Study on the Formation of a Supramolecular Conjugated Graft Copolymer in Solution

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ABSTRACT: The formation in solution of a supramolecular graft copolymer bearing conjugated blocks is demonstrated using diffusion ordered NMR spectroscopy (DOSY). A tailor-made poly(3-(2-ethylhexyl)thiophene) (P3EHT) with a phenol end group is synthesized. For this purpose, the chain-growth mechanism of the polymerization of 2-bromo-5-chloromagnesio-3-alkylthiophenes in the presence of a Ni(dppp) catalyst (dppp = 1,3-bis(triphenylphosphino)propane) is exploited, as it enables the use of functionalized initiators to introduce specific end groups. The so-obtained polythiophene was subsequently mixed in solution with poly(4-vinylpyridine) (P4VP) to enable phenol-pyridine hydrogen bonding. The formation of the supramolecular graft copolymer is studied using DOSY-measurements. Based on the results thereof, the amount of P3EHT attached to the P4VP is calculated and the association constant of the hydrogen bond is estimated. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 804–809

KEYWORDS: conjugated polymers; DOSY; graft copolymers; hydrogen bonding; supramolecular structures

INTRODUCTION Supramolecular interactions can be a useful tool for obtaining block-copolymeric structures, especially when more complex species such as, for example, comb-copolymers are targeted.[1,2] First of all, this approach significantly reduces synthetic difficulties which are encountered when preparing the covalent analogs. Moreover, the reversibility of such interactions affords a high degree of versatility to the system. Hence, the use of supramolecular interactions allows tuning the properties and composition of these materials. This is of prime interest in the field of conjugated polymers, as their macromolecular structure has a large influence on the resulting properties. Among the wide variety of supramolecular interactions, hydrogen bonds (H-bonds) offer the best set of characteristics for this purpose. This is mainly due to the strength and directionality of H-bonds, but also to their temperature- and pH-sensitivities. For these reasons, H-bonds have been widely used for reversibly connecting polymers and other species.[3–5] Ruokolainen et al. have successfully prepared a graft copolymer consisting of varying amounts of pentadecylphenol in combination with poly(4-vinylpyridine) (P4VP), resulting in mesomorphic structures.[6] An all-conjugated covalent graft copolymer with varying numbers of P3HT side chains has also successfully been prepared by Wang et al.[7] However, no supramolecular graft copolymers have, to the best of our knowledge, been made using conjugated polymers, nor has their behavior in solution been the subject of study. As a prerequisite to favor the formation of a comb-polymer, H-bonds should be as strong as possible. Resultantly, phenol and pyridine clearly emerge as suitable partners, as their H-bond is known to be among the strongest. Therefore, we combine P4VP polymer with a tailor-made poly(3-(2-ethylhexyl)thiophene) (P3EHT) containing a phenol end group (Fig. 1). Since P3EHT can be used as an electron-donor in organic electronics, while the pyridine units of P4VP are known to interact with fullerenes (electron acceptors), supramolecular interactions in such systems could be exploited for obtaining stabilized bulk heterojunction morphologies.

Additional Supporting Information may be found in the online version of this article.

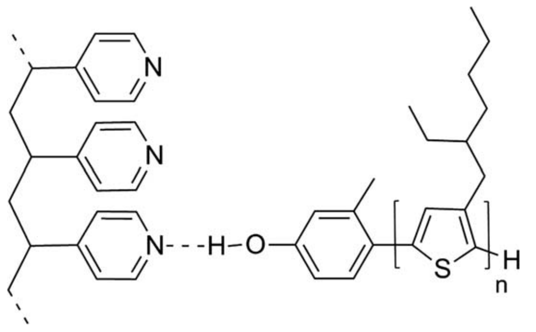


FIGURE 1 Formation of a graft copolymer via hydrogen bonding between P4VP and a P3EHT containing a phenol end group.

