

# Supporting Information

## **Palladium-Containing Polymers *via* a Combination of RAFT and Triazole Chemistry**

Christiane Lang,<sup>a</sup> Claude Kiefer,<sup>b</sup> Elise Lejeune,<sup>a,c</sup> Anja S. Goldmann,<sup>a</sup> Frank Breher,<sup>\*b</sup>

Peter Roesky,<sup>\*b</sup> Christopher Barner-Kowollik<sup>\*a,c</sup>

<sup>a</sup> Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstraße 18, 76131 Karlsruhe, Germany. Fax +49 721 608 45740, E-Mail: christopher.barner-kowollik@kit.edu

<sup>b</sup> Institut für Anorganische Chemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 15, 76131 Karlsruhe, Germany. Fax +49 721 608 44854, E-Mail: breher@kit.edu, roesky@kit.edu

<sup>c</sup> Soft Matter Synthesis Laboratory, Institut für Biologische Grenzflächen I, Karlsruhe Institute of Technology (KIT), Herrmann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

## Calculation of Copolymer Composition

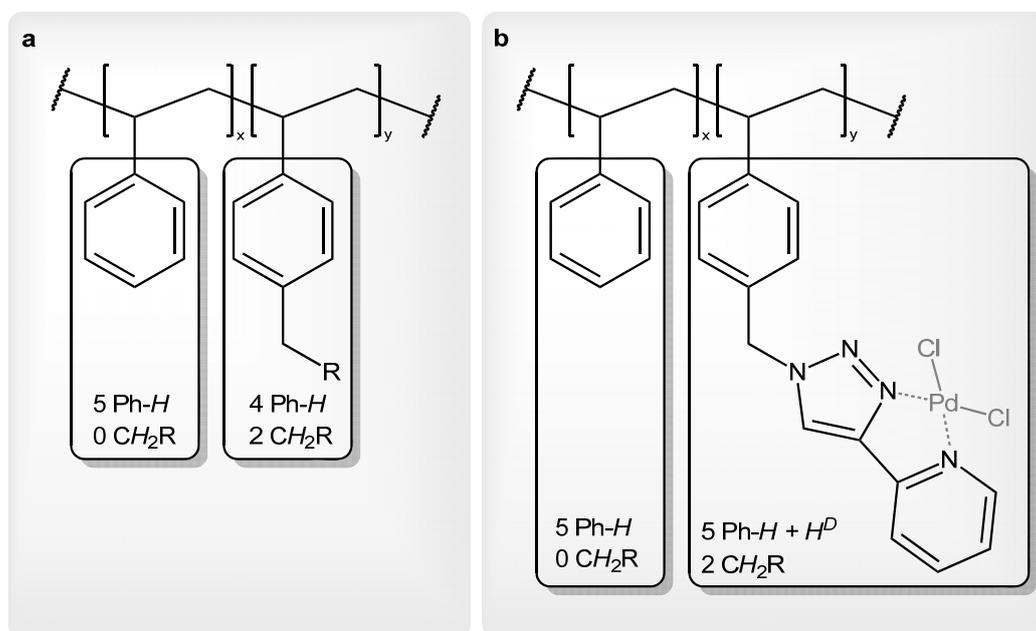
### (a) Expected Values Considering Copolymerization Parameters

Theoretically expected values for the ratio of chloromethyl styrene in the copolymer ( $F_y$ ) were estimated from monomer composition ( $f_x, f_y$ ) employing the copolymerization equation under consideration of the reactivity ratios of styrene ( $r_x = 0.72$ ) and chloromethyl styrene ( $r_y = 1.31$ ) respectively (Eq. S1).<sup>1</sup>

$$F_y = \frac{r_y \cdot f_y^2 + f_x \cdot f_y}{r_x \cdot f_x^2 + 2 \cdot f_x \cdot f_y + r_y \cdot f_y^2} \quad \text{Eq. S1}$$

<sup>1</sup> S. Kondo, T. Ohtsuka, K. Ogura and K. Tsuda, *J. Macromol. Sci. Part A*, 1979, **13**, 767-775.

### (b) <sup>1</sup>H NMR analysis:



**Scheme S1.** Structures of the polymers outlining the assumption for the calculation of the copolymer composition *via* <sup>1</sup>H NMR analysis. (a) Polymers (**P1**, R = Cl) and (**P2**, R = N<sub>3</sub>) containing five phenylic and zero methylenic protons in styrene comonomer and four phenylic and two methylenic protons in chloromethyl styrene or azidomethyl styrene comonomer respectively. (b) Polymers (**P3**, no Pd) and (**P4**, loaded with Pd) containing five phenylic and zero methylenic protons in styrene comonomer and five phenylic and two methylenic protons in ethynylpyridine adducts of the azidomethyl styrene comonomer respectively.

