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Design and Synthesis of a Low Band Gap Conjugated Macroinitiator: Toward Rod−Coil Donor−Acceptor Block Copolymers

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ABSTRACT: A new strategy for the synthesis of a soluble and well-defined dioctylpoly(thienylenevinylene) (DO-PTV), a low band-gap semiconducting polymer, via Horner−Wadsworth−Emmons condensation is presented. The chain length of the DO-PTV can be tuned by varying the amount of end-capping agent employed. This polymer was characterized by ^{1}H NMR, UV−vis absorbance spectroscopy, and GPC. Finally, the DO-PTV was transformed into macroinitiator for nitroxide mediated radical polymerization. A preliminary experiment of polymerization of a mixture of styrene and chloromethylstyrene with this macroinitiator led to a low band gap rod−coil conjugated block copolymer which is a precursor for a donor−acceptor self-organized material.

Introduction

An alternative to silicon-based materials for photovoltaic devices is the semiconducting polymers. The conjugated polymers or oligomers have been used in the recent past to prepare photovoltaic devices so-called "plastic" or organic solar cells.[1−7] This new class of materials looks very promising for the development of low cost solar energy harvesting systems taking advantage of the knowledge in the synthesis and processing capabilities that are offered by the polymer materials. The semiconducting organic materials allow the fabrication of large area thin film mechanically flexible devices challenging the inorganic materials.

For polymer-based photovoltaic (PV) devices the morphology of the active layer is very important. It determines the performance of the device. Efficiency of PV devices dramatically depends on the ability to dissociate the exiton (a pair of an electron and a hole formed by photon absorption). Only at the interface between donor and acceptor material the exciton will be actually dissociated. An exciton has a finite lifetime and therefore has a limited diffusion range on the order of 10 nm.[8−11] To improve the efficiency of PV devices, many materials and processes in order to control the morphology of the active layer have been developed: blends,[1,8,12−18] liquid crystals,[5,19−22] and block copolymers.[23−31] Diblock copolymers are known to phase separate in ordered microphases.[32] The present work focuses on the development of block copolymer materials with the first block being conjugated an electron donor (the rod), and the second flexible block being a functionalized electron acceptor (the coil). It is a general rule that conjugated polymers are not very soluble for this reason the second flexible block will provide higher solubility and processability to the final material.

In recent years several rod−coil diblock copolymers based on poly(phenylenevinylene) (PPV) have been synthesized and used as the active layer in photovoltaic devices.[23−26] However, a major drawback of most conjugated polymers for their application in solar cell devices is the rather poor match of the absorbance spectrum with the solar spectrum. The wavelength of maximum absorbance ($\lambda_{\max}$) for most PPV derivatives lies below 500 nm ($E_g \sim 2.0-2.2$ eV), which is on the far blue side of the spectrum.[12,33] By using low band-gap materials ($E_g < 1.8$ eV), an improved overlap with the solar spectrum would allow an increase in photovoltaic energy conversion. The band-gap of π-conjugated polymers can be controlled through the chemical structure of the system.[34] Recently, few groups have synthesized and studied low band-gap conjugated polymers.[35−40] Poly(thienylenevinylene) (PTV), which has a structure similar to that of PPV (Scheme 1), where the backbone phenyl group is replaced by a thiophene unit, shows a low oxidation potential besides the small band-gap ($\lambda_{\max} \geq 600$ nm, $E_g \approx 1.6$).[41] This low oxidation potential should stabilize the charge-separated state and therefore be advantageous in polymer solar cells. The oligomer counterpart of this polymer (OTVs or *n*TVs) has shown promising results as an electron donor in photovoltaic devices.[41,42]

As PTV exhibits a light absorbance corresponding much more to the solar spectrum than the other common conjugated polymers, rod−coil block copolymers having a PTV segment as the rod block are of potential interest for photovoltaic applications. In this case, PTV should be a good electron donor if the coil block is grafted with electron acceptors, such as fullerenes for example.

There are several requirements that this material has to meet in order to obtain a well-defined block copolymer in the end. For a good microphase separation the control of the chain length distribution and the molecular weight is necessary. It would be also a great advantage if the length of both blocks could be

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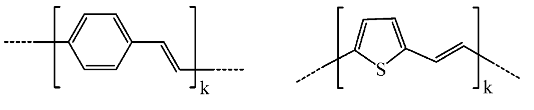
Scheme 1. Chemical Structures for the Backbone of Poly(*p*-phenylenevinylene) (PPV) and Poly(2,5-thienylenevinylene) (PTV)



PPV **PTV**

adjusted. For these reasons, an appropriated route to reach our goal is to design PTV with a controlled length, to convert it into macroinitiator and make the coil block growth from it, in a controlled way. The use of a conjugated macroinitiator has been already successfully used for the synthesis of rod−coil copolymers with PPV,[23,26,27] polythiophene,[43,44] polyfluorene,[45,46] or oligomers[47,48] blocks but not necessary with the control of the rod length. Concerning the coil block, controlled/"living" radical polymerization techniques, such as nitroxide mediated radical polymerization (NMRP),[49] are now well-known as versatile methods to make block copolymers.

In this paper, the synthesis and the characterization of well-defined PTV based low band-gap semiconducting macroinitiators for NMRP are described. For this purpose the control of the PTV length has been studied. Finally, its use as initiator for the polymerization of styrenic monomers in order to obtain a rod−coil diblock copolymer designed as precursor for solar cell is presented.

Results and Discussion

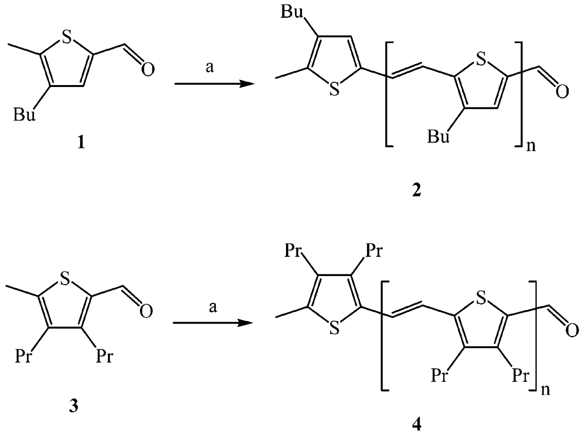
To be able to synthesize a diblock copolymer, the conjugated polymer needs to possess a single functional end group, present in all polymer chains. Preferably, the end group should be an aldehyde, to enable the use of the same method of transformation into a macroinitiator for NMRP as described in previous work.[25] Taking this requirement into account, two different routes have been tested to synthesize a soluble PTV macroinitiator precursor.

Synthesis of PTV via Siegrist Condensation. First, we opted for the Siegrist condensation, since this method of polymerization proved to give good results for the synthesis of PPV.[50] Two different polymers, poly[3-butyl-(2,5-thienylenevinylene)] (3-Bu-PTV) and poly[3,4-dipropyl-(2,5-thienylenevinylene)] (DPr-PTV), were synthesized in this way, with one and two solubilizing side chains, respectively butyl and propyl (Scheme 2).

Monomer **1** was synthesized from 2-bromo-3-butylthiophene via consecutive reaction with *n*-butyllithium, methylation of the lithiated anion with dimethylsulfite,[51] and a Vilsmeier formylation.[52] Monomer **3** was synthesized via the bromination, selective debromination with Zn,[53] nickel-catalyzed Grignard alkylation[54] and Vilsmeier formylation[52] of 2-methylthiophene.

During the polymerizations both reaction mixtures had a promising dark-blue or indigo color, which turned to a dark red/purple after workup procedures. This red-shifted color shows that only very short oligomers could be obtained with this method of polymerization. This observation is confirmed by ^{1}H NMR and UV−vis measurements. When the UV−vis absorbance spectra (Figure 1) are compared to results obtained for well-defined oligothienylenevinylenes (OTVs),[55,56] it can be concluded that only oligomers with a average degree of polymerization ($\overline{\mathrm{DP}}_n$) around 4 are obtained. For instance the λ_{max} values reported by Elandaloussi [55] for dihexyl-substituted OTVs corresponding to degrees of polymerization of 3, 4, and 5 are, respectively, 450, 480, and 505 nm.

