ }^{\dagger}$ Sven Brandau ${ }^{\dagger}$<br>and Christopher Barner-Kowollik* ${ }^{*}$


#### Abstract

$\dagger$ Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany and $\ddagger$ Lanxess Emulsion Rubber, BP 7 - Z.I. Rue du Ried, 67610 La Wantzenau, France


E-mail: christopher.barner-kowollik @kit.edu; Fax: +49 72160845740

## Materials

Acrylonitrile (AN, > 99\%, Acros), 1,3-butadiene (BD, > 99.5\%, Air Liquide), Styrene (S, Acros, $99 \%$ ), $N, N$ '-dicyclohexylcarbodiimide (DCC, $99 \%$, Acros), 4-(dimethylamino)pyridine (DMAP, 99\%, Aldrich), trans,trans-2,4-hexadien-1-ol (> 97\%, SAFC), propane-1,3-diol (98\%, Aldrich), 2-bromo-2-methylpropionyl bromide ( $98 \%$, Acros), sodium azide ( $99 \%$, Acros), copper sulfate pentahydrate ( $98+\%$, Aldrich), sodium (L)-ascorbate (> 98\%, Aldrich), 1,1'-azobis(cyclohexane-1-carbonitrile) (98\%, Aldrich), 2,2'-azobis(N-butyl-2-methylpropionamide) (Wako Ltd.), ethylenediaminetetraacetic acid disodium salt ( $\mathrm{Na}_{2}$-EDTA, Roth, 85\%),
nickelocene ( $99 \%$, strem chemicals), triphenyl phosphine (VWR), NaI (> 99\%, Fluka), butadiene diepoxide ( $97 \%$, Aldrich), trifluoroacetic acid (TFA, Sigma, 99\%), chlorobenzene (Acros, $99+\%$ ), $N, N$-dimethylacetamide ( $99.5 \%$, Acros) and $N, N$-dimethylformamide (DMF, Alfa Aesar, $99 \%$ ), methylene chloride $(99.8 \%$, extra dry, Acros) were used without further purification. Triethylamine ( $99 \%$, ABCR) was dried over $\mathrm{CaH}_{2}$ and distilled prior to use. Other solvents (synthesis grade) were obtained from VWR and used as received. 2((dodecylsulfanyl)carbonothioyl)sulfanyl propanoic acid (DoPAT) was obtained from Orica Pty Ltd., Melbourne, Australia. Prop-2-yn-1-yl 2-(((dodecylsulfanyl)carbonothioyl)-sulfanyl)propanoate, ${ }^{1}$ 3-hydroxypropyl 2 -bromo-2-methylpropanoate, ${ }^{2}$ 1,4-diazidobutane-2,3-diol, ${ }^{3}$ 1benzyl pyridin-2-yldithioformate, ${ }^{4}$ 1-phenylethyl pyridin-2-yldithioformate and 1-phenylethyl (diethoxyphosphoryl)dithioformate ${ }^{5}$ were synthesized according to the literature.

## Experimental Procedures

Synthesis of diene functional chain transfer agent hexa-2,4-dien-1-yl 2((dodecylthio)carbonothioylthio)propanoate (2). DoPAT (6.000 g , 17.1 mmol ), 4(dimethylamino)pyridine ( $0.417 \mathrm{~g}, 3.4 \mathrm{mmol}$ ) and trans,trans-2,4-hexadien-1-ol ( $5.496 \mathrm{~g}, 56.0$ $\mathrm{mmol})(0.523 \mathrm{~g}, 4.28 \mathrm{mmol})$ was dissolved in dry methylene chloride ( 25 mL ) and cooled to $0{ }^{\circ} \mathrm{C}$. A solution of $N, N$ '-dicyclohexylcarbodiimide ( $3.528 \mathrm{~g}, 17.1 \mathrm{mmol}$ ) in dry methylene chloride ( 5 mL ) was added. The cooling bath was removed and the mixture was stirred overnight at ambient temperature. The white precipitate was filtered off and methylene chloride ( 50 mL ) was added. The solution was washed with 0.5 N hydrochloric acid $(2 \times 50 \mathrm{~mL})$ and saturated aqueous $\mathrm{NaHCO}_{3}$ solution ( 50 mL ). The organic layer was dried over $\mathrm{MgSO}_{4}$ and concentrated in vacuum. The crude product was purified by column chromatography on silica gel with nhexane/ethyl acetate ( $15: 1, \mathrm{v} / \mathrm{v}, \mathrm{R}_{\mathrm{f}} 0.59$ ) to give $2(5.024 \mathrm{~g}, 68 \%)$ as a yellow oil.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.26$ (dd, $\left.J=15.2,10.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}=\mathrm{C} H\right), 6.05$ (ddd, $\left.J=14.8,10.5,1.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{3}-\mathrm{CH}=\mathrm{C} H\right), 5.76\left(\mathrm{dq}, J=14.8,6.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}\right), 5.60$ $\left(\mathrm{dt}, J=15.2,6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}=\mathrm{CH}\right), 4.83\left(\mathrm{q}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)\right), 4.63(\mathrm{~d}$, $\left.J=6.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{O}-\mathrm{CH}_{2}\right), 3.34\left(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{S}-\mathrm{CH}_{2}\right), 1.76\left(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}\right)$,
 $\left.\mathrm{CH}_{2}-\mathrm{CH}_{2}\right), 1.33-1.20(\mathrm{~m}, 16 \mathrm{H}$, aliphatic Hs$), 0.88\left(\mathrm{t}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{CH}_{3}-\mathrm{CH}_{2}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 222.11,171.04,135.46,131.70,130.50,123.10,66.37,48.11$, 37.37, 32.04, 29.75, 29.68, 29.56, 29.47, 29.22, 29.03, 28.02, 22.81, 18.26, 17.09, 14.25.

Elemental analysis calculated (\%) for $\mathrm{C}_{22} \mathrm{H}_{38} \mathrm{O}_{2} \mathrm{~S}_{3}$ : C, 61.35; H, 8.89; O, 7.43; S, 22.33, found: C, 59.52; H, 8.77; O, 7.84; S, 23.36.