EXPERIMENTAL

Reagents and Instrumentation

All reagents were purchased and used without further purification. (4-Bromo-3-methylphenoxy) (isopropyl) dimethylsilane (**1**), the nickel initiator (**2**), and 2-bromo-3-(2-ethylhexyl)-5-iodothiophene (**3**) were synthesized according to literature procedures.[8–10]

^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. All DOSY NMR spectra were measured on Bruker Avance II+ 600 NMR spectrometer using a 5-mm direct detection dual broadband probe, with a gradient coil delivering maximum gradient strength of 53 G cm^{-1}. The experiments were performed at a temperature of 293 K and polymer concentrations of 10 mg mL^{-1}. The DOSY spectra were acquired with the double-stimulated echo-pulse sequence, to eliminate possible convection during the experiments.[11] Monopolar sine shaped gradient pulses, gradient recovery delay (τ) of 100 μs, a longitudinal eddy current delay of 5 ms and three spoiling gradients were used. All spectra were recorded with 32K time domain data points in t_2 dimension and 32 t_1 increments, 16 transients for each t_1 increment, and a relaxation delay of 2 s. Diffusion delay ($\triangle$) of 200 ms and gradient pulse length (δ) of 11 ms were used. The gradient strength G was varied in 32 linear steps from 2 to 95% of the maximum gradient output of the gradient unit (from 0.68 to 32.65 G cm^{-1}) to ensure optimal signal attenuation. The spectra were processed with an exponential window function (line broadening factor 1), 32K data points in F2 dimension and 1K data points in the diffusion dimension, using the fitting routine integrated in the Topspin 2.1 package. The evaluation of the diffusion coefficients was performed by fitting the diffusion profile (the normalized signal intensity as a function of the gradient strength G) at the chemical shift of each signal in the DOSY spectrum with an exponential function using the variant of Stejskal–Tanner equation adapted to the particular pulse sequence used:

$$\frac{I}{I_0} = \exp\left[-D(\gamma\delta G)^2 \frac{4}{\pi^2}\left(\Delta - \frac{\delta}{2}\right)\right] \qquad (1)$$

here, γ is the gyromagnetic ratio of ^{1}H (rad T^{-1} s^{-1}), δ is the gradient pulse length (ms), $\triangle$ is the diffusion delay (ms), and D is the translational diffusion coefficient (m^2 s^{-1}). This equation is applicable for free diffusion and usually a short gradient pulse approximation is considered.

Size exclusion chromatography (SEC) measurements were carried out on a Shimadzu 10A GPC system. The column is a PLgel 5-μm mixed-D-type column and the detection system consists of a differential refractometer and a UV–vis spectrophotometer. The GPC system is calibrated towards polystyrene standards (purchased from Polymer Laboratories). Before measuring, the polymers are dissolved in THF ($c \approx 1$ mg mL^{-1}) and filtered over a pore size of 0.2 μm.

Matrix-assisted laser desorption ionization-time-of-flight (MALDI-ToF) mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser of 337 nm with a maximum output of 500 J m^{-2} delivered to the sample in 4 ns pulses at a 20-Hz repeating rate. Time-of-flight mass analyses were performed in the reflection mode at a resolution of about 10,000. The matrix, trans-2-[3-(4-*tert*-butyl-phenyl)-2-methyl-2-propenylidene]malonitrile, was prepared as a 40 mg mL^{-1} solution in chloroform.[12] The matrix solution (1 µL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in chloroform to obtain 1 mg mL^{-1} solutions. Then, 1 µL aliquots of these solutions were applied onto the target area (already bearing the matrix crystals) and then air-dried.

