TEMPO-Substituted PPEs: Polystyrene-PPE Graft Copolymers and Double Graft Copolymers

Yiqing Wang,[†] James N. Wilson,[†] Mark D. Smith,[‡] and Uwe H. F. Bunz*,[†]

School of Chemistry and Biochemistry, Georgia Institute of Technology, 770 State Street, Atlanta, Georgia 30332, and Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received August 17, 2004; Revised Manuscript Received October 9, 2004

ABSTRACT: A PPE containing benzylic TEMPO units on each second benzene ring, **8**, is reported; **8** has been reacted with styrene to give grafted PPE−polystyrene hybrids **10a** and **10b** with unusual optical properties. When **8** is reacted with 4-chloromethylstyrene, polymer **11** forms; **11** carries a poly(4-chloromethylstyrene) side chain that is on average 26 repeat units long. The polymer **11** can be reacted with 2-methyloxazoline to give a "grafted graft", i.e., a polymer in which the polystyrene grafts carry polyoxazoline substitutents. The polymer **12** is water-soluble and fluorescent.

Introduction

Synthesis and characterization of novel graft polymers with a poly(*p*-phenyleneethynylene) (PPE) backbone and polystyrene side chains is reported. The first example of a water-soluble double-grafted PPE is showcased.

In PPEs[1] phenylene groups are separated by alkyne linkages; PPEs are highly fluorescent, chemically robust and useful in sensory applications.[2−4] Their well-known thermochromicity,[5] solvatochromicity,[6] surfactochromicity,[7] and fluorescence quenching upon exposure to certain transition metals and viologen-type cations[8,9] makes them attractive as they combine signal generation, transduction and amplification handily in one package. Concepts such as molecular wire, amplified quenching and superquenching are connected with the PPE's photophysical behavior and have attracted significant attention.

The well-defined photophysics of the PPEs inspires the invention of novel macromolecular architectures that exploits their chromicity.[5−8] An elegant way of changing PPEs' architecture is the postsynthetic modification of side chains.[2,10] This economic approach introduces molecular diversity at the final stage of the synthetic scheme, *after* the polymerization event. In this contribution we describe the synthesis of a TEMPO-substituted PPE, **8**, as a precursor to grafted[11] polystyrene−PPEs,[12] **10**−**12**. The use of the TEMPO−PPE **8** is a conceptual progress in the synthesis of useful PPE-architectures. Polymers **10**−**12** have properties that differ from those of dialkyl−PPEs[5−7] as well as from their TEMPO-substituted precursor **8**. The 4-chloromethyl-substituted graft polymer **11** is functional but cannot be made by a regular Heck−Cassar−Sonogashira−Hagihara[1] reaction of a suitably grafted diiodoarene, due to the interference of the nucleophilic amines popular as solvent in these coupling reactions. Neither can **11** be made by the Breens method,[12] due to the reactivity of benzylic halides under their reaction conditions. The use of the PPE-module **8** as a precursor to **11** solves this problem.

* Corresponding author. Fax: (404) 385-1795. Telephone: (404) 385-1795. E-mail: uwe.bunz@chemistry.gatech.edu.
[†] Georgia Institute of Technology.
[‡] University of South Carolina.

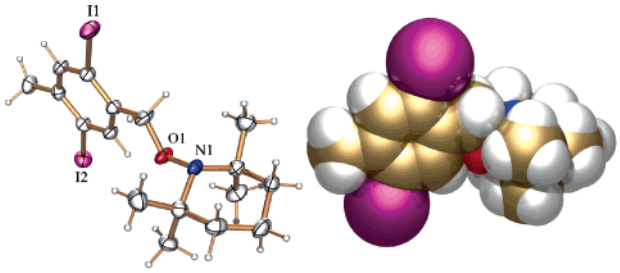


Figure 1. Atomic displacement plot and space filling representations of **6**. Bond lengths and bond angles are in agreement with expected standard values for C=C, C−C, C−H, C−I, C−N, N−O, and C−O bonds.

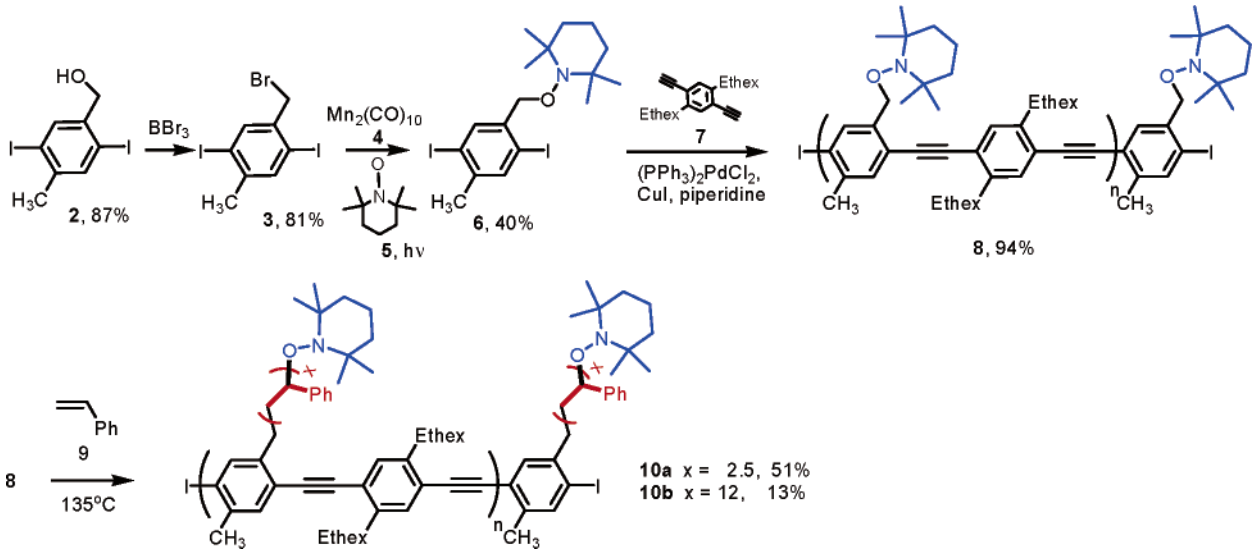
Results and Discussion

Syntheses (Schemes 1 and 2). The reduction of 2,5-diiodo-4-methylbenzoic acid (**1**) with the BH_3−THF complex furnished the benzylic alcohol **2** in 87% yield as sole product. The iodo-functionalities in **1** are not attacked by this mild reducing agent. BBr_3 transforms **2** smoothly into the benzylic bromide **3** (81%). Photochemical reaction of the bromide **3** with dimanganese decacarbonyl (**4**) and TEMPO (**5**)[13] gave rise to the formation of monomer **6** in 40% after chromatography. While the NMR spectra of **6** were supportive of its formation, a single-crystal X-ray structure analysis was performed to prove its topology.[14] Figure 1 shows two representations of **6**. The diiodide **6** was combined with diyne **7** in a Heck−Cassar−Sonogashira−Hagihara coupling.[1,15] The polymer **8** in formed in excellent yields and a degree of polymerization $P_n = 31$ ($M_n = 18 \times 10^3$; >60 phenyleneethynylene units) according to gel permeation chromatography (GPC, polystyrene standard); the obtained polydispersity $M_w/M_n = 3.1$ is typical for PPEs produced by these Pd-catalyzed reactions.[1]

