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# Substituted 2,1,3-Benzothiadiazole- And Thiophene-Based Polymers for Solar Cells − Introducing a New Thermocleavable Precursor

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Alkoxysubstituted and unsubstituted 2,1,3-benzothiadiazoles were prepared and copolymerized with substituted and unsubstituted thiophenes using both Stille and Yamamoto cross-coupling reactions. One class of the materials bore thermally labile ester groups. The materials were all found to have a reduced band gap in the range of 1.69−1.75 eV and were explored in polymer photovoltaic devices as mixtures with the soluble fullerene PCBM. High open circuit voltages of up to 0.93 V and power conversion efficiencies (PCE) of up to 2.22% was observed for materials without the thermally labile groups. The thermocleavable materials have the advantage that they are insoluble after a thermal treatment, enabling a larger degree of processing freedom when preparing multilayer devices and they provide a better operational stability for the devices. So far the process of thermocleavage has led to poorer device performance than for the soluble precursor polymers; however, we found processing conditions that lead to a higher performance for the thermocleaved product, where open circuit voltages of up to 0.9 V could be obtained with power conversion efficiencies of up to 0.42%, representing a doubling as compared to the soluble precursor polymer.

## Introduction

Encouraging progress has been made over the past few years in the field of photovoltaic solar cells using organic materials. Especially conjugated polymers are an attractive alternative to the traditional silicon-based solar cells because they are strong absorbers of visible light and can be deposited onto flexible substrates over large areas using wet-processing techniques such as spin-coating, printing, or roll-to-roll coating.[1−14] Compared to silicon-based solar cells, polymer photovoltaics are inferior when it comes to power conversion efficiency and stability. However, they offer low production cost, low thermal budget, and a very high speed of processing, which makes them competitive in certain applications. Many reviews and special issues on the topic of polymer solar cells have been published during the past 5 years[3,15−38] and the definitions are quite broad spanning all polymer

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solar cells, polymer-fullerene solar cells, small molecule, and hybrid solar cells. Polymer-fullerene solar cells based on composites of an electron-donating conjugated polymer and an electron-accepting fullerene have proven to be the most successful so far with power conversion efficiencies exceeding 6%.[39,40] In addition to the power conversion efficiency, there is, in the context of polymer solar cells, increasing focus on preparation of efficient materials with low optical band gaps and materials that give stable devices. Because the photon flux reaching the surface of the earth from the sun has a maximum of approximately 1.8 eV (700 nm) state-of-the-art materials for polymer solar cells like poly(3-hexylthiophene) (P3HT) is only able to harvest up to $\sim$22% of the available solar photons.[17,30] Therefore, by decreasing the band gap of the active material it is possible to harvest a larger amount of the solar photons and thereby increase the power conversion efficiency. In terms of stability and operational lifetime polymer solar cells generally perform poorly. However, it has been demonstrated that polymer solar cells based on a blend of poly-3-(2-methylhexan-2-yl)-oxy-carbonylbithiophene (P3MHOCT) and PCBM can provide very stable behavior after thermal elimination of the solubilizing ester groups,[41−47] whereas the thermocleavage step was observed to lead to a decrease in performance.[41,42,47,48] It was found that the carboxy groups residing on the backbone after thermocleavage of the ester group could be removed by an even higher thermal treatment[49] and this could then give devices with a higher performance than the devices that had not been thermocleaved.[42] The softness provided by the solubilizing groups is related to the instability of polymer solar cells, and more rigid systems generally give devices with a better stability.[44,50,51] Furthermore, typical nonconjugated solubilizing groups reduce the density of chromophores in the polymer and do not contribute to light harvesting and charge transport. The motivation for preparing materials with thermocleavable side chains are multifold and can be summarized as the possibility to prepare materials with a higher density of chromophores leading to device films with a better operational stability and a higher level of permissible processing conditions due to the insolubility of thermocleaved films in all solvents. This has been explored with success in tandem solar cells based on thermocleavable materials.[52] It should, however, be stressed that these advantages should not come at the expense of the power conversion efficiency for the devices. So far, this has not been the case and there is an urgent need to uncover the processing conditions that are required to get high performance for devices based on thermocleavable materials.

