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Influence of Polymerization Temperature on Molecular Weight, Photoluminescence, and Electroluminescence for a Phenyl-Substituted Poly(*p*-phenylenevinylene)

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ABSTRACT: We present the synthesis and characterization of poly(2-(2″,5′-bis(2″-ethylhexyloxy)phenyl)-1,4-phenylenevinylene) (BEHP-PPV) polymerized at different temperatures. The photoluminescence efficiencies in the solid state of BEHP-PPV obtained at 144 and 0 °C are 28% and 60%, respectively. ^{1}H NMR measurements showed a lower concentration of structural defects for BEHP-PPV obtained at lower temperatures, which can explain the increased photoluminescence efficiencies for these polymers. Polymerization temperatures below 0 °C decrease the molecular weight without changing the photoluminescence efficiency to any large extent. The electroluminescence efficiencies follow the trend in the photoluminescence efficiencies.

Introduction

Although conjugated polymers had been known for a few decades, it was not until 1990 as their use as the active substance in light-emitting diodes (LEDs) was reported.[1] The first conjugated polymer to show electroluminescence was poly(*p*-phenylenevinylene) (PPV).[1,2] Today, PPV and its derivatives are still one of the most frequently used class of conjugated polymers in LEDs.[3] This is due to their good film-forming properties, high photoluminescence (η_{PL}), and electroluminescence (η_{EL}) efficiencies, as well as their readiness to polymerize to high molecular weight polymers. Since singlet excitons are the same whether they are created by either optical or electronical methods,[3] high η_{PL} in the solid state is essential to make LEDs with high η_{EL}. One of the factors that limits the η_{PL} in the solid state is the rate for the excitons to be transported to a defect in the polymer film where nonradiative relaxation to the ground state can occur. It is well-known that excitons live long enough to diffuse a long distance before relaxation to the ground state occurs.[4,5] Since separation of the polymer backbones partially can prevent interchain exciton transfer, it is possible to make a polymer with high η_{PL} by the introduction of appropriate side chains. Too large a separation of the polymer chains must be avoided, since this cause too low mobility of charge carriers in the solid-state LEDs. Another very interesting way to increase the η_{PL} in the solid state is to lower the concentration of structural defects in the polymer. This might be possible if a polymerization method with a minimum of side reactions can be found. The most frequently used polymerization method for PPVs involves dehydrohalogenation of 1,4-bis(halomethyl)benzene derivatives.[6] Unfortunately, these polymerizations occasionally afford polymers with low solubility due to very high molecular weight. Increased solubility for such systems can be achieved by polymerization at elevated temperature[7] or by addition of end-capping groups to the monomer solution.[8,9]

Table 1. Polymerization Parameters and the Molecular Weights of BEHP-PPV

entry	solvent	pol temp (°C)	equiv of *t*-BuOK[b]	$\bar{M}_{\mathrm{n}}/\bar{M}_{\mathrm{w}}$[e] $\times 10^{-3}$	poly-dispersity	yield (%)
1	xylene	144	2.6	50/280	5.6	66
2	THF	66	2.6	gel		
3[a]	THF	0	16	25/1800	72	46
4	THF	0	16	340/1440	4.2	58
5	THF	−35	16	270/1490	5.5	88
6	THF	−78	16	125/536	4.3	71
7[c]	THF			170/731	4.3	77
8[d]	xylene			213/685	3.2	73

[a] 4-*tert*-Butylbenzyl bromide (1 equiv) included as an end-capping group. [b] The base (0.8 M in dioxane for **1** and 1.0 M in THF for **2**−**7**) was added dropwise under 2 min. [c] Polymer **7** was derived from **6** after workup and treatment with excess *t*-BuOK at room temperature. [d] Polymer **8** was derived from **5** after workup and treatment with excess *t*-BuOK in refluxing *o*-xylene. [e] Relative to polystyrene standards in THF at 25 °C.

In this paper, we compare the properties of poly(2-(2′,5′-bis(2″-ethylhexyloxy)phenyl)-1,4-phenylenevinylene) (BEHP-PPV) polymerized under different conditions (Table 1). All polymers originate from the same monomer polymerized with excess potassium *tert*-butoxide (*t*-BuOK) as the base (Scheme 1). The chemical structure of BEHP-PPV was designed to give the polymer high η_{PL} in the solid state, since the bulky side chains should separate the polymer backbones enough to reduce the rate of interchain exciton transfer to defects where nonradiative relaxation can occur. This design with two bulky alkyl groups also gives a polymer with a relatively high solubility even at high molecular weight, which is in contrast to most known PPVs.