Scheme 2. Synthesis of 3-Bu-PTV (2) and DPr-PTV (4) via the Siegrist Polycondensation ($DP_n = k = n + 1$)[a]



[a] Reagents and conditions: (a) aniline, 10 mbar, 60 °C, 1 h, and then KOtBu, DMF, 90 °C, 2.5 h.

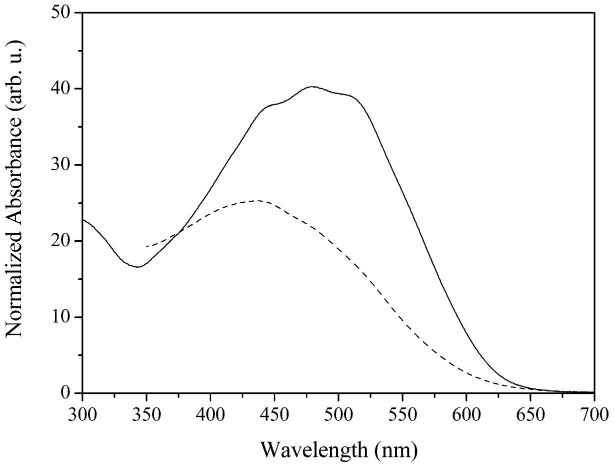


Figure 1. Weight-normalized absorbance spectra for 3-Bu-PTV (—) and DPr-PTV (− − −), synthesized via a Siegrist condensation.

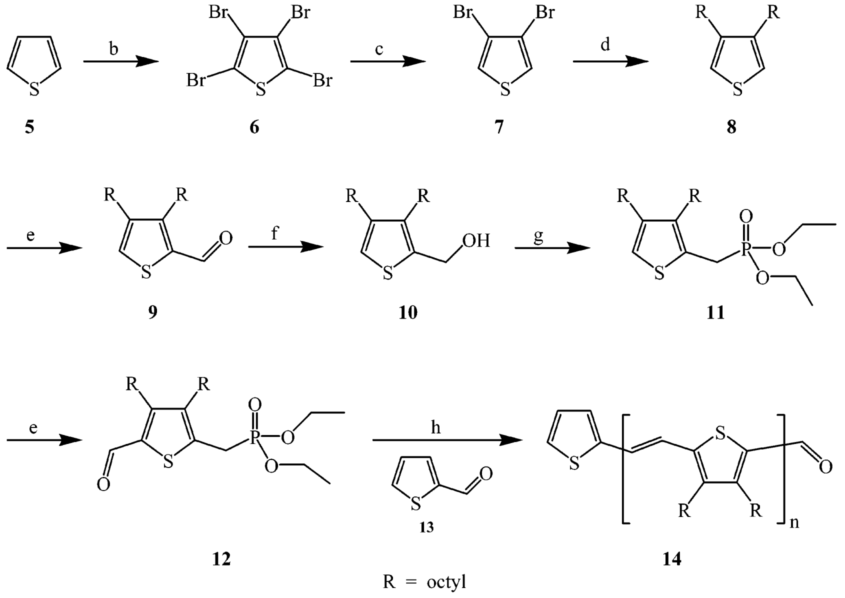
These short oligomers do not only lack the desired low band-gap (they show essentially the same λ_{max} as found for PPV) but will also lead to a very poor phase separation. The products of these Siegrist condensations can therefore not be used for the synthesis of rod−coil block copolymers and a new route for the synthesis of PTV has to be designed.

Synthesis of PTV via Horner—Wadsworth—Emmons Condensation. To improve the synthesis of well-defined PTV, a new synthetic strategy was designed, based on a Horner−Wadsworth−Emmons condensation reaction. An advantage of this method is that a monofunctional end-capper can be employed in order to control the length of the polymer. This type of condensation reaction will generally not lead directly to low polydispersities, but purification via column chromatography is a good method to minimize this drawback.

Poly[3,4-dioctyl(2,5-thienylenevinylene)] (DO-PTV) was synthesized from thiophene following the strategy depicted in Scheme 3.

After bromination[51,53] and selective debromination,[53] the 3 and 4 positions of thiophene are functionalized with solubilizing octyl side chains via a nickel-catalyzed Grignard coupling reaction.[54] Via a Vilsmeier formylation,[52] one side is selectively transformed into an aldehyde, which is subsequently reduced into an alcohol. This alcohol is then transformed into a Horner−Wadsworth−Emmons reagent by in situ reaction of the corresponding unstable bromo-derivative, obtained after reaction with

Scheme 3. Synthesis of DO-PTV (14) via a Horner-Wadsworth-Emmons Polycondensation ($DP_n = k = n + 1$)[a]



[a] Reagents and conditions: (b) Br_2, AcOH, 80 °C, 16 h.; (c) Zn, H_2O/AcOH 7:3, room temperature, 2 h; (d) bromooctane, Mg, $NiCl_2$[dppp], ether, room temperature, 16 h; (e) $POCl_3$, DMF, DCM, reflux, 5 h; (f) $NaBH_4$, DCM/methanol 1:1, 0 °C, 3 h; (g) PBr_3, toluene/benzene 2:1, −30 °C, 5 min and then $(OEt)_2P(O)H$, NaH, THF, −30 °C, 30 min and then reflux, 2 h; (h) 2-thiophenecarbaldehyde (**13**), KOtBu, THF, room temperature, 24 h.

PBr_3, with the anion of diethyl phosphite.[56] After a second Vilsmeier formylation to transform the other side of the monomer into an aldehyde, the final monomer for a Horner−Wadsworth−Emmons self-condensation is obtained.[58,59]

The monomer (**12**) is polymerized under basic conditions in the presence of some monofunctional end-capping agent 2-thiophenecarbaldehyde (**13**) to give the desired DO-PTV (**14**). Care should be taken that monomer **12** is highly pure, because a minor contamination with the precursor **11** could limit the degree of polymerization in an uncontrolled way. Some difficulties had to be overcome before the successful polymerization of **12** could be completed. It was found that under standard conditions for this type of condensation (large excess of strong base and long reaction times) the aldehyde end group was completely removed. Besides reducing thus the length of the polymer, it also renders the product useless for further synthesis of a diblock copolymer. This type of unexpected aldehyde loss was only recently described by Kreher et al.[60] Although it is not clear what causes this aldehyde removal, it is striking that the synthesis attempted by Kreher also concerns a conjugated compound and possibly charge delocalization or doping is at the origin of this problem. Less basic conditions seemed to resolve this problem. Another difficulty was the initial failure of the attempted synthesis of long polymers. Even without any end-capper present, the $\overline{DP}_n$ did not exceed 8−9 repeat units. Slow addition of the base (to prevent aldehyde loss) even reduced this to 6−7 repeat units. A high monomer concentration was needed to drive the polymerization to higher conversions. The reaction conditions were adapted in order to prevent the aldehyde removal and to ensure high conversions: the reaction was performed with 1.5 equiv of base, which is quickly added to a highly concentrated monomer solution (see Experimental Section). Only minor amounts of nonreacted phosphonate end groups could be detected via ^1H NMR spectroscopy, suggesting a conversion of around 96% for all polymerizations.

