ACS Macro Letters
Letter
pubs.acs.org/macroletters

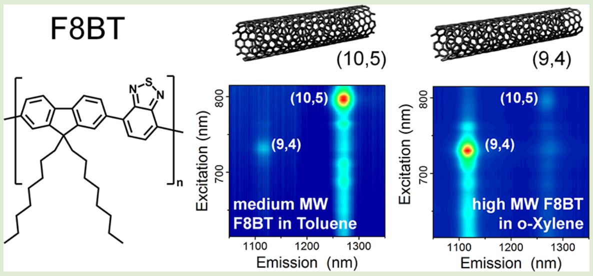
Effect of Polymer Molecular Weight and Solution Parameters on Selective Dispersion of Single-Walled Carbon Nanotubes

Florian Jakubka,† Stefan P. Schießl,† Sebastian Martin,† Jan M. Englert,‡ Frank Hauke,‡ Andreas Hirsch,‡,§ and Jana Zaumseil*,†

†Institute of Polymer Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany
‡Institute of Advanced Materials and Processes (ZMP), Friedrich-Alexander-Universität Erlangen-Nürnberg, 90762 Fürth, Germany
§Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91054 Erlangen, Germany

Supporting Information

ABSTRACT: The selective dispersion of single-walled carbon nanotube species (n,m) with conjugated polymers such as poly(9,9-dioctylfluorene) (PFO) and poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) in organic solvents depends not only on the type of solvent but also on the molecular weight of the polymer. We find an increasing amount of nanotubes and altered selectivities for dispersions with higher molecular weight polymers. Including the effects of different aromatic solvents, we propose that solution viscosity is one of the factors influencing the apparent selectivity by changing the reaggregation rate of the single-walled carbon nanotubes (SWNT). The type of solvent, polymer molecular weight, concentration, and viscosity should thus be taken into account when screening for new polymers for selective SWNT dispersion.



Single-walled carbon nanotubes (SWNTs) have unique electronic and optical properties depending on their chirality index (n,m), which determines their diameter, metallic, or semiconducting character and wavelength of absorbed and emitted light.[1,2] All currently known growth methods for SWNTs produce a mixture of nanotube species. For their application in electronic and optoelectronic devices, such as field-effect transistors,[3] light-emitting diodes,[4] or solar cells,[5] usually only one electronic type (semiconducting or metallic) or only one particular chirality of SWNT is desired. The selective dispersion and sorting of SWNTs is thus crucial for accessing their full potential in large-scale devices.

The sorting of solution-dispersed nanotubes has made tremendous progress in recent years.[6,7] Density gradient ultracentrifugation[8] and gel chromatography[9] of aqueous dispersions using certain surfactants are currently the best methods to separate metallic from semiconducting SWNTs. A direct way of only dispersing specific types of SWNT without further treatment, except centrifugation to remove bundles, was introduced by Nish et al. using solutions of polyfluorenes and their copolymers in organic solvents.[10] Especially poly(9,9-dioctylfluorene) (PFO) and poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) exhibit very high selectivity toward certain semiconducting SWNTs. Dispersions of nanotubes with these and other semiconducting polymers (e.g., polythiophenes) are of particular interest because polymer−SWNT hybrids can be used as active layers in organic electronic devices with improved properties.[4,11]

Two major aspects that influence the morphological and electronic properties of semiconducting polymer films are the casting solvent and the molecular weight (M_w). Boiling point and Hildebrand solubility parameters of the solvent mainly affect nanoscale morphology and crystallinity,[12,13] while increasing molecular weight is linked to higher charge carrier mobilities in many semiconducting polymers.[14,15] We can expect these factors to play a role in the selective dispersion of SWNTs with polymers, too, and hence affecting the properties of the resulting hybrids. Few studies looked at the influence of solvents on polymer−SWNT selectivity. Hwang et al. compared solvents such as chloroform, tetrahydrofuran, toluene, and some xylenes.[16] However, chloroform and tetrahydrofuran resulted in very nonselective dispersions, and no direct correlation between solvent parameters and selectivity has been found so far. A widely ignored aspect is the molecular weight of the conjugated polymer. In many studies the molecular weight is either not mentioned at all, or only low (<25 000 g/mol)[17] or medium (<90 000 g/mol) molecular weight polymers are used.[16,18,19] In contrast to that, high molecular weight semiconducting polymers (>150 000 g/mol) are highly preferable for efficient charge transport and thus for most electronic devices.