For calculation of the copolymer composition, the integrals of Ph-H and CH<sub>2</sub>Cl are correlated (Eq. S2) employing the protons for styrene (5 Ph-H, no CH<sub>2</sub>Cl per monomer unit, compare Scheme S1a) and chloromethyl styrene (4 Ph-H, 2 CH<sub>2</sub>Cl per monomer unit) with disregard of the endgroups. The sum of the fractions of styrene ( $F_x$ ) and chloromethyl styrene ( $F_y$ ) is set to 100% (Eq. S3)

$$\frac{I(\text{Ph}-H)}{I(\text{CH}_2\text{Cl})} = \frac{5 \cdot F_x + 4 \cdot F_y}{2 \cdot F_y} \quad \text{Eq. S2}$$

$$F_x + F_y = 1 \quad \text{Eq. S3}$$

The ratio of chloromethyl styrene ( $F_y$ ) in the copolymer can be estimated employing Eq. S4.

$$F_y = \frac{5}{2 \cdot \frac{I(\text{Ph}-H)}{I(\text{CH}_2\text{Cl})} + 1} \quad \text{Eq. S4}$$

**Table S1.** Comparison of theoretically expected and experimentally measured values for the chloromethyl styrene comonomer content,  $F_y$ , in the copolymers (**P1a-d**) employing equations Eq. S1 and Eq. S4 respectively.

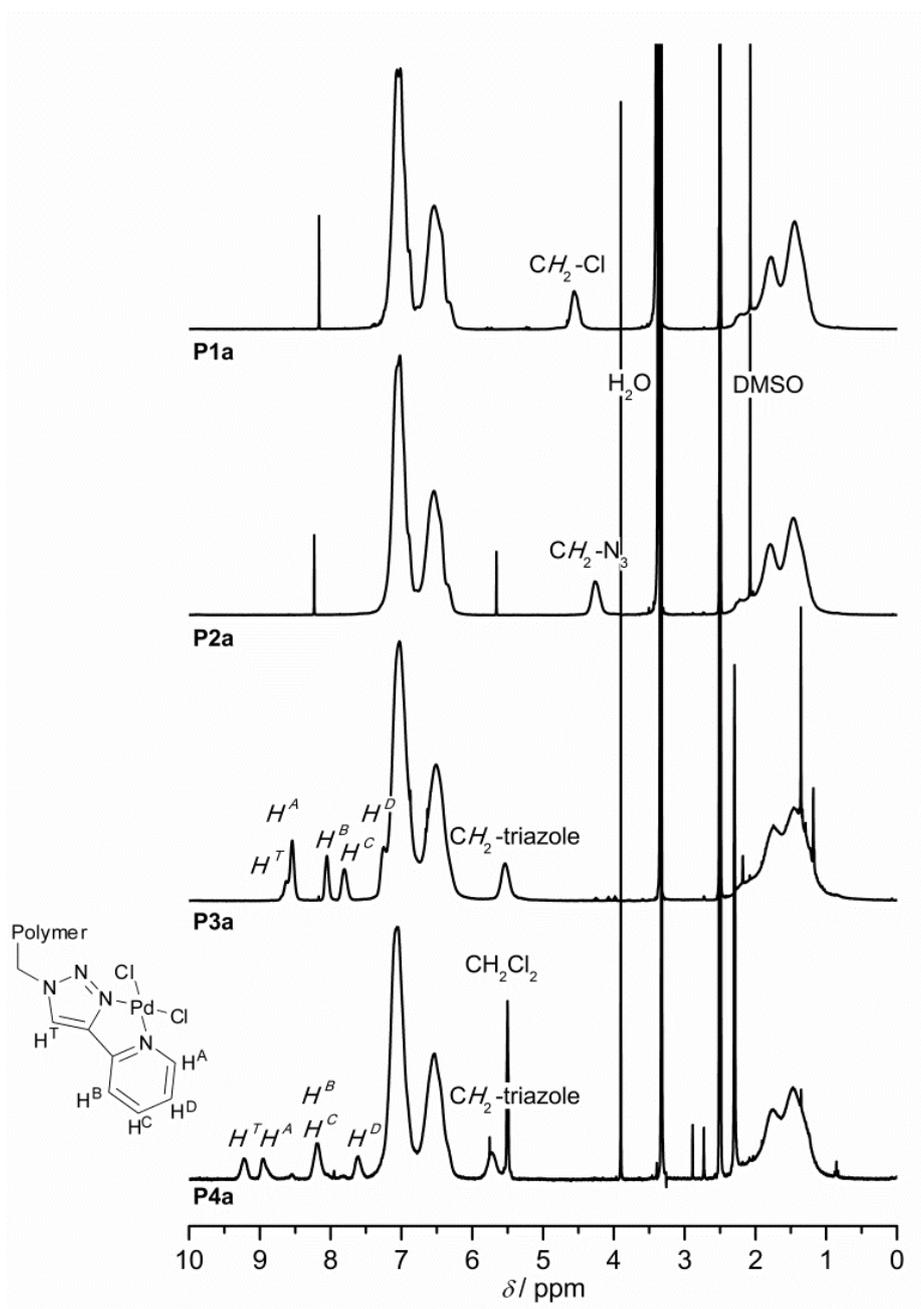
	<b>P1a</b>	<b>P1b</b>	<b>P1c</b>	<b>P1d</b>
Styrene	9.37 g 90 mmol	8.22 g 80 mmol	7.29 g 70 mmol	6.25 g 60 mmol
Chloromethyl styrene	1.53 g 10 mmol	3.05 g 20 mmol	4.58 g 30 mmol	6.10 g 40 mmol
$F_y^{\text{theor}}$	0.134	0.260	0.369	0.474
$F_y^{\text{NMR}}$	0.136	0.266	0.401	0.503

For the calculation of the compositions of the subsequent polymers, similar assumptions are implemented. For the azide functionalized polymers (**P2**), the Ph-*H* and the CH<sub>2</sub>-N<sub>3</sub> resonances are rationed (Eq. S5). After the addition of ethynyl pyridine (**P3**) and the subsequent loading with PdCl<sub>2</sub> (**P4**), the signal of the Ph-*H* resonance, which additionally overlaps with the resonance of the pyridinylic *H<sup>D</sup>* proton, and the CH<sub>2</sub>-triazole resonance are employed for the calculation (Eq. S6 is identical for both polymers **P3** and **P4**, compare Scheme S1b).

