

# NMRP versus "Click" Chemistry for the Synthesis of Semiconductor Polymers Carrying Pendant Perylene Bisimides

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ABSTRACT: The synthesis of well-defined polymers with pendant perylene bisimide (PBI) groups by a combination of nitroxide-mediated radical polymerization (NMRP) of trimethylsilyl propargyl acrylate followed by copper-catalyzed azide—alkyne cycloaddition (CuAAC, "click" chemistry) is described. The kinetics of NMRP of trimethylsilyl propargyl acrylate polymerization was monitored by <sup>1</sup>H NMR and size exclusion chromatography (SEC). Almost quantitative conversion in the "click" reaction with an azide functionalized PBI derivative was proven by FTIR and <sup>1</sup>H NMR analysis. Thus, semiconductor polymers carrying PBI pendant groups with  $M_n$  up to 15800 g·mol<sup>-1</sup> and polydispersity indices as good as 1.16 were obtained by this route. These polymers were compared with poly(perylene bisimide acrylate)s, PPerAcr-(CH<sub>2</sub>)<sub>11</sub>, and PPerAcr(CH<sub>2</sub>)<sub>6</sub>, which were synthesized by direct NMRP of PBI acrylates. These samples do not carry any triazol unit and they differ in their spacer length connecting the PBI unit to the main chain. All polymers were comparatively studied by SEC, thermogravimetry, differential scanning calorimetry, polarization microscopy, UV/vis spectroscopy, and photoluminescence measurements. The crystalline structure of the polymers was analyzed by X-ray diffraction. Inductively coupled plasma mass spectrometry analysis confirmed that copper content in the "click" polymer could be reduced down to 126 ppm (w/w).

## Introduction

Controlled radical polymerization (CRP) techniques are convenient alternatives to living ionic polymerization.<sup>1</sup> They feature the advantage of enhanced functional group tolerance and overcome the rigorous conditions of ionic polymerization, still providing good control over molecular weight and narrow polydispersity indices (PDI =  $M_w/M_n$ ). Nevertheless, control of molecular weight and PDI in CRP can be limited when it comes to the application of high molecular weight monomers, monomers with sterical hindrance, or monomers whose analogue polymers are not soluble in suitable organic solvents. The intention of bypassing such challenging issues in polymerizations by attaching the side groups at an easy to polymerize scaffold polymer block by polymer analogous reactions is often limited by incomplete conversion. However, coupling reactions that lead to quantitative conversions at moderate reaction conditions and in reasonable time, without side products and in a simple manner were summarized by Sharpless et al. in 2001 under the term "click" chemistry.<sup>2</sup> Meanwhile, these types of coupling reactions can be seen as standard reactions in organic synthesis and especially in the design of new functional materials. Upcoming metal-free "click" methods<sup>3</sup> as thiol/ene "click" chemistry<sup>4</sup> or the reversible addition-fragmentation chain transfer hetero Diels-Alder (RAFT-HDA) "click" reaction of cyclopentadienes and dithioesters<sup>5,6</sup> are promising approaches to replenish established techniques such as the Cu(I)-catalyzed 1,3-dipolar cycloaddition of azides and alkynes (CuAAC).<sup>2,7,8</sup> Nevertheless, CuAAC is currently the most commonly used "click" reaction, outstanding for its versatility and easy to introduce clickable groups. Especially the combination of CuAAC, with the three most commonly used CRP methods, atom transfer radical polymerization

(ATRP),<sup>9–12</sup> reversible addition—fragmentation chain transfer polymerization (RAFT),<sup>13,14</sup> and nitroxide-mediated radical polymerization (NMRP),<sup>15–18</sup> has proven to be a powerful tool for material synthesis. The modularity of these concepts allows studying an endless variety of different functional or nonfunctional polymers, all deriving from one synthesized alkyne or azide bearing polymer. By this approach it is possible to compare the influence of small structural changes in the pendant groups on the properties of the final polymer, keeping the degree of polymerization and PDI of the compared polymers exactly constant.

the compared polymers exactly constant. Perylene bisimide<sup>19,20</sup> (PBI = perylene tetracarboxylic acid bisimide) derivatives represent an important class of light absorbing n-type semiconductor materials, exhibiting a relatively high electron affinity among large-bandgap materials.<sup>21</sup> PBIs combine high quantum yields of photoluminescence with excellent photochemical and thermal stability and are promising compounds for application in organic electronic devices.<sup>22–24</sup> Also, suitable substituted PBIs exhibit long-range order via supramolecular self-assembly<sup>25</sup> or liquid crystalline behavior.<sup>26–28</sup>

Polymers with PBI as pendant groups feature high electron mobility combined with good film forming properties.<sup>29</sup> Such polymers were already incorporated as one block in semiconductor donor–acceptor block copolymers for photovoltaic application.<sup>22,23,30–34</sup> Nevertheless, the homopolymerization of PBI containing acrylates remains problematic because it results in polymers with broad molecular weight distributions. Also, limited solubility of resulting PBI polymers, combined with the need to work in highly concentrated solutions, restricts the nature of the substituents of PBI monomers. Considering that narrow molecular weight distributions are important to understand structure– property relationships in polymers and block copolymers, a synthetic route to PBI-containing polymers with narrow PDIs and a higher independence of the chemical nature of the PBI derivative is desirable. With this in mind, a combination of

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Figure 1. "Clicked" PBI polymers 10a,b with a spacer length of  $(CH_2)_6$  and the two reference perylene bisimide polymers PPerAcr $(CH_2)_{11}$  13 and PPerAcr $(CH_2)_6$  14 with spacer length of  $(CH_2)_{11}$  and  $(CH_2)_6$ , respectively, synthesized directly by nitroxide mediated polymerization.



Figure 2. Homopolymerization to poly(perylene bisimide acrylate) PPerAcr(CH<sub>2</sub>)<sub>11</sub> 13 using 11 as initiator in *o*-dichlorobenzene solution at 125 °C and a ratio of  $[M]_0:[I]_0$  of 50:1. (•) Experiment with additional 0.1 equiv of free nitroxide 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO); ( $\blacktriangle$ ) experiment with 0.1 equiv of TIPNO and additional 5 mol % of styrene. (a) First-order kinetic plots. (b) Dependence of  $M_n$  and  $M_w/M_n$  on the monomer conversion.