## Synthesis of Cp-functional RAFT agent

In a glove box, $\mathbf{1}(0.299 \mathrm{~g}, 0.54 \mathrm{mmol}), \mathrm{PPh}_{3}(0.282 \mathrm{~g}, 1.07 \mathrm{mmol}), \mathrm{NaI}(0.483 \mathrm{~g}, 3.22 \mathrm{mmol})$ and nickelocene ( $0.203 \mathrm{~g}, 1.07 \mathrm{mmol}$ ) was dissolved in THF ( 4 mL ) and stirred under argon for 6 h at room temperature. The solution was diluted with THF and filtered over basic aluminum oxide. All volatiles were removed in vacuum, the residue was dissolved in methylene chloride $(10 \mathrm{~mL})$ and washed with deionized water $(2 \times 10 \mathrm{~mL})$. The organic phase was dried over $\mathrm{MgSO}_{4}$, concentrated in vacuum and purified by column chromatography on silica gel with n hexane/ethyl acetate ( $10: 1, \mathrm{v} / \mathrm{v}, \mathrm{R}_{\mathrm{f}} 0.28$ ) to give the modified trithiocarbonate $(0.207 \mathrm{~g}, 71 \%)$ as a yellow liquid. NMR characterization is provided in Fig. S20-21.

## Instrumentation

${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR spectra were recorded at room temperature on a Bruker Advance 400 NMR spectrometer and referenced to the remaining solvent signal.

Molecular weight determination was performed on a SEC system (PL-GPC 50 Plus, Polymer Laboratories) consisting of an auto injector, a guard column (PLgel Mixed C, $50 \times 7.5 \mathrm{~mm}$ ), three linear columns (PLgel Mixed C, $300 \times 7.5 \mathrm{~mm}, 5 \mu \mathrm{~m}$ bead-size) and a differential refractive index detector using THF as the eluent at $35^{\circ} \mathrm{C}$ and a flow rate of $1 \mathrm{~mL} \cdot \mathrm{~min}^{-1}$. The system was calibrated using narrow polystyrene standards (Polymer Standard Service) ranging from 160 to $6 \times 10^{6} \mathrm{~g} \cdot \mathrm{~mol}^{-1}$. Samples were injected from solutions in THF $\left(2 \mathrm{mg} \cdot \mathrm{mL}^{-1}\right)$ and molecular weight distributions were referenced versus polystyrene (PS) standards. Molecular weight evaluations for NBR were performed employing Mark-Houwink parameters of polystyrene $\left(\alpha=0.70, K=14.1 \times 10^{-5} \mathrm{dL} \cdot \mathrm{g}^{-1}\right)$, SAN samples were evaluated using the appropriate Mark-Houwink parameters $\left(\alpha=0.68, K=21.5 \times 10^{-5} \mathrm{dL} \cdot \mathrm{g}^{-1}\right) .{ }^{6}$

ESI-MS spectra were recorded on a LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The system was calibrated with a standard containing caffeine, Met-Arg-Phe-Ala acetate and a mixture of fluorinated phosphazenes (Ultramark 1621), purchased from Aldrich. A spray voltage of 4.5 kV , a dimensionless sweep gas flow rate of 2 and a dimensionless sheath gas flow-rate of 12 were applied. The capillary voltage, the tube lens offset voltage and the capillary temperature were set to $60 \mathrm{~V}, 110 \mathrm{~V}$ and $275^{\circ} \mathrm{C}$, respectively. For SEC-ESI-MS measurements the mass spectrometer was coupled to a Series 1200 HPLCsystem (Agilent, Santa Clara, CA, USA) with THF as the eluent in accordance to a setup
described earlier. ${ }^{7}$ Polymer samples were dissolved in THF at $2 \mathrm{mg} \cdot \mathrm{mL}^{-1}$ and injected onto the HPLC-system.


Figure S1. ${ }^{1} \mathrm{H}$ NMR of ${ }^{t} \mathrm{Br}$ RAFT agent $\mathbf{1}$ recorded in $\mathrm{CDCl}_{3}$ at room temperature.


Figure S2. ${ }^{13} \mathrm{C}$ NMR of ${ }^{t} \mathrm{Br}$ RAFT agent $\mathbf{1}$ recorded in $\mathrm{CDCl}_{3}$ at room temperature.


Figure S3. ESI mass spectrum of ${ }^{t} \mathrm{Br}$ functional RAFT agent 1.


Figure S4. SEC traces of selected RAFT mediated polymerizations employing controlling agent 1. Peak maxima shift towards lower retention times with increasing conversion under preservation of a monomodal molecular weight distribution. Conditions: A) $[\text { RAFT }]_{0}=14.0 \mathrm{mmol} \cdot \cdot^{-1},[\text { Ini }]_{0}=1.7 \mathrm{mmol} \cdot \mathrm{l}^{-1}$, samples taken after $4,5,6$ and 7 h (Table 1 , entry 4); B) $[\mathrm{RAFT}]_{0}=0.9 \mathrm{mmol} \cdot \mathrm{l}^{-1},[\text { Ini }]_{0}=0.2 \mathrm{mmol} \cdot \cdot^{-1}$, samples taken after $2,3,4,5,6$ and 22 h (Table 1, entry 6).


Figure S5. Comparative study of experimentally determined and theoretically calculated mass-to-charge ratios for a polymer 6 with $\mathrm{m}+\mathrm{n}=11$ incorporated monomer units $\left[\mathbf{6}_{11}+\mathrm{Na}\right]^{+}$. A) Magnified view into the region of 1155 to 1190 Dalton of an ESI-MS measurement of bromine-capped NBR 6c. B-G) Simulated isotope patterns of bromine-capped NBR 6 with $m+n=11$ repeat units and various $m / n$ ratios, with $m=$ number of incorporated AN, and $\mathrm{n}=$ number of BD monomer units. B) $7 / 4$, C) $6 / 5$, D) $5 / 6$, E) $4 / 7$, F) $3 / 8$ and G) $2 / 9$.


Figure S6. ESI mass spectra of the open chain diene-functional trithiocarbonate 2 (upper panel) and the obtained Diels-Alder cyclization product (lower panel). Formation of the cyclohexene was observed after reaction of $\mathbf{2}$ with an excess of AN for 22 h at $100^{\circ} \mathrm{C}$ in presence of butylated hydroxytoluene (BHT) as a radical inhibitor. Prior to analysis, the cycloadduct was separated from unreacted trithiocaronate $\mathbf{2}$ by column chromatography.