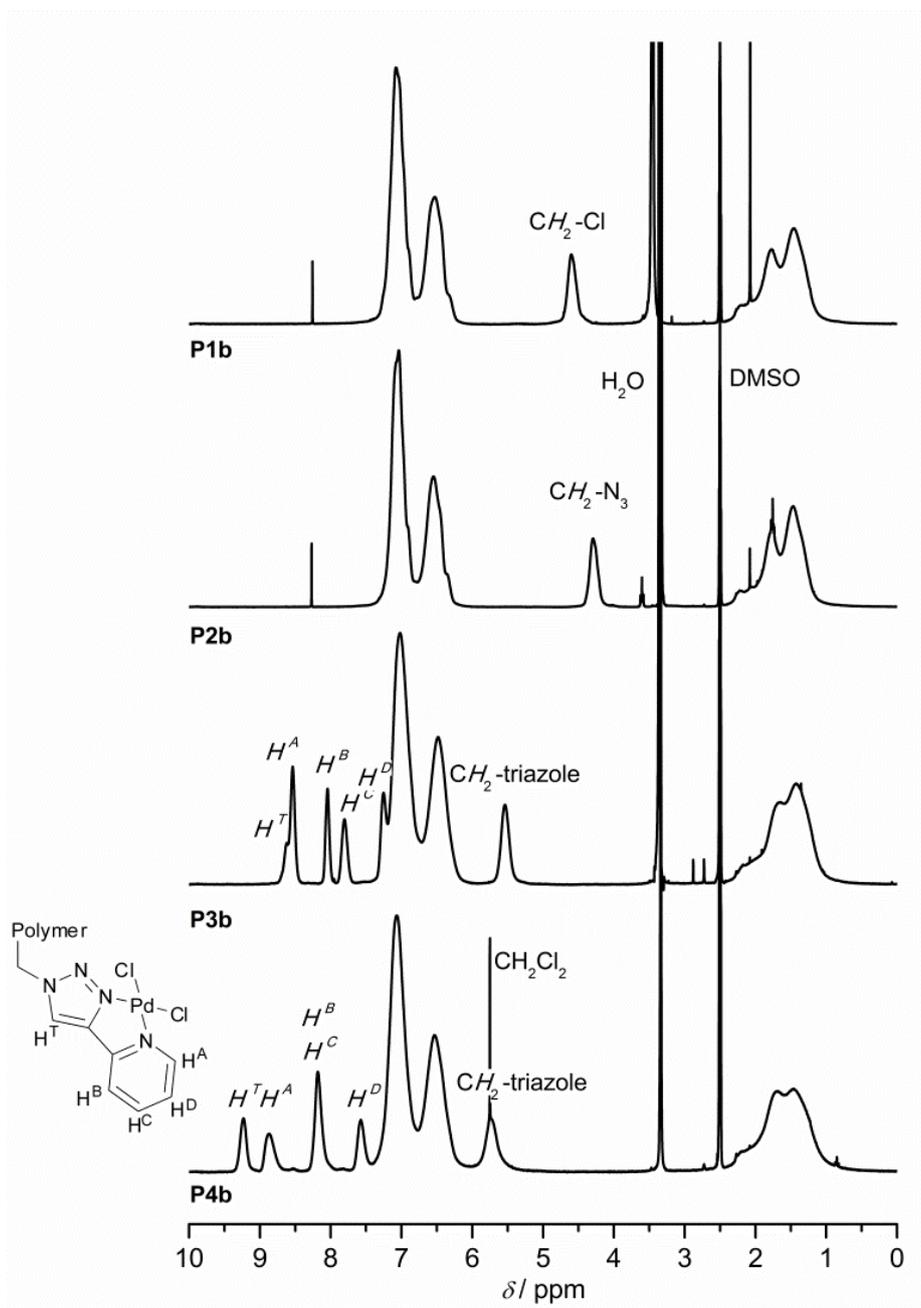
$$F_y = \frac{5}{2 \cdot \frac{I(\text{Ph}-H)}{I(\text{CH}_2\text{N}_3)} + 1} \quad \text{Eq. S5}$$

$$F_y = \frac{5}{2 \cdot \frac{I(\text{Ph}-H + H^D)}{I(\text{CH}_2\text{triazole})}} \quad \text{Eq. S6}$$