Synthesis of Poly(3-(2-ethylhexyl)thiophene) with a Phenol End Group

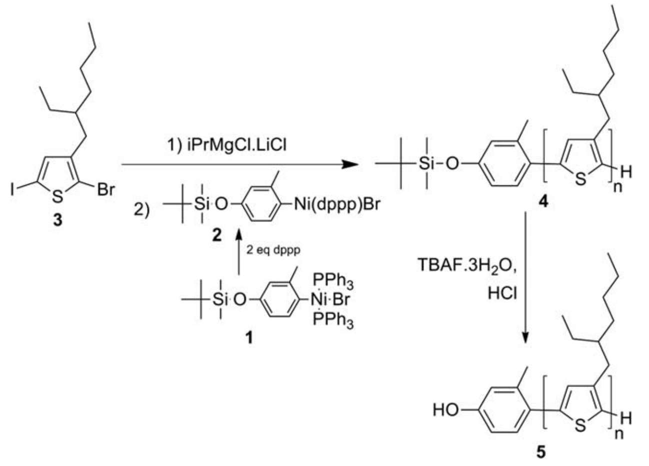
2-Bromo-3-ethylhexyl-5-iodothiophene (1.05 mmol; 0.422 g) was brought under an argon atmosphere and dissolved in dry THF (10 mL). A solution of *i*PrMgCl.LiCl (1.05 mmol; 0.763 mL) in THF was added to this solution and reacted for 1 h at room temperature. In the meantime, a mixture of the functionalized initiator (20.0 μmol; 17.7 mg) and dppp (40.0 μmol; 16.5 mg) was purged with argon and dissolved in dry THF (5 mL). After an initial 15-min reaction period at room temperature, the monomer solution was added to the reaction mixture and the polymerization was allowed to proceed for 60 min. The polymerization was quenched by addition of acidified THF. The latter is obtained by adding a droplet of a 37% HCl solution to 15 mL of THF. The reaction mixture was then precipitated in methanol and filtered off. Next, the polymer was purified with a Soxhlet extraction using methanol and chloroform. The chloroform fraction was again precipitated in methanol, filtered off and dried. The polymer was obtained as a dark red solid.

Yield: 0.150 g (75%); ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.94 (s, 1H, Ar H in P3HT), 2.74 (d, 2H, Ar-CH$_2$-C in P3HT), 22.43 (s, 3H, Ar-CH$_3$), 1.70–1.29 (m, 8H, CH$_2$), 0.88 (m, 6H, CH$_3$).

RESULTS AND DISCUSSION

Synthesis of P3EHT with Phenol End Group

The synthesis of poly(3-alkylthiophene)s (P3AT) has been thoroughly investigated, which has led to protocols enabling



SCHEME 1 Controlled synthesis of P3EHT bearing a phenol end group.

a living polymerization and high degree of control for these materials.[13–18] We have opted to use the selective GRIM for generating the desired monomer, followed by a nickel-catalyzed polymerization. It is known that the polymerization of 2-bromo-5-iodo-3-alkylthiophenes proceeds via a controlled chain-growth mechanism in the presence of a Ni(dppp)-catalyst. The chain-growth mechanism allows the use of external initiators, which will be built in at the beginning of each chain.[19–24] Hence, the use of a functionalized initiator enables us to introduce a phenol end group in every P3AT, capable of engaging in H-bonds. Another benefit of an external initiator is the faster initiation, which results in a lower polydispersity.[25] The initiator is synthesized according to literature procedures.[9] Before polymerization, a ligand exchange is performed with dppp, forming (**2**). This guarantees an optimal control over the polymerization (Scheme 1).[14,15]

By varying the monomer to initiator ratio, the degree of polymerization (DP) can be controlled. We selected a 50/1-ratio, which theoretically results in a DP of 50. It was chosen not to use a higher DP to avoid too much steric hindrance for the supramolecular hydrogen bonding induced by longer chains, as this would reduce the amount of P3EHT chains attached to P4VP. After termination of the polymerization with HCl, the Ni-centers will be replaced by a hydrogen atom. Hence, while a hydrogen at the end of the polymer chain is a signature of the living character, a bromine at the same position implies that the active center, and, consequently, also the living character of the chain, was lost. In a final step, the phenol group of the polymer is deprotected using *tert*-butylammonium fluoride (TBAF) and HCl.