NMRP and "click" chemistry seems to be a very promising approach. PBI was employed successfully in "click" chemistry by Langhals et al. as fluorescence label.<sup>35</sup> Nolte et al. already showed that the clicking of PBI to polyisocyanopeptides is possible quantitatively.<sup>36</sup> However, these polymerizations were not controlled and showed broad polydispersities. Very recently, Segalman et al. obtained PBI-containing block copolymers by a double "click" approach, first coupling P3HT with poly-(trimethylsilyl propargyl acrylate) obtained by ATRP, followed by a second CuAAC with an azide containing PBI.<sup>33</sup>

Motivated by these successful examples of the combination of PBI with "click" chemistry, we investigated the suitability of this synthetic concept in detail to establish a general method toward narrow distributed polymers with pendant PBI units. First, we give a detailed study of the synthesis of a "clicked" PBI polymer with a  $(CH_2)_6$  spacer by combination of CuAAC and NMRP. Second, we examine how the triazol unit of "clicked" polymers changes the polymer properties. For this purpose, we synthesized two reference PBI polymers directly by NMRP that do not carry any triazol unit and which differ in their spacer lengths, for example,  $(CH_2)_6$  and  $(CH_2)_{11}$  spacers. The three PBI polymers depicted in Figure 1 are compared with respect to their structural, optical and thermal properties.

#### **Results and Discussion**

Polymer Synthesis. The polymers 10a,b with different molecular weights were obtained by a combination of NMRP and "click" chemistry, whereas the polymers  $PPerAcr(CH_2)_{11}$  13 and PPerAcr(CH<sub>2</sub>)<sub>6</sub> 14 were obtained by the direct NMRP of acrylate monomers carrying the respective PBI pendant groups with  $(CH_2)_{11}$  or  $(CH_2)_6$  spacers, respectively. As a typical example, the kinetics of the polymerization of 13 is given in Figure 2. The polymerization was conducted with 0.1 equiv of additional free nitroxide to shift the equilibrium to the dormant species and enhance control of the polymerization. The kinetic plots for the polymerization are given in Figure 2a. As can be evidently seen, the polymerization kinetics do not follow a perfect linear first order and the PDI increases continuously with conversion. Further increase of free nitroxide to 0.2 and 0.5 equiv also did not improve the PDI (see Figures S1-S3). On the other hand, even though the addition of 5 mol % of styrene<sup>34,37</sup> as comonomer along with 0.1 equiv of free nitroxide improves the kinetics to a linear progression, the PDI still rises strongly with conversion. This behavior can be ascribed to transfer reactions occurring permanently during the

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polymer	$M_{n} [g/mol]$ (SEC) <sup>a</sup>	$\frac{M_{ m w}/M_{ m n}}{ m (SEC)^a}$	$T_{\text{onset}} [^{\circ}\text{C}]^{b}$	$T_{\mathrm{m},1}  [^{\circ}\mathrm{C}]^c$	$\Delta H  [\mathrm{J/g}]^c$	$T_{\mathrm{m,2}}  [^{\circ}\mathrm{C}]^{c}$	$\Delta H \left[ \mathrm{J/g} \right]^c$	notes
3a	2100	1.17						protected alkyne polymer from 2
4a	1300	1.17						deprotected alkyne polymer from 3a
10a	5200	1.16						"clicked" PBI polymer from 4a
3b	5800	1.20						protected alkyne polymer from 2
4b	4200	1.20						deprotected alkyne polymer from 3b
10b	15800	1.17	310	175	1.2	288	0.5	"clicked" PBI polymer from 4b
13	18400	1.68	359	189	7.6	n.o.		reference polymer $PPerAcr(C_{11})$
14	12500	1.80	356	193	4.6	311	0.5	reference polymer PPerAcr( $C_{4}$ )

 Table 1. Overview of the Analysis Data of the Polymers, with Respect to Molecular Weight and Polydispersity Determined by SEC, Thermal Stability Determined by Thermogravimetric Analysis and Observed Phase Transitions and Enthalpies from Differential Scanning Calorimetry

<sup>*a*</sup> Note: Measured with size exclusion chromatography in tetrahydrofuran and calibrated with polystyrene standards. <sup>*b*</sup> Measured by thermogravimetric analysis under a  $N_2$  atmosphere. <sup>*c*</sup> Measured by differential scanning calorimetry under a  $N_2$  atmosphere.

Scheme 1. S	vnthesis of Alky	vne Polymers 4	a,b by Nit	troxide-Mediated	Radical Polym	nerization of 2 and	Subsequent De	protection of 3a,b
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 ${}^{a}$ DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, TIPNO = 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide, TBAF = tetra-*n*-butylammonium fluoride, THF = tetrahydrofuran, *o*-DCB = *ortho*-dichlorobenzene.

polymerization. Because of these reasons, a new synthetic route for PBI carrying polymers by "click" chemistry is investigated by avoiding the transfer reactions in direct NMRP. The poly(perylene bisimide acrylate) polymers **13** and **14** reported in this work were polymerized without the addition of styrene because it has no beneficial effect on the quality of the polymers at higher conversions and enhances the reaction time. The SEC and thermal data of the polymers are summarized in Table 1.

An overview of the synthetic route to obtain the alkyne polymers **4a,b** from propargyl acrylate **1** is given in Scheme 1 and their conversion to "clicked" PBI polymers **10a,b** is given in Scheme 2. For the sake of comparison with PBI polymers directly synthesized via NMRP, we used an acrylate monomer to build up the alkyne carrying precursor polymer. Thus, propargyl acrylate **1** was prepared by the reaction of acrylic acid chloride with propargyl alcohol.<sup>38</sup> Because the polymerization of the unprotected propargyl acrylate **1** by NMRP is complicated by coupling reactions of the alkyne, which leads to cross-linking,<sup>9,16</sup> the alkyne function was protected with trimethylsilyl chloride under catalysis of AgNO<sub>3</sub> and 1,8-diazabicyclo[5.4.0]undec-7-ene.<sup>16</sup> To avoid deprotection, monomer **2** was stored at -14 °C under inert gas atmosphere and was freshly distilled each time before use.

The polymerization of **2** was conducted at 125 °C using alkoxyamine **11** as initiator and with a ratio of monomer to initiator [M]/[I] = 50:1. An additional 0.1 equiv of free

nitroxide 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) was added to shift the equilibrium of the NMRP more toward the dormant species and thereby to increase the control over the polymerization. The low molecular weight polymer 3a was obtained by quenching the reaction at a lower conversion. Our first attempts to polymerize 2 in bulk showed only very low conversions below 5%, even after 24 h. After dilution with o-dichlorobenzene (o-DCB), reasonable conversions above 60% were observed in this time span. For further investigation of this effect, we studied kinetics of the polymerization at monomer concentrations of 9 mol·L<sup>-</sup> and 27 mol  $\cdot$  L<sup>-1</sup> in *o*-DCB by determining the conversion by <sup>1</sup>H NMR at different intervals during the polymerization. All other reaction conditions were kept constant. The recorded kinetic plots for polymerizations at both concentrations showed linear dependencies of  $\ln([M]_0/[M]_t)$  versus time up to 65% conversion (Figure 3), indicating a constant number of radicals. Interestingly, the apparent rate constant  $k_{\text{app}} \{k_{\text{app}} = \ln([M]_0[M]_t/t] \text{ observed for the higher concentration } ([M]_0 = 27 \text{ mol} \cdot \text{L}^{-1}, k_{\text{app}} = 2.0 \times 10^{-2} \text{ h}^{-1}) \text{ was lower than for the polymerization with the lower monomer concentration } ([M]_0 = 9 \text{ mol} \cdot \text{L}^{-1}, k_{\text{app}} = 3.6 \times 10^{-2} \text{ h}^{-1}).$ This rise of  $k_{app}$  upon dilution stands in contrast to usual rate laws of radical polymerizations, where a deceleration of the polymerization would be expected upon dilution. At further dilution of the monomer, we observed a decline in  $k_{app}$ 



