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Donor–Acceptor Diblock Copolymers Based on PPV and C₆₀: Synthesis, Thermal Properties, and Morphology

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ABSTRACT: An improved synthetic method to nitroxide end-capped poly(p-phenylenevinylene) is presented. The nitroxide-functionalized PPVs are extended with a second coillike block by employing them as macroinitiators in a nitroxide-mediated radical polymerization (NMRP) of monomers like styrene, 4-chloromethylstyrene, 4-vinylpyridine, and n-butyl acrylate. The observed thermotropic properties and morphology of films based on the rod–coil diblock copolymers are identified and described. Some of the block copolymers are subsequently subjected to a coupling with C₆₀ to incorporate electron-accepting properties into these PPV-based diblock copolymers. For this, a statistical copolymer built from styrene and azidomethylstyrene was used as the second coillike block, making it possible to adjust the built-in ratio of C₆₀. The morphology and thermotropic properties of films prepared with these diblock copolymers are investigated.

Introduction

The advantage offered by polymers over the traditional semiconductor materials is the low cost and versatility of processing methods, which allows the polymer film to attain virtually any desired shape. Casting a thin film over a macroscopically large area is feasible and particularly attractive when reducing the processing costs. For this to become reality the parent conjugated polymers, which are often intractable because of their stiff backbone, have to be derivatized without deterioration of their optoelectronic properties. Besides the molecular structure, details of the processing history could play a key role in determining the properties and morphology of such polymeric materials. Therefore, each step has to be carefully carried out and studied in detail when aiming at controlled properties of thin polymer films.

The majority of publications on conjugated polymers and their applications describe polymers based on poly[(1,4-phenylenevinylene) (PPV)] that were synthesized by a precursor route (Gilch,1 Weissing and Zimmerman,2 etc.), Heck coupling,3 Wittig4 (–Horner)5 condensation, McMurry coupling,6 etc.7 These methods yield high molecular weight polymers with a high content of the desired trans double bonds such as for example poly[2-methoxy-5-(2′-ethyl)hexyloxy]-1,4-phenylenevinylene] (MEH–PPV), poly[2-methoxy-5(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO–PPV), and poly[(2,5-dioctyloxy)-1,4-phenylenevinylene] (DOO–PPV) or its analogue DEH–PPV with 2,5-di(2′-ethyl)hexyloxy as side chains. Unfortunately, most PPVs exhibit a high polydispersity (PD), making them less applicable to control the morphology in the solid state. Moreover, the end-group functionality cannot be controlled exactly by one of these methods, and the nature of the end groups is difficult to determine due to their high molecular weight. We aim to control the end groups and modify them to obtain diblock copolymers with a well-defined structure. This can be accomplished in two different ways. One approach is the synthesis of well-defined conjugated oligomers,5–10 in which one has the advantage of controlling the end groups and the molecular weight exactly. Such a multistep route is rather time-consuming when aiming at higher molecular weights. Our approach is based on a second method: the one-step synthesis of conjugated polymers with relatively high, controllable molecular weight (around or above the effective conjugation length) and a relatively low PD.11 The PPV-based homopolymers reported in this paper do contain exactly one end group per chain, which can be modified to obtain a macroinitiator for nitroxide-mediated radical polymerization (NMRP).

Conjugated polymers can be regarded as (rigid) rod-like systems with restricted flexibility compared to conventional polymers like polystyrene (coillike). This may result in complex phase behavior for diblock copolymers containing at least one conjugated block. The presence of such a stiff block puts these diblock copolymers in the class of rod–coil diblock copolymers.12,13 The rodlike block may be the liquid-crystal-forming segment or so-called mesogen,14,15 which plays an important role during the microphase separation. Block copolymers that contain such liquid-crystalline segments have several thermal transitions, namely, a glass transition temperature for each distinct block, a phase transition temperature for the liquid-crystalline block, and the order–disorder transition temperature. They may give rise to an enhanced microphase separation14,17 and morphologies distinctly different from the conventional spheres, cylinders, or lamellar structures,18 which may include arrowhead, zigzag, and wavy lamellae phases.14,15 Stupp and co-workers showed that even low molecular weight rod–coil block copolymers can microphase separate in highly ordered phases as a consequence of a larger Flory–Huggins interaction parameter (χ).19–21 In
related studies by Yu and co-workers, the well-defined rod–coil block copolymers based on substituted PPVs and poly(isoprene) (PI), poly(methyl methacrylate) (PMMA), or poly(ethylene oxide) (PEO) formed liquid-crystalline phases which comprise the substituted PPV. As in the work of Stupp and co-workers, low-molecular-weight hairy-rod blocks were used, and the microphase separation obtained suggests strong mutual interactions of the liquid-crystalline blocks. Additional results presented in our previous work have demonstrated that changes in the thermodynamics of the environment result in quite complex and yet unexplored behavior of the rod–coil diblock copolymers in solution. These forms of self-organization are likely to act as the “nuclei” for solidification and will bring about the morphology of the solid film obtained under certain processing conditions. Thermal treatment of, for example, a film of MEH–PPV was found to improve the device efficiency of diodes, which was attributed to a higher degree of interchain interaction. An enhanced ordering of the microstructure is generally obtained through annealing, both in homopolymers and in conventional block copolymers. Likewise, thermal treatment of films of rod–coil block copolymers results in an enhanced ordering of the microphase-separated morphology.

On the basis of the reported thin film properties, it appears advantageous to be able to correlate the morphology with the optoelectronic properties. The device performance depends on the balance between intrachain and interchain electronic interactions. Hence, the morphology of the thin polymer film plays an important role in determining the optoelectronic properties of light-emitting diodes (LEDs) and photovoltaic (PV) cells. In PV cells, the combination of a poly(p-phenylenevinylene)-type polymer as the donor (D) material and C60 as acceptor (A) has proven promising. Materials that combine the physical properties of fullerene and the processability of polymers can be obtained by covalently connecting the C60 to the polymer. The PPV-based diblock copolymers reported in this paper have a controlled amount of C60 and are used in a systematic study to correlate the morphology and processing conditions to, ultimately, the device performance.

