

SUPPORTING INFORMATION

Donor-acceptor block copolymers carrying pendant PC₇₁BM fullerenes with ordered nanoscale morphology

Martin Hufnagel[†], Matthias Fischer[‡], Thomas Thurn-Albrecht[‡], Mukundan Thelakkat^{†,}*

[†]Applied Functional Polymers, Department of Macromolecular Chemistry I, University of Bayreuth, Universitaetsstr. 30, 95440 Bayreuth (Germany)

[‡] Experimental Polymer Physics Group, Martin-Luther-Universität Halle-Wittenberg, Von-Danckelmann-Platz 3, 06120 Halle, Germany

*Corresponding author: mukundan.thelakkat@uni-bayreuth.de

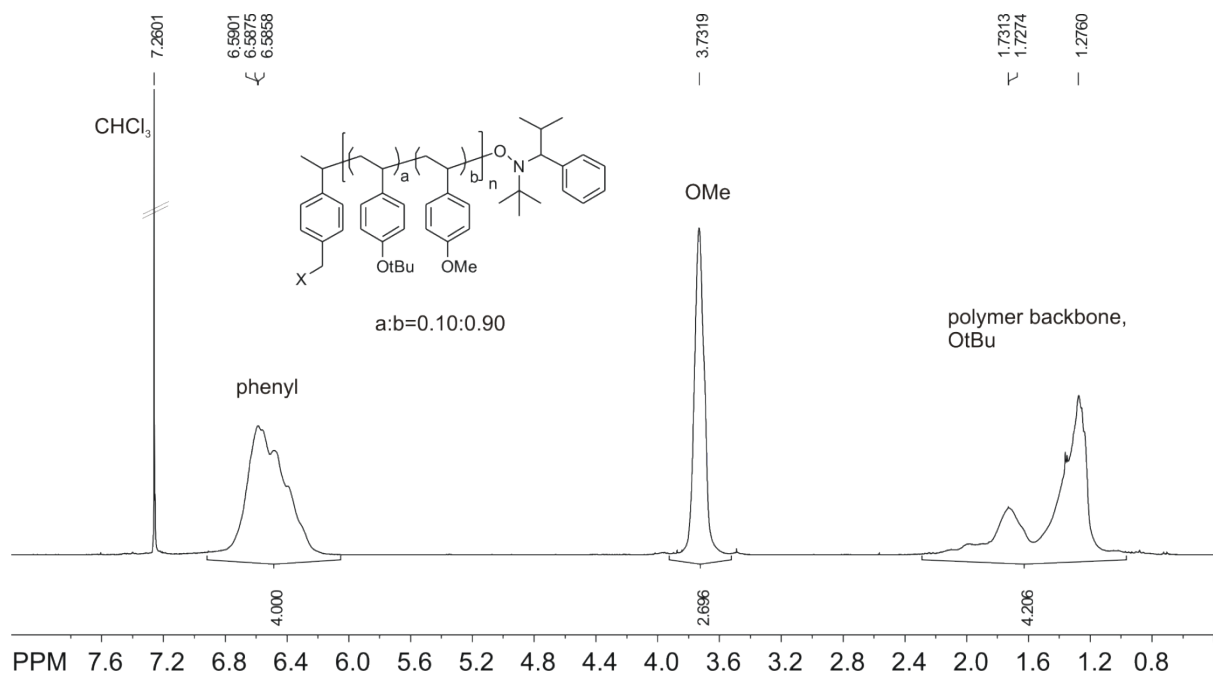


Figure S1. ¹H-NMR spectrum (300 MHz) of poly(4-methoxystyrene-*stat*-4-*tert*-butoxystyrene) PS. The built-in ratio of both monomers in the copolymer can be derived from the signal integrals giving a:b.=0.10:0.90.