Table 1. Results for the Polymerization of DO-PTV via Horner−Emmons Condensation with Varying Amounts of End-Capping Agent

		DP_n			M_n (kg·mol^{-1})			
N_A:$N_{B'}$	r	theor[a]	NMR[b]	abs[c,d]	NMR[b]	GPC[e]	PD[e]	λ_{max}[c] (nm)
0.99:1	0.332	1.99	2.4	2.0	0.588	0.54	1.3	374
2.02:1	0.502	3.02	4.3	4.4	1.21	1.06	1.4	508
3.03:1	0.602	4.03	5.3	6.0	1.55	1.75	1.5	551
5.00:1	0.714	6.00	9.3	9.9	2.87	3.25	1.5	589
7.07:1	0.776	8.07	12.1	11.3	3.80	4.29	1.9	593
8.98:1	0.818	9.98	17.6	17.5	5.63	7.16	4.1	602
14.0:1	0.875	15.0	22.5	-[f]	7.28	6.98	3.8	601
19.2:1	0.906	20.2	35[f]	-[f]	11[f]	9.03	2.2	602
1:0	1.00	∞	66[f]	-[f]	22[f]	10.9	1.8	603

[a] Theoretical value calculated using eq 2 − eq 1 for $p = 1$. [b] Determined by ^1H NMR end group analysis. [c] Determined by UV−vis absorbance spectroscopy (in uvasol $CHCl_3$). [d] Determined by comparison of λ_{max} to the λ_{max} for well-defined DH-OTVs, using eq 4.[41−43] [e] polydispersity index determined by GPC: RI signal with PS standard. [f] The polymer is too long for accurate determination of polymer length.

The end-capper is added in order to be able to control the degree of polymerization and to ensure the complete conversion of the reactive phosphonate group. For a classical step polymerization, $\overline{DP}_n$ can in such case be described by the eq 1[61]

$$\overline{DP}_n = \frac{1 + r}{1 + r - 2rp} \tag{1}$$

where p is the conversion and r is the stoichiometric imbalance, defined by eq 2

$$r = \frac{N_A}{N_B + 2N_{B'}} \tag{2}$$

where N_A, N_B, and $N_{B'}$ are the molar amounts of the different functionalities (aldehyde and phosphonate), so in the case of A−B type monomers with excess monofunctional end-capper (B′), $N_A = N_B$ (monomer **12**), and $N_{B'}$ is the molar excess of monofunctional end-capper (**13**).

The results for a series of polymerizations with different amounts of monofunctional end groups are summarized in Table 1. The length of the polymer was established first by ^1H NMR end group analysis. Comparison of the integration of the side

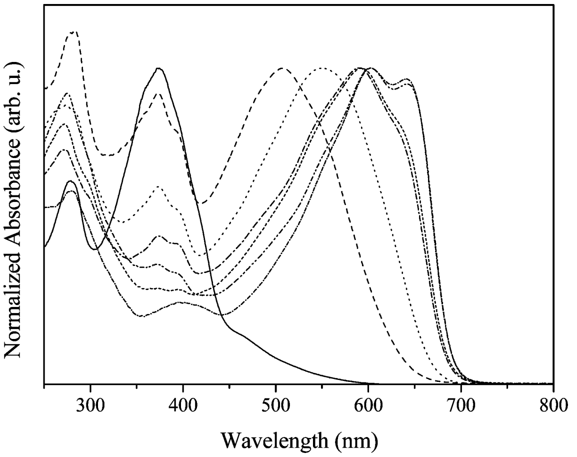


Figure 2. UV−vis absorbance spectra for DO-PTVs synthesized with different amounts of end-capper. $r = 0.33$ (—),0.50 (- - -), 0.60 (• • •), 0.71 (- • -), 0.78 (- - -), 0.82 (- • • -), and 1.0 (- • - • -).

chain CH_2 signal to the aldehyde end group signal gives an estimation of the degree of polymerization. The overlap of vinyl and aromatic thiophene signals in the region ranging from $\delta = 6.5-7.5$ ppm, made a reliable calculation of polymer length using the aromatic thiophene end group signals impossible. The results show an increase of the $\overline{DP}_n$ with a decreasing amount of end-capping agent. The theoretical values for a conversion of 100% are exceeded by a factor 1.5 but a linear relationship exists between this theoretical $\overline{DP}_n$ and the length that was experimentally found. This means that it is possible to control the degree of polymerization by varying the amount of end-capping agent. For longer polymers this method for the calculation of the chain length becomes increasingly inaccurate, due to the decreasing intensity of the aldehyde end group signal.

All these oligomers and polymers have been also characterized by UV−vis absorbance spectrometry. Spectra are depicted in Figure 2. The length of shorter polymers can be determined by comparison of the λ_{max} value (see Table 1) to the λ_{max} obtained for well-defined oligomers.

There is a linear relationship between the band-gap energy (E_g), which is proportional to the reciprocal of the λ_{max} value, and the reciprocal number of carbon atoms in the conjugated chain, *Cn*. From a linear fit to literature λ_{max} values for oligo(3,4-dihexyl-2,5-thienylene vinylene)s (DH-OTVs) with an aldehyde end group,[55−57] the following eq 3 and eq 4 could be derived:

$$\lambda_{max} = \frac{697.3Cn}{Cn + 9.491} \quad \text{for } Cn = 6(\mathrm{DP_n}) - 1 \le 50 \qquad (3)$$

$$\mathrm{DP_n} = \frac{\lambda_{max}}{440.8 - 0.6322\lambda_{max}} + \frac{1}{6} \quad \text{for } \lambda_{max} \le 575 \text{ nm} \qquad (4)$$

Since the length of the side chains has only minor influence on the conjugation length of the conjugated polymer, and thus on its λ_{max}, these equations were used directly for the determination of the length of the different DO-PTVs. For longer polymers, the relationship deviates from linearity and an estimation of the polymer length was performed based on the band-gap values for the DH-OTVs extrapolated to $1/Cn = 0$. For λ_{max} values exceeding the maximum conjugation length (around 601−602), however, even this estimation was too inaccurate to give a good estimation of the $\mathrm{DP_n}$. Results are summarized in Table 1. In all cases (except where λ_{max} exceeds the maximum conjugation length) the values obtained in this way are very similar to those obtained by ^{1}H NMR spectroscopy (see Figure 3). This is again an indication that all polymer chains, constituting the main absorbance peak, contain an aldehyde end group when polymerizations take place in correct conditions.

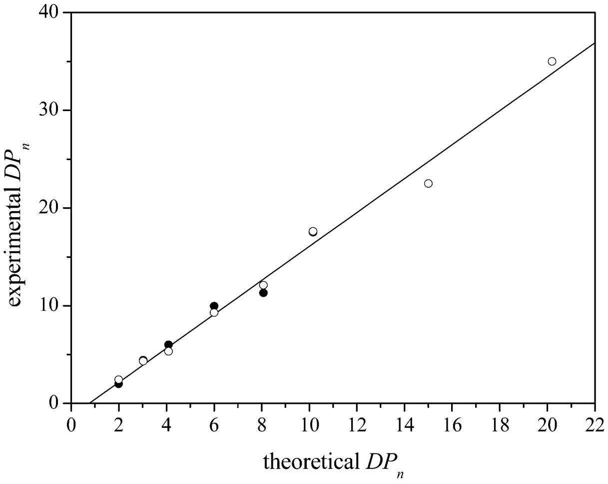


Figure 3. Theoretical (for $p = 1$) vs the experimental degree of polymerization DP_n of DO-PTV, calculated via ^{1}H NMR end group analysis (○) and UV−vis absorbance spectroscopy (●), including a linear fit.

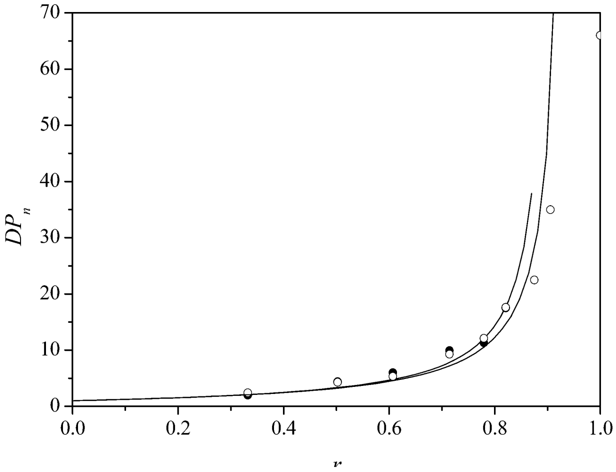


Figure 4. Degree of polymerization as a function of *r*, calculated via ^{1}H NMR end group analysis (○) and UV−vis absorbance spectroscopy (●), including their fits to eq 1.