Results and Discussion

NMRP Copolymerization with PPV-Based Macrorinitiators. The DEH–PPV homopolymer was synthesized via the Siegrist polycondensation of 1 (Scheme 1), which is originally described by Kretzschmann et al. This condensation via a Schiff base results in a narrow molecular weight distribution and exactly one terminal aldehyde group per chain. To obtain the NMRP macroinitiator, the aldehyde end group of the low-molecular-weight polymer (Mn = 7.9 × 10^3 g/mol for DEH–PPVk = 21) is converted to an alkoxyamine based on TIPNO (Table 1).

Both syntheses published in the literature for the comparable DOO–PPV macrorinitiator, either via a Grignard reagent or via an organolithium compound, could not be repeated successfully. The in situ formed lithiated anion (generated from 2) is therefore converted into the more stable Grignard reagent by reaction with MgBr2 (transmetalation). A large excess of 3 guarantees a complete conversion of the aldehyde group (Scheme 2). This improved procedure for the synthesis of the NMRP macroinitiator, which is a combination of the previously reported methods, was found to be very reproducible. The formation of the DEH–PPV–TIPNO macroinitiator is easily visualized by the disappearance of the aldehyde signal at 10.4 ppm in the 1H NMR spectrum and the emergence of a signal at 5.9 ppm from the –CH(OH)– group.

The macroinitiator DEH–PPV–TIPNO is chain extended with a statistical copolymer of styrene (S) and 4-chloromethylstyrene (CMS, Scheme 2). To estimate the chain growth in time of the diblock copolymer, samples were taken during the NMRP copolymerization with DEH–PPVk = 15–TIPNO (Table 1). The monomer conversions were kept below 25% to ensure a low viscosity of the reaction mixture. The monomer composition as well as the chain length of the P(S-stat-CMS) was determined using 1H NMR spectroscopy, assuming that the DEH–PPV block remains unchanged. The nature of the copolymerization is elucidated in a plot of the molecular weight of the growing P(S-stat-CMS) block (Mk) vs time (Figure 1). Using the DEH–PPVk = 15–TIPNO macrorinitiator, a linear growth in time and low polydispersities (Table 1) are observed, confirming the “living” character of the NMRP copolymerization. The values of the comonomer composition obtained in Table 1 clearly illustrate that the determined built-in ratio of the respective monomers is lower than the feed ratio. This is most likely due to the slightly higher reactivity ratio of the CMS comonomer, resulting in a preference to add CMS instead of S. To determine whether the same “living” behavior is observed for a macrorinitiator bearing a longer DEH–PPV block, two additional copolymerizations in separated batches were performed with DEH–PPVk = 21–TIPNO (Table 1, Figure 1). Working with the same relative amount of initiator, AcoO, free TIPNO, and the same total amount of monomer (but with a different feed ratio), we obtained the system twice by adding an equal amount of solvent (relative to the total amount of monomer in the system). In doing so, the concentrations of all components were twice as low compared to the bulk copolymerization with DEH–PPVk = 15–TIPNO. Although we did not investigate the growth in time of these copolymerizations, the NMRP systems with DEH–PPVk = 21–TIPNO are regarded as being “living” because the combined results are in line with the bulk polymerization of DEH–
Diblock Copolymers Based on PPV and C60

In addition to 	extsuperscript{1}H NMR as characterization method, UV–vis spectroscopy can be used to estimate the relative amount of P(S-stat-CMS) in diblock copolymers. Upon chain extension of the DEH–PPV block, its weight-normalized absorbance decreases with increasing P(S-stat-CMS) block length. This relative decrease in absorption is related to the weight percentage (wt %) of P(S-stat-CMS) incorporated in the diblock copoly-mer (Table 2). The results obtained with UV–vis spectroscopy are consistent with those values obtained via 	extsuperscript{1}H NMR spectroscopy. Note that the copolymer composition can only be determined by 	extsuperscript{1}H NMR. Alternatively, the P(S-stat-CMS) block lengths may be determined by means of GPC. However, this technique is only used to determine the PD (Table 1) since it is not appropriate for an absolute molecular weight determination when rigid-rod-like polymers are involved.

**Functionalization of (Di)block Copolymers with C60**

It is our objective to incorporate both the donor (D) and acceptor (A) functionalities into one macromolecule by functionalizing our PPV-based diblock copolymers with C60. During this third step toward D–A diblock copolymers the C60 is attached to the well-defined statistical P(S-stat-CMS) block via the chloromethyl groups (Scheme 2).

Previously, the multifunctional P(S-stat-CMS) block had been functionalized with C60 by employing atom transfer radical addition (ATRA). This approach has proven to be successful. For example, DOO–PPV–7-b-P(S-stat-C60MS)Dk[1:1:1] containing an average of 15 C60 molecules per chain was obtained via this method. Unfortunately, material that is not sufficiently soluble was obtained after employing ATRA. Several research groups use ATRA to graft more than one monofunctional polystyrene chain onto C60 yielding dendritic or starlike macromolecules. A chlorine–C60 bond is left behind after the addition of a polystyrene chain onto C60. This chlorine bond is less stable than the one of the CMS in our P(S-stat-CMS) copolymers, resulting in a high concentration of “polystyrene–C60 radicals” during the course of ATRA. Their recombination with other polystyrene-like radicals is very likely. Since we use multifunctional polystyrenic chains, the occurrence of intrameric and intermolecular cross-linking (multiadditions onto C60) is very likely. The probability of intramolecular cross-linking has been lowered through systematic “dilution” of the reactive CMS groups with styrene moieties (i.e., higher S:CMS built-in ratio). However, the intermolecular cross-linking is hard to overcome by optimization of all reaction parameters when working with radicals as intermediates. Hawker et al. modified the P(S-stat-CMS) copolymers with an azide group to perform a cycloaddition to C60 and obtained soluble polymers. The azidomethyl-substituted polystyrene (the so-called “azide intermediate”, in our case DEH–PPV–b-P(S-stat-N3MS)) reacts in this method with an equimolar amount of C60 to yield triazoline 4 (Scheme 3). The thermal extrusion of nitrogen from this triazoline leads to the formation of aza-bridged fullerences 5 and 6 (and maybe their bisadducts) referred to as bridged iminofullerences. These fullerences can have a bridge between five- and six-membered rings and between two six-membered rings (called [5,6]-bridged and [6,6]-bridged, respectively). In addition, the isomers may either have closed or open transannular bonds. Of the possible Kekulé structures of C60 the ones that have the energetically most favorable arrangement contain exclusively [6,6] double bonds and [5,6] single bonds. So far, and consistent with this “rule”, the closed [6,6]-bridged monoadduct (analogous to 5) and open [5,6]-bridged monoadduct (analogous to 6) have been observed by Prato et al. The number of π-electrons remains unchanged in the case of the open [5,6]-bridge monoadducts. Recently reported (cyclic voltammetric) data of some polymeric fullerene derivatives confirmed