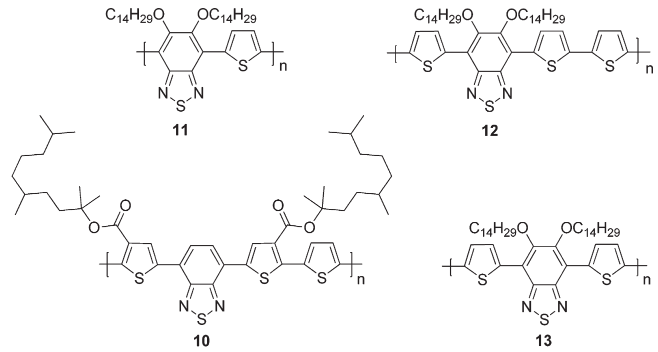

**Figure 1.** Low band gap polymers based on 2,1,3-benzothiadiazole and thiophene units.

Herein, we report the synthesis of four new low band gap polymers and their photovoltaic performance in blends with [6,6]-phenyl $C_{61}$ butyric acid methyl ester (PCBM). Three of the polymers (**11**−**13**) are based on 2,1,3-benzothiadiazole, bearing solubilizing alkoxy side chains at the 5- and 6-position, alternating with thiophene units along the chain (Figure 1). The fourth polymer (**10**) is based on 2,1,3-benzothiadiazole alternating with three thiophene units along the chain. In addition, a branched alkyl chain is attached to the polymer backbone through a labile ester bond to the thiophene segment. When heated, this bond breaks, eliminating a volatile alkene and leaving the polymer component more rigid (Figure 2). The thermal treatment can be viewed as a way of performing an in situ chemical reaction, thereby allowing for the alteration of both physical and chemical properties such as solubility, hardness, hydrogen bonding, chromophore density, and ionicity after the active layer has been deposited.[42]

## Experimental section

Synthetic procedures for synthesis of monomers and polymers according to Schemes 1−3 and their characterization data