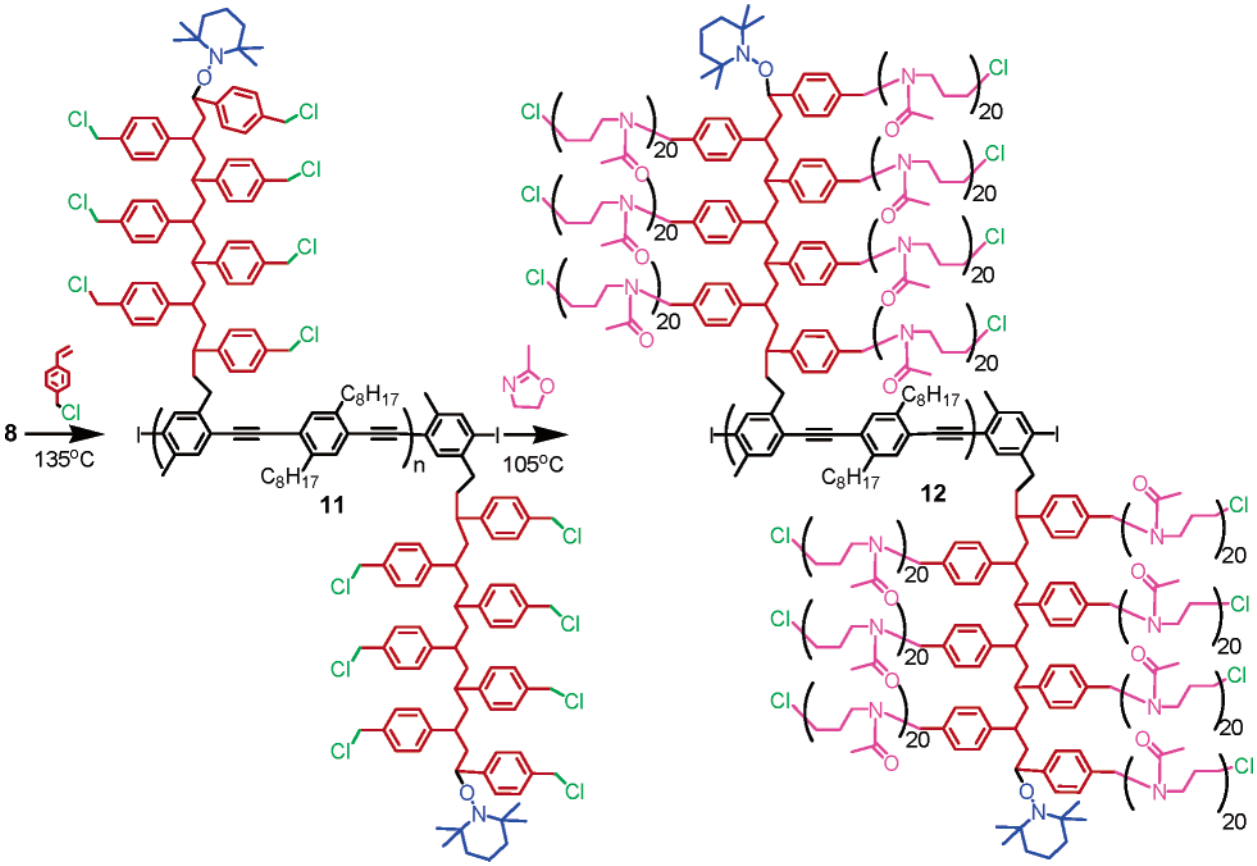
The structural integrity of **8** was proven by ^{1}H NMR, ^{13}C NMR, UV−vis, and fluorescence spectroscopies. Figure 2 shows the ^{13}C NMR spectrum of **8**. It is gratifying to see that the TEMPO group in **6** survives the Pd-catalyzed coupling without any problem. Two sets of signals were obtained by extracting the spectral information on bisethylhexyl−PPE (EPPE) and overlaying the peak positions with those of **8**. The resonances that are virtually identical to those of EPPE are represented in **8** by green arrows. Some of the "green"

10.1021/ma048308o CCC: $27.50
Published on Web 11/24/2004

Scheme 1. Synthesis of TEMPO-Substituted PPE 8 and the Grafted PPE–Polystyrene 10



Scheme 2. Synthesis of Grafted PPE–Polystyrene 11 and Its Super Graft 12



signals are split. Such a split is not visible in EPPE and the split is due to the random orientation of the second, non symmetrically substituted monomer unit that will lead to three dyads in **8** (Scheme 3). This asymmetry does not lead to a split of the signals attributable to the TEMPO-containing building block (red arrows), which is surrounded by the symmetrical bisethylhexylbenzene units. One of the aromatic signals of the TEMPO-carrying units in **8** is missing, masked by one of the "green" peaks. Diagnostic are the resonances at $\delta = 60$ and 76 ppm that represent the signals of the ar–$\boldsymbol{C}$H$_2$–O–N–$\boldsymbol{C}$Me$_2$–(CH$_2$)$_3$–$\boldsymbol{C}$Me$_2$ carbons, respectively. The alkyne peaks are most heavily split due to the stereochemical dyads. Four signals are expected and three are visible, one however with double intensity. The ^{13}C NMR spectrum strongly supports the structure of **8**.