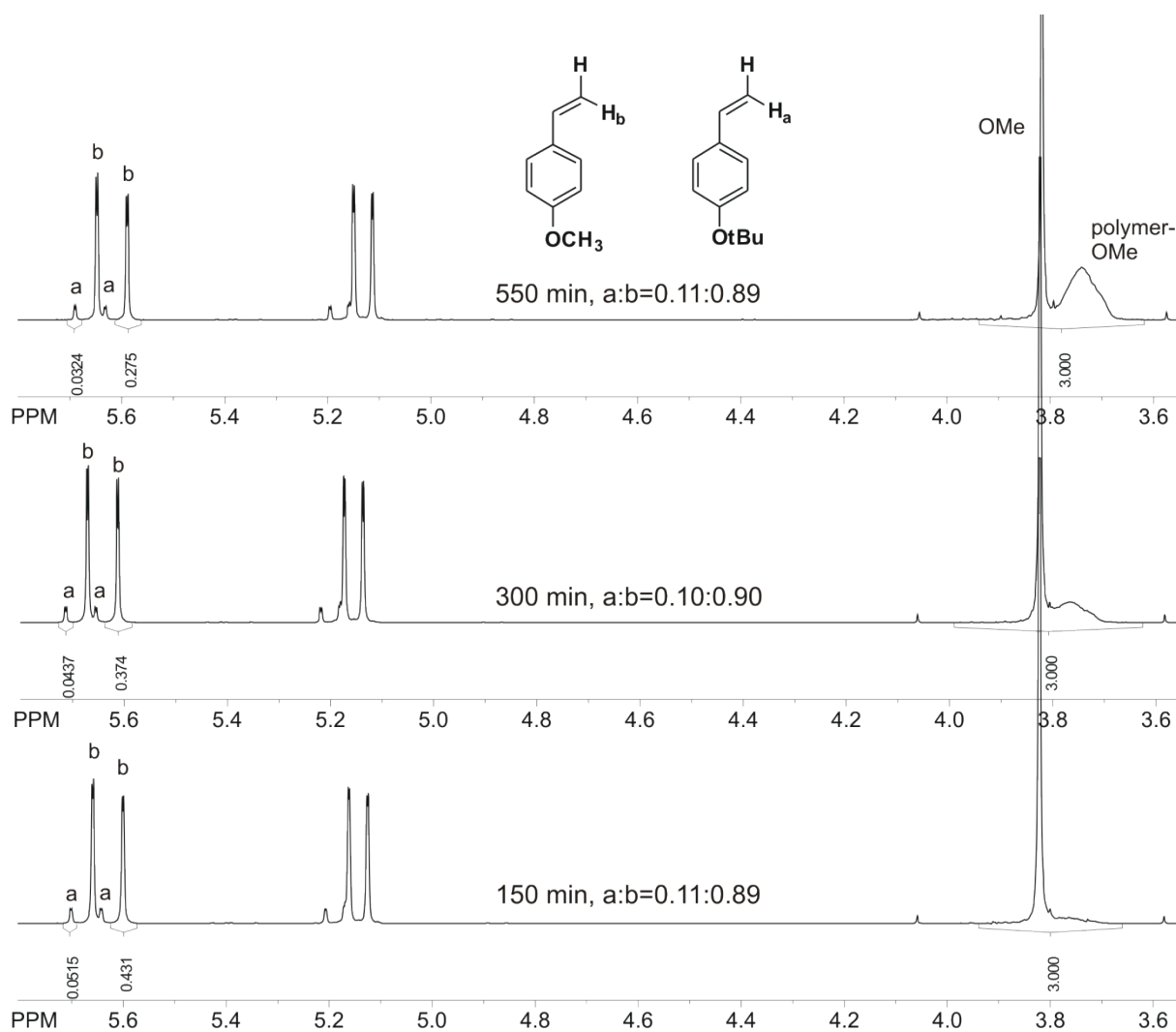


Figure S2. $^1\text{H-NMR}$ monitoring of the copolymerization kinetics of 4-*tert*-butoxystyrene (BS) and 4-methoxystyrene (MS) *via* NMRP for PS. The integral ratio of the vinyl proton resonances *a* (BS at $\delta=5.69$ ppm) and *b* (MS at $\delta=5.59$ ppm) of the unreacted monomers represent the molar ratio of both monomers in solution. It remains almost constant and was a:b=0.11:0.89, 0.10:0.90 and 0.11:0.89 after 150 min, 300 min and 550 min. Therefore the consumption of both monomers is equally fast during the copolymerization. The conversion can be determined from the ratio of proton signals of the methoxygroup (of monomer and polymer) with respect to the vinyl protons. Thus a conversion of 13% after 150 min, 25% after 300 min and 44% after 550 min was calculated.

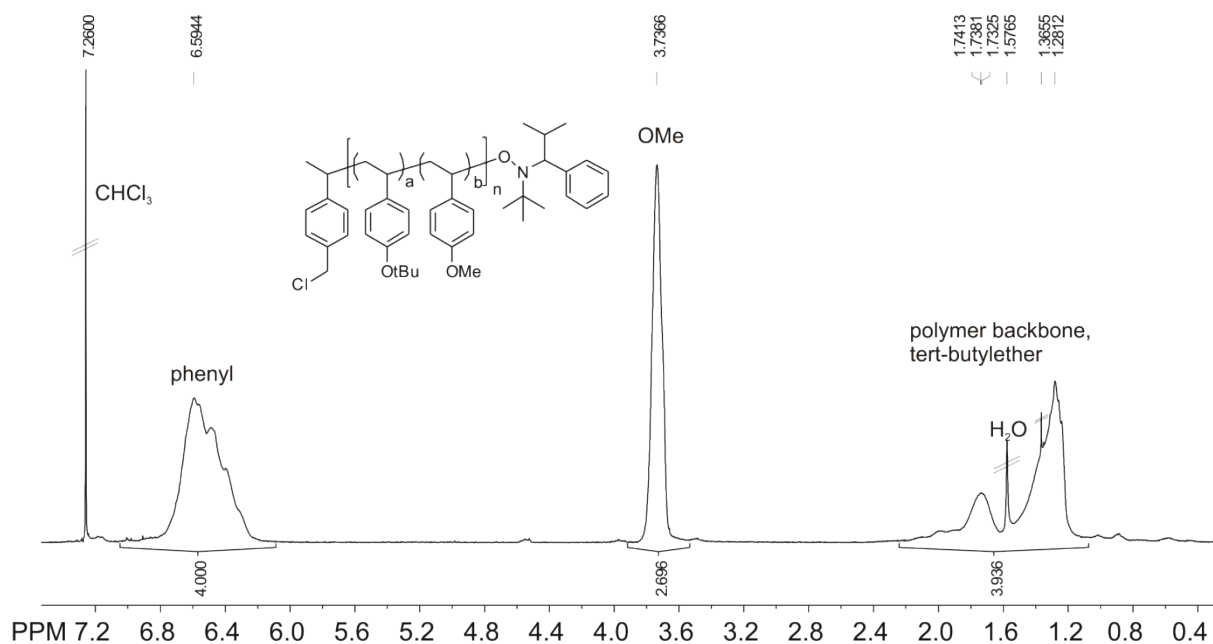


Figure S3. $^1\text{H-NMR}$ spectrum of PS-Cl. The built-in ratio of the monomers BS:MS is determined from the integrals as 0.10:0.90.