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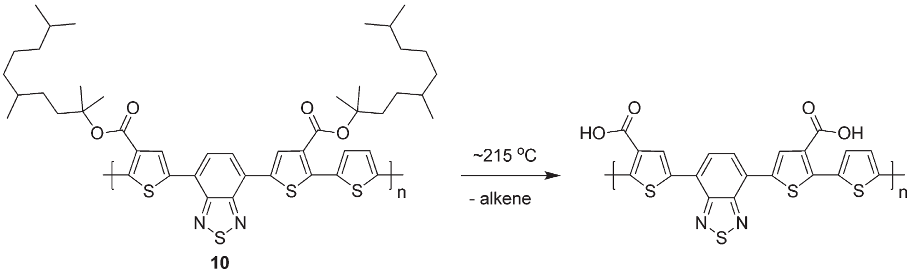
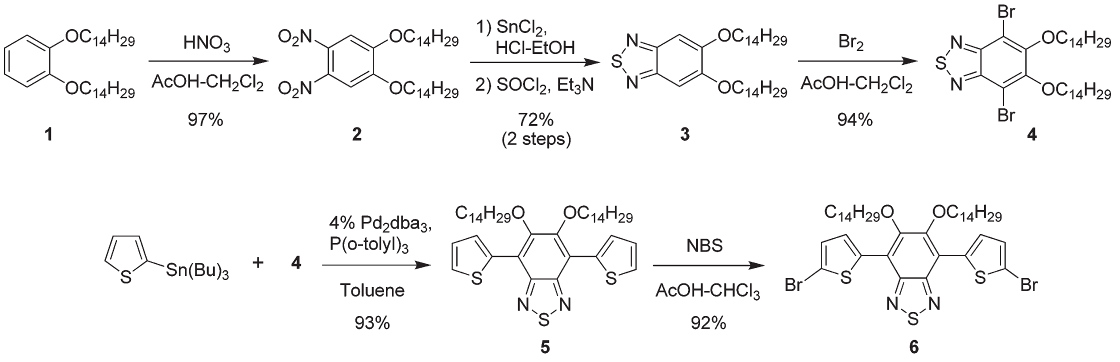
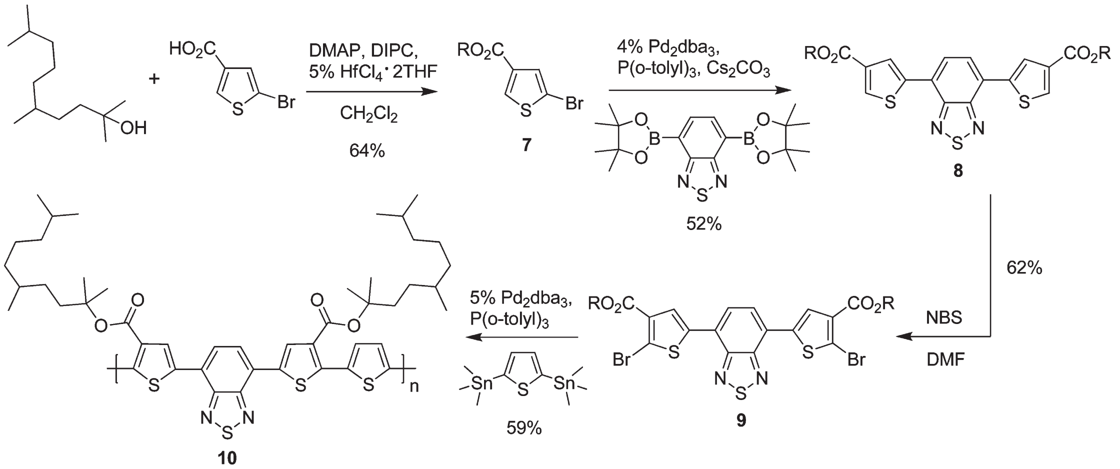


**Figure 2.** Thermocleavable ester groups attached to the polymer backbone of **10**. After a thermal treatment around 215 °C, the solubilizing groups are eliminated.

**Scheme 1. Synthetic Steps Involved in the Preparation of the Monomers 4 and 6**



**Scheme 2. Synthetic Steps Involved in the Preparation of the Thermocleavable Polymer 10; R = 2,5,9-Trimethyl-2-decanyl**



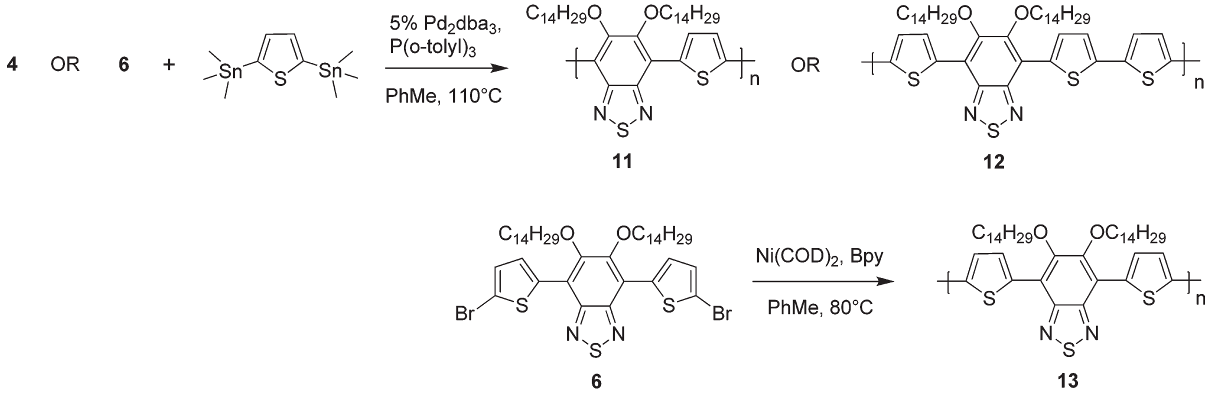
(including $^1$H NMR and $^{13}$C NMR) are described in detail in the Supporting Information, together with general experimental details.