Controlled radical polymerization is a powerful tool in polymer synthesis.[17,18] The TEMPO-substituted PPE **8** should be an excellent precursor to grafted PPE brushes. Heating **8** in the presence of 3 equiv of styrene (**9**) in acetic anhydride furnished polymer **10a** as an almost colorless but strongly blue emitting solid. The acetic anhydride is added to accelerate the reaction as described by Hawker et al.[18c] In **10a** the polystyrene side chains are very short and comprise only two to three repeating units. According to NMR spectroscopy, the

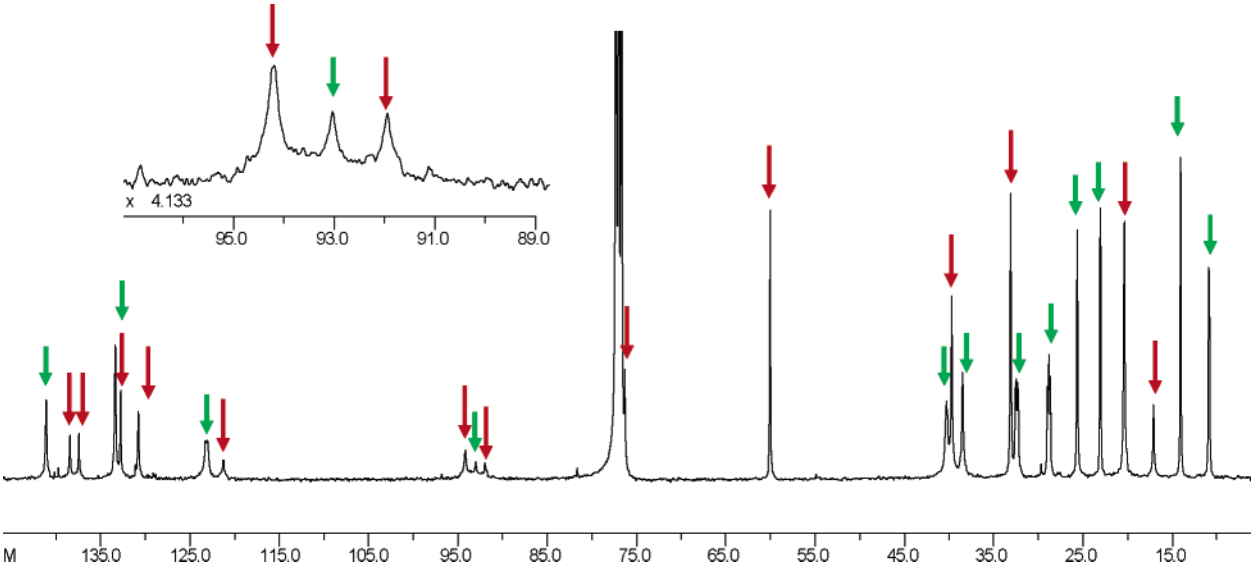
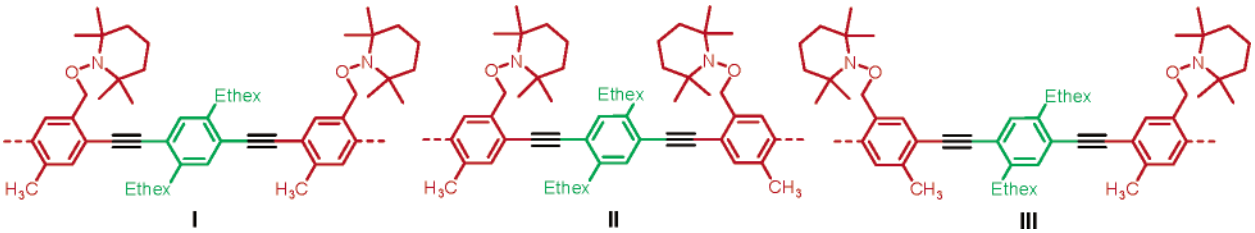


Figure 2. ^{13}C NMR spectrum of polymer **8** in $CDCl_3$. The spectrum is a additive composite of the spectrum of bis(ethylhexyl)−PPE and the spectrum of the TEMPO containing monomer. The green arrows highlight the signals that are attributed to the bis(ethylhexyl) part of the polymer. The interpretation of the signals was performed by overlay of the spectrum of **8** with that of bis(ethylhexyl)−PPE. The signal at $\delta = 77$ is due to $CDCl_3$ while the signal at $\delta = 81$ ppm stems from a solvent impurity.

Scheme 3. Three Dyads Encountered in the Structural Motifs of 8 and 10−12



unmolested TEMPO units are still attached to the polymer. The GPC of the polymer shows $M_n = 20 \times 10^3$ with an $M_w/M_n = 3.5$, similar to the GPC of **8**. In the case of polymer **10b**, the reaction was carried out in a mixture of neat styrene and acetic anhydride.[18c]

The weight amount of isolated polymer **10b** was three times that of the starting material after 3 h at 135 °C. As a consequence, its molecular weight should approximately have tripled. Comparing the GPC data of **8** to that of **10b**, M_n increased from 18×10^3 to 56×10^3 ($M_w/M_n = 3.2$)[5,6,19] which is in good agreement with the amount of uptake of styrene. Polymer **10b** has side chains that are composed of approximately 12 styrene units per phenyleneethynylene repeat unit according to GPC and mass balance. The excellent agreement between the GPC values and the molecular weight values obtained by mass calculations was surprising. A recent report[12b] of a similarly grafted PPE gave inconsistent molecular weight results when comparing the grafted to the "degrafted" polymers and both to the molecular weights of the isolated grafts. The polystyrene PPE grafts **10** modulate the optical properties of the backbone (vide infra). However, polystyrene appendages are nonfunctional to adapt receptor sites. Accordingly, **8** was heated with 4-chloromethylstyrene to 135 °C to furnish the poly(4-chloromethylstyrene) functionalized PPE **11**. According to the increase in weight of the product from 200 mg (**8**) to 760 mg (**11**) (factor of 3.8), the side chains must incorporate on average seven chloromethylstyrene units. The molecular weight (GPC) increases from 1.8×10^4 to 1.0×10^5, giving a factor of 5.6 as the molecular weight increase when going from **8** to **11**. Losses in the workup of **11** could account for this moderate discrepancy in the molecular weights. Because **11** is quite soluble, its ^{13}C NMR spectrum (Figure 3) shows prominent signals due to the polystyrene side chains and a set of signals of much lower intensity that corresponds to the signals seen for polymer **8** in the alkyl region. The alkyne signals of **11** are visible at $\delta = 93.6$ and 91.3 ppm, and the Ph−*C*H(CH_2)−O−N− signal, which is displayed in **8** at $\delta = 60.4$ ppm, is now split into two signals at $\delta = 61.5$ and 60.6. The split is due to the presence of diastereomers in **11**. The signal due to the chloromethyl groups is prominently visible at $\delta = 40.7$. PPE **11** is a functional polystyrene grafted PPE. Exposure of **11** to neat methyloxazoline at 105 °C furnished the polymer **12**.[20,21] The isolated material weighed 9.36 times as much as the starting material. If we neglect loss during workup, on average every chloromethylstyrene group carries a 20-meric polyoxazoline substituent. The overall molecular weight of **12**, $M_n = 9 \times 10^5$ amu. Attempts to perform gel permeation chromatography on **12** were unsuccessful, because **12** never eluted from the column, regardless if THF or chloroform was utilized as elution phase.