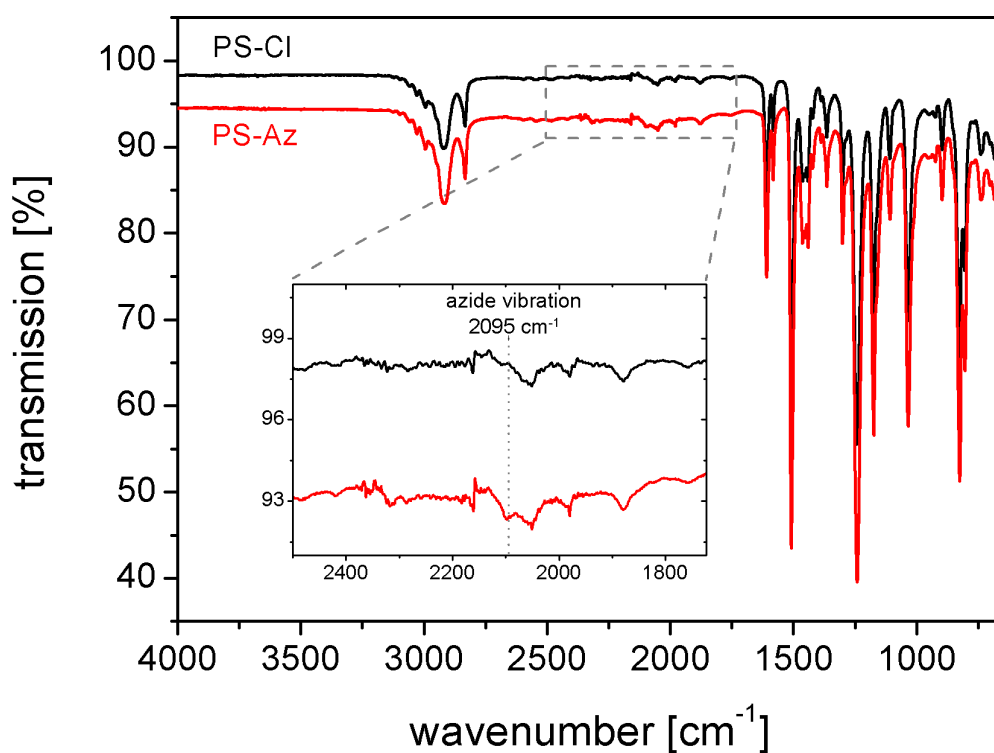


Figure S4. FTIR spectra of PS-Cl and the azido-monoterminated PS-Az. After substitution with sodium azide the copolymer PS-Az carries an azido end group which is evidenced by the weak vibration band at 2095 cm^{-1} .