**Polymer Solar Cell Fabrication and Analysis.** Photovoltaic devices were made by spin coating PEDOT:PSS (Clevios P, VP Al4083) onto precleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The active layer was deposited by spin coating a blend of the polymer and [60]PCBM dissolved in chlorobenzene (20−30 mg/mL). The counter electrode of LiF (1 nm) and aluminum (100 nm) was deposited by vacuum evaporation at $2-3 \times 10^{-7}$ mbar. The active area of the cells was 0.091−0.162 cm$^2$ and the active layer thickness was determined with a Dektak surface profiler. $J-V$ characteristics were measured under 100 mW/cm$^2$ white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. The spectral response (SR) was measured under operating conditions using bias light from a 532 nm solid state laser (Edmund Optics). Monochromatic light from a 50 W tungsten halogen lamp (Philips focusline) in combination with monochromator (Oriel, Cornerstone 130) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford research Systems SR830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. Short circuit currents under AM1.5 conditions were obtained from the spectral response and convolution with the solar spectrum ($J_{sc}$(SR)). The value of $J_{sc}$(SR) was used with $V_{oc}$ and FF from the 100 mW/cm$^2$ white light $J-V$ characteristics to estimate the power conversion efficiency $\eta$.

## Results and Discussion

**Approaches to Thermal Processing of Conjugated Polymers.** Traditionally conjugated materials were prepared by a thermocleavable route whereby a soluble nonconjugated

**Scheme 3. Synthetic Steps Involved in the Preparation of the Polymers 11, 12, and 13**



precursor was heated to provide the insoluble conjugated polymer film. Examples of this include the Wessling route to PPV[53−56] and the Durham routes to polyacetylene.[57−59] These were then replaced by efficient routes to soluble conjugated materials and it is only recently that requirements for better operational stability and processing freedom has spawned new research in this area. Generally, two approaches have been followed. The precursor route where the conjugation in the polymer film is formed upon thermocleavage after formation of a film based on the precursor polymer.[60−64] The other approach is the thermocleavable side chain route where the conjugated backbone is already present in the polymer film during formation but where the side chains are removed upon the thermal treatment to give the unsubstituted conjugated polymer backbone.[41−48,52,65−69] Common to both approaches is that the final film is insoluble and the chromophore density is high. The main difference is that the thermocleavable side chain film is functional as a photovoltaic device before being thermocleaved.

**Synthesis.** The synthetic steps involved in the preparation of the monomers **4** and **6** are outlined in Scheme 1. 1,2-Bis(tetradecyloxy)benzene (**1**) were prepared by a standard alkylation of catechol with 1-bromotetradecane in DMF at 100 °C.[70] Electrophilic aromatic nitration of **1** affords the substituted *o*-dinitrobenzene (**2**).[71] Reduction of the nitro groups with tin(II) chloride[72] gives the diamine as its hydrochloride salt which has to be used directly because of its unstable nature. Treatment of the diamine with thionyl chloride affords **3**, which is brominated with molecular bromine to give monomer **4** in excellent yield.[73] Stille coupling of **4** with 2-tributylstannylthiophene gives **5** as a yellow solid that is highly fluorescent in solution. Finally, NBS bromination of **5** gives monomer **6**.

The synthetic steps involved in the preparation of the thermocleavable polymer **10** are outlined in Scheme 2. A slightly modified procedure, reported in our earlier work[48] for the synthesis of tertiary esters, was used to prepare **7**. The esterification employs a catalytic amount of hafnium(IV) chloride tetrahydrofuran complex (1:2) in combination with *N,N′*-diisopropylcarbodiimide and DMAP. Suzuki cross-coupling of **7** with the boronic ester 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo-[*c*][1,2,5]thiadiazole affords **8** which is NBS brominated to give monomer **9**. Finally copolymerisation of **9** via Stille coupling with 2,5-bis(trimethylstannyl)thiophene affords the thermocleavable polymer **10** as a dark purple-brown solid.