To get a quantitative picture of the molecular weights of the grafts, viscosimetry of **11**, **12**, polystyrene standards, and poly(2-ethyl-2-oxazoline) standards was performed. Table 2 shows the results of the viscosimetry (see the Experimental Section for details). The viscosity of **11** is higher than that of polystyrene with an M_n of 6.6×10^4 amu, and the recorded relative viscosity of 1.35 vs 1.28 is in excellent accord with the M_n obtained by GPC and weight increase. The higher viscosity of **11** when compared to the PS standard is probably due to the relatively rigid phenyleneethynylene backbone, but

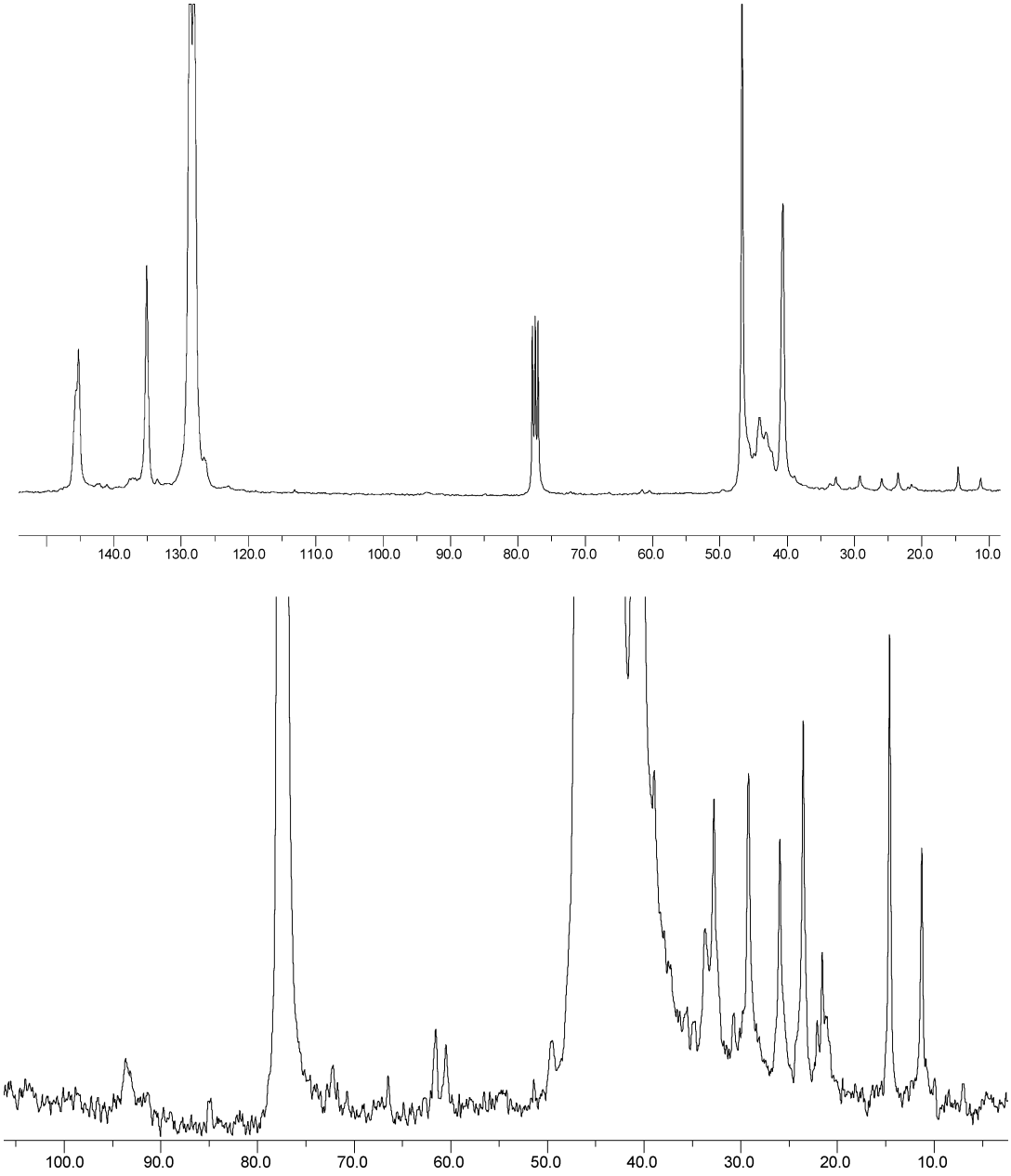


Figure 3. (a) Full spectrum of **11**. (b) Magnified section of the same spectrum. The spectra were taken in chloroform-*d*. The signal at $\delta = 93$ ppm is assigned to the alkyne carbons. The split signal at $\delta = 61$ ppm is due to the Ph−*C*(CH_2)H−O−N units at the active chain ends of the polystyrene substituent.

Table 1. Optical Data and Molecular Weight Information for 8 and 10−12

	8		**10a**		**10b**		**11**		**12**	
	solution	film	solution	film	solution	film	solution	film	solution	film
absorption (nm)	393	418	381	387	379	380	370	366	nd	nd
emission (nm)	428, 450 sh	444 sh, 462	428, 449 sh	436 sh, 473	428, 450 sh	431 sh, 462	428, 450 sh	469	425, 450 sh	427, 450
Φ	0.78	nd	0.62	nd	0.32	nd	0.36	nd	0.11; 0.026 in H_2O	nd
mol wt. by GPC	1.8×10^4		2.0×10^4		5.6×10^4		1.0×10^5		nd	
PDI (M_w/M_n)	3.1		3.5		3.2		3.1		nd	
mol wt. by wt increase	does not apply		2.2×10^4		3.7×10^4		6.8×10^4		9.0×10^5	

the difference is not too dramatic. In the case of **12**, there are no GPC data available. The relative viscosity of **12** (1.09) is in good agreement with the viscosity that has been obtained for the model polymers. While none of the model polyoxazolines have the same molecular weight as **12**, a standard with $M_w = 2 \times 10^5$ is available. Its relative viscosity is 1.08 and close to the relative viscosity measured for **12** suggesting that **12** has a molecular weight in excess of 2×10^5 (M_n determined by mass uptake $= 9 \times 10^5$). The viscosimetry measurements show that the molecular weights calculated by the mass uptake of **8** and **11**, respectively, upon grafting are reasonable. The grafts **11** and **12** behave less like rigid rods but more like floppy coils, as expected from the overall structures.