The excellent control over the polymerization is evidenced by GPC analysis of the polymer, which showed a very low polydispersity of 1.07. The number average molar mass was found to be 12 kg mol^{-1}, based on SEC measurement using a polystyrene standard calibration. The polymer is further analyzed using NMR spectroscopy (Fig. 2). Apart from the structure determination, this spectrum can also provide information on the DP, the efficiency of the initiation and the living nature of the polymerization. Information on these parameters can be deducted from the integration values of the small peaks originating from terminal units of the polymer.[26,27] The polymer has two possible chain ends: one arising from the *o*-tolyl initiating species (signal e) and one from the terminal methylene, with either a Br or H in the 2-position (signal p). Note that given the fact that only one doublet is found for H_p points to the fact that all chains bear either a H- or Br-atom at this end. Hence, the DP is given by:

$$DP = \frac{g}{p/2+e/3} + \frac{p}{p/2+e/3} \tag{2}$$

in which the first term accounts for the inner and the second term for the terminal thiophene units. A DP$_n$ of 41 was found. An equivalent way of determining the DP makes use of the aromatic signals arising from the proton in the 4-position of the thiophene ring. Once again, the ratio of integration values of the peak arising from the hydrogen atoms in the main chain (H_f) and the one from terminal unit (H_x) is calculated, also giving rise to a DP of 41. This is slightly lower than the theoretical value of 50, but can be explained by the fact that the polymerization was not yet fully completed when the polymerization was terminated. However, it was chosen to terminate the polymerization at that time, to assure the living nature prevails over termination. This goal was indeed achieved, as no evidence of chains end-capped with bromine (instead of hydrogen) was found with MALDI-ToF (Fig. 3). In order to verify the efficiency of the initiation, signals p and e were compared. Taking the number of hydrogen atoms that each peak represents into account, this confirms that one initiator is built in for one terminal thiophene unit. Since MALDI-ToF confirms that indeed each chain is equipped with one initiator unit and one terminal unit (Fig. 3), we can conclude that the initiation was very efficient. The MALDI-ToF measurement also shows that the number average molar mass of the polymer is equal to 7.7 kg mol^{-1},

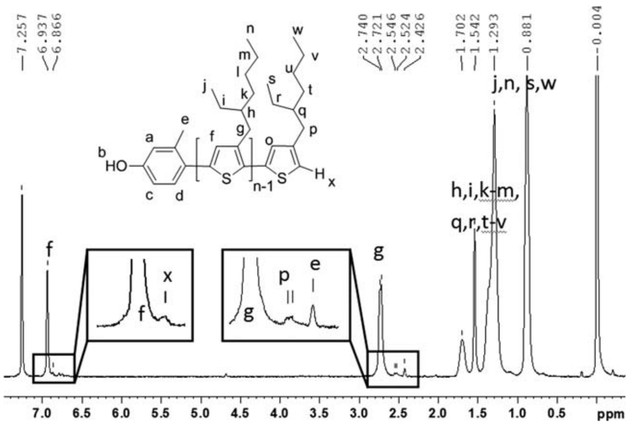


FIGURE 2 ^1H NMR Spectrum of P3EHT bearing a phenol end group.