Both methods (^{1}H NMR or UV−vis) overestimate the Degree of polymerization with respect to the theoretical value. Indeed, fitting of the $\overline{DP}_n$ values obtained by ^{1}H NMR to eq 1 (Figure 4)gives $p = 1.03$ and fitting of the values obtained by UV−vis spectroscopy gives $p = 1.05$. These inconsistent values of conversion are a consequence of this overestimation. However, the shape of the plot of $\overline{DP}_n$ vs *r* corresponds to a classical step polymerization (Figure 4).

This deviation is probably the result of a side reaction due to a specific reactivity of the end-capping agent **13**. In most absorbance spectra there is a clear shoulder around 350−400 nm, indicating the presence of unreacted OTV dimer which can be removed after several precipitations. This dimer, consisting of an end-capped monomer, most likely lacks the aldehyde group (that would allow it to react further) and is probably formed early in the reaction. Test reactions with elevated concentrations of end-capper, proved that this end-capping agent is highly reactive. This high reactivity causes the initial prevalence of dimers formed from reaction of monomer **12** with the end-capper **13**, compared to dimers formed between two monomers. Because of the strongly basic conditions and its

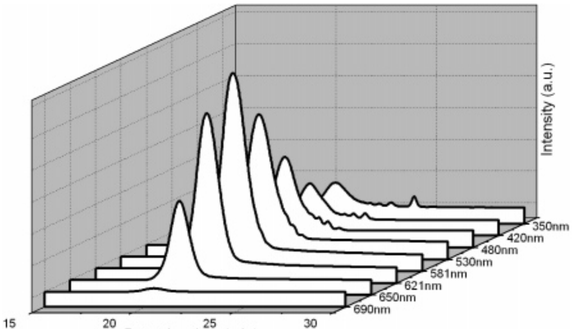


Figure 5. GPC traces (*x* and *z* axis) for 7 different wavelength (*y* axis) of DO-PTV for $r = 0.71$.

particular reactivity, a part of this dimer may loose its remaining aldehyde group and stop growing. Such side reactions may eliminate a part of the end-capping agent from the system which explains the overestimated values of $\overline{\mathrm{DP}}_\mathrm{n}$. This hypothesis will be investigated in the future by kinetic studies and mass spectrometry analysis.

It should be possible to prevent its appearance by slow addition of the base or the use of less concentrated reaction mixtures but, as it has shown previously it will limit the conversion into very long chains (even in absence of end-capper). However, according to correlation between UV−vis and NMR measurements, this side reaction does not affect the functionality of final PTV chain end and the dimer could be easily removed by precipitation in ethanol.

To complete this study, PTV samples were also characterized via gel permeation chromatography (GPC). The GPC analyses were performed with a diodes array detector (see an example on Figure 5). With this detector, it is possible to obtain the UV−vis absorption spectrum for each elution time. With this detector a majority of long chain PTV with large absorbance in the visible have been observed.

As for all conjugated polymers, only a rough estimate of the molecular weight could be obtained in this way due to the calibration with polystyrene standards. It is clear, however, that the molecular weight (reported in Table 1) increases with a decreasing amount of end-capper and the molecular weights obtained do not differ too much from the values obtained by ^{1}H NMR and UV−vis absorbance spectroscopy. The polydispersities (PD) can be also estimated by this way (see Table 1). It remains unclear why the samples with $r = 0.82$ and 0.88 have such extremely high PDs, since the samples with higher r values show more reasonable PD values. The PDs in all other cases are especially low for a simple step polymerization and it is probably due to the presence of the highly reactive end-capping agent. Effectively, when no end-capping agent was added (last line in Table 1) PD trends to the theoretical value of 2 for a maximum conversion ($P = 1$).[61] The presence of a small peak at low molecular weight, comparable to the molecular weight found for the dimer (clearly distinguished in the samples with $r = 0.33$ and 0.50), again shows the presence of OTV dimer in the products. The GPC elugrams do not show enough detail to prove the absence of an aldehyde group on these dimers, but no indication is found for the presence of many other unreacted oligomers. GPC and UV−vis absorbance contour plots (Figure 5), however, demonstrate that the largest part of the absorbance between 200 and 300 nm, and of course between 400 and 700 nm, is mainly due to the contribution of longer polymers rather than to the presence of the dimer.

From all these results (^{1}H NMR, UV−vis absorbance, and GPC), it can be concluded that the length of the DO-PTV can be well controlled with this method of polymerization, although polydispersities are rather high. All products are well-defined (with one aldehyde function) and well soluble in common organic solvents such as THF, DCM and diethyl ether. The deviation of $\overline{\mathrm{DP}}_\mathrm{n}$ from theory does not constitute an obstacle for the synthesis of a PTV based macroinitiator.

Synthesis of a Macroinitiator for NMRP Based on DO-PTV. For the preparation of a block copolymer, a sample with 12 mol % of end-capper was also prepared on a somewhat larger scale. To ensure the complete conversion of the phosphonate group, additional end-capping agent was added at the end of the polymerization. This excess end-capping agent could be easily removed after the reaction by multiple extractions with water. The resulting polymer was purified via precipitation in ethanol, driven to completion by addition of water, to give a polymer with a molecular weight of 3.2 kg·mol^{-1} ($\overline{\mathrm{DP}}_\mathrm{n} = 10.3$), where all three characterization methods give a similar degree of polymerization. A polydispersity index of 1.6 was found by GPC.

This polymer was subsequently transformed into a macroinitiator for NMRP, using the same procedure as the one employed for the synthesis of the PPV macroinitiator.[25] The complete conversion was monitored through the disappearance of the ^{1}H NMR aldehyde signal at $\delta = 9.96$ ppm. The obtained macroinitiator, DO-PTV-TIPNO **15** is then used for the NRMP of styrene derivatives.

PTV-Based Diblock Copolymers. A preliminary attempt was made to synthesize a block copolymer based on the PTV macroinitiator. A diblock copolymer was synthesized by copolymerizing styrene (S) and chloromethylstyrene (CMS) (feed ratio 4:1) from macroinitiator **15**. The synthesis of the final block copolymer **16** is shown in Scheme 4. The use of CMS is performed in order to incorporate later accepting group in the coil block. These conditions are the same as the ones used for the synthesis of a PPV−PS type block.[27] At first, the polymerization was left for 30 min, but only a very low conversion was reached, so the purified product was employed in a second polymerization for another 120 min, yielding a much longer block copolymer. Results are summarized in Table 2.