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**Scheme 2. Synthetic Route to Donor–Acceptor Diblock Copolymers via NMRP with the DEH–PPV (Donor) Macroinitiator and Subsequent C60 Functionalization (Acceptor) of the Second Copolymer Block**

- (i) Ether, 35 °C, 16 h; (ii) styrene, 2-chloromethylstyrene, AcO, cat. TIPNO, anisole, 125 °C, 50 min; (iii) NaNNa, DMF, 130 °C, 16 h; (iv) C60, chlorobenzene, 60 °C, 20 h; (v) 130 °C, 1 h.

PPV<sub>k</sub>–TIPNO (Table 1). While the monomer concentration has been lowered compared to this bulk copolymerization, no significant reduction of the propagation rate is observed during these copolymerizations. As expected, the monomer built-in ratio of the copolymers prepared with DEH–PPV<sub>k</sub>–TIPNO macroinitiator is lower than the feed ratio. Fortunately, it is still possible to adjust and control the monomer composition in the resulting copolymers.
that the electronic properties indeed resemble those of pristine C_60. Therefore, we expect that the C_60 moieties will still serve as electron acceptor when incorporated into the DEH−PPV-b-P(S-stat-CMS) diblock copolymers.

The conversion of P(S-stat-CMS) copolymers (used as a reference compound) to the corresponding azide intermediate is a versatile method with yields varying from 70 to 85%. The chlorine group is completely converted to an azide when a large excess of NaN_3 is used. Both the preparation of DEH−PPV-b-P(S-stat-CMS) and of the reference compound P(S-stat-N_3MS) is easily monitored by ^1H NMR and IR spectroscopy. The methylene proton peak of the P(S-stat-CMS) copolymers shifts from 4.46 to 4.17 ppm, which is in agreement with the ^1H NMR data reported by Ederle and Mathis. The covalent bond connecting the TIPNO group to DEH−C_60 is confirmed by the absence of its characteristic ^1H NMR shift at 0.45 ppm. Moreover, a small aldehyde signal at 10.41 ppm indicates a possible formylation of this radical chain end. The second method used to detect the azide intermediate is IR spectroscopy. The intermediate possesses a strong characteristic band for the azide group at 2094 cm⁻¹. The complete disappearance of this band after cycloaddition to C_60 confirms the completion of the reaction. The formation of the azide and its subsequent functionalization with C_60 are both monitored with IR spectroscopy. Convenient methods to determine the covalent bonding of C_60 and the amount of C_60, like ^1H NMR spectroscopy, could only be used to observe the structural changes after functionalization with C_60. The P(S-stat-C_60MS) reference compounds as well as the DEH−PPV-b-P(S-stat-C_60MS) diblock copolymers are, after complete drying, not sufficiently soluble in common organic solvents like chloroform and chlorobenzene. Nonetheless, a ^1H NMR spectrum of DEH−PPV−PPV−C_60−P(S-stat-C_60MS) that contained a minimum amount of dissolved product clearly demonstrated that the signal of the azide intermediate at 4.17 ppm disappeared after reaction with C_60. In addition, a characteristic C_60 absorption peak around 330 nm is clearly present in UV−vis spectra of the filtered solutions (see Supporting Information). Both observations seem to be an indication of the covalent attachment of C_60 to the polymer.

Other techniques to determine the amount of C_60 in polymers are DSC and TGA.25 The latter one is a convenient method when dealing with poorly soluble materials like our DEH−PPV−PPV−C_60−P(S-stat-C_60MS). Figure 2 shows the TGA thermograms of the starting polymers, C_60-functionalized polymers, and pristine C_60. The molecular weights given for the P(S-stat-CMS) block functionalized with C_60 are their theoretical values (i.e., assuming 100% conversion of azide to C_60). Diblock copolymers with the same copolymer composition ([m:n]) are prepared from the same starting materials. In the DEH−PPV−PPV−C_60−P(S-stat-C_60MS) and P(S-stat-C_60MS) samples, the polymer backbone starts to decompose at 300 °C, leaving a C_60 adduct which shows only minor weight loss up to 600 °C. This decomposition of the backbone is nearly complete at 550 °C (see the corresponding reference compounds), and we can assume that the residue difference at 575 °C corresponds to the C_60 content. This residue was thought not to be unrecovered C_60 given that these polymers are dissolved and filtered twice in THF (solubility of C_60 in THF is <0.01 mg/mL at RT).39 The P(S-stat-CMS) can contain a (theoretical) maximum amount of 68 wt % of C_60 after a complete conversion, which would result in P(S-stat-C_60MS). A value of 55 wt % C_60 is found with the TGA analysis indicating that 80% of the theoretical amount is incorporated, giving P(S-stat-C_60MS). Higher amounts of C_60 are found upon increasing the reaction time. Almost 90% of the theoretical value is incorporated when going from 16 to 20 h and using only 1 equiv of C_60. However, the yields of the reactions are rather low (about 25%). Yields of about 40% are obtained with DEH−PPV−PPV−C_60−P(S-stat-C_60MS) diblock copolymers when 2 equiv of C_60 was used.