Using the same conditions as for **9**, copolymerisation of **4** and **6** via Stille coupling with 2,5-bis(trimethylstannyl)-thiophene gives polymer **11** and **12** as dark purple solids (Scheme 3). Yamamoto coupling of **6**, using bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$) and bipyridine (Bpy)

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Table 1. GPC and Spectroscopic Data for Polymers 10−13

| | solution | | | | | film | | |
|---|---|---|---|---|---|---|---|---|
| polymer | $M_w$ (g/mol) | PDI | $\lambda_{max}$ (nm) | $\lambda_{onset}$ (nm) | $E_g$ (eV) | $\lambda_{max}$ (nm) | $\lambda_{onset}$ (nm) | $E_g$ (eV) |
| **10** | 173000 | 2.6 | 525 | 633 | 1.96 | 593,[a] 570[b] | 732 | 1.69 |
| **11** | 16600 | 1.7 | 563 | 643 | 1.93 | 654 | 711 | 1.74 |
| **12** | 26000 | 2.9 | 570 | 687 | 1.80 | 644 | 707 | 1.75 |
| **13** | 7100 | 1.7 | 543 | 639 | 1.94 | 592 | 715 | 1.73 |

[a] 25 °C. [b] Heated at 250 °C for 1 min.

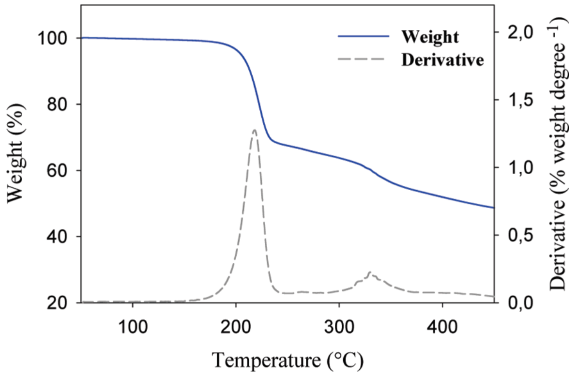

**Figure 3.** Thermogravimetric data for **10** in the temperature range 50−500 °C. The theoretical weight loss for the elimination process around 215 °C is 44%, whereas the observed value is ~31%. A second minor weight loss (~8%) is observed around 330 °C. The data were recorded at 10 °C min$^{-1}$ under an argon atmosphere.

gives polymer **13** in 20% yield (Scheme 3) with a molecular weight ($M_w$) of 7100 g/mol and a polydispersity (PDI) of 1.7. The low yield was caused by the fact that a large portion of the polymer formed was insoluble and could not be isolated by Soxhlet extraction. For the same reason, a low yield of **12** was isolated (28%) but with a higher molecular weight ($M_w$ = 26 000 g/mol, PDI = 2.9). On the contrary Polymer **10** and **11** were isolated in good yields and are very soluble in organic solvents such as chloroform and toluene at room temperature. The large variation in molecular weight between **10** and **11** could be explained by the difference in coupling groups, bromothiophene-stannylthiophene versus bromobenzothiadiazole-stannylthiophene.

**Thermal Behavior.** The sample holders were carefully weighed and the samples introduced. Thermogravimetric analysis (TGA) was then carried out using heating rate of 10 °C min$^{-1}$. TGA of **10** in the temperature range 50−500 °C indicates that the ester bond starts to break around 200 °C (Figure 3). The second loss peak at ~330 °C corresponds to loss of $CO_2$.[48,49]