The length of the second block increases with time of polymerization. Compared to the polymerization based on PPV initiator,[27] the reaction speed is somewhat slower, but still fast enough to give reasonable block lengths with a good control. The PD of the final block copolymer is quite narrow (1.7) if

Scheme 4. Synthesis of Block Copolymer (16) by NMRP from DO-PTV-TIPNO (15)

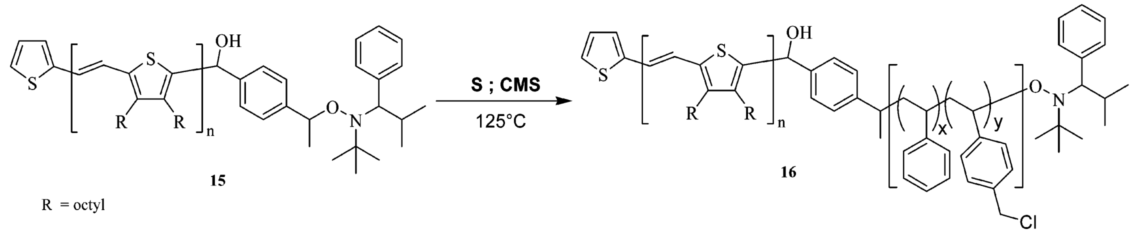


Table 2. Results for the NMRP Bulk Polymerization of S and CMS with Macroinitiator 15

			M_n(kg·mol^{-1})			
t (min)[a]	P[b]	r[b]	NMR[b]	GPC[c]	PD[c]	w_{PPV}[b,d]
0	0		3.5	4.1	1.6	0.91
30	0.039	2.9	5.9	5.1	2.5	0.53
150[e]	0.30	2.9	46.2	31.3	1.7	0.069

[a] Conditions: 1 equiv of **15**, 1100 equiv of S, 275 equiv of CMS, 4 equiv of Ac_2O, 0.1 equiv of TIPNO, 125 °C. [b] Determined by ^{1}H NMR. [c] Determined by GPC measurement; RI signal with PMMA standard. [d] $w_{PPV} = M_{n,PPV}/M_n$; $M_{n,PPV} = 4.0$ kg·mol^{-1}. [e] Starting form purified block copolymer after $t = 30$ min.

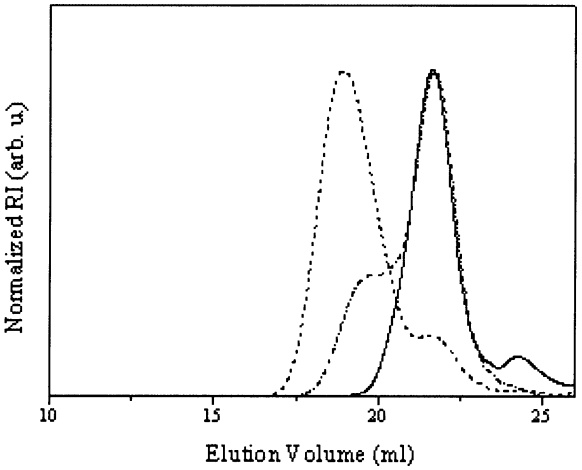


Figure 6. GPC elugrams (RI detection) of DO-PTV$_{3.2K}$-*b*-P(S-*stat*-CMS)-TIPNO at: $t = 0$ (—), 30 (- · -) and 150 min (- - -).

we take into account the high PD of the macroinitiator. The difference built-in ratio of the monomers compared to the feed ratio corresponds to a difference of reactivity between S and CMS.

Figure 6 shows the GPC traces for the first polymerization and the elongation of the coil block. It is clear that the first polymerization attempt gave the chain extension of only a part of the macroinitiator and only upon the second polymerization was all functionalized PTV converted into a block copolymer. That suggests that the chain extension works well and the purified short block copolymer was not dead. For the polymerization time of 150 min, the little shoulder on the elugram suggests that the conversion into efficient macro initiator was not totally complete. However, UV−vis absorbance spectra of long chains (obtained from diodes array detector) show a maximum of absorption around 560 nm, which is a proof of the presence of PTV sequence in the final polymer.

All these results show that it is possible to obtain a block copolymer when starting form a NMRP macroinitiator based on PTV, and it is also possible to elongate the block copolymer after purification.

Conclusion

The successful synthesis of well-defined and monofunctional DO-PTV was performed by using the Horner−Wadsworth−Emmons condensation. Siegrist condensation of PTV derivatives was less successful and led only to short oligomeric species. The length of the polymer could be controlled using an end-capping agent, although the theoretical length was exceeded. This is probably caused by the formation of a nonreactive dimer. These polymers, after precipitation, can be easily transformed into NMRP macroinitiator. A first attempt to make a DO-PTV-*b*-P(S-*stat*-CMS) type block copolymer was successful, although short polymerization times lead to the incomplete initiation of all polymer chains. At higher conversion the product corresponds to a well-defined low band gap conjugated rod−coil block copolymer. Because of the presence of CMS unit, which can be used to grafted electron acceptors, this copolymer is a perfect precursor for a low band gap donor−acceptor rod coil block copolymer.

Experimental Section

Materials and Methods. THF and toluene were distilled from Na/benzophenone, ether from $LiAlH_4$, and DCM from CaH_2, and DMF and triethylamine were dried on activated molecular sieves (4 Å). Column chromatography was performed using Silica gel (Merck Geduran Si 60 (40−63 μm)). All other chemicals and solvents were used as received and all reactions were performed under dry Ar atmosphere, unless noted otherwise.

Measurements. ^{1}NMR spectra were recorded on a Bruker 300 UltrashieldTM 300 MHz NMR spectrometer, with an internal lock on the 2H-signal of the solvent ($CDCl_3$ or acetone-d_6).

Absorbance spectra were recorded on a Shimadzu UV-2101PC UV−vis Scanning spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer Luminscence spectrophotometer LS50-B, using an excitation wavelength 10 nm below λ_{max} and a 2.5 nm bandwidth. Measurements were performed using UV or HPLC grade solvents and quartz cuvettes (path length 10 mm).

GPC measurements were performed in THF (HPLC grade) with a two PL-gel 5 μ mixed-C, a 5μ 100 Å and a 5 μ Guard columns in a Shimadzu LC-10AD liquid chromatograph equipped with a Shimadzu RID-10A refractive index detector and a Shimadzu SPP-M10A diode array (UV) detector.

Synthesis. 2-Methyl-3-butyl-5-formylthiophene (1). 2-methyl-3-butylthiophene was synthesized from 3-butylthiophene following an adaptation of literature procedures.[51,52] Then, 5.01 g (22.9 mmol) of 3-butylthiophene was dissolved in 50 mL of dry ether and cooled to −80 °C. Following this, 25 mL of 2.5 M *n*-butyllithium in ether was added, and the resulting mixture was stirred for 1 h. A cooled (−50 °C) solution of 9.11 g (72.2 mmol) dimethyl sulfate in 25 mL of dry ether was added, and the resulting slurry was stirred for 1 h. The solution was warmed to room temperature and 22 mL of a 4 M NaOH solution was added slowly. The two layers were separated and the water layer was extracted with 20 mL ether. The combined organic layers were washed with 3 × 30 mL water, dried on Na_2SO_4, filtered, and evaporated. The product was purified via flash column chromatography, using hexane as an eluent. Yield: 2.98 g (84%) of a colorless liquid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 7.02 (d, 1H, arom CH-5), 6.85 (d, 1H, arom CH-4), 2.56 (t, 2H, aliph CH_2-1′), 2.40 (s, 3H, arom CH_3), 1.59 (m, 2H, aliph CH_2-2′), 1.41 (m, 2H, aliph CH_2-3′), 0.98 (t, 3H, aliph CH_3-4′).

To a solution of 2.90 g of 2-methyl-3-butylthiophene (18.8 mmol) and 5.0 mL (4.7 g, 64 mmol) of DMF in 15 mL of dry DCM was added 2.60 mL (4.34 g, 28.3 mmol) of $POCl_3$ slowly via a syringe. The reaction mixture was refluxed for 3 h. and cooled to room temperature. Slowly, 30 mL of 1 M sodium acetate was added, and after addition of 20 mL of water, the water layer was extracted with 4 × 30 mL of DCM. The combined organic layers were washed with 3 × 50 mL of water, dried on Na_2SO_4, filtered, and evaporated under reduced pressure. The product was purified via column chromatography, using a gradient of DCM in hexane (from 15 to 30%) as an eluent. Yield: 2.36 g (69%) of a slightly yellowish oil.

^{1}H NMR ($CDCl_3$): δ (ppm) = 9.72 (s, 1H, CHO), 7.46 (s, 1H, arom CH-4), 2.49 (t, 2H, aliph CH_2-1′), 2.39 (s, 3H, arom CH_3), 1.52 (m, 2H, aliph CH_2-2′), 1.31 (m, 2H, aliph CH_2-3′), 0.89 (t, 3H, aliph CH_3-4′).