The synthesized DEH−PPV−PPV−C_60−P(S-stat-C_60MS) diblock copolymers contain 41 and 57 wt % of C_60 (Figure 2). The latter one with a higher fraction of chloromethyl groups in the starting material indeed gives rise to a higher amount of C_60. This agrees well with the initial aim that these groups will determine the C_60 content in diblock copolymers. A similar trend has already been observed in using ATRA as C_60 functionalization method.25 Although the above-presented results are promising, a new problem arises. It seems that after drying the product renders insoluble. Only samples that have not been completely dried could be redissolved.

### Table 1. Diblock Copolymers Obtained with NMRP Copolymerization of S and CMS Using DEH−PPV Macroinitiators

<table>
<thead>
<tr>
<th>Method</th>
<th>DEH−PPV_{k=15}−TIPNO</th>
<th>DEH−PPV_{k=21}−TIPNO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>single batch</td>
<td>batch 1</td>
</tr>
<tr>
<td>time (min)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>feeda</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>built-inb</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Mn (kg/mol)c</td>
<td>4.0</td>
<td>3.2</td>
</tr>
<tr>
<td>PD</td>
<td>1.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Mn (kg/mol)d</td>
<td>6.1</td>
<td>22.5</td>
</tr>
<tr>
<td>PD</td>
<td>1.2</td>
<td>22.5</td>
</tr>
<tr>
<td>PPV−PPV−C_60−P(S-stat-C_60MS)_{54K}</td>
<td>63K</td>
<td>63K</td>
</tr>
<tr>
<td>PD</td>
<td>1.2</td>
<td>8.2</td>
</tr>
<tr>
<td>PD</td>
<td>1.5</td>
<td>38.8</td>
</tr>
<tr>
<td>PD</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>PD</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

a Comonomer S:CMS ratio. b Including the TIPNO end group.

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Figure 1. Polymer chain growth in time during NMRP copolymerization of S and CMS with DEH−PPV_{k=15}−TIPNO macroinitiators.

![Graph showing polymer chain growth](image-url)
Other groups have observed the same problem, and so far its cause is not clarified. The complete removal of solvents should therefore be avoided during the preparation of these C60-functionalized diblock copolymers.

A significant rise in the \( T_g \) of a polystyrenic backbone is expected when the chain stiffness increases due to C60 side groups. Therefore, DSC provides qualitative evidence for the incorporation of C60 in the polymers. However, no transition temperatures were found in DSC scans of DEH-PPV-b-P(S-stat-C60MS) diblock copolymers prepared via the azide intermediate. Instead, an enormous exothermic heat flow during the first heating scan is observed (data not given). After this once-only event starting at 80 °C and ending around 220 °C, the samples exhibit no thermal transitions at all in the first cooling scan and the subsequent second heating scan. Further examination with TGA confirms a physical change of the materials: the premature weight loss observed with TGA starting at 120 °C disappears after the sample has been used for a DSC analysis (Figure 3). We hypothesize that the formation of aza-bridged fullerenes is incomplete (the nitrogen extrusion from triazoline, Scheme 3), resulting in exothermic reactions and weight losses. Unfortunately, this hypothesis could not be confirmed with Gibbs energy calculations based on nitrogen extrusion and the total amount of heat released in the first DSC scan. However, the weight loss monitored with TGA seems to match well with a loss of nitrogen during the DSC analysis. The weight percentage of C60 in the presented polymer (Figure 3) is 95% of the theoretical amount. Upon thermal extrusion of nitrogen from this polymer the maximum weight loss would be 2.2% while a premature weight loss of 2.1% is found with TGA (difference in residue at 300 °C before and after the DSC scan). These values indicate that the polymer and their intermediate triazolines are not fully converted to aza-bridged fullerenes during the

### Table 2. Determination of the P(S-stat-CMS) Amount in Diblock Copolymers

<table>
<thead>
<tr>
<th></th>
<th>NMRP time (min)</th>
<th>( \text{total } M_n ) (^a)</th>
<th>( \text{calcd } M_n ) (^a)</th>
<th>( \text{calcd wt % } \text{P(S-stat-CMS)} )</th>
<th>( \text{UV–vis spectroscopy} ) absorbance (Abs/mg g(^{-1})) (^c)</th>
<th>( \text{calcd wt % } \text{P(S-stat-CMS)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEH-PPV(_{k=21})</td>
<td>0</td>
<td>8.2(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEH-PPV(_{k=21})-b-P(S-stat-CMS)</td>
<td>50</td>
<td>22.4</td>
<td>14.1</td>
<td>63</td>
<td>19.7</td>
<td>64</td>
</tr>
<tr>
<td>DEH-PPV(_{k=21})-b-P(S-stat-CMS)</td>
<td>80</td>
<td>38.8</td>
<td>30.6</td>
<td>79</td>
<td>12.4</td>
<td>77</td>
</tr>
</tbody>
</table>

\(^a\) In kg/mol. \(^b\) Including the TIPNO end group. \(^c\) At \( \lambda_{\text{max}} \) = 496 nm.

### Scheme 3. Cycloaddition of Azide Intermediate DEH-PPV-b-P(S-stat-N3MS) to C60 with Subsequent the Nitrogen Extrusion from the Triazoline Intermediate

![Scheme 3](image)

**Figure 2.** TGA traces of (di)block copolymers recorded under \( N_2 \) and a heating rate of 10 °C/min. The amount of residue left at 575 °C represents the wt % C60 incorporated. Pristine C60 is used as reference compound.