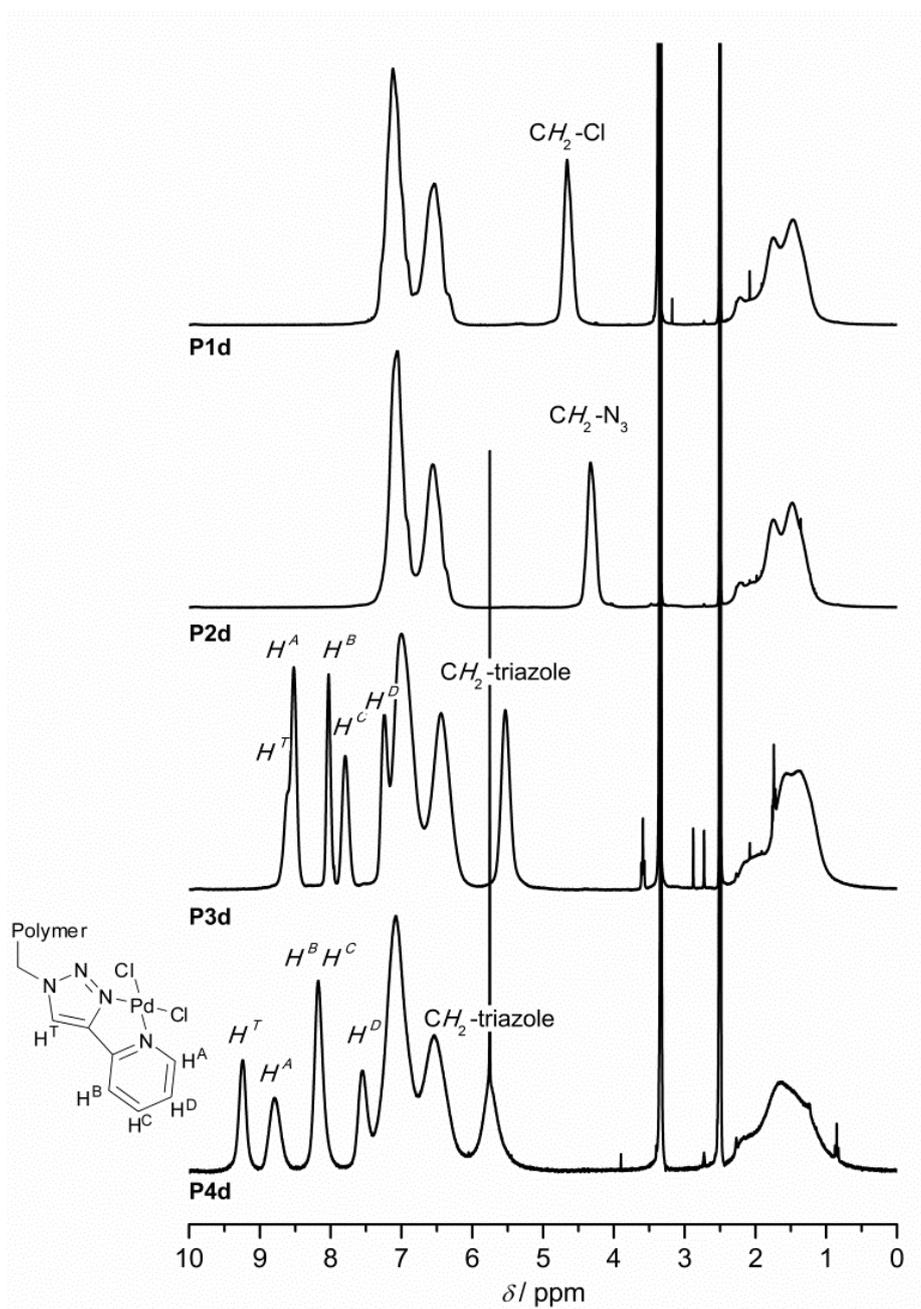
## $^1\text{H}$ NMR Spectra of the Polymers (1a-4a), (1b-4b) and (1d-4d)



**Figure S1.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-d}_6$  of polymers functionalized with chloride (**P1a**), azide (**P2a**) and triazolyl pyridine (**P3a**) at the side chains as well as palladium loaded polymer (**P4a**) with  $F_y \approx 0.1$ . The assignment of the pyridinic resonances is depicted within the structure.



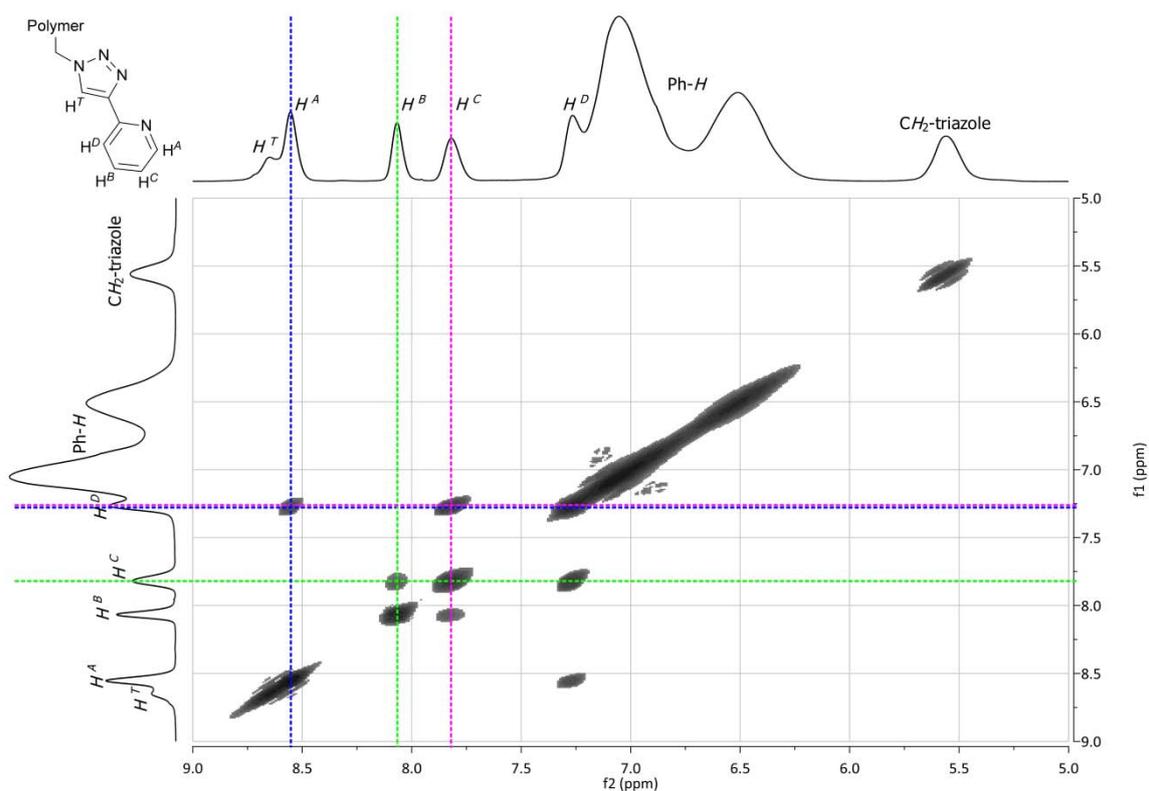
**Figure S2.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-d}_6$  of polymers functionalized with chloride (**P1b**), azide (**P2b**) and triazolyl pyridine (**P3b**) at the side chains as well as palladium loaded polymer (**P4b**) with  $F_y \approx 0.25$ . The assignment of the pyridinyl peaks is depicted within the structure.