2-Methyl-3,4-dipropyl-5-formylthiophene (3). 2-methyl-3,4,5-tribromothiophene was synthesized according to a combination of several literature procedures.[52−54] A solution of 20.0 g (207 mmol) of 2-methylthiophene in 400 mL of glacial acetic acid was placed in a three-neck flask equipped with a dropping funnel and a cooler connected to a trap, containing an concentrated aqueous solution of KOH. Over an hour, 37.0 mL (115 g, 722 mmol) of Br_2 were added dropwise. The reaction mixture was heated to 80 °C and stirred for 3 h. After cooling to room temperature, the reaction was quenched by dropwise addition of 200 mL of a 10% $Na_2S_2O_3$ solution. Water was added to the mixture, and it was extracted with 3 × 200 mL of $CHCl_3$. The combined organic layers were washed with 2 × 400 mL of brine, dried on Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was taken up in ethanol, filtered, and left to crystallize at −20 °C. The product was recrystallized from hot ethanol twice. After filtration, the product was dried under reduced pressure at 30 °C. Yield: 49.9 g (72%) of colorless crystal needles.

^{1}H NMR ($CDCl_3$): δ (ppm) = 2.41 (s, arom CH_3).

2-Methyl-3,4-dibromothiophene was synthesized as follows: 4.00 g (11.9 mmol) of 2-methyl-3,4,5-tribromothiophene was dissolved in 50 mL of dry ether and cooled to −80 °C. Then 12.0 mL of a 1.5 M solution *tert*-butyllithium in pentane was added slowly via a syringe. After being stirred for 10 min, the reaction mixture is poured out into water. The two layers are separated and the water phase is extracted with 3 × 50 mL of $CHCl_3$. The combined organic layers are washed with 2 × 100 mL of brine, dried on Na_2SO_4, filtered, and evaporated. Yield: 1.96 g (64%) of brownish oil, which is used without any further purification.

^{1}H NMR ($CDCl_3$): δ (ppm) = 7.14 (s, 1H, arom CH-5), 2.45 (s, 3H, arom CH_3-2).

2-Methyl-3,4-dipropylthiophene was synthesized as follows: 0.703 g (28.9 mmol) of Mg was placed in 15 mL of dry ether, and over 40 min, 1.50 mL (2.03 g, 16.6 mmol) of propyl bromide was added dropwise. The reaction mixture was heated to reflux and stirred for another hour. This solution was then cooled until room temperature and transferred slowly via a syringe to a mixture of 2-methyl-3,4-dibromothiophene (1.02 g, 3.98 mmol) and 35.0 mg (64.6 μmol) $NiCl_2$[dppp], which was freshly prepared according to ref 45, in 10 mL of dry ether. The reaction mixture was heated to reflux and stirred for 20 h at room temperature. The reaction mixture was cooled until room temperature and subsequently poured out in 200 mL of ice/water containing 10 mL of concentrated HCl. The product was extracted with 3 × 100 mL of ether and the combined organic layers were washed with 2 × 200 mL of water, dried on Na_2SO_4, filtered, and evaporated under reduced pressure. The product was used without any further purification.

^{1}H NMR ($CDCl_3$): δ (ppm) = 7.23 (s, 1H, arom CH-5), 2.5−2.3 (m, 4H, aliph CH_2-1′), 2.3 (s, 3H, arom CH_3), 1.7−1.4 (2 m, 4H, aliph CH_2-2′), 1.0−0.8 (m, 6H, aliph CH_3-3′)

To a solution of ∼0.6 g (∼3 mmol) 2-methyl-3,4-dipropylthiophene and 2.0 mL (1.9 g, 26 mmol) of DMF in 10 mL of dry DCM was added 0.75 mL (1.3 g, 8.2 mmol) of $POCl_3$ slowly via a syringe. The reaction mixture was refluxed for 3 h and cooled to room temperature. Slowly, 8 mL of 1 M sodium acetate was added and after addition of 20 mL of water, the water phase was extracted with 3 × 30 mL of DCM. The combined organic layers were washed with 2 × 50 mL water, dried on Na_2SO_4, filtered and evaporated. The product was purified via column chromatography, using a gradient of DCM in hexane (from 10 to 100%) as an eluent. Yield: 0.2 g (30% over two steps) of a slightly yellowish oil.

^{1}H NMR ($CDCl_3$): δ (ppm) = 9.76 (s, 1H, CHO), 2.84 (m, 2H, aliph CH_2-1(4)′), 2.51 (m, 2H, aliph CH_2-1(3)′), 2.43 (s, 3H, arom CH_3), 1.6−1.3 (2 m, 4H, aliph CH_2-2′), 0.95 (t, 3H, aliph CH_3-3′)

α-Methyl-*ω*-formylpoly(3-butyl-2,5-thienylenevinylene) (2) and α-Methyl-*ω*-formylpoly(3,4-dipropyl-2,5-thienylenevinylene] (4). A solution of **9** or **11** (0.4 mmol/mL) was added to a degassed solution of KOtBu in dry DMF at 90 °C. The solution was stirred for 2.5 h and poured out carefully into excess ice/water containing ∼5% of concentrated HCl. The product was extracted with $CHCl_3$, until the extracted solution became colorless. The combined organic layers were washed with a 5% $NaHCO_3$ solution until the water layer was pH-neutral and finally washed with water. The organic phase was dried on Na_2SO_4, filtered and evaporated under reduced pressure. The polymer was then purified by means of precipitation in methanol with 15% water at −30 °C. The polymer was dried under reduced pressure at 30 °C. Yield: dark brown-purple powder.

^{1}H NMR ($CDCl_3$): **2** δ (ppm) = 9.9 (br s, CHO), 7.5 (br s, arom CH-4), 7.2−6.6 (m, olef. CH), 3.2−3.2−2.4 (br m, aliph CH_2-1′ and arom CH_3), 2.7−1.1 (2 m, aliph CH_2-2′ and CH_2-3′), 0.9 (br s, aliph CH_3-4′), **4** δ (ppm) = 9.9 (br s, CHO), 7.2−6.6 (m, olef. CH), 3.2−2.2 (br m, aliph CH_2-1′), 2.5 (br s, aliph CH_2-2′) 0.9 (br s, aliph CH_3-3′).

Tetrabromothiophene (6). Tetrabromothiophene was synthesized according to a combination of several literature procedures.[51,53] A solution of 70.5 g (0.838 mol) of thiophene in 200 mL of glacial acetic acid was placed in a three-neck flask equipped with a dropping funnel and a cooler connected to a trap, containing a concentrated aqueous solution of KOH. Over a 3-h period, 200 mL (624 g, 3.90 mol) Br_2 was added. The reaction mixture was heated to 80 °C and stirred for 16 h, while care was taken that no HBr escaped from the trap, which was refilled several times. After cooling to room temperature, the reaction was quenched by dropwise addition of ∼60 g of KOH in 400 mL of ethanol. The mixture was again cooled to room temperature and the slightly yellow precipitate filtered of and rinsed with copious amounts of water. The product was redissolved in hot $CHCl_3$, filtered to remove the remaining salts and left to crystallize at −20 °C. After filtration, the product was dried under reduced pressure at 30 °C. Yield: 313.0 g (93%) of colorless crystal needles.

^{1}H NMR ($CDCl_3$ or acetone-d_6): no peaks observed.

^{13}C NMR (acetone-d_6): δ (ppm) = 117.1 (arom Cq-2), 111.0 (arom Cq-3).

3,4-Dibromothiophene (7). 313 g (0.783 mol) **6** was dissolved in 1000 mL of water/acetic acid 7:3. While stirring vigorously, half of the 200 g (3.06 mol) supply of Zn was added and heated until a vigorous reaction started, and it was then cooled on ice. After 30 min, the remainder of the Zn was added ,and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was filtered to remove excess Zn, and the mother liquid was extracted with 3 × 300 mL of ether. The combined organic layers were washed with 4 × 300 mL of water, dried on $MgSO_4$, filtered, and evaporated under reduced pressure. Purity was checked by ^{13}C NMR, and the product was used without any further purification. Yield: 184.9 g (98%) of a colorless oil.