Other groups have observed the same problem, and so far its cause is not clarified. The complete removal of solvents should therefore be avoided during the preparation of these C60-functionalized diblock copolymers. A significant rise in the \( T_g \) of a polystyrenic backbone is expected when the chain stiffness increases due to C60 side groups. Therefore, DSC provides qualitative evidence for the incorporation of C60 in the polymers.
synthesis. On the basis of our observations and the above-mentioned solubility problems (also observed by others), one could conclude that the azide intermediate route is not yet a versatile method to functionalize polymers with C_60.

**Solid-State Properties of Diblock Copolymers Films.** Control over the structure and morphology in the solid state of D–A diblock copolymers is important for the optoelectronic properties of photovoltaic devices based on these materials. Bässler proposed that charge transport in disordered organic materials proceeds mainly by means of hopping across the medium at three levels: intrachain, interchain, and interparticle (across grain boundaries). Factors determining intra- and interchain transport are the conjugation length and structural order, respectively. Side chains attached to the polymer backbone have a contradictory effect on the transport properties at microscopic level. They may introduce torsions along the chain, decreasing thereby the conjugation length or, as insulating side chains will, increase the hopping distance between neighboring chains. On the other hand, the hopping rate increases when the side chains enhance the ordering of polymer segments in the solid state. For example, highly regioregular polymers have an enhanced on-chain energetic order and charge delocalization. Moreover, long side chains may have their own crystallization and melt behavior and can induce liquid crystallinity (LC) in rigid-rod-like macromolecules such as PPV. PPV derivatives and rod–coil diblock copolymers have been shown to possess a rich phase behavior. Oligophenylenevinlenes with alkoxy side chains, so-called “hairy-rod” molecules, are extensively studied because of their reversible LC transitions. This crystallization can lead to dramatic changes in the optical and electronic properties of a material. The alignment of the backbones (with a π-stacking arrangement and side chains acting as spacers) may for example promote the interchain and intersegment electronic interactions. This increased amount of electronic overlap between segments and reduced structural heterogeneity is expected to enhance the charge transport.

LC behavior appears in a restricted temperature range between the crystalline phase and the isotropic melt. Having this, so-called, thermotropic LC behavior in the active layer of a PV device will introduce a temperature-dependent operation mode making the study of thermotropic transitions in thin films important. Moreover, the thermal stability of the conjugated polymer itself is important. In this section we report the thermal transitions of the homopolymers DEH–PPV_15,21_ and DOO–PPV_7 in the solid state and compare them with those of the diblock copolymers. The homopolymers are the same as used for the synthesis of the corresponding diblock copolymers. The thermal properties are studied by DSC, TGA, and optical microscopy. DSC was used to determine the thermotropic transition temperatures like T_g, side-chain melting temperature (T_s), and the liquid-crystal-to-isotropic transition temperature (T_{LC-I}). The LC structure of polymer films was elucidated by optical microscopy using crossed polarizers.

**DOO–PPV-Based Diblock (Co)polymers.** The synthesis of DOO–PPV and its block copolymers is described in refs 25 and 31 and in the Experimental Section. The DSC analysis of DOO–PPV reveals the existence of thermotropic transitions at 55 and 185 °C, of which the lower transition temperature is attributed to melting of the octyloxy side chains (T_s) and the higher one to the isotropic transition temperature (T_{LC-I}). A 1 wt% solution of DOO–PPV in 1,2-dichlorobenzene (or chloroform) was cast onto a glass slide, and the film was investigated with optical microscopy. Figure 4a shows the rough texture of the as-cast film. It reveals reddish elongated domains that are randomly distributed in the film (displayed as gray areas in Figure 4a). Crossed polarizers were used to determine whether the film exhibits highly ordered crystalline domains. The absence of any birefringence in the as-cast film shows that it does not reveal any highly ordered crystalline domains.

A reddish grainy texture (or polydomain texture) is observed upon cooling from the isotropic melt at 90 °C (gray areas in Figure 4b). Such a birefringence
texture is often observed near the isotropic–nematic transition for polydisperse and high-molecular-weight specimens in thick films. The fine grains are believed to correspond to regions of uniform orientation interconnected by disclinations within nematic structures.48 Hence, all diblock copolymers described below based on this symmetrically substituted DOO–PPV moiety have a rodlike diblock that exhibits liquid crystallinity. This does not imply a priori that all diblock copolymers based on this PPV block will also exhibit the same thermotropic behavior.

The thermotropic transitions of the DOO–PPV diblock (co)polymers obtained by a combination of DSC and optical microscopy as well as the decomposition temperature (Tdec) determined by TGA are given in Table 3. Although the Tg depends slightly on the molecular weight of the second coillike block, they represent typical Tg’s (within a margin of ±5 °C) for the (di)block polymers. Tg’s of the corresponding homopolymers (PS, 110 °C; PBA, −60 °C; P4VP, 145 °C)49 differ up to 15 °C. The variation is attributed to the local order and the low molecular weight of the diblock polymers. The statistical copolymer P(S-stat-CMS)21K[2:1] exhibits a lower Tg compared to its corresponding diblock copolymer. Upon functionalization of DOO–PPV-b-P(S-stat-CMS) with C60 the polymer chain becomes stiffer, and consequently, its Tg increases from 95 to 110 °C. The Tg is only observed in the first heating scan of the DSC analysis, implying that the crystallization of the octyloxy side chains is a slow process and depends on the (thermal) history of the sample. The melting temperature of the side chains also depends on the Tg of the second block. With increasing Tg of this coillike block the Tg shifts toward higher temperatures due to a relative higher stiffness of their local environment. Illustrative of this phenomenon is DOO–PPV-b-PBA with a Tg of −45 °C. Its very low Tg results in soft and flexible microdomains that allows the octyloxy side chains to melt at lower temperatures. Vice versa, a PBA homopolymer has a Tg of −60 °C, and the increased Tg of −45 °C for the diblock polymer suggests the presence of PPV blocks between the PBA domains. All other diblock (co)polymers exhibit Tg’s above the side-chain melting temperature, resulting in higher values of Tg compared to that of DOO–PPV homopolymer. This is attributed to the glassy environment induced by the coillike block below its Tg. For the polydisperse DOO–PPV one does not observe a clear isotropic transition temperature (TLC-I) of the backbone with DSC, but merely a continuous increase of the endothermic heat flow above a certain temperature. Hence, the onset of the increased heat flow is taken as the TLC-I of the DOO–PPV backbone. The DOO–PPV-b-P4VP showed a continuous increase of the heat flow directly above its glass transition. The broad Tg of the P4VP block around 150 °C is close to the melting temperature of the PPV backbone and masks the onset of the TLC-I. This latter transition was therefore determined with optical microscopy, resulting in a slightly higher TLC-I compared to a DSC analysis. In general, the series of DOO–PPV-based diblock copolymers reveal distinct transition temperatures for both blocks, suggesting that microphases are involved. For a homogeneous mixture only one transition from the glassy state to the liquid state would have been observed.