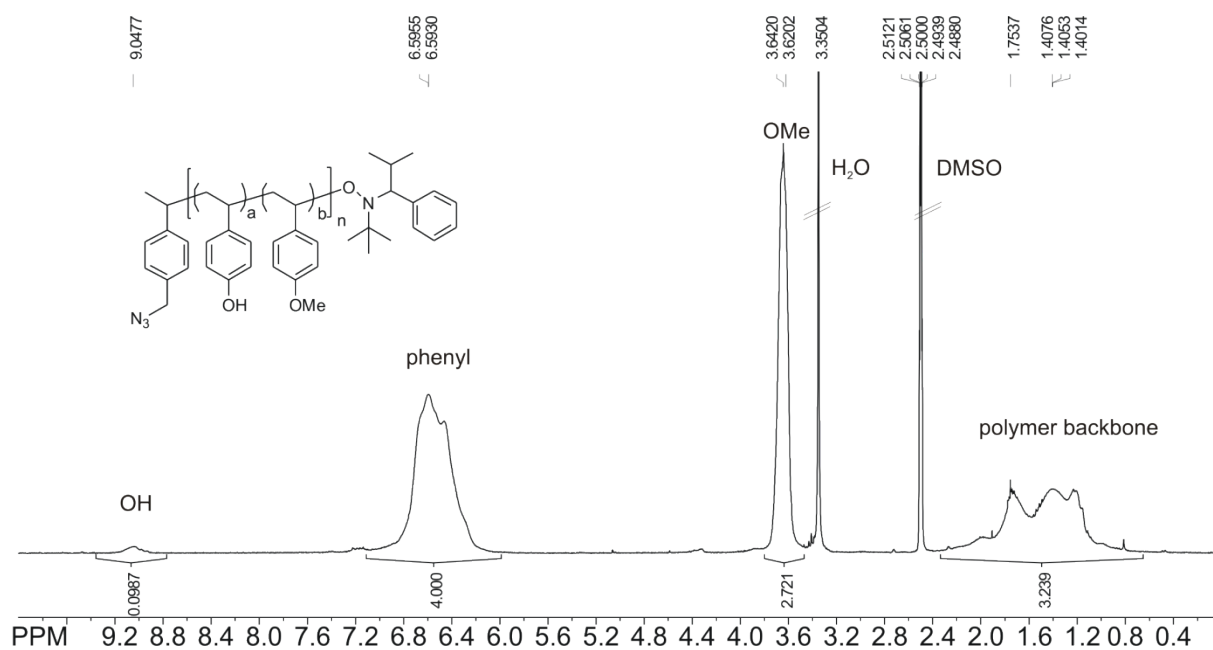
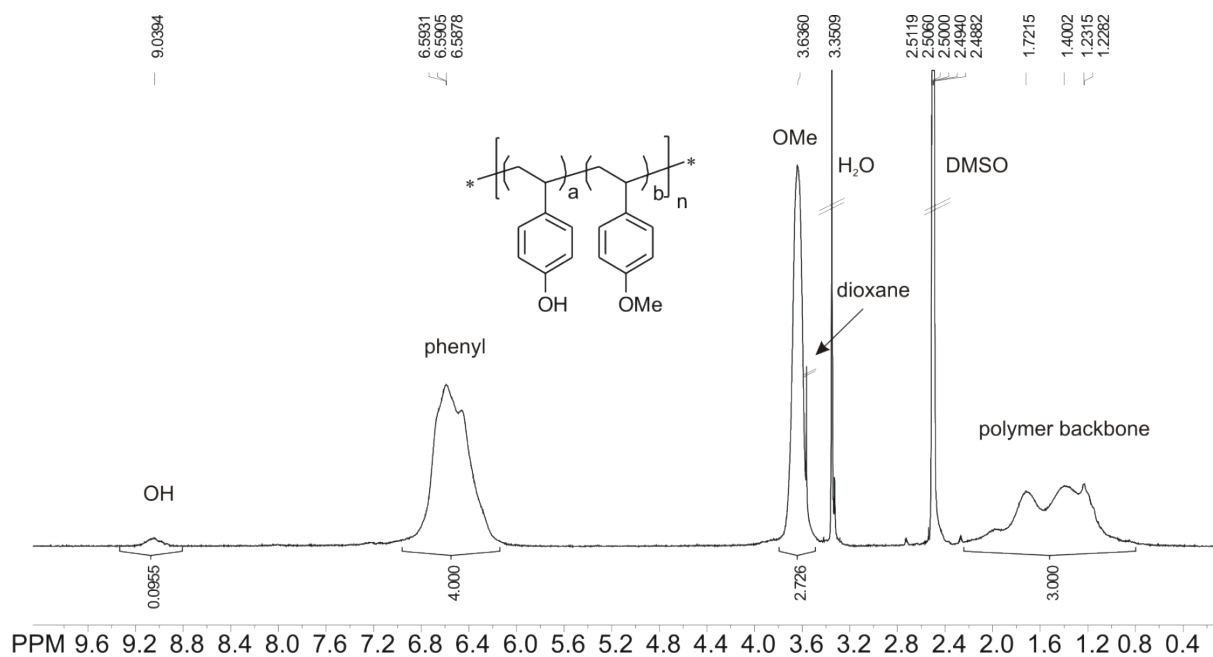


Figure S5. 1H -NMR spectrum of the deprotected copolymer PS_{OH} (top) and PS_{OH-Az} (bottom).