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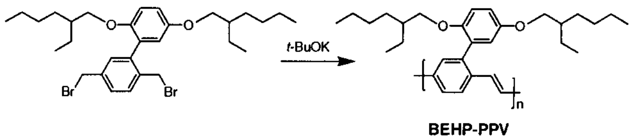
Table 2. PL, EL, and Absorption Data for Polymers 1 and 3−7

entry	Br content (wt %)	abs$_{\max}$ (nm) THF	PL$_{\max}$ (nm) THF	η_{PL} (%) THF	abs$_{\max}$ (nm) film	PL$_{\max}$ (nm) film	η_{PL} (%) film	η_{EL} (%)
1		429	482, 516	84	429	489, 524	28	0.56
3		431	485, 521	90	433	492, 525	60	0.94
4	0.58	425	481, 512	88	423	489, 522	58	0.90
5	0.61	427	481, 512	87	429	489, 522	58	0.80
6	4.4	404	478, 511	50	407	484, 517	44	
7	0.79	426	480, 506	80	429	487, 520	47	
8	0.002	427	481, 512	90	429	489, 522	62	

Scheme 1. Chemical Structure of BEHP-PPV



Experimental Section

Measurements. Molecular weights of the polymers were determined by size-exclusion chromatography (SEC) by a Waters 150 CV using SDVB columns at 25 °C. The calibration was made by a series of monodispersed polystyrene standards in THF. NMR spectra were recorded on a Varian 400 MHz spectrometer with tetramethylsilane as internal reference. UV−vis spectra were recorded on a Lambda 9 spectrometer. Photoluminescence (PL) spectra were measured by exciting the polymer samples with monochromatic light from a tungsten lamp, and the emission was measured with an Oriel Instaspec IV diode matrix spectrometer. An integrating sphere made by Labsphere was used to measure the PL efficiency. Solutions used to detect UV−vis spectra and PL spectra were prepared from the polymer dissolved in $CHCl_3$. UV−vis spectra and PL spectra in the solid state were carried out on films spin-coated onto glass slides. The light-emitting diodes were made with an ITO/glass substrate of 15 × 15 mm with an active area of each device of approximately 0.1 cm^2. The electroluminescence (EL) intensity was measured with a silicon photodiode, and the quantum yield was determined by comparison with devices measured in an integrating sphere.

Materials. All starting materials were purchased from Aldrich and used without further purification. The *o*-xylene was anhydrous and packaged under nitrogen. The synthesis of the monomer (2-(1′,4′-bis(2″-ethylhexyloxy)benzene)-1,4-bis(bromomethyl)benzene) is described in detail in ref 7. THF was distilled over bensophenone and sodium.

Polymer Synthesis. A representative procedure for the preparation and isolation of the polymers follows.

Polymer 5 from 2-(1′,4′-Bis(2″-ethylhexyloxy)benzene)-1,4-bis(bromomethyl)benzene. A stirred solution of the monomer (0.150 g, 0,251 mmol) in freshly distilled THF (10 mL) under nitrogen was cooled by an acetone bath at −35 °C. Potassium *tert*-butoxide at room temperature (4.0 mL, 1.0 M in THF, 4.0 mmol) was added under 2 min. After 4 h at −35 °C, the resulting polymer was precipitated in methanol. The crude polymer was collected, washed with methanol, and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was again collected, washed with methanol, and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was filtered off, washed with methanol, and dissolved in chloroform with stirring at room temperature for 2 h. The resulting solution was filtered through a 325 mesh filter, and the polymer was precipitated by dropwise addition to methanol. The precipitated polymer was collected, washed with methanol, and dried under high vacuum to yield 63 mg (58%) of polymer **5**.

Results and Discussion

Synthesis and Molecular Weights. The reaction parameters for the different polymerizations are summarized in Table 1. The polymerization yields were moderate to good (46−88%), with the best yields obtained for the polymers polymerized at temperatures below 0 °C. Surprisingly the polymerization worked well even at −78 °C. To the best of our knowledge, polymerization of PPVs at this low temperature has not been reported earlier. There was no distinct difference in solubility between the polymers **1** and **3**−**8**. They were all completely soluble in $CHCl_3$, THF, and xylene at room temperature. Attempts to dissolve **2** resulted in gel formation.