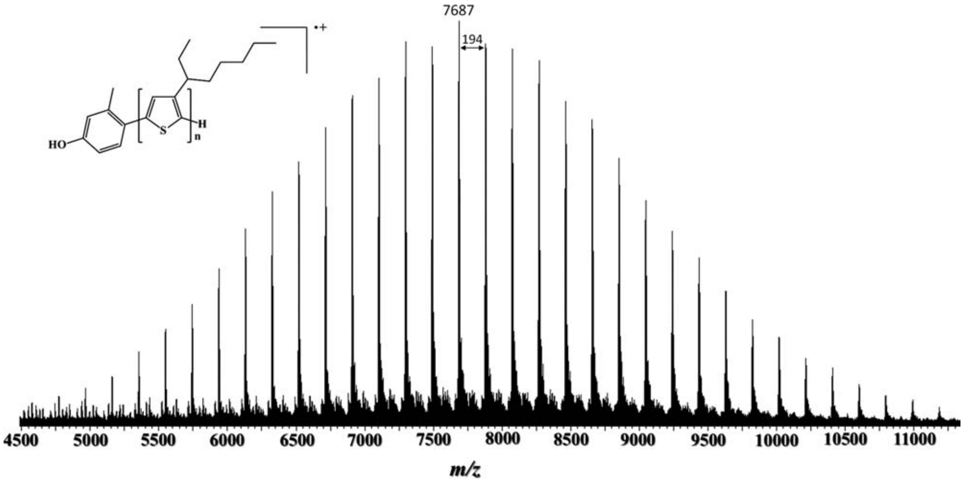


FIGURE 3 MALDI-ToF spectrum of P3EHT containing a phenol end group, evidencing the perfect initiation en living character of the polymerization.

corresponding to a DP$_n$ of 39, in line with the results of ^{1}H NMR spectroscopy. The obtained MALDI-Tof spectrum is representative, as the low PDI of the polymer enables an efficient ionization of the chains. Finally, no significant secondary peaks are observed which could be indicative of side products or uncontrolled polymerization.

Formation of a Supramolecular Graft Copolymer

When the phenol-initiated P3EHT is combined with P4VP, a supramolecular comb-copolymer should arise as a result of phenol-pyridine hydrogen bonding. In order to investigate whether or not hydrogen bonding is taking place, diffusion-ordered NMR spectroscopy (DOSY) is used.[28] This simple and fast technique is capable of determining diffusion coefficients of species in solution. As the diffusion coefficient of the hydrogen-bonded species will differ from their free counterparts, evidence for hydrogen bonding can be found.[29,30] This slightly less common technique is chosen because infrared spectroscopy (often used to detect hydrogen bonding) is difficult in solution and dynamic light scattering is complicated for systems containing polythiophenes, as they do not only scatter but also absorb the light.

First, the diffusion coefficients of the pure materials were measured using DOSY [Fig. 4(a,b)]. These were found to be 5.55×10^{-11} m^{2}s^{-1} for P4VP and 14.4×10^{-11} m^{2}s^{-1} for the phenol-initiated P3EHT. The higher value for the former is expected, as the molar mass of P4VP is more or less five times higher than the molar mass of the polythiophene. On the other hand, the conjugation of the polythiophene causes