**Figure S3.** <sup>1</sup>H NMR spectra in DMSO-d<sub>6</sub> of polymers functionalized with chloride (**P1d**), azide (**P2d**) and triazolyl pyridine (**P3d**) at the side chains as well as palladium loaded polymer (**P4d**) with  $F_y \approx 0.5$ . The assignment of the pyridinic resonances is depicted within the structure.

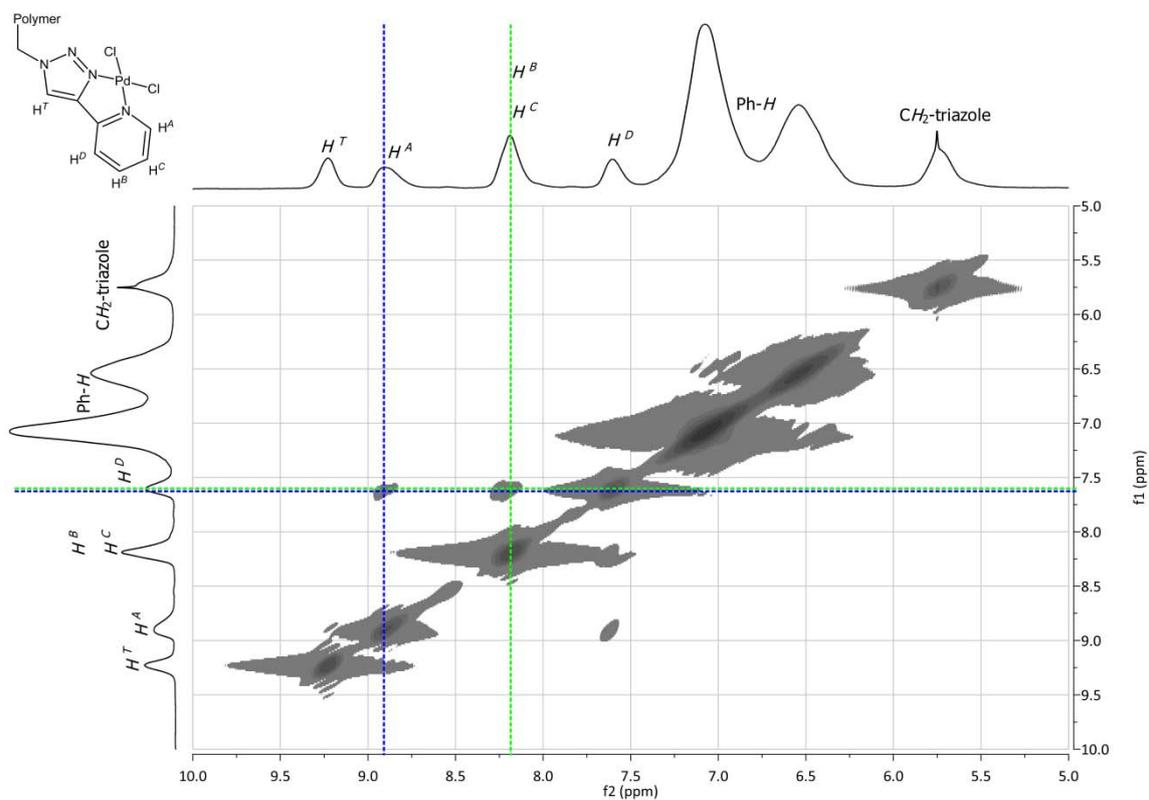
## Two Dimensional NMR Analyses (COSY) of Polymers (P3) and (P4)

For the assignment of the pyridinyl proton resonances, 2D NMR spectra of the polymers **P3** and **P4** were recorded (Figures S4 and S5). For polymer **P3**, three cross-resonances caused by  $^3J$  interaction of adjacent protons are observed. Thus,  $H^D$  is interacting with both  $H^A$  and  $H^C$  as well as  $H^C$  is interacting both with  $H^B$  and  $H^D$ . This implies that  $H^C$  and  $H^D$  are in *meta*- and *para*-position respectively relative to the pyridine-*N*.  $H^A$  and  $H^B$  are thus located in *ortho*-position. Considering the electron withdrawing effect of the nitrogen atom, the resonance for  $H^A$  shows a higher downfield-shift. The protons  $H^T$  and  $CH_2$ -triazole are isolated and show no cross-resonances.