Figure S7. ${ }^{1} \mathrm{H}$ NMR characterization of the Diels-Alder product of $\mathbf{2}$ and AN recorded in $\mathrm{CDCl}_{3}$ at room temperature. Prior to analysis, the cycloadduct was separated from unreacted trithiocaronate $\mathbf{2}$ by column chromatography.


Figure S8. SEC traces of dienophile SAN copolymers 7a (black), 7b (blue), 7c (red) and 7d (green line). The origin of different molar masses of $\mathbf{7 a}$ and $\mathbf{7 d}$ (also see Table 1 , entry 11 and entry 14) at almost similar SEC traces is a result of the permanent updating of calibration curves to ensure an exact molecular weight determination.


Figure S9. ${ }^{1} \mathrm{H}$ NMR spectrum of SAN 7 recorded in $\mathrm{CDCl}_{3}$ at room temperature. Proton resonances of pure controlling agent $\mathbf{3}$ are indicated as blue dotted lines (see inset).


Figure S10. FT-IR analysis of SAN copolymer 7a.

# Experimental determination of the benzylthio dihydrothiopyranyl pyridine structure 3+BD responsible for the loss of control in AN/BD copolymerizations utilizing controlling agent 3. 

A high pressure glass reactor was charged with controlling agent $3(100 \mathrm{mg}, 0.41 \mathrm{mmol})$ and butylated hydroxytoluene ( $450 \mathrm{mg}, 2.04 \mathrm{mmol}$ ) as an inhibitor. Oxygen was removed by three consecutive vacuum/nitrogen cycles and 1,3-butadiene ( $45 \mathrm{~mL}, 542 \mathrm{mmol}$ ) was added via a metal burette. The reactor was sealed and heated to $100^{\circ} \mathrm{C}$. After 54 h the reactor was vented. Residual BD was removed in high vacuum and a crude ${ }^{1} \mathrm{H}$ NMR was recorded. The crude product was purified by column chromatography on silica. After residual controlling agent 3 eluted from the column with hexane/methylene chloride $\left(1: 1, \mathrm{v} / \mathrm{v}, \mathrm{R}_{\mathrm{f}} 0.47\right)$, the methylene chloride content of the liquid phase was increased to $1: 2(\mathrm{v} / \mathrm{v})$. The cyclization product $\mathbf{3 +} \mathbf{B D}$ $\left(\mathrm{R}_{\mathrm{f}} 0.2\right.$ in hexane/methylene chloride $\left.1: 1, \mathrm{v} / \mathrm{v}\right)$ was washed from the column and analyzed by NMR spectroscopy.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ spectra of $\mathbf{3 + B D}$ are provided in Fig. S 11 B and S 12 B , respectively, and are compared to the spectra of controlling agent 3 (Fig. S11A and S12A). In the ${ }^{1} \mathrm{H}$ NMR spectrum, olefinic proton resonances $d$ and e and allyl resonances $c$ and $f$ of the formed heterocycle indicate the degradation of controlling agent $\mathbf{3}$ via HDA reaction with BD (see Fig. S11). The formation of $\mathbf{3}+\mathbf{B D}$ is accompanied by a shift of the aromatic signals $\left(\mathrm{H}^{\mathrm{Py}}\right.$ and $\mathrm{H}^{\mathrm{Bn}}$ to $\mathrm{H}^{\mathrm{Py}}$ and $\left.\mathrm{H}^{\mathrm{Bn}}\right)$ as well as the methylene protons of the benzyl moiety (a to b). Moreover, ${ }^{13} \mathrm{C}$ NMR experiments (see Fig. S12) reveal the loss of the downfield resonance at 226 ppm assigned to the dithioester carbonyl of $\mathbf{3}$ when reacting with BD.

Integration of signals a and $b$ of the crude ${ }^{1} \mathrm{H}$ NMR taken after the reaction of $\mathbf{3}$ and BD allows evaluation of the conversion of $\mathbf{3}+\mathbf{B D}$ formation to be $>95 \%$. A steady removal of controlling
agent 3 from AN/BD copolymerization system via HDA cyclization over the polymerization is therefore expected. The resonances of the protons $\mathrm{H}^{\prime P y}, \mathrm{H}^{\prime \mathrm{Bn}}, \mathrm{b}, \mathrm{c}, \mathrm{d}$, e and f of the cyclic adduct are also observed when analyzing polymerization mixtures of $\mathrm{AN} / \mathrm{BD} / \mathbf{3}$ polymerization system via ${ }^{1} \mathrm{H}$ NMR spectroscopy. These results indicate formation of $\mathbf{3}+\mathbf{B D}$ and the respective macromolecular HDA cyclization adducts to cause the loss of control over RAFT copolymerization of AN/BD when using controlling agent 3.


Figure S11. ${ }^{1} \mathrm{H}$ NMR spectra $\left(\mathrm{CDCl}_{3}\right)$ of A) controlling agent $\mathbf{3}$ and B) controlling agent $\mathbf{3}$ after reaction with BD at $100^{\circ} \mathrm{C}$ and a successive purification via column chromatography.


Figure S12. ${ }^{13} \mathrm{C}$ NMR spectra $\left(\mathrm{CDCl}_{3}\right)$ of A) controlling agent $\mathbf{3}$ and B) controlling agent $\mathbf{3}$ after reaction with BD at $100^{\circ} \mathrm{C}$ and a successive purification via column chromatography.