Figure 3. Kinetics and evolution of molecular weight and PDI for the homopolymerization of protected propargyl acrylate 2 using 11 as initiator in o-dichlorobenzene solution at 125 °C at a ratio of  $[M]_0/[I]_0$  of 50:1 and with additional 0.1 equiv of free nitroxide 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide to improve the control of the polymerization. The two experiments only differ in the concentration of the monomer in o-dichlorobenzene. It can be observed that the polymerization with the lower monomer concentration has a higher apparent rate constant  $k_{app}$  than the more concentrated one: ( $\blacktriangle$ ) 27 mol·L<sup>-1</sup> and ( $\bigcirc$ ) 9 mol·L<sup>-1</sup>. (a) First-order kinetic plots. (b) Dependence of  $M_n$  and  $M_w/M_n$  on the monomer conversion.

Scheme 2. Synthesis of Perylene Bisimide (PBI) Azide 9 Followed by "Click" Reaction to Model Monomer 12 and "Clicked" PBI Polymers 10a,b with Different Molecular Weights"



 $^{a}$ DMF = dimethylformamide, PPTS = pyridinium p-toluenesulfonate, DPPA = diphenylphosphoryl azide, DEAD = diethyl azodicarboxylate, PMDETA = N, N, N', N'', Pentamethyldiethylenetriamine, THF = tetrahydrofuran.

according to usual polymerization rate laws for diluted systems.<sup>39</sup> Considering the still low rate of polymerization of 3-(trimethylsilyl)prop-2-ynyl acrylate in NMRP, this technique is applicable for the synthesis of lower molecular weight polymers, but not ideal for polymers with very high molecular weights. In both polymerizations the plot of molecular weight ( $M_{n,SEC}$ ) against conversion initially correlates with the theoretical molecular weight, calculated from conversion. Above a conversion of 20%, a low molecular shoulder around 2500 g·mol<sup>-1</sup> emerges in size exclusion chromatography (SEC) curves (see Figure S4) and the plotted  $M_n$  declines under the theoretical calculated line. Simultaneously, the PDI rises. It is noted that after cleaning the polymers from monomer and solvent by dialysis against THF for 5 days, the SEC curves were monomodal and did not show the low molecular weight shoulder anymore.

Dialysis was used here because the precipitation of poly-(3-(trimethylsilyl)prop-2-ynyl acrylate) from THF in MeOH/ $H_2O$  leads to a turbid dispersion and a high loss of polymer. After dialysis, the observed PDIs were narrow and the  $M_n$  were closer to the theoretical values, calculated from conversion. This was also observed for polymers cleaned by reprecipitation.

The deprotected polymers **4a,b** were obtained by removing the trimethylsilyl group using tetra-*n*-butylammonium fluoride, buffered with acetic acid according to a published procedure of Haddleton et al.<sup>10</sup> SEC analysis indicates a decrease in hydrodynamic volume of the polymers after deprotection, as expected. The observed PDIs remained unchanged (Figure 4). The complete removal of the trimethylsilyl group was confirmed by <sup>1</sup>H NMR by the appearance of the C=CH proton at 2.45 ppm and the disappearance



Figure 4. Normalized UV-signal of SEC traces (detection at 254 nm) of protected polymer 3b (dotted line), deprotected polymer 4b (dashed line), and "clicked" PBI polymer 10b (straight line). A clear decrease in molecular weight after deprotection of 3b to 4b and a clear increase in molecular weight after the "click" reaction from 4b to 10b as well as monomodal narrow distribution of molecular weight can be observed.



**Figure 5.** FTIR spectra of "clicked" PBI polymer **10b**, PBI azide **9**, and alkyne polymer **4b**. After the "click"-reaction between alkyne polymer **4b** and PBI azide **9** the superposition of the C=O stretching vibrations of **4b** and **9** can be observed in the product **10b**. The strong azide vibration in **9** and the alkyne vibration in **4b** cannot be observed anymore in **10b**, indicating complete conversion of these groups.

of the Si(CH<sub>3</sub>)<sub>3</sub> protons at 0.18 ppm. Additionally, FTIR analysis shows the expected C=C vibration at 2129 cm<sup>-1</sup> and the C=C-H vibration at 3288 cm<sup>-1</sup> (Figure 5). The SEC, TGA, and thermal data of all polymers are given in Table 1.

The synthesis of azide functionalized PBI **9** for the cycloaddition reaction with the alkyne polymers **4a,b** is presented in Scheme 2. PBI **5** was synthesized according to literature procedures for asymmetric PBIs<sup>28</sup> and was coupled with 2-(6-bromohexyloxy) tetrahydro-2*H*-pyran **6** to give PBI **7** with a protected alcohol group.<sup>40</sup> The subsequent deprotection with pyridinium *p*-toluenesulfonate and HCl yielded PBI alcohol **8**, which was converted into azide **9** elegantly by a Mitsunobu reaction with diphenyl phosphoryl azide and diethyl azodicarboxylate/PPh<sub>3</sub>.<sup>41</sup>

To obtain a model monomer 12 for the "clicked" PBI polymers and for a first test of the "click" chemistry, the azide functionalized PBI 9 was used in a "click" reaction with 4 equiv of propargyl acrylate 1 at RT in degassed THF with 0.1 equiv of CuBr/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) as a catalyst/ligand system. After 1 h, complete conversion was observed (<sup>1</sup>H NMR and FTIR). The triazol carrying PBI acrylate monomer 12 was obtained



**Figure 6.** <sup>1</sup>H NMR spectra of alkyne polymer **4a**, "clicked" PBI polymer **10a**, PBI azide **9**, and "clicked" PBI model-monomer **12** in CHCl<sub>3</sub>. It can be seen that the signals of the "clicked" PBI polymer **10a** match very well with the signals of the model compound **12**. Signals from residual alkyne cannot be observed in the <sup>1</sup>H NMR spectrum of **10a**.

in pure form after filtering through a short silica column and precipitation in MeOH/water. The <sup>1</sup>H NMR spectrum in Figure 6 clearly shows the shift of the  $CH_2N_3$  protons of **9** from 3.28 to 4.38 ppm in **12**. It also features the OCH<sub>2</sub> protons of **12** at 5.36 ppm, the protons of the acrylic double bond between 5.8 and 6.6 ppm, the signal of the 1,2,3-triazol proton at 7.64 ppm as a singlet, and the protons of the perylene core between 8.55 and 8.74 ppm. A direct polymerization of **12** was not feasible due to its low solubility.