In this study we compare the SWNT dispersion selectivity of conjugated polymers (F8BT and PFO) with a range of molecular weights and for a selection of nonhalogenated aromatic solvents that are good solvents for the polymers but

Received: March 26, 2012
Accepted: June 11, 2012
Published: June 15, 2012

dx.doi.org/10.1021/mz300147g | *ACS Macro Lett.* 2012, 1, 815−819

do not disperse SWNT themselves. We find that some of the observed differences in selectivity and concentration of dispersed SWNT might be explained by the different reaggregation rates of metastable SWNT−polymer complexes depending on the viscosity of the solution, which depends on the solvent and molecular weight of the polymer.

Figure 1 shows photoluminescence (PL) excitation−emission maps of SWNT dispersions in F8BT and PFO solutions with different molecular weights and solvents (see Table 1).

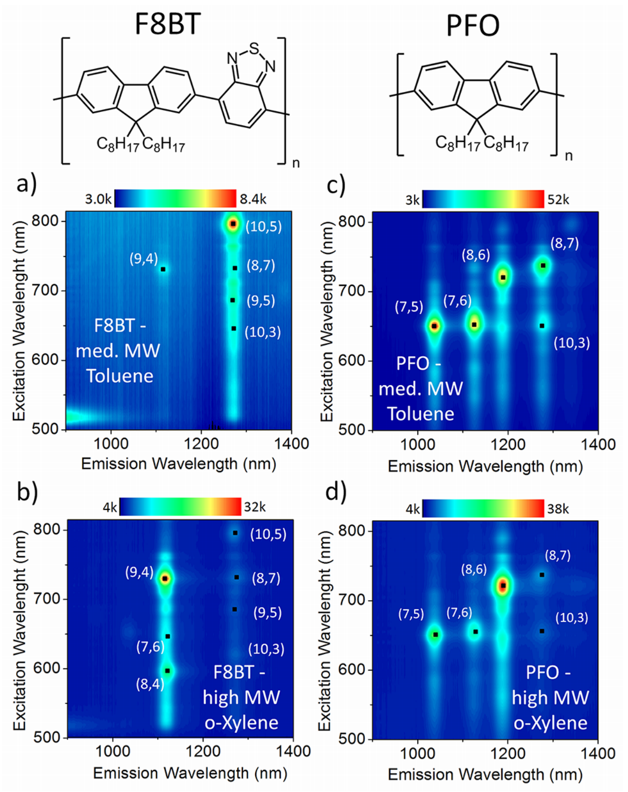


Figure 1. PL excitation−emission maps for (a, b) F8BT- and (c, d) PFO-based SWNT dispersions with different combinations of molecular weight and solvent. Identified SWNT species are labeled.

Table 1. Polymer and Solution (2 mg/mL) Parameters[a] **(Molecular Weight Distributions and ^{1}H NMR Spectra of All Polymers Are Shown in Figure S1 of the SI)**

polymer	M_w	PD	solvent	ρ	ν	η
F8BT low MW	27	3.66	toluene	0.83	0.705	0.590
			o-xylene	0.86	0.956	0.828
F8BT med. MW	64.5	1.78	toluene	0.82	0.775	0.639
			o-xylene	0.87	1.061	0.923
F8BT high MW	189	3.01	toluene	0.82	0.979	0.805
			o-xylene	0.86	1.333	1.149
PFO low MW	15.4	2.29	toluene	0.82	0.684	0.564
			o-xylene	0.88	0.923	0.818
PFO med. MW	90.3	6.25	toluene	0.83	0.760	0.638
			o-xylene	0.87	1.057	0.921
PFO high MW	257	2.62	toluene	0.80	0.969	0.777
			o-xylene	0.86	1.389	1.195

[a] M_w: weight average molecular weight (kg/mol), PD: polydispersity, ρ: density (g/cm^3), ν: kinematic viscosity (mm^2/s), η: dynamic viscosity (mPa·s).