The ^{13}C NMR of **12** shows intense signals due to the polyoxazoline side chains. Signals due to the PPE backbone are not visible anymore. Polymers **10**−**12** are

Table 2. Viscosity Measurements of the Newly Synthesized Polymers

sample	efflux time, t (s)	mol wt [a]	concn (mg/mL)	relative viscosity, η_r [b]	specific viscosity, η_s [c]	reduced viscosity, η_{red} [d] (mL/mg)
polymer **11**	607	$M_n = 1.0 \times 10^5$	10	1.35	0.35	0.035
polystyrene standard	574	$M_n = 6.6 \times 10^4$	10	1.28	0.28	0.028
polystyrene standard	520	$M_n = 2.8 \times 10^4$	10	1.16	0.16	0.016
polymer **12**	489	M_w (estimated) $= 9.0 \times 10^5$	2.0	1.09	0.09	0.045
poly(2-ethyl-2-oxazoline)	467	$M_w = 5.0 \times 10^4$	2.0	1.04	0.04	0.020
poly(2-ethyl-2-oxazoline)	485	$M_w = 2.0 \times 10^5$	2.0	1.08	0.08	0.040

[a] PS standard from Showa Denko. Poly(2-ethyl-2-oxazoline) from Aldrich. [b] Relative viscosity $\eta_r = t/t_0$. [c] Specific viscosity, $\eta_s = (t - t_0)/t_0$. [d] Reduced viscosity, $\eta_{red} = \eta_s/c$.

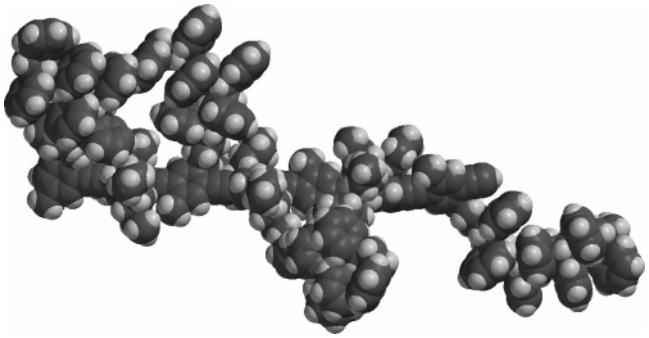


Figure 4. MM2 representation of an oligomer of **10b**.

freely soluble in chloroform and toluene and therefore are not cross-linked. Both polymer **10b** and **11** were investigated by DSC to show a glass transition point at 94 and 106 °C, respectively. These values are in good agreement with those of linear polystyrene that shows a glass transition point of 104 °C. Polymers **8** and **12** have more complex DSC traces that are difficult to interpret. They do not show clear melting or glass transition points. To visualize the shape of the PPEs, Figure 4 shows a MM2 representation of an oligomer of **10b**. During the minimization the main chain adopted a twisted conformation. The shown conformer is a *representative* conformer but probably not the global minimum.

Optical and Emissive Properties of 8 and 10—12. While TEMPO−PPE **8** is yellow in appearance in the solid state, the color of the grafted polymers **10** and **11** is consecutively lighter. The graft **12** displays only a slightly off-white hue, which stems mostly from the polyoxazoline side chain. All of the materials are strongly blue-turquoise emissive in the solid state. To quantify these observations we took UV−vis and emission spectra of **8**−**12** in solution and in the solid state. Figures 5 and 6 show the spectra of **8**−**11**, while Figures 7 and 8 show the emission spectra of **12** (Table 1).

In solution **8**, **10a,b**, and **11** show spectroscopic properties that are similar to those observed for dialkyl−PPEs (Figure 3).[1,5,7] We attribute the blue shift when going from **8** to **10** and **11** to an increased torsional twist of the benzene units in the PPE main chain with respect to each other. As a consequence, **11** has an absorption maximum of only 370 nm. The alternative explanation would be the disruption of the conjugated backbone by the addition of the radical centers to the CC-triple bond of the backbone. Upon cross-linking a *red* shift of the absorption would be expected. Why? Addition of a radical center to the triple bonds, followed by further reaction, would lead to a trisubstituted or tetrasubstituted double bond. Such a reaction would transform parts of the PPEs into PPVs *with a considerably smaller band gap*. A further radical reaction of the sterically shielded tri- or tetrasubstituted double bonds is not probable with a tetra- to hexasubstituted ethane derivative as end product. To exclude the radical addition scenario further, styrene was polymerized by a TEMPO starter, **6**, in the presence of didodecyl−PPE. After workup, the PPE was unchanged in absorption, emission, molecular weight, and polydispersity. From these experiments, we conclude that the changes in absorption and emission are not due to the production of defect structures, and that dialkyl−PPEs survive the process of radical polymerization unmolested. Attempts to obtain a UV−vis spectrum of **12** however failed, due to the tailing background absorption of the polyoxazoline side chains and the dilution of the PPE.

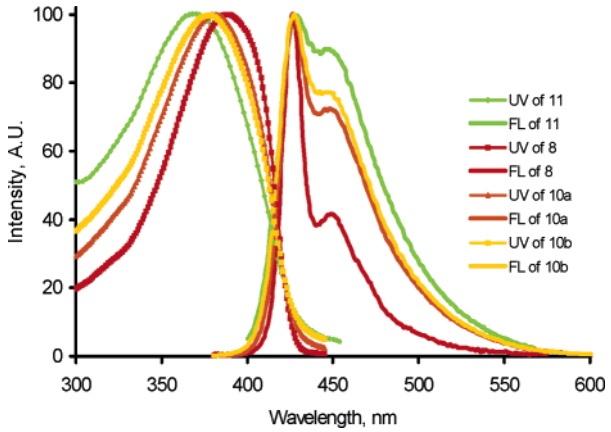


Figure 5. UV−vis spectra of **8**, **10**, and **11** in chloroform.

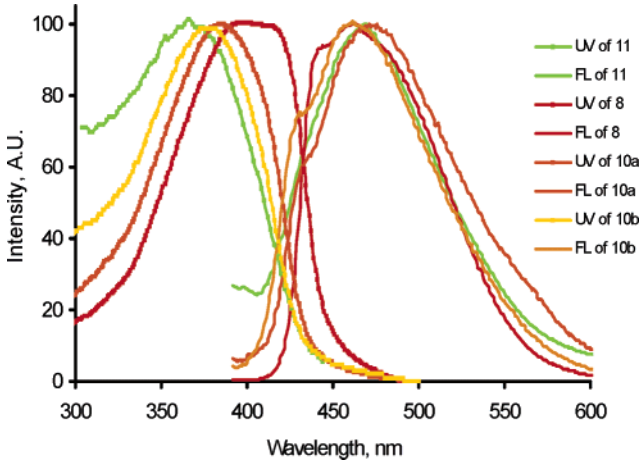


Figure 6. Optical data (emission and absorption) of **8**, **10**, and **11** in thin films.