For the CuAAC of PBI azide 9 with the deprotected polymers 4a,b, PMDETA/CuBr was used as catalyst system. The reaction mixture was degassed before addition of CuBr and was stirred for 5 h under an inert gas atmosphere. We also monitored the "click" reaction by online <sup>1</sup>H NMR measurements. The completion of the reaction was achieved in  $\sim$ 1 h. To remove the catalyst, the reaction mixture was filtered over a short silica column and precipitated in MeOH/ H<sub>2</sub>O. Further purification was achieved by Soxhlet extraction with methyl ethyl ketone to remove the remaining PBI 9. The rest amount of copper, determined by inductively coupled plasma mass spectrometry was found to be 188 ppm (w/w) and could be further decreased by an additional precipitation step in aqueous ammonia solution to 126 ppm. SEC traces show a clear increase of the hydrodynamic volume of the polymers after the "click" reaction. The molecular weights and PDIs determined by SEC were found to be 5200  $g \cdot mol^{-1}$  and 1.16 for 10a and 15800  $g \cdot mol^{-1}$  and 1.17 for 10b, respectively. Their molecular weights are strongly underestimated by the polystyrene calibration. Because the alkyne polymers 4a and 4b have an average degree of polymerization of 9 and 35 respectively, the theoretical molecular weights for 10a and 10b are 8000 and 29000  $g \cdot mol^{-1}$  respectively. A determination of the molecular weight by analysis of end groups by <sup>1</sup>H NMR was not possible because all reliable signals of the initiating group were superimposed by the signals of the polymer. The <sup>1</sup>H NMR spectra of 10a and 10b prove the quantitative conversion of the alkyne groups by the disappearance of the signals of the alkyne proton at 2.45 ppm and the complete shift of the  $OCH_2$ protons from 4.69 ppm in 4 to 5.23 ppm in 10 (Figure 6). The  $CH_2N_3$  protons of the azide at 3.28 ppm shift to 4.00 ppm,



Figure 7. Optical density of "clicked" PBI polymer 10b (solid line), reference polymer 13 (dashed line), and reference polymer 14 (dotted line) in chloroform solution ( $c = 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ). The fluorescence spectra of 10b, 13, and 14 excited at 490 nm, are also shown.

residual azide signal in the cleaned polymer was not observed. The 1,2,3-triazol proton was not observed as a single signal but can be determined by integration together with the broad signal of the perylene protons between 7.28 and 8.44 ppm. The spectrum exhibits all other expected signals of PBI 9 broadened to featureless signals. FTIR measurements also indicate complete conversion by disappearance of the C=C vibration at 2129 cm<sup>-1</sup> and of the C=C-H vibration at 3288 cm<sup>-1</sup> (Figure 5). Also, the strong azide vibration at 2090 cm<sup>-1</sup> cannot be observed any more. Further, the spectrum of 10b shows a superposition of the imide C=O<sub>imide</sub> vibration of PBI at 1695 cm<sup>-1</sup> and the acrylate C=O<sub>ester</sub> vibration at 1732 cm<sup>-1</sup>.

**Polymer Characterization.** Because it is important to know how the properties of the "clicked" PBI polymer differ from PBI homopolymers without the triazol unit, we compared the "clicked" PBI polymer **10b** with the two reference PBI polymers PPerAcr(CH<sub>2</sub>)<sub>11</sub> **13** and PPerAcr(CH<sub>2</sub>)<sub>6</sub> **14** obtained by direct NMRP. The polymer **13** with spacer lengths of (CH<sub>2</sub>)<sub>11</sub> relatively matches the length from the imide nitrogen to the ester bond in the polymer backbone of **10a**, **b** and polymer **14** with a (CH<sub>2</sub>)<sub>6</sub> spacer fits the length of the (CH<sub>2</sub>)<sub>6</sub> spacer used in the azide PBI. In the following we discuss differences and similarities of the polymer **10b** in comparison to **13** and **14**; polymer **10b** is chosen for its similarity in molecular mass compared to **13** and **14**.

All three polymers exhibit good solubility in CHCl<sub>3</sub> and a low solubility in THF. Films out of CHCl<sub>3</sub> could be cast easily and showed similar absorption spectra (see Figure S11). Absorption and fluorescence of the polymers 10b, 13, and 14 in solution are shown in Figure 7. The absorption spectra in solution (CHCl<sub>3</sub>,  $10^{-5}$  M) show the characteristic fingerprint spectra for aggregated PBIs with vibronic bands of PBI at 464, 490, and 527 nm. The relative intensity of the vibronic bands for the  $S_0 - S_1$  transition can be compared to assess the degree of aggregation.<sup>42</sup> The absorption spectra of PBI polymer 13 and "clicked" PBI polymer 10b are almost identical and the quotients of the vibronic bands  $A_{490/527}$  are 1.12 and 1.09, respectively. Polymer 14 shows higher quotients of the absorption with  $A_{490/527}$  of 1.36. This indicates that in CHCl<sub>3</sub> solution the perylene cores in polymer 14 aggregate stronger than the perylene cores in the polymers 10b and 13. All three polymers exhibit a weak red, featureless fluorescence at 611 nm (CHCl<sub>3</sub>,  $10^{-5}$  M, excited at 490 nm). The small shoulder at 527 nm in the fluorescence spectra derives from minimal amounts of residual low molecular weight PBIs, which show a much stronger fluorescence compared to the polymer.

To understand the influence of the triazol unit and spacer length on bulk properties, the phase behavior of compounds **10b**, **13**, and **14** was investigated by DSC measurements,



**Figure 8.** Second heating (solid line) and second cooling (dashed line) of "clicked" PBI polymer **10b**, PPerAcr(CH<sub>2</sub>)<sub>11</sub> **13**, and PPerAcr(CH<sub>2</sub>)<sub>6</sub> **14** in DSC. The DSC traces of **14** and **10b** are scaled up  $2 \times$  and  $10 \times$ , respectively, to enhance the visibility of the phase transitions. Enlarged temperature region between 250 and 350 °C is given in Supporting Information (Figure S10).



**Figure 9.** X-ray diffraction of "clicked" PBI polymer 10b, PPerAcr-(CH<sub>2</sub>)<sub>11</sub> 13, and PPerAcr(CH<sub>2</sub>)<sub>6</sub> 14 at RT. The location of the scattering vector corresponding to the  $\pi - \pi$  stacking of perylene bisimide is marked.

polarized optical microscopy (POM), and X-ray diffraction experiments. The DSC thermograms and the X-ray diffractograms are shown in Figures 8 and 9, respectively.