These PL maps allow us to identify individualized semiconducting nanotube species. Note that we cannot make any assumptions about type and amount of metallic nanotubes in the F8BT solution as their absorption peaks would overlap with the strong F8BT absorption. Raman measurements are also restricted due to F8BT fluorescence. However, for PFO it is well-established that almost no metallic SWNTs are left even after centrifugation at moderate speeds.[10,20] Using HiPco nanotubes as the source material, F8BT with a low or medium molecular weight in toluene predominantly disperses (10,5)-SWNT (see Figure 1a) as previously shown.[10] Increasing the molecular weight of F8BT and using *o*-xylene as the solvent results in an apparent shift of selectivity toward (9,4)-SWNT (Figure 1b). Compared to the distribution of nanotube species in the source material (e.g., nonselectively dispersed with sodium dodecyl sulfate in D_2O, Figure S2 of the Supporting Information (SI)), the selectivity toward (10,5)-nanotubes is still high, but (9,4)-nanotubes become more abundant. Note that these two nanotube species have similar chiral angles but different diameters. PFO with a medium molecular weight in toluene preferably disperses nanotubes with high chiral angles; among the four most prominent species, the (7,5) nanotubes seem to dominate (Figure 1c). For high molecular weight PFO in *o*-xylene (8,6)-SWNT are the most abundant (Figure 1d). These examples show that the molecular weight of the dispersing polymer and its solvent have a large impact on the apparent selectivity and need to be taken into account when SWNT−polymer dispersions are used to draw conclusions about the interaction of a polymer with a certain nanotube species. Detailed PL maps and selectivity distributions for all samples and SWNT-species are presented in Figure S3 (SI).

We first investigate the influence of solubility parameters, that is, the Hildebrand and Hansen parameters,[21,22] of various solvents on the chirality distribution of SWNT dispersions in F8BT solutions. To account for the inhomogeneous distribution of nanotube species in the source material and their different PL efficiencies, we define a selectivity fraction *S* that is independent of these factors. For F8BT dispersions we examine the dispersion selectivity of (10,5) versus (9,4) nanotubes given as

$$S = \frac{(I_{(10,5)\mathrm{F8BT}}/I_{(10,5)\mathrm{SDS}})}{(I_{(9,4)\mathrm{F8BT}}/I_{(9,4)\mathrm{SDS}}) + (I_{(10,5)\mathrm{F8BT}}/I_{(10,5)\mathrm{SDS}})}$$

using background-corrected PL intensities of the individual nanotubes in the polymer solution ($I_{(10,5)\mathrm{F8BT}}$ and $I_{(9,4)\mathrm{F8BT}}$) and an essentially nonselective aqueous sodium dodecyl sulfate (SDS) dispersion of the HiPco nanotubes ($I_{(10,5)\mathrm{SDS}}$ and $I_{(9,4)\mathrm{SDS}}$) as a reference (Figure S2, SI). Within the limited range of solubility parameters of aromatic solvents we find no clear correlation between the solubility parameters and the selectivity (see Figure S4, SI). Since only good solvents for F8BT were used, we can assume that the polymer chains form expanded coils in solution in all cases[23] and should have a similar tendency to wrap around the SWNT, which might explain the lack of correlation. Looking at various other solvents we find that only benzene-based, nonhalogenated solvents result in good selectivity (see Figure S5, SI).

Cheng et al. reported that solvent viscosity had some influence on the individualization and stabilization of SWNT dispersions in pure solvents.[24] The kinematic viscosities ν ($\nu = \eta/\rho$ with η as dynamic viscosity and ρ as density) of toluene (0.657 mm^2/s) and *o*-xylene (0.886 mm^2/s) are quite different.

In addition, the molecular weight of the polymer has a large impact on the overall solution viscosity according to the Mark–Houwink equation: $[\eta] = KM_w^a$, with $[\eta]$ as the intrinsic viscosity, M_w as the weight average molecular weight, and K and a as system-dependent constants.[25] Table 1 lists the kinematic and dynamic viscosities of 2 mg/mL solutions of F8BT and PFO with low, medium, and high molecular weight in toluene and *o*-xylene, showing a clear increase of viscosity with M_w although the concentrations are far from the ideal dilution assumed for the Mark–Houwink equation. The measured kinematic viscosities range from 0.68 to 1.39 mm^2/s.

Figure 2a shows the (10,5) versus (9,4) selectivity of SWNT dispersions with F8BT as defined above versus the kinematic viscosities of solutions with three different molecular weights in toluene and *o*-xylene. We observe a clear trend toward lower (10,5) nanotube dispersion selectivity versus (9,4) with increasing viscosity. Considering Figure 1a and b as examples with low (0.78 mm^{2}s^{-1}) and high (1.33 mm^{2}s^{-1}) viscosities, Figure 2a shows the gradual transition between the two most abundant nanotube species. For very high molecular weights of F8BT and *o*-xylene the dispersion seems to become more selective for (9,4) nanotubes; however, this might be exaggerated due to the larger uncertainty of the ratio of two very small PL intensities obtained for (10,5) nanotubes.