When going into the solid state, the UV−vis absorption of **8** is significantly red shifted as expected for a dialkyl−PPE and λ_{max} is 418 nm. In thin films of

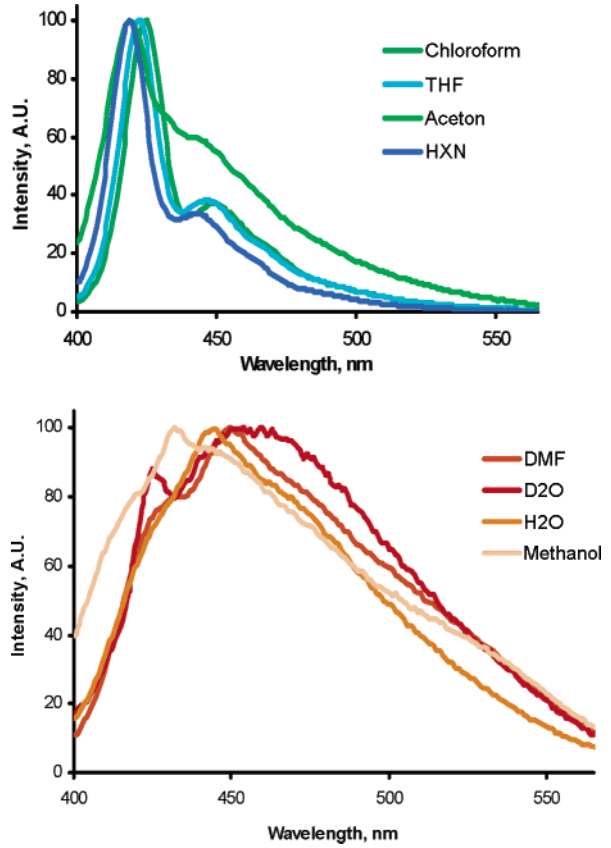


Figure 7. Emission spectra of **12** in different solvents. Top: Solvents in which **12** dissolves unaggregated. Bottom: Highly polar solvents which dissolve **12** in an aggregated form.

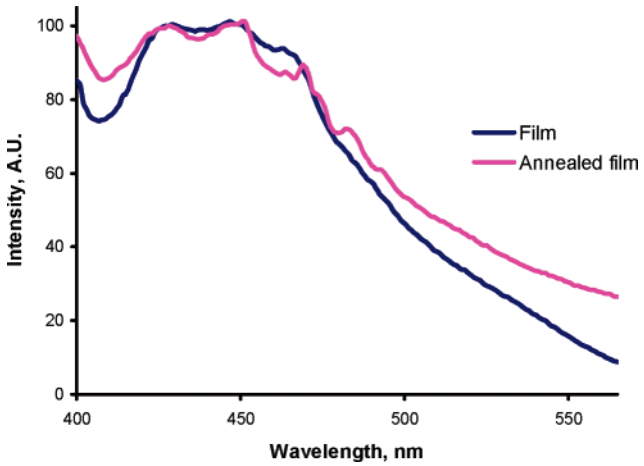


Figure 8. Emission spectra of **12** in the solid state.

didodecyl−PPE, λ_{max} is 445 nm. In the case of **8**, the bulky tetramethylpiperidine substituent perhaps decreases the propensity toward full planarization. In the case of **10b** and **11** the solid state absorption is almost unchanged compared to their solution spectra (Figure 6), even though the emission is significantly red shifted. Here, the polystyrene side chains act as "added on" disordered solvent and there is no significant difference in the UV−vis spectra in these materials in the solid state and in solution. These data suggest that in the main chain of **10b** and **11** the phenyl rings are twisted with respect to each other in the thin films. The UV−vis spectra of the PPE **10b** are mainly determined by the conformation of the side chain and not by the formation of aggregates. The polystyrene side chains lead to a rotational disorder in the conformation of the main chain by acting as disordered/disordering solvent.

The emission spectra of **8** and **10**−**11** in chloroform, a good solvent for all of these polymers, are shown in Figures 5−7. All of the investigated PPEs emit at 428 nm and show a shoulder at 450 nm. It is noteworthy that the shoulder grows when going from **8** to **10b** and then to **11**. It was ruled out that this spectral change was due to self-absorption. The interpretation of the increase of the shoulder at 450 nm is nontrivial and connected to increasing vibronic coupling of ground and excited states.[22] These bands are not a sign of aggregation or excimer formation. In the emission spectrum of **12** the shoulder at 450 nm is decreased when compared to that of its precursor **11**. The quantum yield of emission decreases from 0.78 for **8** to 0.11 for **12** (in chloroform). There could be two reasons for the decrease: (a) the increased vibronic coupling opens up nonradiative vibronically coupled pathways, in corroboration with the increase observed for the shoulder at 450 nm, and (b) in the case of **12**, small amounts of absorbing impurities will quench the fluorescence of the main chain by a FRET[23] mechanism. And indeed, we were not able to obtain a satisfactory UV−vis spectrum of **12** due to a general background and tailing absorbance observed after the addition of the polyoxazoline chains suggesting that the latter explanation is the correct one. Polymer **12** shows an interesting fluorescence behavior. In polar solvents, including water and D_2O, the emission of **12** shifts to 450 nm, and broadens considerably. The broadening is so severe that both increased vibronic coupling as well as excimer formation via aggregation could play a role, while the emission quantum yield drops from $\Phi = 0.11$ to $\Phi = 0.026$.

In the solid state the emission of **8**−**11** is centered between 460 and 470 nm. The emission is broad and unstructured, suggesting some excimer formation of twisted chains. Excimer formation of *planarized chains*[24a] leads to a strong and broad emission centered around 540 nm. This is in good agreement with the finding that emission of twisted PPE chains is blue shifted.[24b] An additional blue-shifted shoulder is observed at 430−440 nm. Again the interpretation of the data is somewhat ambiguous; the broad emission could either be due to excimers combining twisted chains, or it could be due to a broadening brought about by the increase in the Huang-Rys factors and the increased vibronic coupling.[22] In the future we will investigate the emissive lifetimes of **10**−**12** in solution and in the solid state to gain insight into the operating mechanisms of excimer formation.

Conclusions

In conclusion we have made the novel TEMPO substituted PPE **8** by the Pd-catalyzed reactions of the Heck−Cassar−Sonogashira−Hagihara type, with the TEMPO groups surving the Pd catalysis without problems. We have shown that **8** undergoes controlled radical polymerization at elevated temperatures to give the graft copolymers **10** and **11**. The radical reaction proceeds without interference of the triple bonds of the PPE-backbone. The graft copolymers **10** and **11** show interesting optical properties that are interpreted as a result of the twisted nonplanar conformation of neighboring phenyl groups due to the steric needs of the long side chains. These PPEs therefore should show more of a cylindrical than a lamellar morphology in the solid-

state according to a model proposed by Neher.[24] The grafted PPE **11** is attractive because it has potential to be transformed into novel functionalized polymers. A proof of concept experiment was the synthesis of the doubly grafted water-soluble PPE **12**. In future, we will report upon the reaction of **8** with other polymerizable groups to give grafted PPEs with unusual sensory and structural properties and explore the physical properties and photophysical traits of these fascinating conjugated grafts in more detail.