Table 3. Transition Temperatures of DOO–PPV and DEH–PPV-Based Diblock (Co)polymers and Their Corresponding Homopolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Tg (°C)</th>
<th>Ts (°C)</th>
<th>TLC-I (°C)</th>
<th>Tdec (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOO–PPV</td>
<td>55</td>
<td>185</td>
<td>380</td>
<td>n.d.</td>
</tr>
<tr>
<td>DOO–PPV-b-PS</td>
<td>95</td>
<td>60</td>
<td>370</td>
<td>n.d.</td>
</tr>
<tr>
<td>DOO–PPV-b-P4VP</td>
<td>150</td>
<td>90</td>
<td>330</td>
<td>n.d.</td>
</tr>
<tr>
<td>DOO–PPV-b-PBA</td>
<td>−45</td>
<td>50</td>
<td>340</td>
<td>n.d.</td>
</tr>
<tr>
<td>P(S-stat-CMS)21K[2:1]</td>
<td>90</td>
<td>0</td>
<td>320</td>
<td>n.d.</td>
</tr>
<tr>
<td>DEH–PPV</td>
<td>100</td>
<td>200</td>
<td>360</td>
<td>n.d.</td>
</tr>
<tr>
<td>DEH–PPV-b-P(S-stat-N2MS)k[3:1]</td>
<td>100</td>
<td>85</td>
<td>325</td>
<td>n.d.</td>
</tr>
<tr>
<td>DEH–PPV</td>
<td>110</td>
<td>285</td>
<td>390</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

* In combination with optical microscopy. b Given for 5 wt % loss during TGA. c Determined by optical microscopy. d n.d. = not determined.

Figure 5. Optical micrographs at RT using crossed polarizers of (a) DOO–PPV-b-P4VP12.1K as-cast and (b) after cooling from the melt and annealing for 1 h at 150 °C.
an optical micrograph of DOO–PPV-b-P4VP displays the typical crystalline texture at RT that was obtained by cooling from the melt down to 150 °C and subsequent annealing at 150 °C for 1 h prior to the cooling to RT. Generally, this cooling from the melt gave rise to larger crystalline domains compared to the as-cast films (Figure 5, b vs a, respectively). The drop-casting of more diluted diblock copolymer solutions (0.1 wt %) followed by rapid evaporation of the solvent did not give rise to birefringence or crystalline domains. This is attributed to a fast solidification process rendering a long-range order in the polymer films. The microphases can be ordered locally on a length scale of several tens of nanometers (see AFM images in ref 24). On a large scale, however, the films appear to be isotropic due to the overall random orientation of small domains. Because the resolution of optical microscopy is limited to the wavelength of light, one cannot reveal the local order in these films using this technique and has to utilize other techniques like AFM or TEM.  31

**Figure 6.** Optical micrographs at RT using crossed polarizers of (a) DEH–PPVk=15, (b) DEH–PPVk=21, and (c) DEH–PPVk=21–b-P(S-stat-CMS)24k(2:1:1).

**DeH–PPV-Based Diblock Copolymers.** The DEH–PPV homopolymers show a similar behavior as the DOO–PPV with the PPV backbone as the mesogenic group. The DEH–PPVk=15 shows two transitions at low temperatures (55 and 75 °C, Table 3), which are both attributed to melting of the side chains. For DEH–PPVk=21 only a single transition is found, which covers the same temperature range. Since we observed several crystalline-like textures in films of this polymer (optical microscopy is described below), it is reasonable to assume that this single and broad transition comprises to the two transition temperatures found for the DEH–PPVk=15 homopolymer. Clear isorotopic transition temperatures of the DEH–PPV (TLC–1) are not found with DSC. The observed continuous increase of heat flow may be due to crystallites that differ in size and perfection. To circumvent these difficulties, we used optical microscopy to determine the TLC–1 as the onset of the fast disappearance of birefringence.

The amorphous P(S-stat-CMS) block in the DEH–PPV diblock copolymers gives rise to a clear Tg transition. In line with the theory this Tg increases (from 85 to 90 or 100 °C) for increasing P(S-stat-CMS) block lengths (14, 21, and 66 kg/mol, respectively). However, the Tg is now more difficult to elucidate because it coincides with the Tg of the P(S-stat-CMS) block. For both chain extended DEH–PPVk=15,21 polymers the Tg increases with 10 °C. The mobility of segments at specific temperatures seems to be lower due to the glassy environment introduced by the P(S-stat-CMS). Furthermore, the Tg for the DEH–PPV-b-P(S-stat-CMS) diblock copolymer is only found during the first heating scan. After crystallization upon cooling, the corresponding endothermic peak in the following heating scan is absent probably due to a smaller volume fraction of crystalline material.