## Investigation of Alternative Pathways to synthesize SAN- $b$-NBR

The inverse approach, i.e. the conjugation of enophile SAN with NBR copolymers synthesized from dithioester 3, was also investigated. In contrast to the SAN system, RAFT polymerization of AN and BD employing 3 to synthesize hetero-dienophile NBR did not yield the targeted RAFT polymers. Under the applied polymerization conditions - i.e. elevated temperatures, a high excess of BD versus the RAFT agent and in absence of an acidic proton $\mathbf{- 3}$ partly reacts with BD. The herein obtained structure was identified as a benzylthio dihydrothiopyranyl pyridine in an experiment described in the Supporting Information. The heterocycle no longer behaves as a transfer agent, since the thiocarbonyl moiety is crucial for the degenerative chain transfer within the RAFT process. A similar reaction of the $\mathrm{C}=\mathrm{S}$ double bond of RAFT polymers with BD proceeds during polymerization. SEC traces of a polymerization of AN and BD in the presence of $\mathbf{3}$ at various reaction times are shown in Fig. S13. As a result of the steady degradation of the moiety controlling the polymerization process, molecular weight distributions broaden with increasing reaction time. Nevertheless, at the early polymerization stages narrow dispersities <1.1 are obtained. Similar problems arise when utilizing RAFT agent 4 and broad molecular weight distributions are obtained at later polymerization stages (see Fig. S14). AN/BD copolymerizations with controlling agent 5 yield high molecular weights and high dispersities after reaction times as short as 1 h (Fig. S15). This is not surprising, since the Z-group of 5 is a strongly electron withdrawing moiety and HDA reactions of 5 proceed without further activation of the $\mathrm{C}=\mathrm{S}$ double bond.


Figure S13. SEC traces of a copolymerization of AN/BD employing controlling agent $\mathbf{3}$ and 2,2'-azobis( $N$-butyl-2-methylpropionamide) in $N, N$-dimethylacetamide at $100{ }^{\circ} \mathrm{C}$ after 5 h (dashed line, $M_{\mathrm{n}}=4800 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$, dispersity 1.1 ), 6 h (dotted line, $M_{\mathrm{n}}=5600 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$, dispersity 1.1), 8 h (dash-dotted line, $M_{\mathrm{n}}=7900 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$, dispersity 1.1 ) and 22 h (solid line, $M_{\mathrm{n}}=23000 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$, dispersity 1.8). Broad molecular weight distributions are obtained after long reaction times while at the early polymerization stages narrow distributions are observed. Experimental details are provided in Table 1, entry 8.


Figure S14. SEC traces of a copolymerization of AN/BD utilizing controlling agent 4. Samples were taken after 8 h (solid line, $M_{\mathrm{n}}=6600 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$, dispersity 1.1 ) and 22 h (dashed line, $M_{\mathrm{n}}=25000 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$, dispersity 3.1) and clearly demonstrate a broadening of molecular weight distributions with reaction time. Polymerizations were performed in chlorobenzene under azeotropic conditions employing $2,2^{\prime}$-azobis( $N$-butyl-2-methylpropionamide) as the initiator at $100^{\circ} \mathrm{C}$ (Table 1 , entry 9).


Figure S15. Evolution of $M_{\mathrm{n}}$ and dispersity with conversion for a polymerization of AN/BD utilizing controlling agent 5 exhibiting characteristics of a conventional free radical polymerization. At low conversion, high molecular weights and broad molecular weight distributions are obtained, demonstrating the degradation of controlling agent $\mathbf{5}$. Degradation of $\mathbf{5}$ is further documented by the complete loss of the red color of the phosphoryl dithioester moiety within the first hour of polymerization and was identified to proceed via HDA cyclization with BD. The blue solid line depicts the theoretically expected evolution of $M_{\mathrm{n}}$ with conversion, strongly deviating from the obtained molar masses.


Figure. S16. Integral over double and triple charges of the sodium adducts $\left[\mathbf{8}_{m+n}+2 N a\right]^{2+}$ and $\left[8_{m+n}+3 \mathrm{Na}\right]^{3+}$ of a SEC-ESI mass spectrum of Cp-capped NBR 8d of $10000 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$.


Figure S17. Full ESI mass spectrum of linear ${ }^{\dagger}$ Br-functional NBR $\mathbf{6 c}$.


Figure S18. Full ESI mass spectrum of linear Cp-functional NBR 8c.


Figure S19. Full ESI mass spectrum of linear Cp-functional NBR 8c after reaction with an excess of $\mathbf{3}$ in presence of TFA.

Table S1. Experimental details of $\mathrm{Br}-\mathrm{Cp}$ substitution reactions.

| entry |  | $\mathrm{m}(\mathbf{6}) / \mathrm{g}$ <br> or $\mathrm{m}(\mathbf{1 2}) / \mathrm{g}$ | $\mathrm{n}\left(\mathrm{NiCp}_{2}\right) / \mathrm{mmol}^{2}$ | $\mathrm{n}\left(\mathrm{PPh}_{3}\right) / \mathrm{mol}$ | $\mathrm{n}(\mathrm{NaI}) / \mathrm{mol}$ | $\mathrm{v}(\mathrm{THF}) / \mathrm{mL}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathbf{6 a} \Rightarrow \mathbf{8 a}$ | 0.585 | 0.176 | 0.089 | 0.263 | 10 |
| 2 | $\mathbf{6 b} \Rightarrow \mathbf{8 b}$ | 1.054 | 0.263 | 0.131 | 0.396 | 15 |
| 3 | $\mathbf{6 c} \Rightarrow \mathbf{8 c}$ | 0.101 | 0.444 | 0.222 | 0.667 | 1.5 |
| 4 | $\mathbf{6 d} \Rightarrow \mathbf{8 d}$ | 0.435 | 0.513 | 0.258 | 0.770 | 4 |
| 5 | $\mathbf{1 2 a} \Rightarrow \mathbf{1 3 a}$ | 0.818 | 1.963 | 0.988 | 2.938 | 10 |
| 6 | $\mathbf{1 2 b} \Rightarrow \mathbf{1 3 b}$ | 0.586 | 0.176 | 0.089 | 0.264 | 10 |



Figure S20. ${ }^{1} \mathrm{H}$ NMR characterization $\left(\mathrm{CDCl}_{3}\right)$ of Cp -functional RAFT agent obtained from substitution of the bromine of controlling agent $\mathbf{1}$.


Figure S21. ${ }^{13} \mathrm{C}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ of Cp -functional RAFT agent obtained from substitution of the bromine of controlling agent $\mathbf{1}$.


Figure S22. ESI-MS analysis of Cp-functional RAFT (RAFT-Cp) agent A) before and B) after HDA cyclization with controlling agent $\mathbf{3}$ in presence of 1.5 equivalents of TFA. The HDA cycloadduct (RAFT-Cp-3) was neutralized by washing with saturated sodium bicarbonate solution prior to ESI-MS analysis.


Figure S23. ${ }^{1}$ H NMR characterization of Cp-functional RAFT agent after reaction with 1.05 eq. of $\mathbf{3}$ in presence of TFA recorded in $\mathrm{CDCl}_{3}$ at room temperature. Excess controlling agent $\mathbf{3}$ was removed via column chromatography prior to analysis.