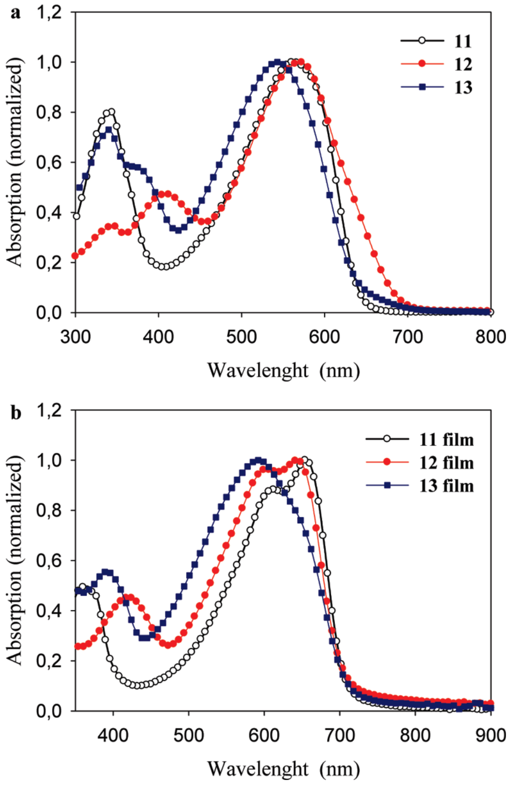

**Figure 4.** UV−vis absorption spectra of polymers **11**−**13** in (a) chloroform solution and (b) thin film.

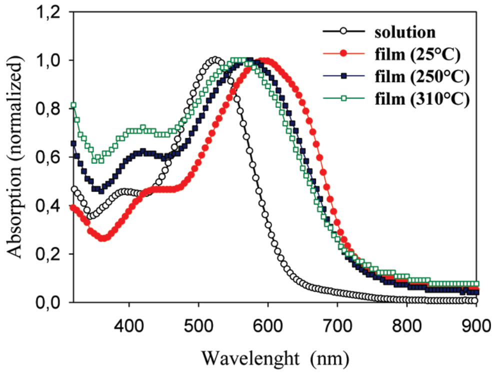

**Figure 5.** UV−vis absorption spectra of **10** in chloroform solution and in thin film before and after thermocleavage.

**Optical Properties.** The absorption spectra for polymer **10**−**13** in chloroform solution are shown in Figure 4a and Figure 5. The optical band gaps, defined by the onset of absorption, are rather similar ranging from 1.8 to 1.96 eV (Table 1). **12** exhibits a lower optical band gap in solution due to partial aggregation of the polymer in solution. The difference in absorption maxima ($\lambda_{max}$) is relatively small but **10** is blue-shifted compared to polymers **11**−**13** (Table 1), indicating a more twisted backbone because of the branched ester side chains. The film absorption spectra for polymers **10**−**13** are shown in Figures 4b and 5. Again, the optical band gaps are very similar ranging from 1.69 to 1.75 eV (Table 1). The polymers have absorption maxima ranging from 525 to 570 nm in chloroform, and these are red-shifted further to 592−654 nm when in a solid film (Table 1), indicating significant interchain association in the solid state. In addition polymers **11** and **12** show vibronic fine structure

Table 2. Photovoltaic Performance of Devices Based on Blends of Polymer and PCBM

| polymer | thermal treatment[a] (°C) | layer thickness (nm) | $V_{oc}$ (V) | $J_{sc}$(SR) (mA/cm$^2$) | FF | $\eta$ (%) |
|---|---|---|---|---|---|---|
| **10** | | 92 | 0.75 | 1.07[b] | 0.26 | 0.21 |
| **10** | 200 | 92 | 0.90 | 0.72[b] | 0.37 | 0.24 |
| **10** | 285 | 78 | 0.90 | 1.36 | 0.34 | 0.42 |
| **11** | | 63 | 0.93 | 5.18 | 0.46 | 2.22 |
| **12** | | 80 | 0.61 | 6.21 | 0.47 | 1.78 |
| **13** | | 65 | 0.76 | 2.56 | 0.32 | 0.62 |

[a] Heated for 20−30 s. [b] Unestimated.