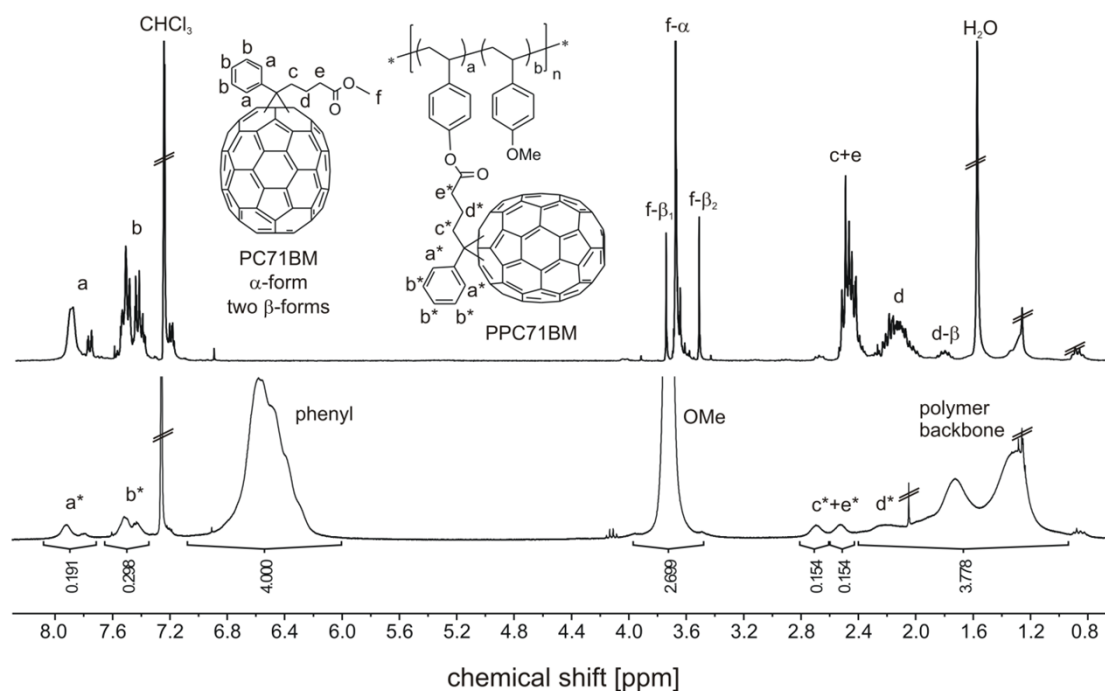


Figure S6. ¹H-NMR spectra of the small molecule compound PC₇₁BM (top) in comparison to the PC₇₁BM-grafted copolymer PPC₇₁BM (bottom). Basically, the anisotropic shape of C₇₀ is the reason why the starting material phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM), is usually obtained as isomeric mixture from synthesis with one major regioisomer, α-form [6,6]-methanofullerene, and two minor isomers, β-form achiral stereoisomers, in the ratio 85:7:8.31,32 These isomers can be distinguished in ¹H-NMR, where the methyl protons of PC₇₁BM show three different singlets at δ=3.68, 3.74 and 3.51 ppm in the ratio 83:8:9 (Figure 3). The corresponding methylene protons of the major isomer appear as fine structured multiplets at δ=2.55-2.33 ppm (4H) and δ=2.27-1.94 ppm (2H) and overlap with the multiplets of the minor isomers. Now, the grafting reaction, i.e. the ester bond formation between PC₇₁BA and the hydroxyl groups of the copolymer, can be verified by the proton NMR spectrum of PPC₇₁BM: First, all the multiplets of PC₇₁BM with its pronounced fine structure experience the same strong polymer-related signal broadening in PPC₇₁BM. Second, the methylene multiplet of PC₇₁BM at δ=2.55-2.33 ppm is split up into two separated broad resonances in PPC₇₁BM at δ=2.79-2.61 ppm and δ=2.61-2.44 ppm with equal intensity. The middle methylene group is very broad around δ=2.21 ppm and overlaps with the resonances from the polystyrene backbone. Both aspects give strong evidence for the covalent bonding of PC₇₁BA to the polymer backbone in PPC₇₁BM.

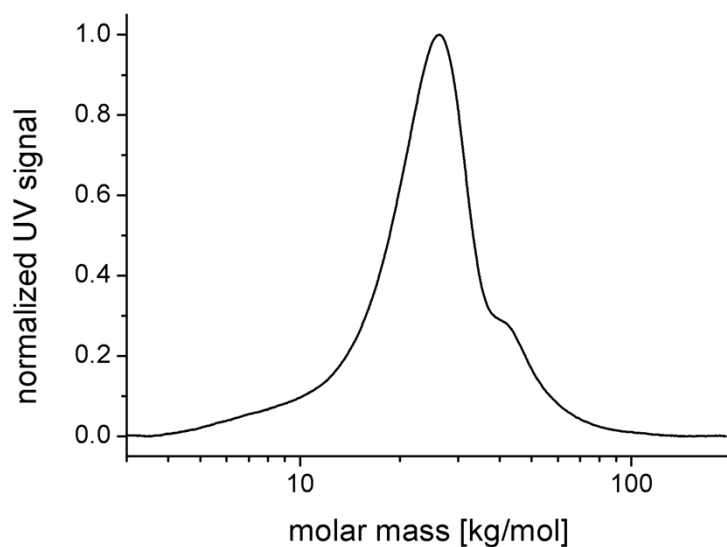


Figure S7. SEC trace of PPC₇₁BM in chloroform as eluent.

Table S1: Experimental data on molecular weights of PS, PSOH and the PC₇₁BM-grafted copolymer PPC₇₁BM.

Polymer	Molar ratio a:b	SEC [kg/mol]			MALDI [kg/mol]
		M _n	M _p ^{c)}	M _w /M _n	M _p ^{c)}
PS ^{a)}	0.1:0.9	19.6	24.6	1.19	
PSOH ^{a)}	0.1:0.9	16.7	21.7	1.19	24.4
PPC ₇₁ BM ^{b)}	0.1:0.9	20.8	26.3	1.27	42.5

a) SEC in tetrahydrofuran as eluent.

b) SEC in chloroform as eluent.

c) M_p is the peak maximum of the MW distribution curve.

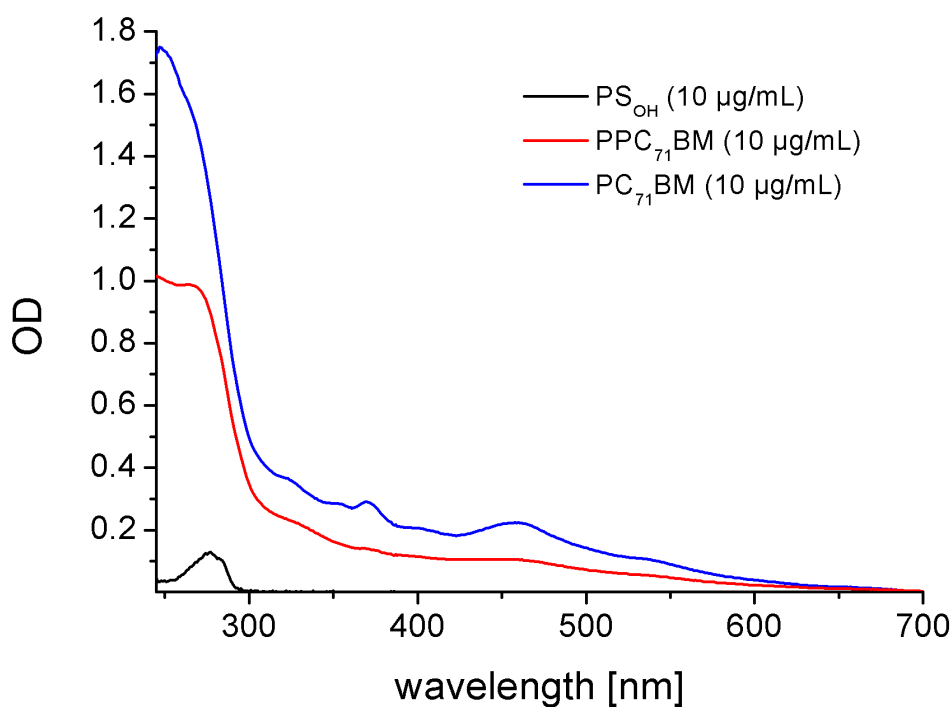


Figure S8. UV-vis absorption spectra in chloroform solution of PPC₇₁BM and the precursor copolymer PS_{OH}. The spectrum of PC₇₁BM is given as reference.