In DSC, PPerAcr $(CH_2)_{11}$  13 shows an endothermic phase transition at 189 °C with  $\Delta H = 7.6$  J/g on heating. The examination of the sample by polarized optical microscopy showed, that this phase transition observed at 200 °C in POM is a transition into isotropic melt from an easy to shear, birefringent liquid crystalline state. Upon cooling from isotropic melt and annealing at 194 °C a birefringent phase appears, which corresponds to the transition at 168 °C in DSC on cooling. At lower temperature and RT, the polymer could not be sheared any more, but does not show a change in texture or growth of crystallites. The difference in transition temperature in DSC and POM could arise due to differences in rate of heating/cooling and possible differences in calibration in addition to supercooling effects. It is not clear if this effect could also derive from two superimposed phase transitions of a melting and a liquid crystallineisotropic phase transition. A temperature-dependent X-ray study shows a decrease in sharp reflexes beginning at 172 °C and a complete isotropization at 192 °C (see Supporting Information, Figure S7) indicating the presence of two different transitions. In X-ray diffraction at RT, distinct reflections at q = 2.09, 3.37, and  $4.19 \text{ nm}^{-1}$  can be observed as well as mixed reflections between 5 and 8 nm<sup>-1</sup>. The reflexes at 2.09 and 4.19 nm<sup>-1</sup> indicate a lamellar structure, following the ratio 1:2. The reflex at 3.37 nm<sup>-1</sup> does not belong to a hexagonal packing but represents the (110) reflection. The broad reflection at 18.09 nm<sup>-1</sup> derives from the  $\pi$ - $\pi$  stacking order of the perylene bisimides representing a mean distance of 0.347 nm. The observed reflections cannot be observed at 210 °C, clearly indicating the isotropic phase (see Figure S6).

PPerAcr(CH<sub>2</sub>)<sub>6</sub> 14 shows an endothermic phase transition at 193 °C with  $\Delta H = 4.6$  J/g in DSC on heating. In POM studies, polymer 14 exhibits an easy to shear intermediate phase showing birefringence between 193 and 325 °C, which clears at about 325 °C. The DSC measurement confirms a melting point at 311 °C (see Figure S10) with a very small enthalpy of  $\Delta H = 0.5$  J/g. In X-ray diffraction at RT, distinct reflections at  $q = 1.31, 2.62, \text{ and } 3.94 \text{ nm}^{-1}$  can be observed as well as unresolved mixed reflections between 5 and 8 nm<sup>-1</sup>. The ratios of the q values are 1:2:3, indicating a lamellar 2D structure similar to polymer 13. But polymer 14 has a lower order compared to polymer 13, in which the region between 5 and 8  $\text{nm}^{-1}$  is better resolved. These observations also explain the lower  $\Delta H$  of the phase transition in this polymer. The broad reflection at 17.64  $\text{nm}^{-1}$ . which is weaker in polymer 14 than in polymer 13, derives from the  $\pi - \pi$  stacking order of the perylene bisimides representing a mean distance of 0.356 nm. In temperaturedependent X-ray studies, the first reflections at 1.31 and 2.92  $nm^{-1}$  remain unaffected in the high temperature regime (up to 250 °C; see Figure S9).

It is now interesting to compare "clicked" PBI polymer 10b with the reference polymers 13 and 14 concerning their structural properties and phase behavior. "Clicked" PBI polymer 10b shows a small endothermic phase transition at 175 °C with  $\Delta H = 1.2 \text{ J/g in DSC}$  on heating. As in polymer 14, no transition into the isotropic phase was observed in POM after the phase transition at 175 °C, but an easy to shear liquid crystalline, birefringent phase between 175 and 280 °C, which clears at about 280 °C. The DSC measurement confirms a melting point at 288 °C with a very small enthalpy of  $\Delta H = 0.5$  J/g. This shows that the thermal behavior of **10b** is quite similar to the one of polymer 14. In X-ray diffraction, distinct reflections at the same q values as in polymer 14 at q = 1.31 and 2.62 nm<sup>-1</sup> can be observed, and mixed reflections between 5 and 8 nm<sup>-1</sup> were not observed at all. Together with the even lower  $\Delta H$  of the phase transition, this indicates a lower order compared to polymers 13 and 14. The ratios of the q values are 1:2 and indicate a lamellar 2D structure as in 13 and 14. The broad reflection at  $17.74 \text{ nm}^{-1}$ , which is even weaker than in polymer 14, derives from the  $\pi - \pi$  stacking order of the perylene bisimides, representing a mean distance of 0.354 nm.

It is evident that, in bulk, the length of the spacer is decisive for the phase behavior of the PBI-polymers. The triazol unit of "clicked" PBI polymer **10b** seems to be quite stiff and does not enhance the flexibility of the PBI unit and main chain. The long spacer in polymer **13** enables a higher flexibility that allows better packing of the PBI pendant groups and correspondingly enthalpy of transition was higher in polymer **13** compared to **14** and **10b**. A more detailed X-ray study of PBI polymers by SAXS and WAXS is planned for the future to elucidate the unit cell dimensions and to obtain a clear picture of molecular packing.

## Conclusion

evidence for transfer reactions during the polymerization, leading to continuously rising PDIs. To overcome this drawback of this polymerization, we studied the suitability of the NMRP of trimethylsilyl propargyl acrylate for the first time followed by a "click" reaction of PBI azide. We were able to obtain well-defined precursor polymers with molar masses up to  $5800 \text{ g} \cdot \text{mol}^{-1}$  and PDIs as good as 1.17, which maintained their good PDIs after deprotection of the alkyne group. The deprotected polymer could be coupled with PBI azide, quantitatively, to give fully functionalized semiconductor polymers with molecular weights up to 15800  $g \cdot mol^{-1}$  and PDIs as good as 1.16. Comparison of the properties of these polymers with PBI containing polymers from direct NMRP with different spacer lengths of  $(CH_2)_6$  and  $(CH_2)_{11}$ showed that the phase behavior of PBI containing polymers strongly depends on the alkyl spacer length between the PBI and the backbone. All three polymers showed a lamellar 2D ordering at RT and showed a liquid crystallinelike phase behavior at high temperatures. Further detailed studies on the influence of spacer length and of substitution pattern at the PBI nitrogen on the phase behavior of PBI-polymers are currently undertaken.

### **Experimental Section**

General. PBI 5 was prepared according to a literature procedure.<sup>43</sup> The initiator 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexan 11 and the free nitroxide N-tert-butyl- $\alpha$ isopropyl- $\alpha$ -phenylnitroxid were also synthesized according to published procedures.<sup>44</sup> Dialysis was carried out in THF with a dialysis tubing of regenerated cellulose with a molecular weight cutoff of 1000 purchased from Roth. Acrylic acid chloride  $(\geq 97\%)$ , o-dichlorobenzene (99%), tetrabutylammonium fluoride (1 M solution in THF), 6-bromo-1-hexanol (97%), 2-(6bromohexyloxy)tetrahydro-2H-pyran (97%), dimethylformamide (99.8%), diethyl azodicarboxylate (40% in toluene), diphenylphosphoryl azide (97%), pyridinium p-toluenesulfonate (98%), silver nitrate ( $\geq$ 99.0%), and triphenylphosphine ( $\geq$ 95.0) were purchased from Sigma-Aldrich. 1,8-Diazabicyclo[5.4.0]undec-7-ene ( $\geq$ 99.0%), trimethylsilyl chloride (98%), and PMDETA ( $\geq 98\%$ ) were purchased from Fluka. CuBr (98%) was bought from Acros. All reagents were used without further purification unless otherwise noted.