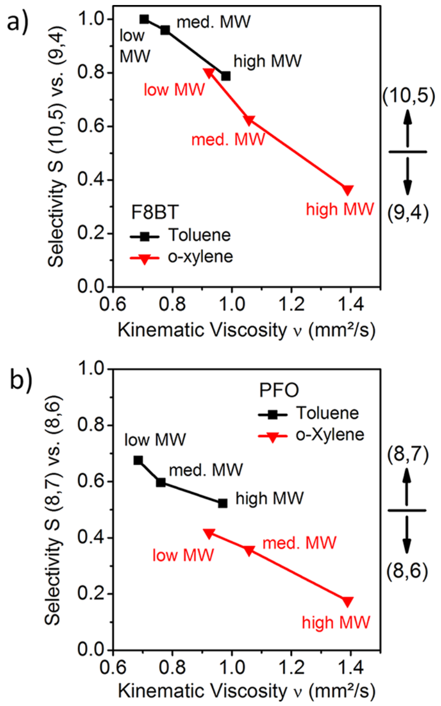


Figure 2. Selectivity *S* of (a) (10,5) vs (9,4) nanotubes dispersed in F8BT solutions and (b) (8,7) vs (8,6) nanotubes dispersed in PFO solution depending on their kinematic viscosity, varied by using different solvents (toluene and *o*-xylene) and different polymer molecular weights.

PFO solutions disperse several different SWNT species at much higher concentrations than F8BT but show similar behavior of decreasing selectivity for (8,7) versus (8,6)-SWNT with increasing molecular weight and solution viscosity (see Figure 2b and S3c of the SI). According to recent molecular modeling studies these two SWNT species are the most stable in PFO dispersions.[18] Interestingly (7,5) nanotubes remain quite abundant in all PFO dispersions, although their relative selectivity is somewhat lower compared to (8,7) and (8,6).

These deviations of both types of dispersions from previously published results[10] also highlight the role of the nanotube source material. Without using normalized values the selectivity for certain nanotube species might be over- or underestimated. The changeover of selectivity from lower viscosity toluene solutions to higher viscosity *o*-xylene solutions for two different polymers suggests that the selectivity for specific nanotube types depends, among other factors, on the solution viscosity.

To deconvolute the influence of solvent type and molecular weight on the selective dispersion, Figure 3 shows the PL intensities of individual nanotube species versus the kinematic viscosities of F8BT solutions. Here the viscosity is only varied by using different solvents while keeping polymer type and molecular weight (M_w = 85 kg/mol) constant. The range of viscosities is thus quite limited. PL intensities were corrected by chirality-specific fluorescence action cross sections (Φ) as determined by Tsyboulski et al.[26] Corresponding PL maps and absorption spectra are shown in Figures S3b and S5a of the SI, respectively. Overall, the amounts of both (10,5) and (9,4) nanotubes increase, and the selectivity for (10,5) nanotubes decreases with increasing viscosity although not as clearly as in Figure 2a. For PFO solutions (see Figure S6, SI), which disperse more species at much higher concentrations, we observe no clear correlation between solvent viscosity and selectivity.

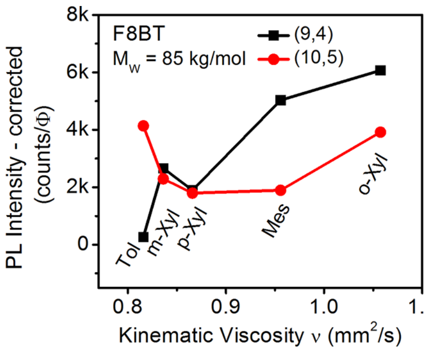


Figure 3. Corrected PL-intensities of (9,4) and (10,5) nanotubes in F8BT (M_w = 85 kg/mol) vs kinematic viscosity of solutions with different solvents (toluene, *m*-xylene, *p*-xylene, mesitylene, *o*-xylene).

Another way of increasing the viscosity without changing the molecular weight or solvent is varying the polymer concentration. For increasing F8BT (M_w = 153 kg/mol) concentrations (from 2 mg/mL to 10 mg/mL) with viscosities up to 3.3 mm^2/s (see Table S8, SI) we find larger amounts of nanotubes and a significantly reduced selectivity as expected (shown in Figure S7, SI).