Figure S24. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY NMR spectrum of Cp -functional RAFT agent after reaction with 1.05 eq of $\mathbf{3}$ in presence of TFA recorded in $\mathrm{CDCl}_{3}$ at room temperature. Excess controlling agent $\mathbf{3}$ was removed via column chromatography prior to analysis.


Figure S25. ${ }^{13} \mathrm{C}$ NMR spectrum of Cp -functional RAFT agent after reaction with 1.05 eq. of $\mathbf{3}$ in presence of TFA recorded in $\mathrm{CDCl}_{3}$ at room temperature. Excess controlling agent $\mathbf{3}$ was removed via column chromatography prior to analysis.


Figure S26. ${ }^{1} \mathrm{H}$ NMR spectrum of linear NBR/SAN block copolymer 8a-b-7a recorded in $\mathrm{CDCl}_{3}$ at room temperature.


Figure S27. ${ }^{1} \mathrm{H}$ NMR spectrum and signal assignments of hydroxy functional symmetrical controlling agent $\mathbf{1 0}$ recorded in $\mathrm{CDCl}_{3}$ at ambient temperature.


Figure S28. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY NMR experiment of hydroxy functional symmetrical controlling agent 10 recorded in $\mathrm{CDCl}_{3}$ at room temperature.


Figure S29. ${ }^{13} \mathrm{C}$ NMR spectrum of hydroxy functional symmetrical controlling agent $\mathbf{1 0}$ recorded in $\mathrm{CDCl}_{3}$ at room temperature. Carbon resonances of the triazole are broad and thus poorly resolved from the noise.


Figure S30. ${ }^{1} \mathrm{H}$ NMR spectrum of ${ }^{t}$ Br-functional symmetrical controlling agent $\mathbf{1 1}$ recorded in $\mathrm{CDCl}_{3}$ at room temperature.


Figure S31. ${ }^{13} \mathrm{C}$ NMR spectrum of ${ }^{t} \mathrm{Br}$-functional symmetrical controlling agent $\mathbf{1 1}$ recorded in $\mathrm{CDCl}_{3}$ at room temperature.


Figure S32. ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ HSQC NMR spectrum of ${ }^{t} \mathrm{Br}$-functional symmetrical controlling agent $\mathbf{1 1}$ recorded in $\mathrm{CDCl}_{3}$ at room temperature allowing signal assignments of a , b and b' (see Fig. S30).


Figure S33. ESI mass spectrum of ${ }^{t} \mathrm{Br}$-functional symmetrical controlling agent $\mathbf{1 1 .}$


Figure S34. SEC trace (A) and ESI mass spectrum (B) of a SEC-ESI mass spectrometric analysis of NBR star precursor 12a. The blue area highlights the retention time from 15.85 to 16.00 min in the low molecular weight region over which ESI-MS signal averaging was performed. Besides the targeted bromo-functional NBR star precursor, sodium adducts of dead polymer chains Z-NBR-I (see inset) are observed. These chains are an inevitable side product of the RAFT process and are, however, not observed at the higher molecular weight regions (also see Fig. S35, providing double and triple charged species).


Figure S35. Integral over double and tripple charges of a SEC-ESI-MS of mid-chain ${ }^{t} \mathrm{Br}$ functional polymer 12a.


Figure S36. ${ }^{1} \mathrm{H}$ NMR of mid-chain ${ }^{t} \mathrm{Br}$ functional NBR copolymer 12a.


Figure S37. Evolution of number average molecular weight and dispersity of an AN/BD polymerization employing controlling agent 11. Conditions: $[\mathbf{1 1}]_{0}=2.2 \mathrm{mmol} \cdot \mathrm{L}^{-1}$, $[\text { Ini }]_{0}=0.3 \mathrm{mmol} \cdot \mathrm{L}^{-1}, 24 \mathrm{~h}, 100^{\circ} \mathrm{C}$, chlorobenzene, for further details see Table 1, entry 16 .


Figure S38. SEC traces at various reaction times of a polymerization of AN/BD employing controlling agent 11. Conditions: $[\mathbf{1 1}]_{0}=2.2 \mathrm{mmol} \cdot \mathrm{L}^{-1},[\mathrm{Ini}]_{0}=0.3 \mathrm{mmol} \cdot \mathrm{L}^{-1}, 24 \mathrm{~h}, 100{ }^{\circ} \mathrm{C}$, chlorobenzene, for further details see Table 1, entry 16.


Figure S39. ${ }^{1} \mathrm{H}$ NMR spectrum of mid-chain Cp functional star precursor 13a in $\mathrm{CDCl}_{3}$ at room temperature.


Figure S40. Integral over double and tripple charges of a SEC-ESI-MS of mid-chain Cpfunctional polymer 13a.


Figure S41. ${ }^{1} \mathrm{H}$ NMR spectrum of NBR/SAN 4-miktoarm star (13a)(7d) $\mathbf{2}_{\mathbf{2}}$ in $\mathrm{CDCl}_{3}$ at room temperature.

## Predici Simulations/Deconvolution

The implemented model for AN/BD copolymerization is illustrated in Scheme S1 with the relevant rate coefficients in Table $S 2$. Scheme S 2 illustrates the model implemented for simulation of AN/S copolymerization, with the employed rate coefficients shown in Table S 3 . In both Schemes S1 and S2, termination reactions are not shown but were included in the implemented models at rates governed by the rate coefficients shown in Tables S 2 and S 3 , respectively. The "Q-type" system for the description of RAFT equilibrium reactions was adopted in both simulations. ${ }^{8-9}$ A comparison of conversion and $M_{\mathrm{n}}$ data obtained experimentally, with that obtained from PREDICI ${ }^{\circledR}$ simulation is shown in Tables S4 and S5. Good correlation between experimental and simulated data is observed in both copolymerization processes. From simulation results in both cases of SAN and NBR preparations, the weight fractions of chains bearing the desired end group functionality required for subsequent conjugation reaction were computed.