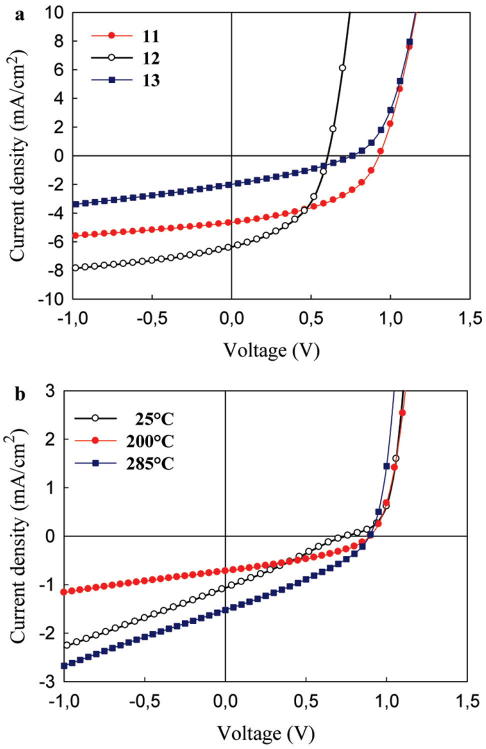

**Figure 6.** (a) $J-V$ characteristics of the **11**:PCBM, **12**:PCBM and **13**:PCBM solar cells measured under 100 mW/cm$^2$ white light; (b) $J-V$ characteristics of solar cells based on **10** and PCBM measured under 100 mW/cm$^2$ white light before and after a thermal treatment.

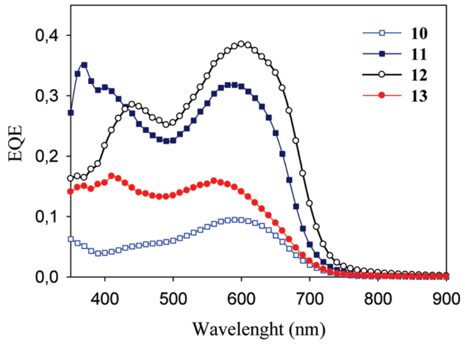

**Figure 7.** EQE spectra of polymer:PCBM solar cells. **10** were thermocleaved at 285 °C.

at 625 nm in the solid state. A weak vibronic transition may also account for the observed shoulder of **13** (Figure 4b). With regard to the thermocleavable polymer **10**, a blue shift of the absorption maxima is observed when the film is heated at 250 °C for 1 min (Figure 5), but no clear color change is observed. Only a minor blue shift in the absorption maxima is observed when the film is heated at 310 °C for 1 min compared to heating at 250 °C. After the thermal treatment, the film was completely insoluble.

**Photovoltaic Performance.** Bulk heterojunction solar cells were fabricated on an indium tin oxide (ITO) covered glass substrate, using conventional device architecture. A thin layer of poly(3,4-ethylenedioxythiophene)−poly-(styrenesulfonate) (PEDOT-PSS) was spin coated on top of the ITO coating followed by spin coating of the active layer. The active layer contained a blend of the respective polymer and [60]PCBM. After spin coating of the active layer the devices were either processed directly into a solar cell by evaporation of LiF (1 nm) and aluminum (100 nm) as back electrode or subjected to a thermal treatment at the temperature of thermocleavage immediately before evaporation of the back electrode. The most efficient devices comprised a polymer/PCBM ratio of 1:2 spin-coated from chlorobenzene with a polymer concentration of 7.5 mg/mL. The optimal layer thickness was around 60−80 nm.