The observation of an immediate color change from colorless to bright yellow-green when the *t*-BuOK was added to the monomer solution (for polymer **1**−**5**) shows that the polymerization rate is fast and that 4 h reaction time is enough to obtain a good quality material. The lower polymerization rate at −78 °C, observed as a slower color change when the *t*-BuOK was added to the monomer solution, indicates that the decrease in molecular weight at lower polymerization temperatures in THF is due to a slower reaction rate, which is in line of what one would expect.

Workup of the polymer obtained at −78 °C followed by treatment with *t*-BuOK (1 equiv per repeating unit) in THF at room temperature for 2 h yielded polymer **7**, and workup followed by treatment of the material polymerized at −35 °C with *t*-BuOK (1 equiv per repeating unit) in refluxing *o*-xylene for 2 h yielded polymer **8**. A comparison of the bromine content of **4**−**8** (Table 2) shows that the dehydrobromination at −78 °C is a much slower process than at 0 and −35 °C. This observation clearly shows that 4 h reaction time is not enough to complete the polymerization at −78 °C. Although **7** was more dehydrobrominated than **6**, it still contained a considerable amount of bromine. Polymer **8**, on the other hand, was almost completely dehydrobrominated. This clearly shows that the dehydrobromination process is more effective at elevated temperatures. The molecular weight of **8** was halved compared to **5**. This shows that chain scission of the polymer backbones occurs at high temperatures and explains why the molecular weight of **1** (polymerized in refluxing xylene for 4 h) is relatively low compared to those of the polymers obtained at lower temperatures. This behavior is in agreement of what our group has observed for other PPVs where we see chain scission for polymers refluxed in xylene without base treatment. We have used this method to prepare highly soluble poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4- phenylenevinylene) (MEH-PPV) after polymerization at −35 °C.[10]

Addition of 4-*tert*-butylbenzyl bromide as an end-capping group to the monomer solution was not necessary to obtain a soluble material when the polymerization was carried out at 0 °C. This additive might initiate an anionic polymerization as proposed by Hsieh et al.,[8] but if so, only to a small extent. The preferred reaction is the dimerization forming 4,4′-di-*tert*-butylstilbene as described in the literature.[6] The extremely high polydispersity of **3** shows that 4-*tert*-butylbenzyl bromide

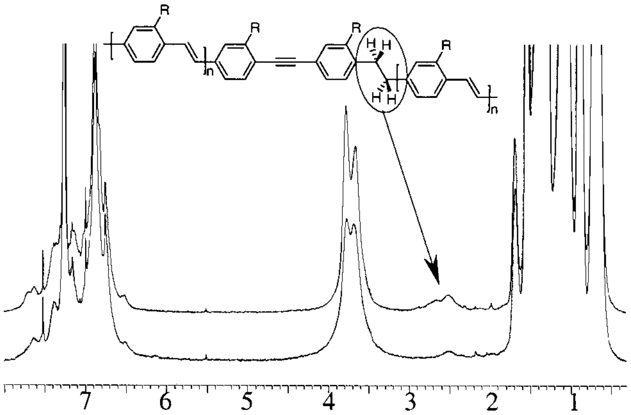


Figure 1. Chemical structure of the segment resulting from a HH coupling and ^{1}H NMR for **1** (top) and **4** (bottom). Peaks around 3.7 ppm in both spectra have the same integrated area.

reacts with some polymer chains, giving a portion of the polymer with low molecular weight. However, it leaves some polymer chains unaffected, and these can grow to a high molecular weight material.

Photoluminescence, Electroluminescence, and UV−vis Properties. The most important result of lowering the polymerization temperature is the increase of the η_{PL} in films as shown in Table 2. The most probable explanation is that a decrease in the polymerization temperature reduces the rate of the reactions leading to defects where nonradiative quenching of the excited states can occur. From ^{1}H NMR measurements and IR spectroscopy data it is clear that all the polymers (except **6**, which is not sufficiently dehydrobrominated) are quite similar. These observations clearly show that a small variation in defect concentration might have a remarkable effect on the η_{PL}. It is known that carbonyls can effect luminescence quantum yields in a negative manner. However, it cannot explain our results since no carbonyls were detected in NMR or IR measurements for any of the polymers.