In both copolymerization processes, the rate coefficient of addition of primary radical to monomer was assumed to be an order of magnitude larger than the corresponding rate coefficient of propagation for the respective monomer. The rate coefficient of addition of radicals to the RAFT agent in the pre-equilibrium steps was set to $1.0 \times 10^{6} \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$. The rate coefficients of addition $\left(k_{\beta}\right)$ and fragmentation $\left(k_{-\beta}\right)$ to the macro-RAFT were both set to $1.0 \times 10^{6} \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$ and $1.0 \times 10^{6} \mathrm{~s}^{-1}$. For termination processes, the rate coefficient of termination for processes involving primary radicals was set to $1.0 \times 10^{9} \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$, while it was set to $1.0 \times 10^{8} \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$ for termination process involving two macro-radical.

Table S2. Relevant rate coefficients for AN/BD copolymerization.

| Coefficient | A | $\mathrm{E}_{\mathrm{a}}\left(\mathrm{KJ} \mathrm{mol}^{-1}\right)$ | Coefficient | Ref. |
| :---: | :---: | :---: | :---: | :---: |
| $k_{p}^{A}$ | $1.79 \times 10^{6}$ | 15.4 |  | 10 |
| $k_{p}^{B}$ | $1.20 \times 10^{8}$ | 38.91 |  | 11 |
| $r_{A}$ |  | 0.016 | 11 |  |
| $r_{B}$ |  | 0.408 | 11 |  |

Scheme S1. Implemented model for AN/BD copolymerization.

| $\mathrm{I}_{2}$ |  |  | $\rightarrow 2 \mathrm{I}$. |  |  | $k_{d} f$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I. | $+$ | A | $\rightarrow$ I-PA. |  |  | $k_{p, i}{ }^{\text {a }}$ |
| I. | + | B | $\rightarrow \mathrm{I}-\mathrm{PB}_{1}$. |  |  | $k_{p, i}{ }^{B}$ |
| 1. | $+$ | DoPAT | $\rightarrow$ I-DoPAT | + | R (DoPAT) . | $k_{\text {pre } e_{q}}$ |
| $\mathrm{I}-\mathrm{PA}{ }_{\mathrm{n}}$. | + | DoPAT | I-PA ${ }_{n}$-DoPAT | + | R (DoPAT). | $k_{\text {pre } e^{\prime} \text { q }}$ |
| $\mathrm{I}-\mathrm{PB}_{n}$. | + | DoPAT | I-PB ${ }^{\text {-DoPAT }}$ |  | R (DoPAT). | $k_{\text {pre } E_{\text {E }}}$ |
| $\mathrm{I}-\mathrm{PA}_{\mathrm{n}}{ }^{\text {. }}$ | + | I-DoPAT | $\rightarrow \mathrm{I}-\mathrm{PA}_{\mathrm{n}}$-DoPAT | + | I | $k_{\text {pre } e^{\prime} \text { q }}$ |
| $\mathrm{I}-\mathrm{PB}_{\mathrm{n}}$. | + | I-DoPAT | $\rightarrow \mathrm{I}-\mathrm{PB}_{\mathrm{n}}$-DoPAT | + | I. | $k_{\text {pre_Eq }}$ |
| R(DoPAT) | $+$ | A | $\rightarrow \mathrm{R}-\mathrm{PA}_{1}$. |  |  | $k_{p, i}{ }^{\text {a }}$ |
| R (DoPAT) . | $+$ | B | $\rightarrow \mathrm{R}-\mathrm{PB}_{1}$. |  |  | $k_{p, i}{ }^{\text {B }}$ |
| $\mathrm{R}-\mathrm{PA}{ }_{\mathrm{n}}$. | $+$ | I-DoPAT | $\rightarrow \mathrm{R}-\mathrm{PA}_{\mathrm{n}}$-DoPAT | + | I | $k_{\text {pre } e_{\text {Eq }}}$ |
| $\mathrm{R}-\mathrm{PB}_{\mathrm{n}}$. | + | I-DoPAT | $\longrightarrow \mathrm{R}-\mathrm{PB}_{\mathrm{n}}$-DoPAT | + | I. | $k_{\text {pre_Eq }}$ |
| $\mathrm{I}-\mathrm{PA}_{\mathrm{n}}$. | $+$ | A | $\longrightarrow \mathrm{I}-\mathrm{PA}_{\mathrm{n}+1}$. |  |  | $k_{p}^{\text {AA }}$ |
| $\mathrm{I}-\mathrm{PA}_{\mathrm{n}}$. | + | B | $\longrightarrow \mathrm{I}-\mathrm{PB}_{\mathrm{n}+1}$. |  |  | $k_{p}^{A B}$ |