The obtained current−voltage curves are presented in figure 6 which shows the current−voltage characteristics of the **10**:PCBM, **11**:PCBM, **12**:PCBM and **13**:PCBM solar cells measured under 100 mW/cm$^2$ white light. The devices based on **11**, with only one thiophene unit alternating with benzothiadiazole, and PCBM showed power conversion efficiencies of up to 2.22% (Table 2). The devices had high open-circuit voltages ($V_{oc}$) of 0.93 V, moderate fill factors (FF) of 0.46 and current densities ($J_{sc}$) of 5.18 mA/cm$^2$. The external quantum efficiency (EQE) for **11**:PCBM is higher than 23% in the wavelength range between 350 and 650 nm, and the maximum was found to be 35% around 370 nm where PCBM also absorbs (Figure 7). Polymer **12**:PCBM gives an EQE higher than 22% in the range between 400 and 680 nm with a maximum of 39% at around 600 nm. Compared to **11**:PCBM, the EQE is enhanced by up to 10% in the range 450−720 nm, which gives a current density of 6.21 mA/cm$^2$. The devices based on **12**:PCBM performed slightly poorer due to a lower $V_{oc}$ of typically 0.61 V, which resulted in power conversion efficiencies of up to 1.78%. Solar cells based on polymer **13**:PCBM gave significantly lower EQE with quantum efficiencies around 10−15% in the range of 350−650 nm, giving current densities of 2.56 mA/cm$^2$. Together with a typical $V_{oc}$ of 0.76 V and low fill factors of 0.32, power conversion efficiencies of up to 0.62% were obtained. The lower performance of **13** compared to **11** and **12** could be due to the different polymerization procedure where excess of nickel(0) was used instead of a catalytic amount of palladium employed in the Stille coupling. The devices based on the thermocleavable polymer **10** and PCBM showed the lowest power conversion efficiencies of up to 0.42% (Table 2). Without thermal treatment of **10**:PCBM devices a typical $V_{oc}$ of 0.75 V was obtained. Upon heating the device to 200 °C the $V_{oc}$ increases to 0.90 V and resides there when annealing at 285 °C. The FF increased from 0.26 to 0.37 after thermal treatment at 200 °C and then drops a bit upon heating the device at 285 °C. The current density first drops after thermal treatment and then increases again when heating at 285 °C. The EQE of **10**:PCBM (cleaved at 285 °C) is relatively low with quantum efficiencies of about 5−10% in the range 350−670 nm (figure 7) giving it an estimated current density of 1.36 mA/cm$^2$. A general observation was that the devices based on **10**:PCBM performed better after thermocleavage due to an increase in mainly the current and fill factor. $J-V$ curves for uncleaved and cleaved **10**:PCBM devices are shown in figure 6b. Despite the lower efficiency of polymer **10** compared to the polymers **11-13** the thermocleavable polymer **10** does show promising results with increased performance after thermocleavage. In the majority of cases where thermocleavable materials have been employed in polymer solar cells, a drop in performance has been observed when thermocleaving the polymer and only one previous case has demonstrated an advantage of thermocleavage in terms of performance.[42] The lower performance of polymer **10** compared to the polymers **11−13** can be an effect of the more electron-attracting ester groups situated on thiophene (**10**) compared to the electron-donating alkoxy groups on benzothiadiazole (**11−13**).

## Conclusion

In conclusion, four new low band gap polymers have been synthesized. They are based on 2,1,3-benzothiadiazole alternating with thiophene units along the chain, bearing solubilizing chains on either benzothiadiazole (**11−13**) or thiophene (**10**). The solubilizing chain on **10** is attached to the polymer backbone through a labile ester bond which is thermocleavable around 215 °C. When heated, this bond breaks, eliminating a volatile alkene and leaving the polymer component more rigid. The four polymers optical properties and photovoltaic performance in blends with PCBM have been investigated. In chloroform solution, the polymers had very similar optical band gaps ranging from 1.8 to 1.96 eV. The optical band gaps are lowered to 1.69−1.75 eV in thin film (Table 1), indicating significant interchain association in the solid state. Furthermore polymer **11** and **12** showed vibronic fine structure centered at 625 nm in the solid state. The best performing polymer in a bulk heterojunction solar cell was **11** with $J_{sc}$ = 5.18 mA/cm$^2$, $V_{oc}$ = 0.93 V, FF = 0.46, and $\eta$ = 2.22%. Devices based on **10**:PCBM performed better after thermocleavage because of an increase in mainly current and fill factor giving power conversion efficiencies up to 0.42%.

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**Supporting Information Available:** General procedures and characterization data including NMR spectra; experimental procedures for the synthesis of the monomers and polymers according to Schemes 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.