**Figure S4.** Cross-resonance section in the COSY NMR of polymer **P3** between 5.00 and 9.00 ppm in DMSO- $d_6$ . Interactions of the protons are indicated by the coloured lines. The resulting assignment of the pyridinyl protons is depicted in the structure within the figure.

For the polymer **P4**, the signals of the protons  $H^B$  and  $H^C$  overlay with each other. Therefore, only the cross-resonances between this peak and either  $H^A$  or  $H^D$  are observed (Figure S5).



**Figure S5.** Cross-resonance section in the COSY NMR of polymer **P4** between 5.00 and 10.00 ppm in DMSO- $d_6$ . Interactions of the protons are indicated by the coloured lines. The resulting assignment of the pyridinyl protons is depicted in the structure within the figure.

## Calculation of Loading Efficiency Employing Elemental Analysis

For the determination of the loading efficiency, elemental analysis is employed. The mass fractions of C, H, N and S are measured.

The theoretically expected mass fraction of palladium for complete loading is equal to the mass ratio of palladium ( $m_{Pd}$ ) and the polymer ( $m_{polymer}$ ) (Eq. S7). For completely loaded polymers, the molar amount of palladium ( $n_{Pd}$ ) equals the molar amount of ethynylpyridine functionalized comonomer ( $n_y$ ) (Eq. S8). The mass of the polymer can be estimated as the product of the summed molar amounts of both comonomers ( $n_x$  and  $n_y$ ) with the weighted molar mass of the polymer ( $M_{polymer}$ ) (Eq. S9). Taking equations Eq. S10 and Eq. S11 into account, describing the relationship of the molar amounts of the comonomers within the polymer, the weight fraction of palladium can finally be estimated employing the resulting equation Eq. S12. The weighted molar mass of the polymers is calculated employing equation Eq. S13.

$$\omega_{Pd}^{theor} = \frac{m_{Pd}}{m_{polymer}} \quad \text{Eq. S7}$$

$$m_{Pd} = n_{Pd} \cdot M_{Pd} = n_y \cdot M_{Pd} \quad \text{Eq. S8}$$

$$m_{polymer} = (n_x + n_y) \cdot M_{polymer} = \frac{n_y}{F_y} \cdot M_{polymer} \quad \text{Eq. S9}$$

$$\frac{n_x}{n_y} = \frac{F_x}{F_y} \quad \text{Eq. S10}$$

$$F_x + F_y = 1 \quad \text{Eq. S11}$$

$$\omega_{Pd}^{theor} = F_y \cdot \frac{M_{Pd}}{M_{polymer}} \quad \text{Eq. S12}$$

$$M_{polymer} = F_x \cdot M_x + F_y \cdot M_y \quad \text{Eq. S13}$$

The experimentally determined mass fraction of  $PdCl_2$  in the polymers **P4a-d** has to be calculated from the missing mass since palladium and chloride are both not detected (Eq. S14). The mass fraction of palladium itself can thus be calculated considering the quotient of the molar masses of Pd compared to  $PdCl_2$  (Eq. S15).

$$\omega_{PdCl_2}^{EA} = 1 - \sum \omega(C, H, N, S) \quad \text{Eq. S14}$$

$$\omega_{Pd}^{EA} = \omega_{PdCl_2}^{EA} \cdot \frac{M_{Pd}}{M_{PdCl_2}} = [1 - \sum \omega(C, H, N, S)] \cdot \frac{M_{Pd}}{M_{PdCl_2}} \quad \text{Eq. S15}$$

The loading efficiency ( $f^{EA}$ ) is finally calculated as the ratio of the experimentally determined mass fraction divided by the theoretical expected mass fraction for full loading (Eq. S16).

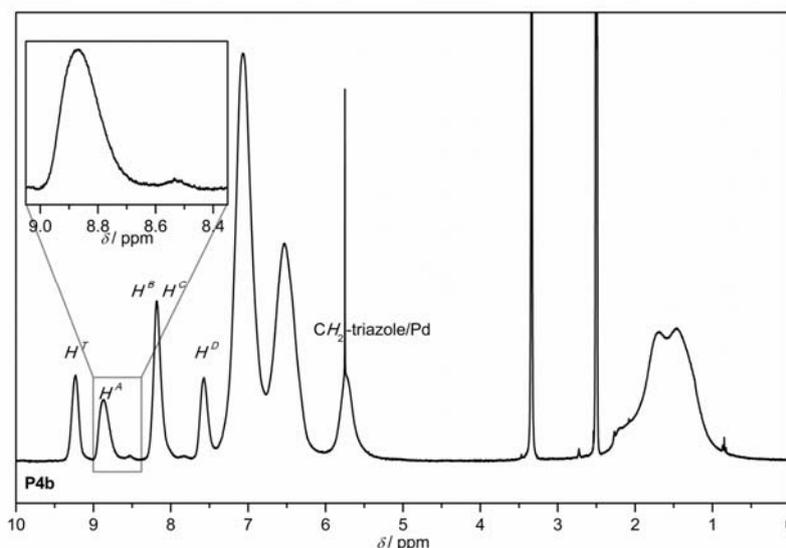
$$f^{EA} = \frac{\omega_{Pd}^{EA}}{\omega_{Pd}^{theor}} \quad \text{Eq. S16}$$

Table S2 collates the theoretically expected ( $\omega_{Pd}^{theor}$ ) and the experimentally determined ( $\omega_{Pd}^{EA}$ ) mass fractions for the polymers P4a-d as well as the respective loading efficiencies ( $f^{EA}$ ).