| $\mathrm{I}-\mathrm{PB}_{\mathrm{n}}$. | + | A | $\rightarrow \mathrm{I}-\mathrm{PA}_{\mathrm{n}+1}$. |  |  | $k_{p}^{B A}$ |
| $\mathrm{I}-\mathrm{PB}_{\mathrm{n}}$. | $+$ | B | $\longrightarrow \mathrm{I}-\mathrm{PB}_{\mathrm{n}+1}$. |  |  | $k_{p}{ }^{B B}$ |
| $\mathrm{R}-\mathrm{PA}_{\mathrm{n}}$. | + | A | R-PA ${ }_{n+1}$ |  |  | $k_{p}^{\text {AA }}$ |
| R-PA ${ }_{\mathrm{n}}$. | + | B | $\longrightarrow \mathrm{R}-\mathrm{PB}_{\mathrm{n}+1}$. |  |  | $k_{p}^{A B}$ |
| $\mathrm{R}-\mathrm{PB}_{\mathrm{n}}$. | $+$ | A | $\rightarrow \mathrm{R}-\mathrm{PA}_{\mathrm{n}+1}{ }^{\text {. }}$ |  |  | $k_{p}^{B A}$ |
| $\mathrm{R}-\mathrm{PB}_{\mathrm{n}}$. | + | B | $\rightarrow \mathrm{R}-\mathrm{PB}_{\mathrm{n}+1}{ }^{\text {. }}$ |  |  | $k_{p}^{B B}$ |
| I-PA ${ }_{\text {n }}$. | + | I-PB ${ }_{\mathrm{m}}$-DoPAT | $\longrightarrow$ I-PA ${ }_{\mathrm{n}}$-DoPAT | + | $\mathrm{I}-\mathrm{PB}_{\mathrm{m}}$. | $k_{\beta} k_{-\beta}$ |
| I-PA ${ }_{n}$. | + | R-PA ${ }_{\text {m }}$-DoPAT | $\longrightarrow I-P A_{n}$-DoPAT | + | $\mathrm{R}-\mathrm{PA} \mathrm{m}$. | $k_{\beta} k_{-\beta}$ |
| $\mathrm{I}-\mathrm{PA}_{\mathrm{n}}$. | + | R-PB ${ }_{\mathrm{m}}$-DoPAT | $\longrightarrow I-P A_{n}$-DoPAT | + | $\mathrm{R}-\mathrm{PB}_{\mathrm{m}}$. | $k_{\beta} k_{-\beta}$ |
| $\mathrm{R}-\mathrm{PA}_{\mathrm{n}}$. | + | $\mathrm{I}-\mathrm{PB}_{\mathrm{m}}$-DoPAT | $\longrightarrow \mathrm{R}^{\text {PA }} \mathrm{n}_{\mathrm{n}}$-DoPAT | + | $\mathrm{I}-\mathrm{PB}_{\mathrm{m}}$. | $k_{\beta} k_{-\beta}$ |
| $\mathrm{R}-\mathrm{PA}_{\mathrm{n}}$. | + | R-PB ${ }_{\mathrm{m}}$-DoPAT | $\longrightarrow$ R-PA ${ }_{\mathrm{n}}$-DoPAT | + | $\mathrm{R}-\mathrm{PB}_{\mathrm{m}}$. | $k_{\beta} k_{-\beta}$ |
| $\mathrm{R}-\mathrm{PA} \mathrm{n}_{\mathrm{n}}$. | + | I-PA ${ }_{\text {m }}$-DoPAT | $\longrightarrow$ R-PA ${ }_{\mathrm{n}}$-DoPAT | + | $\mathrm{I}-\mathrm{PA} \mathrm{m}_{\mathrm{m}}$ | $k_{\beta} k_{-\beta}$ |
| $\mathrm{I}-\mathrm{PB}_{\mathrm{n}}$. | + | I-PA ${ }_{\text {m }}$-DoPAT | $\longrightarrow \mathrm{I}-\mathrm{PB}_{\mathrm{n}}$-DoPAT | + | $\mathrm{I}-\mathrm{PA} \mathrm{m}_{\text {. }}$ | $k_{\beta} k_{-\beta}$ |
| $\mathrm{I}-\mathrm{PB}_{\mathrm{n}}$. | + | R-PA ${ }_{\text {m }}$-DoPAT | $\longrightarrow \mathrm{I}-\mathrm{PB}_{\mathrm{n}}$-DoPAT | + | $\mathrm{R}-\mathrm{PA}_{\mathrm{m}}$. | $k_{\beta} k_{-\beta}$ |
| $\mathrm{I}-\mathrm{PB}_{\mathrm{n}}$. | + | R-PB ${ }_{\mathrm{m}}$-DoPAT | $\longrightarrow \mathrm{I}-\mathrm{PB}_{\mathrm{n}}$-DoPAT | + | $\mathrm{R}-\mathrm{PB}_{\mathrm{m}}$. | $k_{\beta} k_{-\beta}$ |
| $\mathrm{R}-\mathrm{PB}_{\mathrm{n}}$. | + | $\mathrm{I}-\mathrm{PB}_{\mathrm{m}}$-DoPAT | $\longrightarrow$ R-PB ${ }_{\mathrm{n}}$-DoPAT | + | $\mathrm{I}-\mathrm{PB}_{\mathrm{m}}$. | $k_{\beta} k_{-\beta}$ |
| $\mathrm{R}-\mathrm{PB}_{\mathrm{n}}$. | + | I-PA ${ }_{\text {m }}$-DoPAT | $\longrightarrow$ R-PB ${ }_{\mathrm{n}}$-DoPAT | + | $\mathrm{I}-\mathrm{PA}_{\mathrm{m}}$. | $k_{\beta} k_{-\beta}$ |
| $\mathrm{R}-\mathrm{PB}_{\mathrm{n}}$. | + | R-PA ${ }_{\text {m }}$-DoPAT | $\longleftrightarrow \mathrm{R}-\mathrm{PB}_{\mathrm{n}}$-DoPAT | + | $\mathrm{R}-\mathrm{PA} \mathrm{m}$. | $k_{\beta} k_{-\beta}$ |