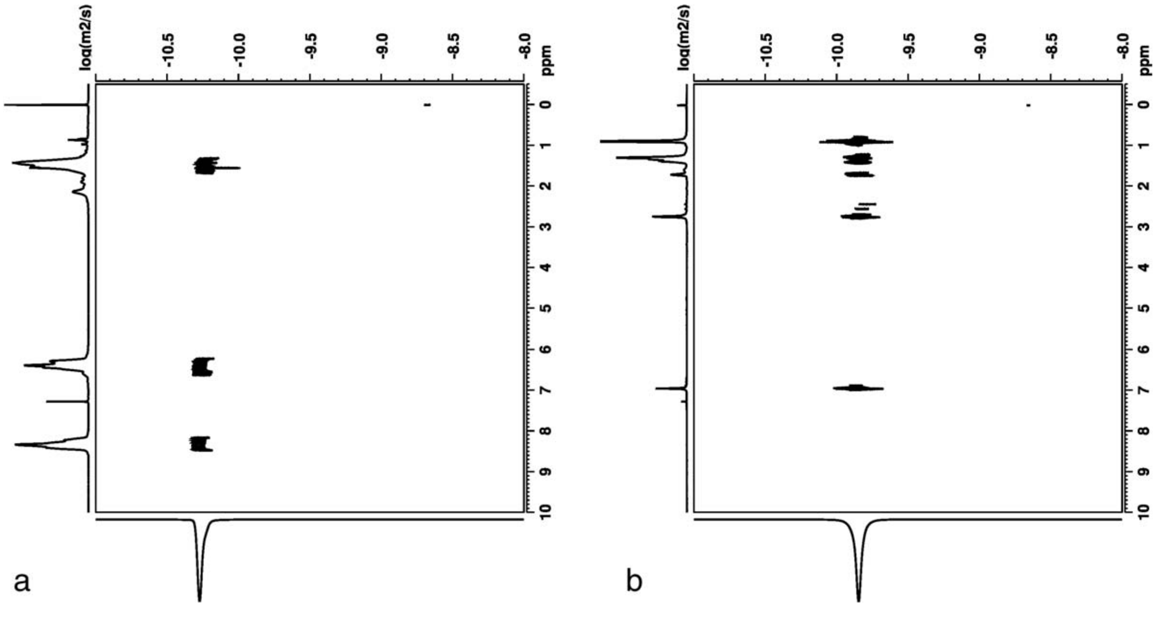


FIGURE 4 (a) DOSY spectrum of P4VP in CDCl$_3$ (10 mg mL^{-1}). (b) DOSY spectrum of P3EHT with phenol end group in CDCl$_3$ (10 mg mL^{-1}).

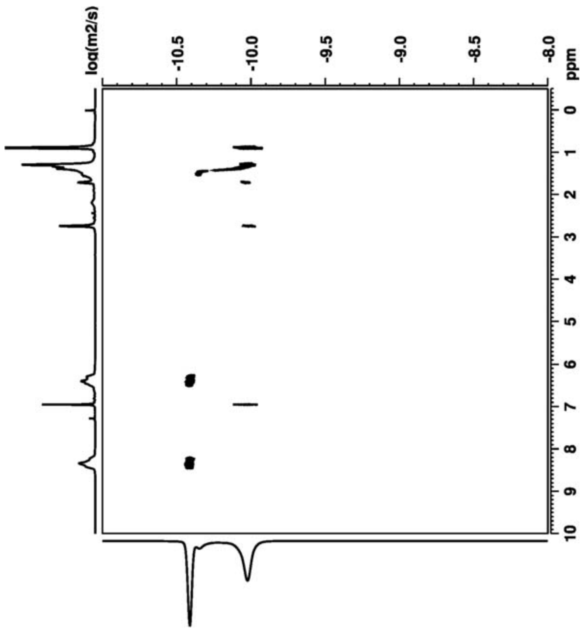


FIGURE 5 DOSY specrum of the 50/50 wt% mixture of P4VP and the phenol-initiated P3EHT. Two different diffusion coefficients are clearly observed, although there is a shift towards lower values compared to the spectra of the pure materials.

the chain to be more rigid than P4VP, which generally leads to a larger hydrodynamic radius and lower diffusion coefficient. However, this effect is obviously not large enough to compensate for the large difference in molar mass.

Subsequently, a 50/50 wt % mixture of both polymers in solution is measured. This ratio is chosen because it combines the advantages of sufficiently intense signals for both polymers and an excess of binding partners available for the phenol-initiated polythiophene. The latter is beneficial, as upon binding between PV4P and P3EHT the largest shift in diffusion coefficient is expected for P3EHT. The DOSY spectrum of the mixture shows the presence of species with two different diffusion coefficients (Fig. 5). If complete association between both materials occurs, only one diffusion coefficient of the combined species would be detected. Clearly, this is not the case. The results from DOSY spectra imply that not all P3EHT chains are attached to P4VP, despite the large excess of binding partners. Nevertheless, there is a shift in the diffusion coefficients toward lower values for both species in the blend as compared to their individual solutions (Table 1 and Supporting Information Fig. S1). This decrease of the diffusion coefficients can be explained by the formation of a supramolecular complex with a smaller diffusion coefficient. This complex is in dynamic equilibrium with the unbound polymer chains, so that an average diffusion coefficient of the associated and free polymers is measured.