Experimental Section

Materials. Styrene (99%) and 4-vinylbenzyl chloride (95%) were purchased from Aldrich. Both of these monomers were passed through a basic alumina column to remove the inhibitor and used immediately. All other reagents were used as received from Acros or Aldrich. Solvents were utilized unpurified and are ACS or technical quality.

Instrumentation. The ^{1}H and ^{13}C NMR spectra were taken on a Varian 300 MHz spectrometer using a broadband probe operating at 300 MHz (proton) and 75 MHz (^{13}C). UV−vis measurements were made with a Shimadzu UV-2401PC recording spectrophotometer. Fluorescence data were obtained with a Shimadzu RF-5301PC spectrofluorophotometer. Fluorescence quantum yields were determined in relation to quinine sulfate ($\approx 10^{-6}$ M in 0.1 M H_2SO_4, $\Phi_F = 0.54$) according to ref 26. The concentration of the polymers was such that their absorptivity was <0.1 at the excitation wavelength. It was as well made sure that the absorptivity of the solution was <0.05 at the half-intensity of the fluorescence. The polymers were utilized in concentrations that ranged from 0.3 to 8 mg L^{-1}. IR data were collected by a Shimadzu FTIR-8400S infrared spectrophotometer. A Headway Research model PWM32 instrument was used to spin-coat dilute chloroform saturated solutions (~10 mg/mL) and filtered off polymer onto quartz slides at 1500 rpm for 30 s for thin film experiments. The average thin film thickness is about 50 nm. GPC measurements were conducted in chloroform (25°C) with a Shimadzu SCL-10A VP UV−vis detector. The molecular weights were determined vs polystyrene standards.

Molecular Modeling. The modeling was performed utilizing the SPARTAN program suite from Wavefunction (www.wavefun.com) implemented on a Pentium IV 3.6 GHz windows machine. The utilized force field was MM2.

Polymer Viscosity Measurements. Polymer relative viscosity was measured by a Cannon-Fenske viscometer (Size 25) in DMF at 25 °C. DMF efflux time, $t_0 = 450$ s was set as the relative standard.

Synthesis of 2. To a nitrogen-purged 250 mL round-bottom flask was added **1** (7.76 g, 20.0 mmol) and dry THF (50 mL). The mixture was stirred under nitrogen at 0 ° C until the acid dissolved. BH_3·THF (1.0 M in THF, 30.0 mL, 30.0 mmol) was added dropwise. The solution was stirred at 0 °C for another 30 min and then warmed to room temperature for 24 h. The solution was quenched with ice-cold water (100 mL), and a white precipitate formed in the water after the THF was removed. The crude product was dissolved in ether and purified by column chromatography with eluent ether to obtain the product as a colorless solid (6.50 g, 87%). IR (KBr, cm^{-1}) = 3351, 3206, 2969, 2850, 1701, 1694, 1466, 1437, 1376, 1325, 1294, 1255, 1183, 1136, 1063, 1039, 1002, 984, 896, 880, 862, 688. Mp = 186−187 °C. ^{1}H NMR ($CDCl_3$): δ = 7.78 (s, 1H), 7.73 (s, 1H), 4.30 (s, 2H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 143.13, 142.23, 139.87, 138.24, 101.96, 97.31, 68.47, 27.05. Anal. Calcd for $C_8H_8I_2O$: C 25.69, H 2.16; Found: C 25.53, H 2.16.

Synthesis of 3. To a nitrogen purged 250 mL round-bottom flask were added **2** (6.50 g, 17.4 mmol) and toluene (50 mL). BBr_3 (5.30 g, 21.2 mmol) was added via syringe. The reaction was stirred at room temperature for 3 h under inert atmosphere. The reaction mixture was poured into ice-cold water, and the organic layer was washed with water (3 × 100 mL) and then dried over $MgSO_4$. The solvent was subsequently removed in vacuo. The crude product was purified by crystallization from hexanes to yield a colorless solid (6.12 g, 81%). Mp = 157−158 °C. IR (KBr, cm^{-1}) = 3027, 3060, 2958, 2916, 2847, 1574, 1465, 1434, 1419, 1371, 1340, 1260, 1220, 1208, 1190, 1002, 894, 888, 870, 794, 788, 759, 709, 627. ^{1}H NMR ($CDCl_3$): δ = 7.84 (s, 1H), 7.73 (s, 1H), 4.42 (s, 2H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 141.21, 141.13, 140.82, 140.26, 100.58, 99.83, 37.91, 27.80. Anal. Calcd for $C_8H_7BrI_2$: C 21.99, H 1.62. Found: C 21.85, H 1.64.

Synthesis of 6. To a 100 mL Schlenk tube were added **3** (2.18 g, 5.00 mmol), **5** (1.24 g, 7.94 mmol), **4** (0.390 g, 1.00 mmol), and toluene (20 mL). The tube was degassed and then filled with nitrogen. The flask was irradiated by a broadband sunlight lamp for 24 h. The reaction mixture was filtered and purified by column chromatography (hexanes) to obtain **6** as a colorless solid (1.03 g, 40%). Mp = 126−128°C. IR (KBr, cm^{-1}) = 2962, 2959, 2903, 2842, 1444, 1373, 1352, 1335, 1260, 1256, 1243, 1183, 1132, 1129, 1041, 1036, 1025, 926, 876. ^{1}H NMR ($CDCl_3$): δ = 7.87 (s, 1H), 7.62 (s, 1H), 4.72 (s, 2H), 2.38 (s, 3H), 1.60−1.20 (m, 6H), 1.20−1.10 (d, 12H). ^{13}C NMR ($CDCl_3$): δ = 142.10, 140.45, 139.48, 138.38, 101.16, 96.55, 81.38, 60.41, 40.07, 33.36, 27.62, 20.85, 17.48. Anal. Calcd for $C_{17}H_{25}I_2NO$: C 39.79, H 4.91, N 2.73. Found: C 40.06, H 5.04, N 2.69.