Table S3. Relevant rate coefficients for the AN/S copolymerization.

| Coefficient | $A$ | $E_{\mathrm{a}}\left(\mathrm{KJ} \mathrm{mol}^{-1}\right)$ | Coefficient | Ref. |
| :---: | :---: | :---: | :---: | :---: |
| $k_{p}^{A}$ | $1.79 \times 10^{6}$ | 15.4 |  | 10 |
| $k_{p}^{S}$ | $4.27 \times 10^{7}$ | 32.5 |  | 12 |
| $r_{A}$ |  |  | 0.078 | 13 |
| $r_{S}$ |  | 0.36 | 13 |  |

Scheme S2. Implemented model for AN/S copolymerization.

| $\mathrm{I}_{2}$ |  |  | $\longrightarrow$ | 2 I . |  |  | $k_{d}, f$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I. | + | A | $\rightarrow$ | $\mathrm{PA}_{1}$. |  |  | $k_{p, i}{ }^{\text {a }}$ |
| I | + | S | $\rightarrow$ | $\mathrm{PS}_{1}$. |  |  | $k_{p, i}{ }^{s}$ |
| I. | + | BPDF | $\rightarrow$ | I-BPDF | + | R(BPDF) | $k_{\text {pre_Eq }}$ |
| $\mathrm{PA}_{\mathrm{n}}$. | + | BPDF | $\rightarrow$ | $\mathrm{PA}_{\mathrm{n}}$-BPDF | + | R(BPDF) . | $k_{\text {pre_Eq }}$ |
| $\mathrm{PS}_{\mathrm{n}}$. | + | BPDF | $\rightarrow$ | $\mathrm{PS}_{\mathrm{n}}$ - - PDF | + | R(BPDF) . | $k_{\text {pre_Eq }}$ |
| $\mathrm{PA}_{\mathrm{n}}$. | + | I-BPDF | $\rightarrow$ | $\mathrm{PA}_{\mathrm{n}}$-BPDF | + | I. | $k_{\text {pre_Eq }}$ |
| $\mathrm{PS}_{\mathrm{n}}$. | + | I-BPDF | $\longrightarrow$ | $\mathrm{PS}_{\mathrm{n}}$ - BPDF | + | I. | $k_{\text {pre_Eq }}$ |
| R(BPDF). | + | A |  | PA ${ }_{1}$. |  |  | $k_{p, i}{ }^{\text {a }}$ |
| R(BPDF). | $+$ | S | $\longrightarrow$ | $\mathrm{PS}_{1}$. |  |  | $k_{p, i}{ }^{s}$ |
| $\mathrm{PA}_{\mathrm{n}}$. | + | A | $\rightarrow$ | $\mathrm{PA}_{n+1}$. |  |  | $k_{p}^{\text {AA }}$ |
| $\mathrm{PA}_{\mathrm{n}}$. | + | S | $\longrightarrow$ | $\mathrm{PS}_{\mathrm{n}+1}$. |  |  | $k_{p}^{\text {AS }}$ |
| $\mathrm{PS}_{\mathrm{n}}$. | + | A | $\longrightarrow$ | $\mathrm{PA}_{\mathrm{n}+1}$. |  |  | $k_{p}{ }^{S A}$ |
| $\mathrm{PS}_{\mathrm{n}}$. | + | S | $\longrightarrow$ | $\mathrm{PS}_{\mathrm{n}+1}$. |  |  | $k_{p}^{\text {SS }}$ |
| $\mathrm{PA}_{\mathrm{n}}$. | + | $\mathrm{PS}_{\mathrm{m}}$ - BPDF | $\longleftrightarrow$ | PA ${ }_{\text {n }}$-BPDF | $+$ | $\mathrm{PS}_{\mathrm{m}}$. | $k_{\beta}, k_{-\beta}$ |
| $\mathrm{PS}_{\mathrm{n}}$. | + | PA ${ }_{\mathrm{m}}$-BPDF | $\longleftrightarrow$ | $\mathrm{PS}_{\mathrm{n}}$ - - PPDF | + | $\mathrm{PA}_{\mathrm{m}}$. | $k_{\beta}, k_{-\beta}$ |

Table S4. Comparison of conversion and $M_{\mathrm{n}}$ data for AN/BD copolymerizations.

| Experiment number | Conversion / \% |  |  | $M_{\mathrm{n}} / \mathrm{g} \mathrm{mol}^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Experimental | PREDICI $^{\circledR}$ |  | Experimental | PREDICI $^{\circledR}$ |
| 6e | 11.6 | 16.6 |  | 15600 | 15000 |
| 6b | 12.3 | 15.3 |  | 39000 | 36000 |
| 6f | 10.3 | 13.0 |  | 68000 | 68000 |
| 6a | 29.1 | 11.0 |  | 5900 | 2900 |

Table S5. Comparison of conversion and $M_{\mathrm{n}}$ data for AN/S copolymerizations.

| Experiment number | Conversion / \% |  |  | $M_{\mathrm{n}} / \mathrm{g} \mathrm{mol}^{-1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Experimental | PREDICI $^{\circledR}$ |  | Experimental | PREDICI $^{\circledR}$ |
| $\mathbf{7 a}$ | 9.8 | 10.0 |  | 7900 | 7600 |
| $\mathbf{7 c}$ | 11.2 | 5.0 |  | 76000 | 56000 |
| 7b | 22.9 | 9.7 |  | 28000 | 14000 |



Figure S42. SEC traces of miktoarm block copolymer. 8a-b-7a (black solid line), Cp-functional star precursor 8a (red line), dienophile SAN 7a (blue line) and deconvolution data obtained via the Peak Fit program. The dashed line represents the deconvoluted peak of the actual NBR- $b$ SAN block copolymer, the dotted lines indicate the deconvoluted side products, i.e. remaining SAN (blue) or NBR (red line).


Figure S43. SEC traces of miktoarm block copolymer. 8b-b-7b (black solid line), Cp-functional star precursor 8b (red line), dienophile SAN 7b (blue line) and deconvolution data obtained from Peak Fit program. The dashed line represents the deconvoluted peak of the actual NBR-b-SAN block copolymer, the dotted lines indicate the deconvoluted side products, i.e. remaining SAN (blue) or NBR (red line).


Figure S44. SEC traces of miktoarm star copolymer (13b)(7b)2 (black solid line), Cp-functional star precursor 13b (red line), dienophile SAN 7b (blue line) and deconvolution data obtained via the Peak Fit program. The dashed line represents the deconvoluted peak of the 4-miktoarm star copolymer, the dotted line exhibits the deconvoluted overall side products, i.e. remaining SAN, NBR and 3-miktoarm star copolymer.

Equation S1. Calculation of the predicted weight fraction $w_{\text {pred }}(\mathbf{8}-\boldsymbol{b}-\mathbf{7})$ of the actual block copolymer 8-b-7 of the total sample mass of the apparent block copolymer sample under consideration of the fraction of "dead" polymer chains present in the starting materials (i.e. building blocks $\mathbf{8}$ and 7). Calculation was performed comprising the weight fractions of actual diene and dienophile functional polymers $w_{\text {pred }}(\mathbf{8})$ and $w_{\text {pred }}(\mathbf{7})$ within the starting materials, assuming full conversion of the HDA cyclization and an equimolar ratio of the actual diene and dienophile functionalized polymers $\mathbf{8}$ and $\mathbf{7}$ (excluding NBR and SAN polymer not possessing the diene oder dienophile functionality). Weight fractions of diene and dienophile polymers $w_{\text {pred }}(\mathbf{8})$ and $w_{\text {pred }}(7)$, respectively, were obtained via PREDICI ${ }^{\circledR}$ simulations. $M_{\mathrm{n}}(\mathbf{8})$ and $M_{\mathrm{n}}(\mathbf{7})$ are the molar masses of the polymer building blocks as determined from SEC.

$$
\begin{equation*}
w_{\text {pred }}(8-\mathrm{b}-7)=\frac{M_{n}(8)+M_{n}(7)}{M_{n}(8) / w_{\text {pred }}(8)+M_{n}(7) / w_{\text {pred }}(7)} \tag{S1}
\end{equation*}
$$

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