Optical microscopy reveals the presence of birefringent textures in thick films of DEH–PPV and DEH–PPV-b-P(S-stat-CMS). The films were obtained after drop-casting a 1 wt % solution in chlorobenzene onto glass slides and a subsequent slow evaporation of the solvent. The as-cast films appeared to be highly birefringent when examined under crossed polarizers. They exhibit reddish needlelike domains that are isotropically distributed in the film (Figure 6). The amorphous domains (black) as well as the crystalline domains increase in size with increasing DEH–PPV block lengths (Figure 6, a and b, respectively). A significant increase in size of both domains is observed in films of DEH–PPV-b-P(S-stat-CMS) (Figure 6, b vs c). Apparently, this second coillike block enhances the mobility of the DEH–PPV, resulting in a facilitated crystallization from solution and larger domains. Heating of the films resulted in melting of the crystalline domains, but no reversible birefringence was observed after the subsequent cooling from the melt. This indicates that the crystallization of the bulk polymer is a slow process. No efforts have been made to (re)crystallize the polymer by means of annealing at temperatures just above the Tg or Tc, as has been done for DOO–PPV-b-P4VP (Figure 5b). In addition to the randomly distributed needlelike domains, we find spherical aggregates often called spherulites.

The thermotropic transitions of the C60-functionalized DEH–PPV diblock copolymers are not included in this study since they show exothermic reactions upon heating (i.e., extrusion of nitrogen, see discussion of Figure 3). The C60 incorporated in DOO–PPV-b-P(S-stat-CMS) did increase the chain stiffness and changed its thermotropic LC behavior. Similar results are expected for the DEH–PPV polymers, suggesting a temperature-dependent operation mode for optoelectronic devices based on these donor–acceptor diblock copolymers.

**Conclusions**

An improved synthesis of the NMRP macroinitiator based on PPV and TIPNO is presented, which is used for the preparation of donor–acceptor diblock copolymers. A “living” character of the NMRP polymerizations is observed for these PPV-based macrominitiators. The block lengths as well as the built-in ratio of the comonomers in the second P(S-stat-CMS) block can be con-
controlled during the course of the polymerization. The macroinitiator allows for the adjustment of the donor–acceptor ratio in the C_{60}-functionalized diblock copolymers. In addition, the method to introduce the C_{60} has been improved by circumventing the formation of radicals through the utilization of azide intermediates. Further improvement of this new approach is necessary to enhance the solubility of the donor–acceptor diblock copolymers. This could be achieved by means of a complete conversion of the azide intermediates.

The structure–property relationship of the (diblock) copolymers is investigated using the DOO–PPV and DEH–PPV homopolymers as reference compounds. They are both liquid-crystalline and exhibit thermotropic behavior due to the combination of a mesogenic rod-like block and the adjacent coil-like block. An additional thermotropic transition was identified for the diblock copolymers that is attributed to the T_g of the polystyrene-like block.

We have shown that this approach of rational design and controlled synthesis is a systematic method to explore the correlation between (self-)organization of rod–coil diblock copolymers and the morphology of films thus produced (and ultimately the correlation between self-organization and the device performance).

Experimental Section

Measurements. ^1H NMR spectra were recorded on a Varian Gemini-300 spectrometer operating at 300 MHz in the Fourier transform mode. All measurements were performed at room temperature (RT) in chloroform-d (CDCl_3) internal lock on the ^1H signal. Absorbance spectra were recorded on a Perkin-Elmer Instruments Lambda 900 UV/Vis/NIR spectrometer and normalized of clarity. Fluorescence spectra were recorded on a Perkin-Elmer luminescence spectrometer LS50-B using an excitation wavelength of 10 nm below the absorption maximum and a 2.5 nm bandwidth. The optical measurements were performed in Uvasol chloroform with quartz cuvettes (light path 10 mm) unless mentioned otherwise. Gel permeation chromatography (GPC) analyses were performed in THF (HPLC grade) with PL-gel mixed-C columns in a Waters PowerTec system (717+ autosampler, 600 controller, and a 610 fluid unit), equipped with a Waters 996 photodiode array detector (on-line UV–vis measurements), a Wyatt Dawn DSP laser photometer (light scattering detector), and a 410 differential refractometer. All solutions (~1 mg/mL) were filtered over a polystyrene filter (0.45 μm) to a cloudy, white suspension, containing compound 1. A cloudy, white suspension, containing compound 2 was obtained. This was allowed to warm to RT. After 30 min, a cloudy, white suspension, containing compound 3 was obtained. The mixture was stirred at RT for 30 min. From the resulting two-phase mixture, a quarter of lower phase was extracted with ether (200 mL), the organic layer was dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure at RT. After this period, the mixture was degassed by freeze–pump–thaw cycles (3×), flushed with N_2, and polymerized at 110 °C. Samples were taken after 4 and 8 h and precipitated in hexane (1 L). The polymer was precipitated from CHCl_3 into hexane (1 L). Yields: 189 mg (4 g), 217 mg (8 g), and 357 mg (10 g), respectively, determined by ^1H NMR. ^1H NMR: δ = 8.0–8.6 (br d, C_H^1), 7.4 (br s, C_H^2), 7.11 (br s, C_H^3), 6.2–6.6 (br d, C_H^4), 4.0 (br s, OCH_3), 2.2 (br s, C_H^5), 1.3–1.8 (m, CH, C_H^6), 0.8 (s, C_H^7).

DEH–PPV. The synthesis of DEH–PPV was accomplished by the Siegrist polycondensation (originally described in ref 30 of compound 1). The average degree of polymerization (i.e., number of repeat units k) of the DEH–PPV is determined with ^1H NMR spectroscopy using the ratio of integrals of the OCH_3 groups and the terminal CH_3 group. For a DEH–PPV polymer prepared at 80 °C in 3 h, a k of 21 units is calculated by this method. This so-called DEH–PPV has a polydispersity (PD) of 1.23 (determined by means of GPC vs polystyrene standards) and a M_n = 7.9 × 10^3 g/mol. By only changing the temperature to 50 °C, the DEH–PPV in ref 21 was synthesized in 3 h with PD = 1.16 and M_n = 5.6 × 10^3 g/mol. Representative ^1H NMR of DEH–PPV in ref 21: δ = 10.41 (s, C_H(end group)), 7.49 (br s, C_H^1), 6.67–7.16 (br s, C_H^2), 3.91 (br m, C_H^3), 2.20–2.34 (br s, C_H(end group)), 1.71–1.85 (m, C_H^4), 1.14–1.68 (m, C_H^5, C_H^6), 0.8–1.0 (m, C_H^7).