Recently, Becker et al.[11,12] reported that PPVs with side chains similar to BEHP-PPV polymerized in refluxing dioxane contained head-to-head (HH) couplings as the result of a side reaction. They assigned the CH_2-CH_2 groups resulting from HH couplings (Figure 1) to peaks around 2.7−2.9 ppm.[11] Our results are consistent with theirs, where we observe a relatively large amount of HH couplings for BEHP−PPV polymerized at 144 °C. From Figure 1 where the ^{1}H NMR of **1** and **4** is shown, it is clear that this side reaction is suppressed at a lower polymerization temperature. The HH content for **1** and **4** was 9% and 3%, respectively. Polymerization at −35 °C resulted only in a minor decrease in HH content compared to polymerization at 0 °C. The peaks in the ^{1}H NMR at 3.7−3.8 ppm correspond to the methylene protons next to the oxygens in the side chains. In an ordered structure these two signals should have equal intensity. As seen in Figure 1, this is the case for **4** but not for **1**. A more ordered structure in **4** is also in line of what one would suspect from a reaction at a lower temperature. Although an increased polymerization temperature yields a more irregular structure with higher HH content, it does not influence the crystallinity since both **1** and **3** turned out to be completely amorphous in X-ray studies of polymer powder. Thus, the increase in η_{PL} is not caused by a change in crystallinity. Although the HH coupling is the structural defect with the highest concentration, there are most certainly more defects with a lower concentration, not detectable with NMR measurements, in the high-temperature polymerized polymer that contributes to the lower η_{PL}.

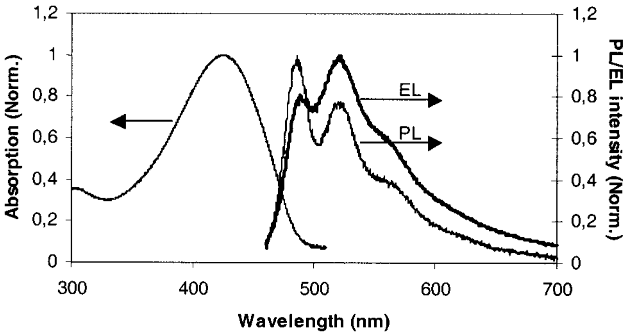


Figure 2. Absorption, PL, and EL spectra in the solid state of polymer **5**.

From the bromine content and absorption maxima in film and solution (Table 2) it is clear that polymerization at −78 °C leads to a polymer that is not fully conjugated. This indicates that the chemical structure of the polymer backbone of **6** is something in between precursor polymer and conjugated polymer. The incomplete dehydrobromination of **6** is also reflected as a decrease in the η_{PL}, and the absorption and photoluminescence of this polymer are somewhat blue-shifted. Although **7** has the same absorption maxima as **1** and **3**−**5**, its η_{PL} in the solid state still is slightly lower than for **3**−**5**. The reason for the lower η_{PL} for **7**, compared to those for **4** and **5**, is most probably due to the incomplete dehydrobromination even after additional base treatment at room temperature.

A bromine content of 0.6 wt % (as for **4** and **5**) corresponds to one nonconjugated repeating unit per 30 conjugated repeating units. The number of the conjugated repeating units per one nonconjugated for **6** and **7** is 3 and 22, respectively. It is known from the literature that shortening of the conjugation length improves the photoluminescence yields by decreasing the probability of exciton diffusion to defects where nonradiative decay to the ground state can occur.[2] The fact that **8**, which has a very low bromine content and at the same time the highest η_{PL}, rules out that shortening of the conjugation length can explain the η_{PL} behavior in our case.

Double-layer devices (ITO/PEDOT/polymer/Ca) of **1** and **3** show that the external electroluminescence efficiency (η_{EL}) follows the trend in the η_{PL}. For **1** and **3** the η_{EL} are 0.56 and 0.94, respectively. The thickness of the polymer layer in the devices was ~1000 Å. It is important to get a good balance between electrons and holes injected into the polymer film in LEDs in order to form diodes with high η_{EL}. The oxidized conducting polymer poly(3,4-ethylenedioxythiophene), PEDOT, which has the work function value 5.2 eV,[13,14] together with modified ITO (cleaned with acetone and 2-propanol and treated with oxygen plasma) was used to make it easier to inject holes and thereby to achieve a better balance between the injected holes and electrons in the LEDs. The electroluminescence spectra, as well as the absorption and photoluminescence spectra, for **1**−**5** are almost identical. Representative absorption and luminescence spectra of BEHP-PPV are shown in Figure 2.

Conclusions

We have shown that the molecular weight of BEHP-PPV decreases by polymerization at lower temperatures in THF. Lower polymerization temperatures also give polymers with a lower content of structural defects which is reflected in a much higher η_{PL} in the polymers. The drawback of a high bromine content in the low-temperature polymerized materials can be avoided by additional base treatment at elevated temperature. It should be possible to find other PPVs that improves their properties as a result of a decrease of the polymerization temperature in the same way as shown for BEHP-PPV.

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