The apparent dependence of selectivity and total amount of nanotubes on viscosity for F8BT may be explained by the relation between diffusion and rate of aggregation. For diffusion-limited aggregation of colloidal particles the rate constant is directly proportional to the diffusion constant. This also holds true for interaction-limited aggregation although multiplied with an exponential term for the aggregation activation energy.[27] This term would account for the steric stabilization of SWNT by the polymer wrapping, which is expected to depend on the nanotube–polymer interaction. If the activation energies are roughly similar for two types of nanotubes the diffusion constants become important again.

While F8BT-dispersed SWNT are significantly less stable than PFO-dispersed SWNT the energetic differences between (9,4) and (10,5) SWNT in F8BT, and similarly between (8,6) and (8,7) SWNT in PFO, might be small. Tsyboulski et al. showed that the translational diffusion constant D for nanotubes is inversely proportional to the dynamic viscosity η of the solution,[28] including L as the nanotube length, d as the diameter, and γ as a combined end-correction parameter:

$$D = \frac{k_B T}{6\pi\eta}\cdot\frac{2\ln(L/d) - \gamma}{L}$$

Due to the logarithmic dependence the diameter of the nanotubes has a negligible effect on the final diffusion constant for the nanotube species in question. The length distribution is expected to be similar for all. Assuming that during sonication all types of nanotubes are initially debundled and more or less wrapped by polymer, the rate of reaggregation for unstable and metastable SWNT-polymer complexes will depend on the diffusion constant and thus inversely on the viscosity. High viscosity solutions could kinetically stabilize slightly less-stable nanotube-polymer configurations such as (9,4)-SWNT/F8BT. This hypothesis is further supported by the fact that high viscosity solutions also disperse more nanotubes in total than low viscosity solutions.

An alternative explanation for the observed molecular weight dependence of selectivity involves nanotube surface coverage. A longer polymer chain could conceivably wrap itself around a certain length of nanotube (tens of nanometers) whereas for the same length several short polymer chains would be required, thus potentially leaving more or larger gaps of exposed SWNT and more polymer end-groups that could lead to reaggregation and lower PL efficiencies. Alternatively, one could speculate that longer polymer chains adopt a different wrapping geometry than shorter polymers, which could favor nanotubes with different chiralities. However, both concepts cannot explain the large differences between dispersions with high molecular weight polymer in toluene and *o*-xylene (see Figures 2 and S3a of the SI). They also assume perfectly equilibrated states of wrapping, which is unlikely to be completed directly after sonication when centrifugation takes place.[29]

To further corroborate the influence of viscosity on the reaggregation behavior of polymer−nanotube dispersions we investigated their long-term stability. Figure 4 shows absorption spectra of SWNT-dispersions with F8BT of different molecular weights recorded directly after sonication and centrifugation and after 32 days of storage and recentrifugation. The background-corrected maximum absorbance (A) and thus nanotube concentration increase with molecular weight of the polymer. This is consistent with the lower stability of oligomer dispersions shown by Berton et al.[30] After storage and recentrifugation the absorption background decreases significantly. In all three cases the amount of (9,4)-SWNT drops relative to that of (10,5)-SWNT. This agrees with the notion that the latter are ultimately more stable in dispersion than the former. The fraction of (10,5) compared to (9,4) nanotubes (defined as $A_{(10,5)}/(A_{(10,5)} + A_{(9,4)})$, without taking into account the HiPco source distribution) increases only slightly for high molecular weight solutions (from 0.33 to 0.37) compared to medium molecular weight (from 0.42 to 0.52). For low molecular weight F8BT the (10,5) peak is the only clearly distinguishable peak after 32 days. The different reaggregation kinetics over longer periods of time support the hypothesis that higher viscosities and reduced diffusion constants lead to a kinetic stabilization of less favorable SWNT−polymer complexes. PFO dispersions are more stable and hardly change in concentration or SWNT distribution over several weeks. Studying the reaggregation kinetics of polymer−nanotube dispersions with different viscosities could result in a stability ranking of the various polymer−nanotube combinations to confirm or refute molecular modeling results.