<sup>1</sup>H NMR (300 MHz) spectra were recorded on a Bruker AC 300 spectrometer and calibrated to CHCl<sub>3</sub> (7.26 ppm for  $^{1}$ H). UV-vis spectra of solutions in CHCl<sub>3</sub> with a concentration of  $10^{-5}$  mol·L<sup>-1</sup> were recorded on a Hitachi 3000 spectrophotometer and photoluminescence spectra were acquired on a Shimadzu RF 5301 PC spectrofluorophotometer upon excitation at 490 nm. SEC measurements were carried out in THF with two Varian MIXED-C columns  $(300 \times 7.5 \text{ mm})$  at room temperature and at a flow rate of 0.5 mL/min using UV (Waters model 486) with 254 nm detector wavelength and refractive index (Waters model 410) detectors. Polystyrene standards and o-DCB as an internal standard were used for calibration. Differential scanning calorimetry experiments were conducted at heating rates of 10 or 40 K  $\cdot$  min<sup>-1</sup> under a N<sub>2</sub> atmosphere with a Perkin-Elmer Diamond DSC, calibrated with indium. The endothermic maximum was taken as  $T_{\rm m}$ . Thermogravimetry measurements were conducted on a Mettler Toledo TGA/SDTA 851<sup>e</sup> under a N<sub>2</sub> atmosphere at a heating rate of 10 K/min. Temperature of decomposition  $(T_{onset})$  was calculated from the onset of the respective curve. ICP-MS was measured on Agilent 7500ce. X-ray diffraction experiments were performed on a Huber Guinier Diffractometer 6000 equipped with a Huber quartz monochromator 611 with Cu  $K_{\alpha 1}$ : 1.54051 Å.

**3-(Trimethylsilyl)prop-2-ynyl Acrylate (2).** Silver nitrate (2.45 g, 14.5 mmol) was suspended in 320 mL of dry methylene chloride. Propargyl acrylate (1; 32.02 g, 290.8 mmol) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (46.50 g, 305.3 mmol) were added to the suspension. The reaction mixture was heated to 40 °C and

trimethylsilyl chloride (44.20 g, 407.1 mmol) was added dropwise. The solution was stirred for 24 h at 40 °C, cooled to RT, and concentrated under reduced pressure. Protected propargyl acrylate (2) was obtained after distillation in high vacuum. The colorless liquid weighed 29.7 g (56.0%): <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$  (ppm) 6.49 (dd, 1H, J = 17.4, J = 1.4, CH=CHH), 6.15 (dd, 1H, J = 17.3, J = 10.4, CH=CH<sub>2</sub>), 5.87 (dd, 1H, J = 10.4, J = 1.4, CH=CHH), 4.76 (s, 2H, OCH<sub>2</sub>), 0.18 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

General Procedure for Preparation of Trimethylsilyl Protected Poly(propargyl acrylate) (3). Freshly distilled 3-(trimethylsilyl)prop-2-ynyl acrylate (2; 1.00 g, 5.5 mmol), alkoxyamine 2,2,5trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexan (11; 35.74 mg, 109.8  $\mu$ mol) and free nitroxide *N*-tert-butyl- $\alpha$ -isopropyl- $\alpha$ -phenylnitroxid (2.410 mg, 10.98 µmol) were dissolved in 200 µL of o-DCB and degassed by three freeze-pump-thaw cycles. The reaction mixture was heated to 125 °C and guenched in an ice bath after the reaction time. The solvent and monomer were removed by dialysis against THF for 5 days. The solvent was changed every second day. Poly(3-(trimethylsilyl)prop-2-ynyl acrylate) (3) was obtained as a slightly yellow substance. The low molecular weight polymer 3a was obtained by quenching the reaction at a lower conversion. <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$  (ppm) 4.68 (br s, 2H, OCH<sub>2</sub>), 2.44 (br s, 1H, CH<sub>2</sub>CH), 2.09–1.35 (br s, 2H, CH<sub>2</sub>CH), 0.19 (br s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 2954, 2178 (C=C), 1736 (C=O), 1444, 1355, 1249, 1147, 1029, 948, 829, 758, 698. GPC (**3a**) conv.: 22%,  $M_n = 2100$  g/mol, PDI = 1.17; (**3b**) conv.: 63%,  $M_{\rm n} = 5800$  g/mol, PDI = 1.20.

General Procedure for Deprotection of Trimethylsilyl Protected Poly(propargyl acrylate) (4). Poly(3-(trimethylsilyl)prop-2-ynyl acrylate) (3; 400 mg, 2.19 mmol based on monomer units) was dissolved in 30 mL of tetrahydrofuran. The solution was purged with argon for 10 min and cooled to -20 °C. Subsequently, a likewise degassed solution of acetic acid (172 mg, 2.87 mmol) and 1 M tetrabutylammonium fluoride in THF (2.87 mL, 2.87 mmol) was added dropwise. The reaction mixture was stirred for 30 min at -20 °C and 2 h at RT. The mixture was passed through a short silica column to remove an excess of tetrabutylammonium fluoride, concentrated under reduced pressure and dialyzed against THF for 5 days. The solvent was changed every second day. The product (4) was obtained after freeze-drying as a slightly yellowish powder. <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$  (ppm) 4.68 (br s, 2H,  $OCH_2$ ), 2.56 (br s, 1H, C=CH), 2.44 (br s, 1H, CH<sub>2</sub>CH), 2.07–1.35 (br s, 2H, CH<sub>2</sub>CH). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 3288 (=C-H), 2954, 2129 (C=C), 1732 (C=O), 1438, 1384, 1361, 1249, 1149, 1028, 989, 954, 927, 841, 817. GPC: (4a)  $M_n = 1300$  g/mol, PDI = 1.17; (**4b**)  $M_{\rm n} = 4200$  g/mol, PDI = 1.20.