^{1}H NMR (CDCl3): δ (ppm) = 7.30 (s, arom CH).

^{13}C NMR (CDCl3): δ (ppm) = 123.7 (arom CH-2), 113.9 (arom Cq-3).

3,4-Dioctylthiophene (8). A 65.0 g (3.90 mol) sample of Mg was placed in 100 mL of dry ether and cooled to 0 °C. Over 2 h, 225 mL (252 g, 1.30 mol) of bromooctane was added dropwise, and the reaction mixture was stirred for another hour. This solution was then transferred slowly via a cannula to a mixture of **7** (135 g, 559 mmol) and 7.14 g (13.1 mmol) of $NiCl_2$[dppp] in 200 mL of dry ether while cooling on ice. The reaction mixture was stirred for 16 h at room temperature and subsequently poured out in 1000 mL of ice/water containing 50 mL of concentrated HCl. The product was extracted with 3 × 300 mL of ether and the combined organic layers were washed with 2 × 300 mL of water, dried on Na_2SO_4, filtered, and evaporated under reduced pressure. The product was purified via silica gel column chromatography, using cyclohexane as an eluent. Yield: 142.2 g (82%) of a slightly yellowish liquid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 6.91 (s, 2H, arom CH-2), 2.53 (q, 4H, aliph CH_2-1′), 1.7−1.2 (m, 24H, aliph CH_2-2′, CH_2-3′, CH_2-4′, CH_2-5′, CH_2-6′, CH_2-7′), 0.92 (t, 6H, aliph CH_3-8′).

^{13}C NMR ($CDCl_3$): δ (ppm) = 139.6 (arom C_q-3), 117.4 (arom CH-2), 29.3, 27.2, 26.8, 26.7, 26.5 26.3 (aliph CH$_2$-1′, CH$_2$-2′, CH$_2$-3′, CH$_2$-4′, CH$_2$-5′, CH$_2$-6′,), 20.17 (aliph CH$_2$-7′), 11.61 (aliph CH$_3$-8′).

2-Formyl-3,4-dioctylthiophene (9).[56] To a solution of **8** (142 g, 461 mmol) and 100 mL (94 g, 1.29 mol) of DMF in 500 mL of dry DCM was added 85.0 mL (142 g, 926 mmol) of $POCl_3$ slowly via a dropping funnel. The reaction mixture was refluxed for 3 h and cooled to room temperature. Slowly, 100 g of sodium acetate was added into 300 mL of water and the two layers were separated. The water layer was extracted with 3 × 300 mL of DCM, and the combined organic layers were washed with a 5% $NaHCO_3$ solution until the water layer was pH-neutral and finally washed with 2 × 300 mL of water. The organic phase was dried on Na_2SO_4, filtered, and evaporated under reduced pressure. The product was used without further purification.

^{1}H NMR ($CDCl_3$): δ (ppm) = 10.0, (s, 1H, C*H*O), 7.34 (s, 1H, arom C*H*-5), 2.88 (t, 2H, aliph C*H*$_2$-1′a), 2.53 (t, 2H, aliph C*H*$_2$-1′b), 1.7−1.1 (m, 24H, aliph C*H*$_2$-2′, C*H*$_2$-3′, C*H*$_2$-4′, C*H*$_2$-5′, C*H*$_2$-6′, C*H*$_2$-7′), 0.88 (t, 6H, aliph C*H*$_3$-8′).

^{13}C NMR ($CDCl_3$): δ (ppm) = 180.1 (*C*HO), 149.1 (arom C_q-2), 141.9 (arom C_q-3), 135.6 (arom C_q-4), 127.8 (arom *C*H-5), 29.3, 29.1, 29.0, 27.2, 26.8, 26.7, 26.7, 26.6, 25.7, 24.5 (aliph *C*H$_2$-1′, *C*H$_2$-2′, *C*H$_2$-3′, *C*H$_2$-4′, *C*H$_2$-5′, *C*H$_2$-6′), 20.04, 20.01 (aliph *C*H$_2$-7′), 11.51, 11.48 (aliph *C*H$_3$-8′).

2-Hydroxymethyl-3,4-dioctylthiophene (10). A solution of 155 g of unpure **9** in 600 mL of DCM/methanol 1:1 was cooled to 0 °C. Then 34.9 g (922 mmol) of $NaBH_4$ was added in portions to the solution over a period of 30 min. The reaction mixture was stirred vigorously for 18 h, and water was added carefully to quench the reaction. The product was extracted with 2 × 400 mL of DCM and the combined organic layers were washed with acidified water and subsequently with 5% $NaHCO_3$ until the water layer was pH-neutral. The organic phase was then dried on Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified via column chromatography, using a gradient of DCM in cyclohexane (from 0 to 100%) as an eluent. Yield: 24.3 g (16% over two steps) of a colorless oil.

^{1}H NMR ($CDCl_3$): δ (ppm) = 6.85 (s, 1H, arom C*H*-5), 4.74 (d, 2H, C*H*$_2$OH), 2.50 (m, 4H, aliph C*H*$_2$-1′), 1.73 (t, 0.5H, CH$_2$O*H*), 1.7−1.1 (m, 24H, aliph C*H*$_2$-2′, C*H*$_2$-3′, C*H*$_2$-4′, C*H*$_2$-5′, C*H*$_2$-6′, C*H*$_2$-7′), 0.89 (t, 6H, aliph C*H*$_3$-8′).

^{13}C NMR ($CDCl_3$): δ (ppm) = 142.9, 139.4, 137.1 (arom C_q-2, C_q-3, C_q-4), 118.9 (arom *C*H-5), 58.3 (*C*H$_2$OH), 31.7, 31.6, 31.1, 29.7, 29.5, 29.3, 29.1, 29.0, 29.0, 26.9 (aliph *C*H$_2$-1′, *C*H$_2$-2′, *C*H$_2$-3′, *C*H$_2$-4′, *C*H$_2$-5′, *C*H$_2$-6′), 22.6 (aliph *C*H$_2$-7′), 14.0 (aliph *C*H$_3$-8′).

3,4-Dioctyl-5-methyldiethylphosphonate Thiophene (11). A suspension of 14.1 g (60% in min oil, 354 mmol) NaH in 50 mL of dry THF was cooled to −30 °C. A solution of 40.0 mL (43.2 g, 354 mmol) diethyl phosphite in 50 mL of dry THF was added dropwise over 30 min. In a separate flask, 3.0 mL (32 mmol) of PBr_3 was added to a cooled (−30 °C) solution of 24.3 g (71.7 mmol) **10** in 150 mL of toluene/benzene 2:1. This solution was then transferred quickly to the first flask via a cannula. The reaction mixture was refluxed for 2 h and finally quenched in ice. The two layers were separated and the water layer was extracted with 4 × 100 mL of DCM. The combined organic layers were washed with 3 × 200 mL brine, dried on Na_2SO_4, filtered, and evaporated under reduced pressure. The product was purified via column chromatography, using a gradient of DCM in cyclohexane (60−100%) as eluent. Yield: 27.1 g (82%) of a slightly yellow oil.

^{1}H NMR ($CDCl_3$): δ (ppm) = 6.82 (d, 1H, arom C*H*-5), 4.05, (m, 4H, C*H*$_2$ (OEt)), 3.34, 3.23 (2s, 2H, C*H*$_2$−P(O)(OEt)$_2$), 2.46 (m, 4H, aliph C*H*$_2$-1′), 1.7−1.1 (m, 30H, aliph C*H*$_2$-2′, C*H*$_2$-3′, C*H*$_2$-4′, C*H*$_2$-5′, C*H*$_2$-6′, C*H*$_2$-7′ and C*H*$_3$ (OEt)), 0.88 (m, 6H, aliph C*H*$_3$-8′).