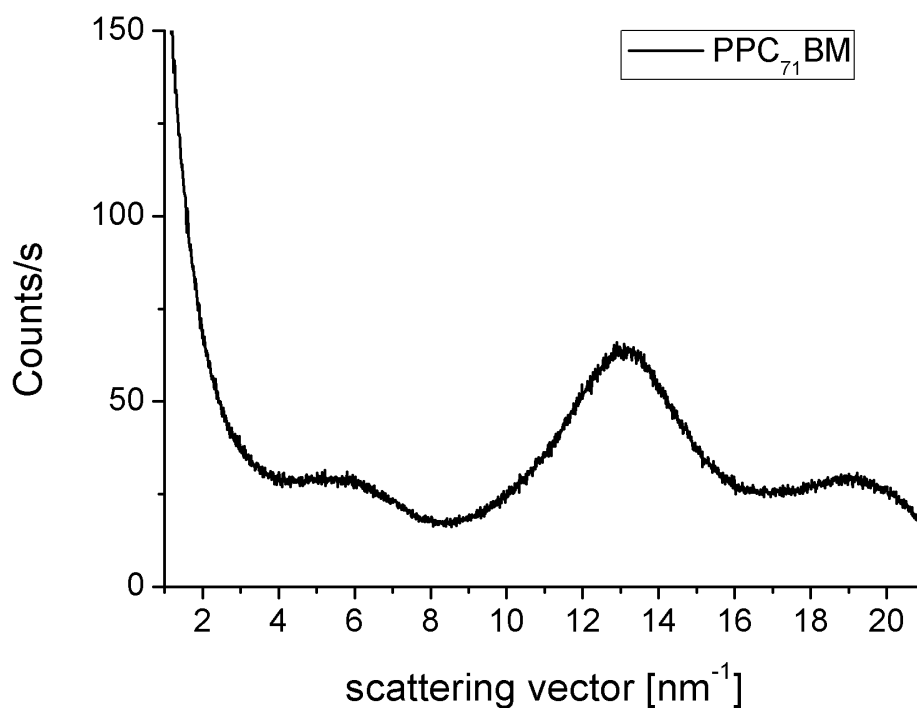


Figure S9. X-ray diffractogram of PPC₇₁BM prepared by film-casting from DCB at 70 °C in vacuum. The film was scratched and the powder filled into a glass capillary for XRD measurement.