Perlylene-THP (7). N-(1-Heptyloctyl)-perylene-3,4,9,10-tetracaboxylic acid bisimide (5; 3.00 g, 5.0 mmol), 2-(6-bromohexyloxy)tetrahydro-2H-pyran) (6; 1.85 g, 7.0 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.00 g, 9.0 mmol) were dissolved in a mixture of 56 mL of dry dimethylformamide and 19 mL of dry tetrahydrofuran. The reaction mixture was heated to 60 °C, and the progress of the reaction was monitored by thin film liquid chromatography in CHCl<sub>3</sub>. After 24 h, the reaction mixture was cooled to RT. The product was precipitated in 300 mL of MeOH, filtered, washed with MeOH again and dried under vacuum. The product was obtained as a red powder and weighed (3.64 g, 93%). <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>): δ (ppm) 8.72–8.46 (m, 8H, ArH), 5.26–5.11 (m, 1H, N–CH), 4.57 (t, 1H, J = 3.8 Hz, OCH), 4.18 (t, 2H, J = 7.7 Hz, N-CH<sub>2</sub>), 3.90-3.81 (m, 1H, OCHH<sub>ring</sub>), 3.79-3.69 (m, 1H, OCHH), 3.54–3.44 (m, 1H, OCHH<sub>ring</sub>), 3.44–3.34 (m, 1H, OCHH), 2.33-2.17 (m, 2H, 2aCHH), 1.93-1.43 (m, 16H, 2αCHH, 7CH<sub>2</sub>), 1.41-1.14 (m, 20H, 10CH<sub>2</sub>), 0.82 (t, 6H, J = 6.8 Hz, 2CH<sub>3</sub>).

*N*-(1-Heptyloctyl)-*N*-(hexyl-6'-hydroxy)-perylene-3,4,9,10-tetracaboxylic Acid Bisimide (8). Perylene-THP (7; 3.64 g, 4.6 mmol) was dissolved in 60 mL of tetrahydrofuran. Pyridinium *p*-toluenesulfonate (0.120 g, 0.46 mmol), 20 mL of MeOH, and 1 mL of concentrated HCl were added. The reaction mixture was heated to 55 °C for 5 h, cooled to RT, precipitated in 300 mL of MeOH, filtered, washed with MeOH, and dried under reduced pressure. The obtained raw product was purified by column chromatography with hexane:THF 4:1 on a silica column to remove impurities. The pure product was obtained by applying a gradient of hexane/ THF from 1:1 to pure THF. The fractions containing the pure product (8) were combined and the solvent removed under reduced pressure. The obtained red powder weighed 2.34 g (72%). <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$  (ppm) 8.74–8.57 (m, 8H, Ar*H*), 5.25–5.12 (m, 1H, N–C*H*), 4.22 (t, 2H, *J* = 7.63 Hz, N–C*H*<sub>2</sub>), 3.66 (dd, 2H, *J* = 12.69 Hz, *J* = 5.90 Hz, C*H*<sub>2</sub>OH), 2.33–2.17 (m, 2H, 2 $\alpha$ CH*H*), 1.94–1.73 (m, 4H, 2 $\alpha$ C*H*H, N–CH<sub>2</sub>C*H*<sub>2</sub>), 1.66–1.44 (m, 6H, 3C*H*<sub>2</sub>), 1.39–1.17 (m, 20H, 10C*H*<sub>2</sub>), 0.83 (t, 6H, *J* = 6.8 Hz, 2C*H*<sub>3</sub>).

N-(1-Heptyloctyl)-N'-(hexyl-6'-azido)-perylene-3,4,9,10-tetracaboxylic Acid Bisimide (9). Triphenylphosphine (740 mg, 2.82 mmol) was dissolved in 25 mL of dry tetrahydrofuran. N-(1-Heptyloctyl)-N'-(hexyl-6'-hydroxy)-perylene-3,4,9,10-tetracaboxylic acid bisimide (8; 900 mg, 1.28 mmol) was added and dissolved. Subsequently, a mixture of diethyl azodicarboxylate (1280 mg, 2.98 mmol, 40% in toluene) and diphenylphosphoryl azide (871 mg, 3.07 mmol) was added. The reaction mixture was stirred for 24 h at RT and poured into MeOH, and the precipitate was filtered, washed with MeOH, and purified over a short silica column with CHCl<sub>3</sub>/acetone 95:5. The fractions containing the pure product were combined and evaporated under reduced pressure. The obtained red powder weighed 753 mg (81%). <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$  (ppm) 8.72-8.51 (m, 8H, ArH), 5.26-5.13 (m, 1H, N-CH), 4.21 (t, 2H, J = 7.6, N-CH<sub>2</sub>), 3.30 (t, 2H, J = 6.9, CH<sub>2</sub>-N<sub>3</sub>), 2.35-2.18 (m, 2H, 2αCHH), 1.97-1.73 (m, 4H, 2αCHH, N-CH<sub>2</sub>CH<sub>2</sub>), 1.72–1.60 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 1.54–1.18 (m, 24H, 12CH<sub>2</sub>), 0.84 (t, 6H, J = 6.8, 2CH<sub>3</sub>). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 2923, 2855, 2092 (-N<sub>3</sub>), 1964, 1650, 1593, 1578, 1507, 1437, 1404, 1338, 1248, 1174, 1163, 1125, 1108, 1084, 958, 851, 809, 795, 745, 724.

General Procedure for "Click" Reaction of Azide Functionalized Perylene Bisimide and Propargyl Acrylate to "Click" Monomer (12). Propargyl acrylate (1; 60.8 mg, 0.55 mmol) and PMDETA (3.6 mg, 20  $\mu$ mol) were added to a solution of PBI-N<sub>3</sub> (9; 100.0 mg, 0.138 mmol) in 2 mL of THF. The mixture was degassed by two freeze-pump-thaw cycles. Subsequently, CuBr (1.00 mg, 6.9  $\mu$ mol) was added under an argon stream. The reaction was stirred at RT for 1 h to completeness, and the product was precipitated in MeOH/H<sub>2</sub>O: 10:4 and filtered. The product (12) was obtained as a red powder. <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$ (ppm) 8.75-8.58 (m, 8H, ArH), 7.63 (s, 1H, triazol-H) 6.43 (dd, 1H, J = 17.3 Hz, J = 1.5 Hz, CH=CHH), 6.13 (dd, 1H, J = 17.4 Hz, J = 10.4 Hz, CH=CH<sub>2</sub>), 5.83 (dd, 1H, J = 10.4 Hz, J = 1.5 Hz, CH=CHH), 5.30 (s, 2H, OCH<sub>2</sub>), 5.25–5.11 (m, 1H, N–CH), 4.36 (t, 2H, J = 7.2 Hz, N-CH<sub>2,perylene</sub>), 4.19 (t, 2H, J = 7.5 Hz, N-CH<sub>2,triazol</sub>), 2.32-2.15 (m, 2H, 2αCHH), 2.03-1.70 (m, 6H, 2αCHH, N-CH<sub>2</sub>CH<sub>2,perylene</sub>, N-CH<sub>2</sub>CH<sub>2,triazol</sub>), 1.60-1.12 (m, 24H, 12CH<sub>2</sub>), 0.82 (t, 6H, J = 6.20 Hz, 2CH<sub>3</sub>). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 3094, 2924, 2855, 1723, 1693, 1651, 1594, 1578, 1508, 1483, 1460, 1438, 1404, 1338, 1295, 1253, 1219, 1175, 1125, 1109, 1081, 1048, 983, 964, 851, 809, 795, 745, 658.