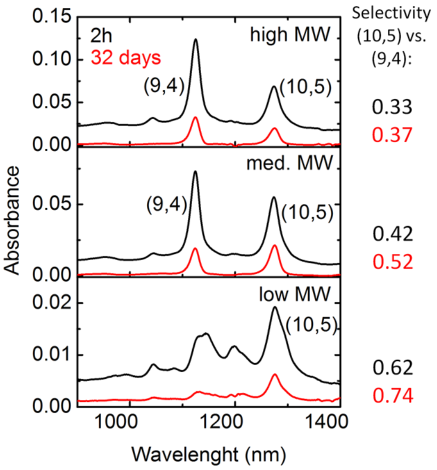


Figure 4. Absorption spectra of freshly prepared and centrifuged F8BT-based nanotube dispersions (black) and after 32 days of storage at room temperature and recentrifugation (red).

In conclusion, we find that both polymer molecular weight and type of solvent influence nanotube selectivity and concentration, possibly due to their impact on solution viscosity. We propose that reducing the diffusion constant of SWNT in dispersion by increasing viscosity allows for kinetic stabilization of less favorable polymer−SWNT hybrids. The viscosity can be tuned by the polymer molecular weight, concentration, and type of solvent. In particular the molecular weight of the dispersing polymer has a strong effect on the apparent selectivity and should always be taken into account when screening for suitable conjugated polymers for nanotube dispersion. If high selectivity is desired, low to medium molecular weights and low concentrations are preferable. High molecular weight polymers and more concentrated solutions are better suited for achieving high SWNT loadings and long-term dispersion stability although at the cost of selectivity.

■ EXPERIMENTAL METHODS

All conjugated polymers used in this study were supplied by Cambridge Display Technology Ltd. (low M_w, medium M_w, and high M_w F8BT and high M_w PFO) or purchased from American Dye Source (medium M_w F8BT-ADS, F8BT-ADSn, and low M_w PFO) and Sigma Aldrich (medium M_w PFO). Solvents (anhydrous, Sigma-Aldrich) were used as received. HiPco single-walled carbon nanotubes (diameter 0.8−1.2 nm, <13 wt % iron) were purchased from Unidym Inc. and used without further purification. Polymer solutions (2 mg/mL) were heated for 30 min at 70 °C to remove aggregates. After cooling nanotube powder was added at 2 mg/mL, and dispersions were homogenized in an ultrasonic bath (Branson 2510) for 60 min, followed by vigorous sonication using a tip sonicator (Sonics Vibra Cell) for 10 min. After centrifugation at 60 000 g for 30 min (Beckman Coulter Avanti J26XP centrifuge) the supernatant was collected and characterized. Absorption spectra (optical path length 10 mm) were recorded with a Varian Cary 6000i spectrometer. A Fluorolog-3 (Horiba Jobin-Yvon) spectrometer with an InGaAs array detector was used for PL excitation−emission measurements. Molecular weight distributions of all polymers were determined by gel permeation chromatography (GPC). Kinematic viscosity measurements of all solutions were performed with a Micro-Ostwald viscometer (capillary diameter 0.43 mm, length 290 mm) at 23 °C (AVS-470, Schott Instruments).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further information about the polymers, nanotube source material, solvent parameters, and dispersion selectivity. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jana.zaumseil@ww.uni-erlangen.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Cambridge Display Technologies Ltd. for the generous supply of conjugated polymers (PFO and F8BT). The authors are grateful to S. Michler for help with viscosity measurements and to M. Malter and I. Herzer for GPC measurements. This research was funded by the Deutsche Forschungsgemeinschaft (DFG ZA 638/3) and the Alfried Krupp von Bohlen and Halbach Foundation. Carbon nanotube research at the ZMP is supported by the SFB 953 "Synthetic Carbon Allotropes".

■ REFERENCES

(1) Charlier, J.-C.; Blase, X.; Roche, S. *Rev. Mod. Phys.* **2007**, *79*, 677−732.

(2) Lefebvre, J.; Maruyama, S.; Finnie, P. *Carbon Nanotubes*, Jorio, A.; Dresselhaus, G.; Dresselhaus, M. S., Eds.; Springer: Berlin/Heidelberg, 2008; Vol. *111*, pp 287−319.

(3) Rouhi, N.; Jain, D.; Burke, P. J. *ACS Nano* **2011**, *5*, 8471−8487.

(4) Sung, J.; Choi, Y. S.; Kang, S. J.; Cho, S. H.; Lee, T.-W.; Park, C. *Nano Lett.* **2011**, *11*, 966−972.

(5) Bindl, D. J.; Safron, N. S.; Arnold, M. S. *ACS Nano* **2010**, *4*, 5657−5664.