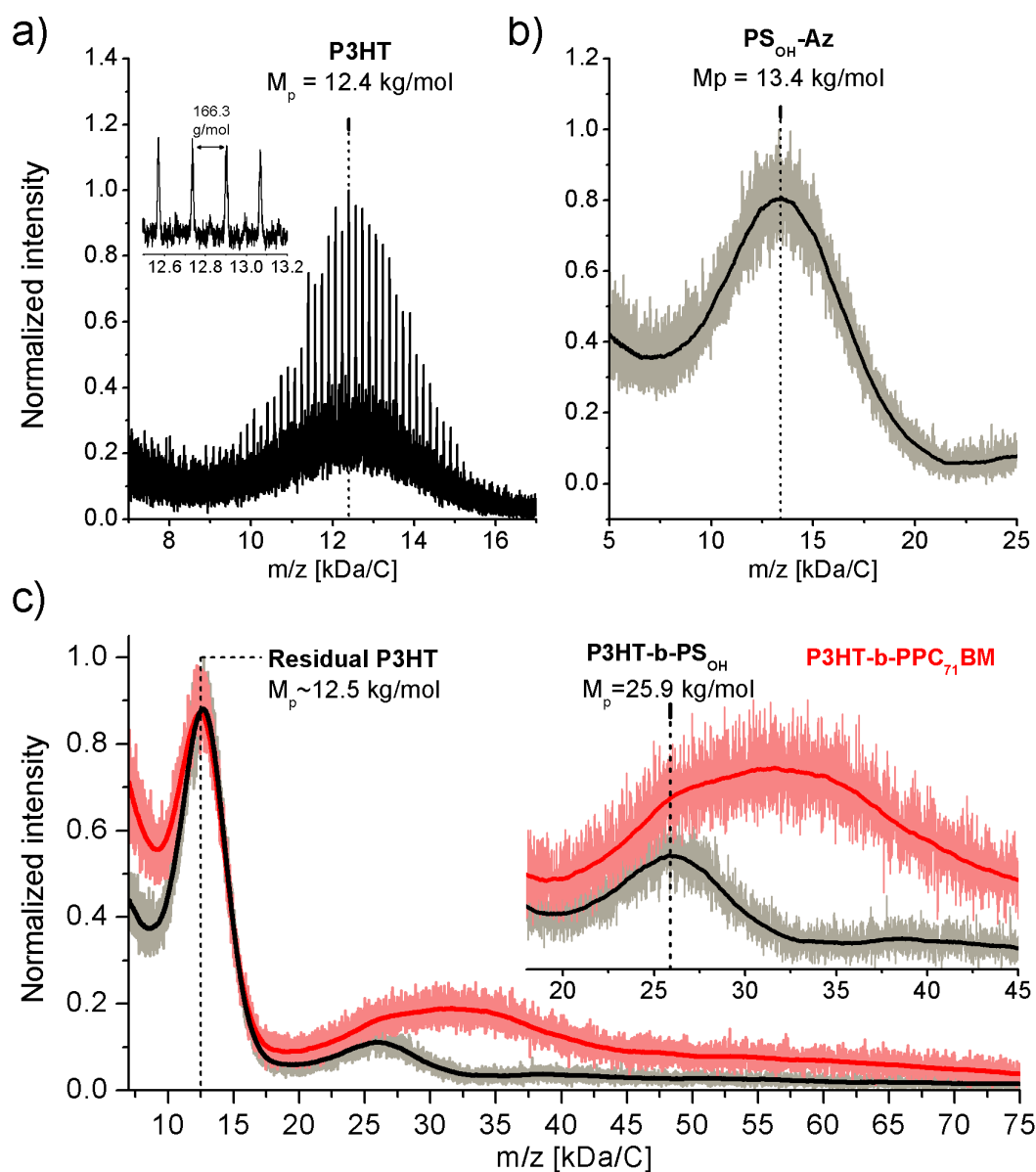


Figure S10. MALDI-TOF mass spectra of the polymer blocks (a) P3HT and (b) PS_{OH}-Az with the individual peak maxima M_p of 12.4 and 13.4 kg/mol, respectively. The block copolymers P3HT-b-PS_{OH} (black) and P3HT-b-PPC₇₁BM (red) are shown in the mass spectra in (c) containing residual P3HT and the block copolymer signal (magnified detail in the inset).

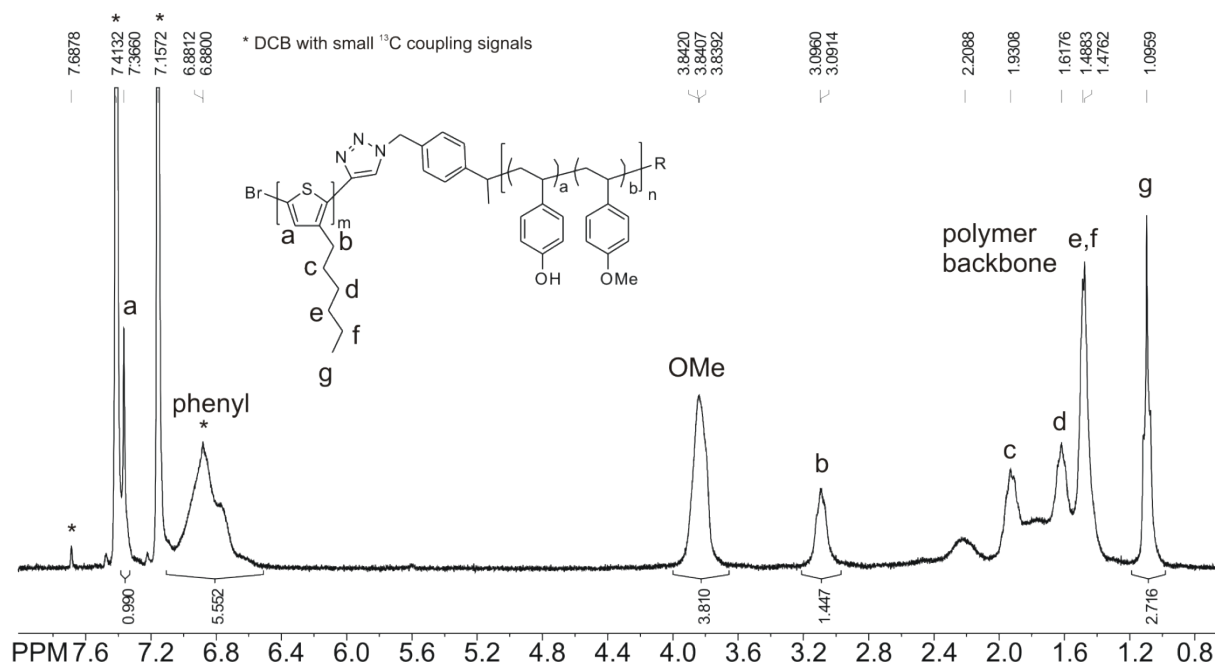


Figure S11. $^1\text{H-NMR}$ spectrum of blockcopolymer P3HT-b-PS_{OH} in DCB-d₄. The solvent residue signals of DCB were calibrated to $\delta = 7.4132$ ppm and $\delta = 7.1572$ ppm.