DEH–PPV–TIPNO. The Br_Mg–O(CH_3)_2Br was prepared prior to the synthesis from a stirred mixture under a dry N_2 atmosphere of Mg turnings (0.17 g, 7.0 mmol) and ether (5 mL). Via a syringe, 1,2-dibromoethane (0.55 mL, 6.38 mmol), a cloudy, white suspension, containing compound 1 was slowly added, and the mixture was stirred at RT for 30 min. From the resulting two-phase mixture, a quarter of lower gray layer was used in the synthesis of DEH–PPV–TIPNO. For this, 2,2,5-trimethyl-3-(1-(4-bromophenyl)ethoxy)-4-phenyl-3-azahexane in ref 32 (2) (0.62 g, 1.5 mmol) was dissolved in ether (10 mL) and cooled to −80 °C (cryostat). After the addition of tert-butyl lithium (1.5 M in pentane, 2 mL, 3 mmol), the solution was stirred at −80 °C. After this period, the color turned to yellow when the stirred solution was immersed in a thermostat oil bath kept at 35 °C. A solution of DEH–PPV in ref 21 (1.4 g, 0.18 mmol) in ether (40 mL) was added via a syringe and stirred for 16 h at 35 °C. The mixture was quenched in water (150 mL) that contained HCl (37%, 3 mL) and stirred for 30 min at RT. After this period, the mixture was extracted with ether (200 mL), the organic layer was washed with water (2 × 300 mL) and with saturated NaHCO_3 (1 × 200 mL), dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure at RT. The red solid was dissolved in CHCl_3 (10 mL) precipitated twice in cold
methanol (400 mL, ca. –30 °C), washed with ethanol until a colorless filtrate was obtained (to remove excess of 3), and dried under reduced pressure (RT, 16 h). Yield: 1.08 g (76%) of red powder. Using the same conditions, the reaction has also been performed with DEH–PPVk=15, resulting in 0.39 g (68%) of DEH–PPVk=15–TIPNO. 1H NMR: δ = 7.49 (br s, C–H), 6.67–7.16 (br s, C–H), 5.90 (br m, CHOH), 4.85 (br m, OCH2C6H), 3.91 (br m, OCH2), 3.73 (d, NCH2C6H), 2.99 (st, CH2O), 2.38–2.50 (s, CH3, CH2). 1H NMR (50 mL). After stirring for 15 min, the mixture was extracted with CHCl3 (34 mg/g chlorobenzene) of reddish-brown solution. The corresponding diblock copolymer and NaCl (2 equiv relative to the amount of N2MS comonomer) were dissolved in chlorobenzene and degassed by bubbling dry N2 through the solution for 15 min. The mixture was stirred at 60 °C for 20 h using a thermostated oil bath. Subsequently, it was refluxed for 1 h at 130 °C (no N2 atmosphere). After cooling to RT, saturated NaCl (10 mL) was added, and the mixture was vigorously stirred for 1 h as an attempt to remove unreacted azide groups. The organic layer was washed with water (4 × 500 mL) and dried over Na2SO4, and the solvent was almost completely removed. The residue was diluted with THF (500 mL), filtered, and washed until a colorless filtrate, and the THF was removed under reduced pressure. After repeating this latter step, the polymer was precipitated in methanol (200 mL), filtered, and taken in chlorobenzene (10 mL). This latter precipitation and filtration were repeated, and the product was either dried under reduced pressure (70 °C, 16 h) or stored in chlorobenzene (10 mL).

DEH–PPVk=15–b–P(S-stat-C60MS)31K[2.6:1] (1.0 g, 0.026 mmol), NaN3 (2.41 g, 37.1 mmol); yield: 0.87 g (85%). Representative 1H NMR of DEH–PPVk=15–b–P(S-stat-C60MS)31K[2.6:1]: δ = 10.41 (s, CHO/end group), 7.49 (br s, C=CH2), 6.66–7.01 (br s, C–H), 4.17 (br d, CH2N1), 3.91 (br m, OCH2), 2.20–2.34 (br s, CH2), 1.04–1.19 (m, CH, CH2O). 1H NMR (sample of 110 min): δ = 6.50–7.00 (br s, C=CH2), 4.33–4.47 (br d, CH2Cl), 1.36–1.73 (br s, CH3, CH2). 1H NMR (sample of 90 min): δ = 6.50–7.00 (br s, C=CH2), 4.33–4.47 (br d, CH2Cl), 1.36–1.73 (br s, CH3, CH2).
References and Notes

Supporting Information Available: Additional FT-IR and UV–vis spectra of DEH–PPV-b-P(S-stat-CMS), DEH–PPV-b-P(S-stat-NiCMS), DEH–PPV-b-P(S-stat-C06), and DEH–PPV–TIPNO (UV–vis only) visualize the functionalization with the azide group and incorporation of C06. This material is available free of charge via the Internet at http://pubs.acs.org.

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References and Notes


(50) This high-molecular-weight DEH-PPV (Mn ~ 90,000 g/mol) was prepared by the anionic polymerization of α,α′-dibromo-2,5-di(2′-ethylhexyloxy)xylene as described by: Neef, C. J.; Ferraris, J. P. Macromolecules 2000, 33, 2311–2314. The synthesis of the monomer was accomplished in two steps from hydroquinone. The hydroquinone reaction with 2′-ethylhexyl bromide (for details of this etherification see ref 51) was followed by a treatment with paraformaldehyde as described by Neef et al. To control the molecular weight, we used 1 mol % of the initiator (method B). The two additional precipitations were from toluene (0.5 wt %) into acetone/methanol (1:1).


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