^{13}C NMR ($CDCl_3$): δ (ppm) = 142.9, 139.4, 137.1 (arom C_q-2, C_q-3, C_q-4), 118.9 (arom *C*H-5), 58.26 (*C*H$_2$OH), 32.2, 31.7, 31.6, 30.3, 30.2, 29.7, 29.5, 29.2, 29.1, 29.1, 29.0, 27.3, 26.3, 26.1 (aliph *C*H$_2$-1′, *C*H$_2$-2′, *C*H$_2$-3′, *C*H$_2$-4′, *C*H$_2$-5′, *C*H$_2$-6′ and *C*H$_2$−P(O)(OEt)$_2$), 22.5 (aliph *C*H$_2$-7′), 16.3, 16.2 (*C*H$_3$ [OEt]), 13.9 (aliph *C*H$_3$-8′).

2-Formyl-3,4-dioctyl-5-methyldiethylphosphonate Thiophene (12). A 2.00 mL (3.34 g, 21.8 mmol) of $POCl_3$ was added slowly to a solution of **11** (7.01 g, 15.3 mmol) and 2.00 mL (1.88 g, 25.7 mmol) of DMF in 20 mL of DCM. The reaction mixture was refluxed for 2 h and cooled to room temperature. Slowly, 5 g of sodium acetate in 20 mL of water was added and the two layers were separated. The water layer was extracted with 2 × 50 mL of DCM and the combined organic layers were washed with a 5% $NaHCO_3$ solution until the water layer was pH-neutral and finally washed with 3 × 100 mL of water. The organic phase was dried on Na_2SO_4, filtered, and evaporated under reduced pressure. The product was purified multiple times via column chromatography, using a gradient of DCM in cyclohexane (from 60 to 100%) as an eluent and flushing the column with 2% ethanol in DCM. The product was checked for the absence of **11** by NMR spectroscopy. Yield: 1808 g (24%) of a highly viscous yellow oil.

^{1}H NMR ($CDCl_3$): δ (ppm) = 9.91 (s, 1H, C*H*O), 4.02 (m, 4H, C*H*$_2$ (OEt)), 3.33, 3.25 (2s, 2H, C*H*$_2$ (OEt)), 2.80 (t, 2H, C*H*$_2$-1′a), 2.50 (t, 2H, aliph C*H*$_2$-1′b), 1.6−1.1 (m, 30H, aliph C*H*$_2$-2′, C*H*$_2$-3′, C*H*$_2$-4′, C*H*$_2$-5′, C*H*$_2$-6′, C*H*$_2$-7′, and C*H*$_3$ (OEt)), 0.83 (m, 6H, aliph C*H*$_3$-8′).

^{13}C NMR ($CDCl_3$): δ (ppm) = 182.0 (*C*HO), 151.9, 142.4, 138.2, 136.2 (arom C_q-2, C_q-3, C_q-4, C_q-5), 62.4 (*C*H$_2$ [OEt]), 32.2, 31.7, 31.6, 30.3, 30.2, 29.7, 29.5, 29.2, 29.1, 29.1, 29.0, 27.3, 26.3, 26.1 (aliph *C*H$_2$-1′, *C*H$_2$-2′, *C*H$_2$-3′, *C*H$_2$-4′, *C*H$_2$-5′, *C*H$_2$-6′, and *C*H$_2$−P(O)(OEt)$_2$), 22.5 (aliph *C*H$_2$-7′), 16.3, 16.2 (*C*H$_3$ [OEt]), 13.9 (aliph *C*H$_3$-8′).

α-2-(Thiophen-2-yl)vinyl-ω-formyl-poly(3,4-dioctyl-2,5-thienylenevinylene) (14). To **12** the correct amount of a 2-thiopenecarbaldehyde **13** solution (20 mg·mL^{-1}) in dry THF was added and the solution was diluted with dry THF to give a final monomer concentration of ~100 mg·mL^{-1}. Then 1.5 equiv of a 20 wt % solution of KO*t*Bu in THF was added to this solution at once, and the reaction mixture was stirred for 15 h. The reaction was quenched in water/ice containing a small amount of NH_4Cl. The product was extracted with DCM until the organic layer was almost colorless, and the combined organic layers were washed with water twice. The organic phase was then dried on Na_2SO_4, filtered, and evaporated under reduced pressure to give the final red to dark blue polymers. Yield 86−93%

To the polymer used for the synthesis of the macroinitiator **15**, 2 equiv of 2-thiophenecarbaldehyde were added after 15 h and the reaction mixture was stirred for another 3 h. This batch was washed with water five times in order to remove excess end-capping agent. The polymer was purified via precipitation from THF in methanol, using a small amount of water to force the precipitation.

^{1}H NMR ($CDCl_3$): δ (ppm) = 9.97 (s, 1H, C*H*O), 7.3−6.8 (m, (2n+3)H, vinyl C*H*, end group arom C*H*), 2.9−2.7, 2.6−2.3 (2m, 4nH, aliph C*H*$_2$-1), 1.6−1.1 (m, 24nH, aliph C*H*$_2$-2′, C*H*$_2$-3′, C*H*$_2$-4′, C*H*$_2$-5′, C*H*$_2$-6′, and C*H*$_2$-7′), 1.0−0.8 (m, 6nH, aliph C*H*$_3$-8′).

Macroinitiator DO-PTV-TIPNO (15). The synthesis of DO-PTV-TIPNO was performed according to the procedure described for the synthesis of DEH-PPV-TIPNO.[25] Yield: dark blue powder.

^{1}H NMR ($CDCl_3$): δ (ppm) = 7.7−6.7 (m, arom C*H* and vinyl C*H*), 5.98, 5,93 (2d, C*H*OH), 4.85 (m, PhC(O)*H*CH$_3$), 4.05−3.85 (m, aliph OC*H*$_2$), 3.38, 3.34 (2d, PhC(N)*H*-*i*Pr), ~3 (br s, CHO*H*), 2.25 (s, 3H, C*H*$_3$ end-group), 1.82 (m, aliph C*H*), 1.7−1.3 (m, aliph C*H*$_2$), 0.92 (m, aliph C*H*$_3$), 1.04, 0.76 (2s, CH(C*H*$_3$)$_2$, two diastereoisomers), 0.55, 0.22 (2d, C*H*$_3$CH, one of two methyl groups, two diastereoisomers).

DO-PTV-*b*-P(S-*stat*-CMS) Block Copolymer (16). A 60.6 mg (17 μmol) sample of DO-PTV$_{3.2k}$-TIPNO (**15**) was dissolved in 2.19 mL (1.99 g, 19.1 mmol) of styrene and 686 μL (0.739 g, 4.76 mmol) of 4-chloromethylstyrene. Then 6.5 μL (7 mg) of Ac_2O and 0.38 mg of free TIPNO were added. The mixture was degassed by performing three freeze−pump−thaw cycles and the reaction vessel was subsequently placed in a preheated oil bath at 125 °C. After 30 min, the reaction mixture was precipitated in cold methanol and dried under vacuum. For the second attempt, this whole procedure was repeated with the entire amount of product and the same quantities of reagents.

^{1}H NMR ($CDCl_3$) spectra, DP$_n$ was calculated by comparison with the DO-PTV side chain peaks at δ = 2.6 ppm: δ (ppm) = 7.2−6.3 (m. arom C*H* [PTV, S and CMS]), 4.51 (br s, C*H*$_2$Cl [CMS]), 2.6 (br s, C*H*$_2$-1 [PTV]), 2.0−1.2 (m, aliph C*H* and C*H*$_2$ [PTV] and main chain C*H* and C*H*$_2$ [P(S-*stat*-CMS)]), 0.88 (m, aliph C*H*$_3$ [PTV]).

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