(6) Hersam, M. C. *Nat. Nanotechnol.* **2008**, *3*, 387−394.

(7) Zhang, H.; Wu, B.; Hu, W.; Liu, Y. *Chem. Soc. Rev.* **2011**, *40*, 1324−1336.

(8) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. *Nat. Nanotechnol.* **2006**, *1*, 60−65.

(9) Liu, H.; Nishide, D.; Tanaka, T.; Kataura, H. *Nat. Commun.* **2011**, *2*, 309−309.

(10) Nish, A.; Hwang, J.-Y.; Doig, J.; Nicholas, R. J. *Nat. Nanotechnol.* **2007**, *2*, 640−646.

(11) Gwinner, M. C.; Jakubka, F.; Gannott, F.; Sirringhaus, H.; Zaumseil, J. *ACS Nano* **2011**, *6*, 539−548.

(12) Khan, A. L. T.; Sreearunothai, P.; Herz, L. M.; Banach, M. J.; Köhler, A. *Phys. Rev. B* **2004**, *69*, 085201−085201.

(13) Chang, J.-F.; Sun, B.; Breiby, D. W.; Nielsen, M. M.; Sölling, T. I.; Giles, M.; McCulloch, I.; Sirringhaus, H. *Chem. Mater.* **2004**, *16*, 4772−4776.

(14) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Fréchet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312−3319.

(15) Donley, C. L.; Zaumseil, J.; Andreasen, J. W.; Nielsen, M. M.; Sirringhaus, H.; Friend, R. H.; Kim, J. S. *J. Am. Chem. Soc.* **2005**, *127*, 12890−12899.

(16) Hwang, J.-Y.; Nish, A.; Doig, J.; Douven, S.; Chen, C.-W.; Chen, L.-C.; Nicholas, R. J. *J. Am. Chem. Soc.* **2008**, *130*, 3543−3553.

(17) Lemasson, F.; Berton, N.; Tittmann, J.; Hennrich, F.; Kappes, M. M.; Mayor, M. *Macromolecules* **2011**, *45*, 1324−1336.

(18) Gao, J.; Loi, M. A.; de Carvalho, E. J. F.; dos Santos, M. C. *ACS Nano* **2011**, *5*, 3993−3999.

(19) Stürzl, N.; Hennrich, F.; Lebedkin, S.; Kappes, M. M. *J. Phys. Chem. C* **2009**, *113*, 14628−14632.

(20) Gaufrés, E.; Izard, N.; Vivien, L.; Kazaoui, S.; Marris-Morini, D.; Cassan, E. *Opt. Lett.* **2009**, *34*, 3845−3847.

(21) Hansen, C. M. *Hansen Solubility Paramters - A Users Handbook*, 2nd ed.; CRC Press: Boca Raton, FL, 2007.

(22) Bergin, S. D.; Sun, Z.; Rickard, D.; Streich, P. V.; Hamilton, J. P.; Coleman, J. N. *ACS Nano* **2009**, *3*, 2340−2350.

(23) Kitts, C. C.; Vanden Bout, D. A. *Polymer* **2007**, *48*, 2322−2330.

(24) Cheng, Q.; Debnath, S.; Gregan, E.; Byrne, H. J. *J. Phys. Chem. C* **2010**, *114*, 8821−8827.

(25) Ravve, A. *Principles of Polymer Chemistry*; Plenum Press: New York, 1995.

(26) Tsyboulski, D. A.; Rocha, J.-D. R.; Bachilo, S. M.; Cognet, L.; Weisman, R. B. *Nano Lett.* **2007**, *7*, 3080−3085.

(27) Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*, 3rd ed.; CRC Press: Boca Raton, FL, 1997.

(28) Tsyboulski, D. A.; Bachilo, S. M.; Kolomeisky, A. B.; Weisman, R. B. *ACS Nano* **2008**, *2*, 1770−1776.

(29) Cathcart, H.; Nicolosi, V.; Hughes, J. M.; Blau, W. J.; Kelly, J. M.; Quinn, S. J.; Coleman, J. N. *J. Am. Chem. Soc.* **2008**, *130*, 12734−12744.

(30) Berton, N.; Lemasson, F.; Tittmann, J.; Stürzl, N.; Hennrich, F.; Kappes, M. M.; Mayor, M. *Chem. Mater.* **2011**, *23*, 2237−2249.