Another explanation for the observed changes in diffusion coefficients could be an increase in viscosity. In the mixture, the total polymer concentration is higher than for the pure polymers. Nevertheless, all solutions were still of very low viscosity because of the small polymer concentrations. In order to fully exclude the effect of the viscosity on the measurement, some tetramethyl silane was added as a reference material.[31] It was observed that there was no shift in the TMS signal going from the pure materials to the mixture. The diffusion coefficient was found to be 2.23×10^{-9} m^2s^{-1} in all samples. This proves that the effect of the increased viscosity is negligible and that the shift toward lower diffusion coefficients can be ascribed to supramolecular complex formation.

The results of the DOSY measurements prove the formation of hydrogen bonds between P4VP and phenol-initiated P3EHT. However, the strength of this noncovalent interaction is limited, as only a fraction of the P3EHT chains are coupled with the P4VP. The measured diffusion coefficients of the polymers in the blend are represented by the following equation.

$$D_{\text{measured}} = x_{\text{free}} D_{\text{free}} + x_{\text{bound}} D_{\text{bound}} \tag{3}$$

with x_{free} and x_{bound} the fractions of the polymer in the free and bound state and D_{free} and D_{bound} their respective diffusion coefficients. From this equation, it is possible to determine the average fraction of P3EHT chains that is involved in the supramolecular association. In order to do so, the assumption has to be made that the diffusion coefficient of P3EHT in the bound state is equal to the diffusion coefficient of P4VP in the mixture. This means that we assume that all P4VP chains have a certain number of binding partners in the mixture. This is a reasonable assumption, since the molar mass of the P4VP is sufficiently large and it is likely that the P3EHT chains are more or less equally distributed over the P4VP chains for interaction. With the values extracted from the DOSY spectra, we obtain a value for $x_{(\text{HO-P3EHT})\text{free}}$ of 0.54. This means that, on average, slightly more than half of the HO-P3EHT chains is not interacting with the P4VP via hydrogen bonding. Hence, 46% is involved in supramolecular complex formation.

As the total concentration of pyridine units and P3EHT chains in solution is known, and also the fraction of P3EHT chains attached to a pyridine unit, it is possible to calculate the association constant (see Supporting Information). It was found to be 8.8. In comparison, the association constant for hydrogen bonding between free pyridines and phenols in CCl_4 was found to be 44.6.[32] The difference between both values could tentatively be ascribed to a lower "availability" of both interacting partners in the polymer system.

TABLE 1 The diffusion coefficients of P4VP and P3EHT in $CDCl_3$ as determined by DOSY

Polymer	Diffusion Coefficient – Pure Material (10^{-11} m^2s^{-1})	Diffusion Coefficient – In Mixture (10^{-11} m^2s^{-1})
P4VP	5.55	3.90
P3EHT	14.4	9.55

The formation of this supramolecular complex was found not to have an influence on the absorption spectrum of P3EHT (Supporting Information Fig. S2). Hence, the aggregation behavior of P3EHT was not affected by the addition of P4VP, which can be understood by the relatively low number of P3EHT chains per P4VP and the only partial complexation.

CONCLUSIONS

A phenol-initiated P3EHT with a successful initiation, good control over the molar mass and a low polydispersity was prepared. This polymer was subsequently mixed in solution with P4VP in order to form a supramolecular graft-copolymer in solution through phenol-pyridine hydrogen bonding. This blend was studied using DOSY, which showed that the diffusion coefficients of both components in the blend decreased with respect to their diffusion coefficients in pure solution. This effect is ascribed to the formation of a supramolecular complex, being the first supramolecular graft-copolymer with a conjugated polymer in solution.

ACKNOWLEDGMENTS

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