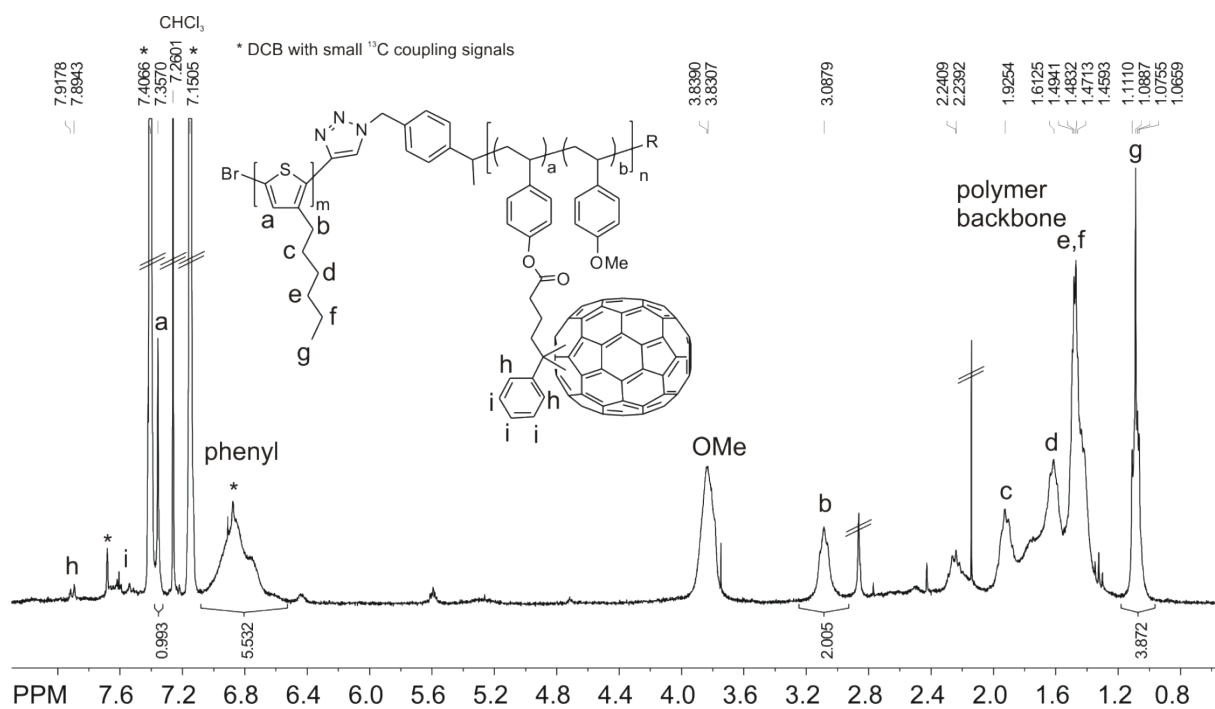


Figure S12. $^1\text{H-NMR}$ spectrum of donor-acceptor block copolymer P3HT-b-PPC₇₁BM measured in DCB-d₄. The solvent CDCl₃ was added for calibration.

Quantitative UV-Vis spectroscopy for the determination of P3HT and PC71BM content in the block copolymers

P3HT-b-PS_{OH}:

The weight content of P3HT was calculated by the ratio of mass extinction coefficients $\epsilon(\text{P3HT-b-PS}_{\text{OH}})/\epsilon(\text{P3HT})$ at the absorption maximum of 450 nm (Figure 6a). The calculated amount of P3HT is 39 wt%.

P3HT-b-PPC₇₁BM:

To determine the PC₇₁BM content, we use the mass extinction coefficients at 274 nm (Figure 6a) for PC₇₁BM and P3HT-b-PPC₇₁BM in solution due to the high absorption of the C70 fullerene in the UV range. Further it is necessary to subtract the absorption originating from polystyrene, which is clearly visible in the UV-vis spectrum of P3HT-b-PS_{OH} (Figure 6a). We can now estimate the PC₇₁BM content in P3HT-b-PPC₇₁BM from the ratio $[\epsilon(\text{P3HT-b-PPC}_{71}\text{BM}) - 0.75 \times \epsilon(\text{P3HT-b-PS}_{\text{OH}})]/\epsilon(\text{PC}_{71}\text{BM})$ which is 24 wt% PC₇₁BM in the block copolymer.

Similar approach was done for P3HT, but at a wavelength of 424 nm. Here, a correction of $\epsilon(\text{P3HT-b-PPC}_{71}\text{BM})$ by $\epsilon(\text{PC}_{71}\text{BM})$ is required due to overlapping absorption with PC₇₁BM. Note that the wavelength 424 nm is not at the absorption maximum of P3HT but shifted slightly to avoid correction errors from the distinct vibration band in PC71BM which is weaker when PC₇₁BM is grafted to a polymer. The P3HT content is then calculated using $[\epsilon(\text{P3HT-b-PPC}_{71}\text{BM}) - 0.25 \times \epsilon(\text{PC}_{71}\text{BM})]/\epsilon(\text{P3HT})$. From this calculation a weight fraction of 28 wt% of P3HT in P3HT-b-PPC₇₁BM is obtained.

Analysis of the SAXS and GISAXS scattering curves

The SAXS experiments were performed in transmission geometry on bulk samples with a typical thickness of around 1- 2 mm. We performed in addition GISAXS measurements on thin film samples prepared in different ways (crystallization from the melt and drop cast, i.e. dried from solution). We analyzed the GISAXS data in a quantitative way using a similar model function as for the analysis of the bulk SAXS data, which consists of a power law background and a Gaussian to describe the peak:

$$I = B q^{-D} + \frac{I_0}{\sqrt{2\pi} \sigma} e^{-\frac{(q - q_0)^2}{2 \sigma^2}}$$

The periodicity of the structure is calculated based on Bragg's equation, $d=2\pi/q_0$, where q_0 is the position of the first order peak. The peak position is determined by modeling the data with a function consisting of a power law background and a Gaussian describing the peak itself. The inset in the manuscript in Fig.6 shows the data after Lorentz correction, i.e. multiplication with a factor q^2 together with the model function given below.

$$I q^2 = \left(y_0 + B q^{-D} + \frac{I_0}{\sqrt{2\pi} \sigma} e^{-\frac{(q - q_0)^2}{2 \sigma^2}} \right) q^2 * q^2$$