**Table S2.** Summary of the results from elemental analysis for the polymers **P4a-d**. The theoretically expected mass fractions were calculated according to Eq. S13, whereby the experimentally determined values and the loading efficiencies ( $f^{EA}$ ) were calculated according to Eq. S15 and Eq. S16 respectively with  $M_{Pd} = 106.40 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_{PdCl_2} = 177.33 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_x = 104.15 \text{ g}\cdot\text{mol}^{-1}$  (styrene) and  $M_y = 262.31 \text{ g}\cdot\text{mol}^{-1}$  (4-methyltriazolyl-pyridinyl functionalized styrene). The molar fraction of functionalized comonomer ( $F_y$ ) was determined *via*  $^1\text{H}$  NMR (see Table 1). For calculation, the values of  $F_y$  determined in the polymers **3a-d** are employed.

	<b>P4a</b>	<b>P4b</b>	<b>P4c</b>	<b>P4d</b>
$F_y$	0.128	0.252	0.386	0.485
$\sum \omega(C, H, N, S)$	n.d.	0.741	0.683	0.662
$\omega_{Pd}^{theor}$	0.1095	0.1862	0.2486	0.2853
$\omega_{Pd}^{EA}$	n.d.	0.1554	0.1902	0.2028
$f^{EA}$	n.d.	0.835	0.765	0.711

## Calculation of Loading Efficiencies from the $^1\text{H}$ NMR Spectra



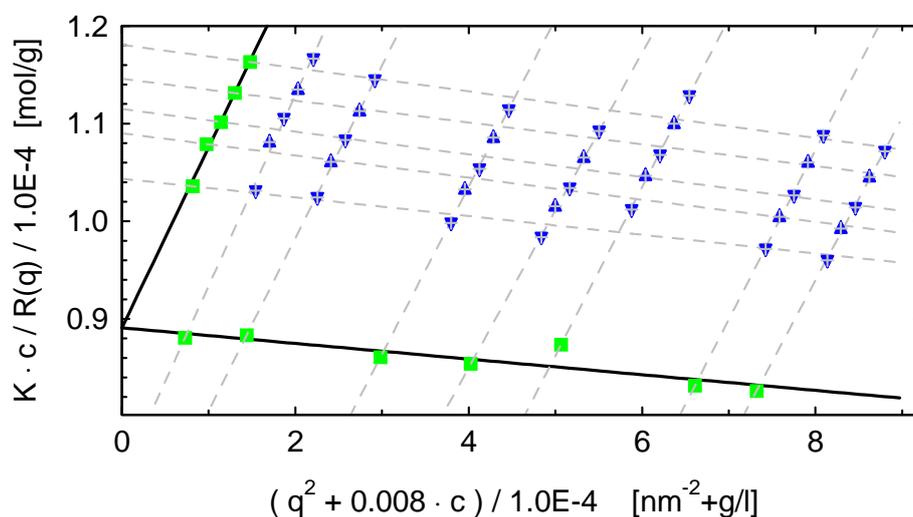
**Figure S6.**  $^1\text{H}$  NMR spectrum of polymer **P4b**. The enlarged area between  $\delta = 9.0$  ppm and  $8.3$  ppm shows the residual resonance at  $\delta = 8.52$  ppm of non-loaded pyridine moieties in the polymer. By comparing the integral of this signal with the integral of the resonance for the loaded pyridine moieties at  $\delta = 8.79$  ppm, the loading efficiency can be calculated.

## Static Light Scattering (SLS) Measurements

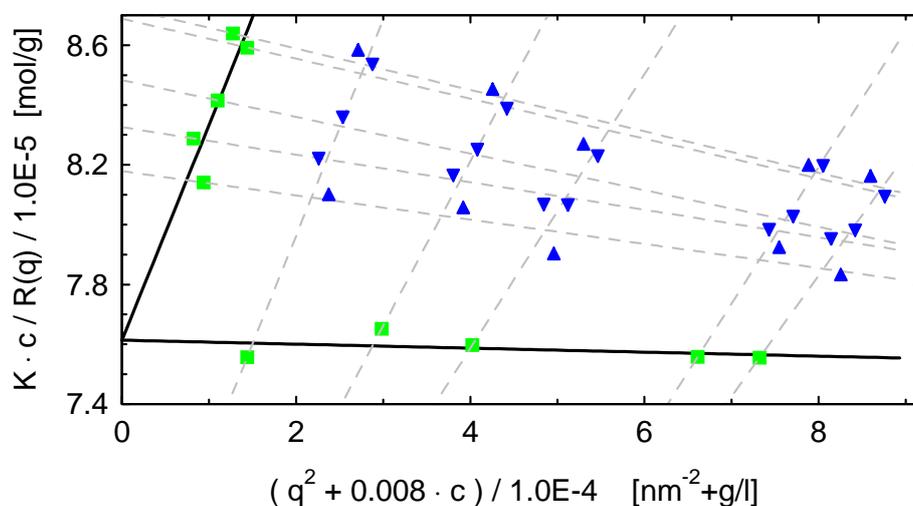
SLS provides information on the time-averaged properties of the system. The apparent weight-averaged molecular weight ( $M_w$ ) can be obtained by the Debye relationship:

$$\frac{K \cdot c}{I_r} = \frac{1}{M_w} \cdot \left( 1 + \frac{R_g^2 \cdot q^2}{3} \right) + 2 \cdot A_2 \cdot c \quad \text{Eq. S15}$$

where  $c$  is the concentration (in  $\text{g} \cdot \text{L}^{-1}$ ),  $I_r$  is the relative excess scattering intensity,  $K$  gathered optical parameters,  $R_g$  is the radius of gyration,  $q$  is the scattering wave vector, and  $A_2$  is the second virial coefficient. The absolute weight-averaged molecular weight,  $M_w$ , was obtained by extrapolating  $\frac{K \cdot c}{I_r}$  values to  $q = 0$  and  $c = 0$  according to Eq. S15 (see Figures S6 and S7 for the Zimm-Plots of polymers **P3c** and **P4c** respectively in dimethyl acetamide). SLS obtained molecular weights are collected in Table 1.

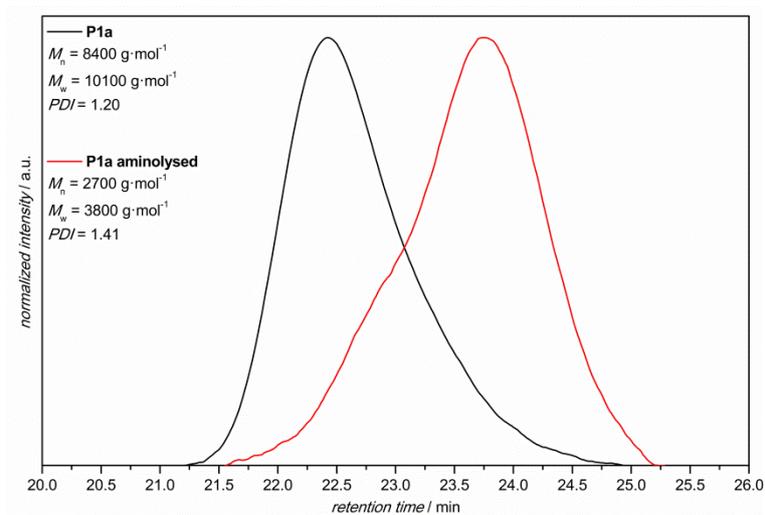


**Figure S7.** Zimm-plot obtained by SLS measurement for polymer **P3c** dissolved in DMAc for 5 concentrations ranging from 10 to 20  $\text{g} \cdot \text{L}^{-1}$ .

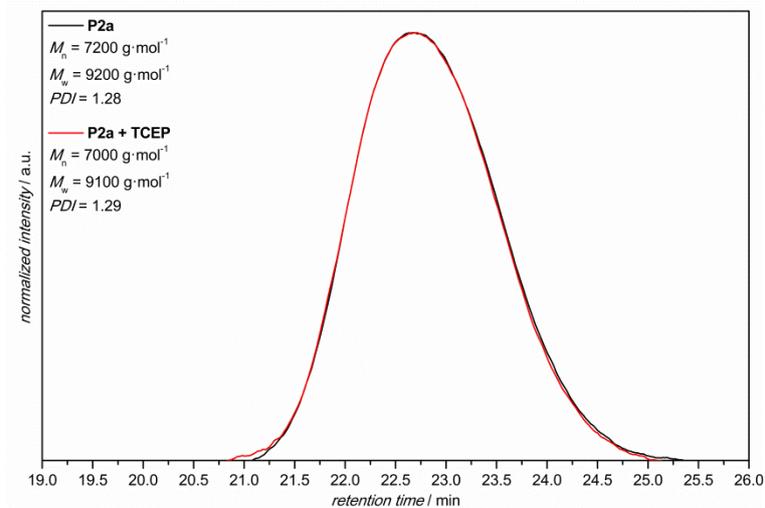


**Figure S8.** Zimm-plot obtained by SLS measurement for polymer **P4c** dissolved in DMAc for 5 concentrations ranging from 10 to 20  $\text{g} \cdot \text{L}^{-1}$ .

## SEC Elugrams of the Control Reactions Regarding the Nature of the RAFT-Group within the Azide Transformation Sequence



**Figure S9.** SEC elugrams of the chloride functionalized polymer **P1a** and the resulting polymer **P1a aminolysed** after the aminolysis reaction with *n*-butylamine. The reduction of the molecular weight in the product evidences the symmetric addition of monomers on both sides of the transfer agent DBTTC within the polymerization process.



**Figure S10.** SEC elugrams of the azide functionalized polymer **P2a** and the resulting polymer **P2a + TCEP** after the reaction with tris(2-carboxyethyl)phosphine (TCEP). There is no change in the molecular weight observed excluding the formation polymers coupled *via* disulfide bridges.