General Procedure for "Click" Reaction of Poly(propargyl acrylate) (4) and PBI-N<sub>3</sub> (9). Poly(propargyl acrylate) (4; 10.0 mg, 0.091 mmol based on monomer units), PBI-N<sub>3</sub> (9; 79.3 mg, 0.109 mmol), and PMDETA (1.58 mg, 9.1  $\mu$ mol) were dissolved in 2.0 mL of THF in a Schlenk flask and degassed by three freeze-pump-thaw cycles. Subsequently, CuBr (1.30 mg, 9.1  $\mu$ mol) was added under an argon stream. The reaction mixture was stirred for 6 h, run over a short pad of silica to remove catalyst, precipitated into MeOH, filtered, dried, and purified further by Soxhlet extraction with methyl ethyl ketone. The "clicked" PBI polymer was obtained as a red powder. <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$  (ppm) 8.29–6.97 (br s, 9H, Ar*H*, triazol-*H*), 5.46–5.10 (br s, 2H, OCH<sub>2</sub>), 5.11–4.85 (br s, 1H, N–CH), 4.67–4.30 (br s, 2H, N–CH<sub>2,perylene</sub>), 4.09–3.76 (br s, 2H, N–CH<sub>2,triazol</sub>), 2.58–1.00 (br s, 35H, 17CH<sub>2</sub>, CH<sub>backbone</sub>), 0.95–0.67 (br s, 6H, 2CH<sub>3</sub>). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 2924, 2855,

6-Bromo-1-hexyl Acrylate (15). 6-Bromo-1-hexanol (5.0 g, 28 mmol) and Na<sub>2</sub>CO<sub>3</sub> (4.5 g, 42 mmol) were dissolved in 30 mL of dry THF and cooled to 0 °C. Acrylic acid chloride (4.98 g, 55.0 mmol) was added to the solution dropwise and the reaction was stirred for 24 h. The mixture was extracted with diethyl ether, washed with NaHCO<sub>3</sub> solution two times, and dried with Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated. The pure product was obtained by column chromatography with THF/cyclohexane 1:3 and weighed 1.5 g (22.7%). <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$  (ppm) 6.36 (dd, 1H, J = 17.2 Hz, J = 1.5 Hz, CH=CHH), 6.07 (dd, 1H, J = 17.3 Hz, J = 10.4 Hz, CH=CH<sub>2</sub>), 5.38 (dd, 1H, J = 10.5 Hz, J = 1.5 Hz, CH=CHH), 4.12 (t, 2H, J = 6.6 Hz, OCH<sub>2</sub>), 3.37 (t, 2H, J = 6.8Hz, CH<sub>2</sub>Br), 1.89–1.77 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>Br), 1.71–1.59 (m, 2H,  $CH_2CH_2O$ , 1.51–1.30 (m, 4H, 2 $CH_2$ ). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 2937, 2860, 1721, 1636, 1620, 1462, 1436, 1407, 1295, 1271, 1186, 1057, 984, 967, 810, 729, 668.

N-(1-Heptyloctyl)-N'-(hexyl-6'-acrylate)-perylene-3,4,9,10tetracaboxylic Acid Bisimide (16). The asymmetric perylene bisimide (5; 623 mg, 1.04 mmol) was dissolved in a mixture of 7.5 mL of DMF and 2.5 mL of THF together with 6-bromo-1hexyl acrylate (15; 489 mg, 2.07 mmol) and  $K_2CO_3$  (258 mg, 1.86 mmol) and heated to 50 °C for 3 d. After cooling to RT, the solution was precipitated in MeOH/H2O, filtered, washed with MeOH, dried in vacuum, and cleaned by column chromatography with THF/hexanes 1:3.5. The product was obtained after removal of the solvents as a red powder and weighed 300 mg (38.2%). <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>): δ (ppm) 8.73-8.50 (m, 8H, ArH), 6.38 (dd, 1H, J = 17.3 Hz, J = 1.5 Hz, CH=CHH), 6.11 (dd, 1H, J = 17.1 Hz, J = 10.3 Hz,  $CH=CH_2$ ), 5.80 (dd, 1H, J = 10.5 Hz, J = 1.5 Hz, CH=CHH), 5.24-5.12 (m, 1H, N-CH), 4.19 (t, 2H, J = 7.4 Hz, N-CH<sub>2</sub>), 4.16 (t, 2H, J = 6.6Hz, OCH<sub>2</sub>), 2.32-2.17 (m, 2H, 2αCHH), 1.94-1.65 (m, 6H, 2αCHH, N-CH<sub>2</sub>CH<sub>2</sub>, OCH<sub>2</sub>CH<sub>2</sub>), 1.53-1.44 (m, 4H, CH<sub>2</sub>), 1.40-1.14 (m, 20H, 10CH<sub>2</sub>), 0.82 (t, 6H, J = 7.1 Hz, 2CH<sub>3</sub>). IR (ATR): ν (cm<sup>-1</sup>) 2923, 2855, 1712, 1694, 1652, 1594, 1578, 1507, 1461, 1437, 1404, 1338, 1251, 1194, 1125, 1059, 983, 961, 851, 809, 795, 745, 664.

**Poly(perylene bisimide**  $(CH_2)_6$  acrylate) (14). Perylene bisimide acrylate (16; 276 mg, 0.36 mmol), initiator (11; 0.794 mg, 2.44  $\mu$ mol), and free nitroxide TIPNO (0.054 mg, 0.24  $\mu$ mol) were added to 140  $\mu$ L of *o*-DCB degassed by three freeze–pump–thaw cycles and stirred at 125 °C. The reaction was quenched in an ice bath and precipitated into MeOH. The rest of the monomer was removed by Soxhlet extraction with methyl ethyl ketone. The polymer was obtained as a red powder. <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>):  $\delta$  (ppm) 8.29–7.09 (br s, 8H, Ar*H*), 5.15–4.84 (br s, 1H, C*H*), 4.42–3.76 (br s, 4H, OC*H*<sub>2</sub>, NC*H*<sub>2</sub>), 2.71–1.16 (br s, 35H, 17C*H*<sub>2</sub>, C*H*<sub>backbone</sub>), 0.94–0.79 (br s, 6H, 2C*H*<sub>3</sub>). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 2924, 2855, 1730, 1695, 1653, 1593, 1579, 1506, 1454, 1437, 1404, 1389, 1337, 1248, 1216, 1166, 1125, 1107, 1089, 999, 958, 851, 809, 795, 745, 724. GPC: (14)  $M_n = 12500$  g/mol, PDI = 1.80.

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**Supporting Information Available:** Additional experimental, SEC, X-ray, and kinetics data. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **References and Notes**

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