Synthesis of Polymer 8. A 50 mL Schlenk flask was charged with **6** (513 mg, 1.00 mmol), **7** (351 mg, 1.00 mol), THF (5 mL), piperidine (1.50 mL), $(PPh_3)_2PdCl_2$ (2 mg, 2.8 μmol), and CuI (1 mg, 5.3 μmol). The flask was degassed and filled with nitrogen. The reaction was allowed to stir at room temperature for 24 h. The reaction mixture was filtered over silica on a fritted funnel with hexane. After the hexanes were evaporated off, the crude product was dissolved in chloroform (10 mL) and was slowly added into methanol (300 mL). A bright yellow solid (603 mg, 94%) was obtained. IR (KBr, cm^{-1}) = 2949, 2924, 2920, 2915, 2907, 2891, 2870, 2853, 1501, 1464, 1456, 1447, 1378, 1373, 1359, 893. ^{1}H NMR ($CDCl_3$): 7.68 (br s, 1H), 7.42−7.20 (br m, 3H), 5.10 (br s, 2H), 2.93−2.61 (br s, 4H), 2.47 (br s, 3H), 1.90−1.05 (m, 36H), 1.00−0.75 (bd, 12H). ^{13}C NMR ($CDCl_3$): δ = 141.29, 138.60, 137.64, 133.65, 133.08, 123.43, 121.57, 94.50, 93.32, 92.29, 76.51, 60.39, 40.67, 40.12, 38.82, 33.42, 32.78, 26.05, 23.47, 20.81, 17.54, 14.53, 11.39. GPC (vs polystyrene standards in chloroform): $M_n = 18 \times 10^3$, $P_n = 31$, $M_w/M_n = 3.1$. Quantum yield (in chloroform): 0.78.

Synthesis of 10a. An oven-dried 50 mL Schlenk flask was charged with **8** (200 mg, 0.329 mmol; counted by the TEMPO functional group), **9** (208 mg, 2.00 mmol), xylene (3 mL), and acetic anhydride (20 mg, 0.196 mmol). The flask was degassed by three freeze−pump−thaw cycles and refilled with nitrogen. The reaction was allowed to stir at 135 °C for 8 h. The solution was precipitated slowly into methanol (200 mL). A light yellow solid was obtained (242 mg, 51% with respect to utilized styrene). GPC (vs polystyrene standards in chloroform): $M_n = 20 \times 10^3$, $M_w/M_n = 3.5$. IR (KBr, cm^{-1}) = 3080, 3059, 3025, 2917, 2907, 2897, 2846, 1945, 1900, 1780, 1701, 1600, 1492, 1451, 1373, 1359, 1180, 1027, 905, 892, 758, 698. ^{1}H NMR ($CDCl_3$): δ = 7.83−6.75 (m, 28H), 5.10−5.00 (br s, 2H), 3.03−2.00 (m, 14H), 2.00−0.20 (m, 54H). ^{13}C NMR ($CDCl_3$): δ = 145.82, 143.29, 141.27, 138.61, 137.59, 133.57, 132.99, 130.99, 128.181, 123.38, 121.54, 94.52, 93.81, 92.24, 60.37, 40.68, 38.87, 33.49, 32.85, 30.10, 29.22, 26.52, 23.51, 20.80, 17.55, 14.55, 11.27. Quantum yield (in chloroform): 0.62.

Synthesis of 10b. An oven-dried 50 mL Schlenk flask was charged with **8** (200 mg, 0.329 mmol counted by the TEMPO functional group), styrene (5 mL), and acetic anhydride (20 mg, 0.196 mmol). The flask was degassed and filled with nitrogen. The reaction was allowed to stir at 135 °C for 3 h during which the reaction mixture solidified. Chloroform (20 mL) was added into the flask to dissolve the solid, and the solution was precipitated into methanol (200 mL). A very lightly yellow polymer was obtained (631 mg, 13% with respect to used styrene). IR (KBr, cm^{-1}) = 3081, 3057, 3024, 3000, 2921, 2912, 2896, 2849, 1600, 1492, 1451, 1374, 1360, 1180, 1066, 1027, 906, 747, 697. ^{1}H NMR ($CDCl_3$): 7.45 (br m), 7.42−6.30 (br m), 2.40−1.0 (br m), 1.00−0.85 (br s). ^{13}C NMR ($CDCl_3$): δ = 145.51, 128.16, 125.87, 44.11, 43.89, 40.67, 32.86,

29.14, 25.96, 23.47, 20.75, 14.54. GPC (vs polystyrene standards in chloroform): $M_n = 56 \times 10^3$, $M_w/M_n = 3.2$. Quantum yield (in chloroform): 0.32.

Synthesis of 11. An oven-dried 50 mL Schlenk flask was charged with **8** (200 mg, 0.329 mmol counted by the TEMPO functional group), 4-vinylbenzyl chloride (5 mL), and acetic anhydride (20 mg, 0.196 mmol). The flask was degassed and filled with nitrogen. The reaction was allowed to stir at 135 °C for 3 h during which the reaction mixture solidified. Chloroform (20 mL) was added into the flask to dissolve the solid and the solution was precipitated into methanol (200 mL). A lightly yellowish polymer was obtained (760 mg, 14% with respect to used styrene). IR (KBr, cm^{-1}) = 638, 665, 672, 708, 744, 798, 814, 821, 832, 911, 946, 965, 1018, 1108, 1182, 1213, 1240, 1265, 1315, 1352, 1421, 1443, 1507, 1610, 1909, 2848, 2923, 2988, 3015, 3025, 3050, 3087. ^{1}H NMR ($CDCl_3$): 7.60−6.90 (br s), 6.90−6.20 (br s), 4.90−4.20(br s), 2.40−0.50 (br m). ^{13}C NMR ($CDCl_3$): δ = 145.1 (ps), 145.0 (ps), 134.8 (ps), 128.7 (ps), 128.1 (ps), 93.6 (alkyne), 91.3(alkyne), 61.5, 60.6, (both *C*H−O−N), 46.7 (ps), 44.1 (ps), 43.1 (ps), 42.3 (ps), 40.7 (ps), 33.6, 32.8, 29.2, 26.0, 23.5, 21.6, 14.6, 11.3 (ethylhexyl signals and signals due to the TMP group). GPC (vs polystyrene standards in chloroform): $M_n = 10 \times 10^4$, $M_w/M_n = 3.1$. Quantum yield (chloroform): 0.36.

Control Experiment. An oven-dried 50 mL Schlenk flask was charged with **6** (103 mg, 0.200 mmol), styrene (1 mL), *p*-xylene (5 mL), didocecyl−PPE (381 mg, 0.872 mmol, P_n = 252 according to GPC, PDI = 2.33), and acetic anhydride (5 mg, 0.05 mmol). The flask was degassed and filled with nitrogen. The reaction was allowed to stir at 135 °C for 24 h. Chloroform (5 mL) was added into the flask and the solution was precipitated from methanol (200 mL).

Synthesis of 12. To a 50 mL nitrogen purged round-bottom flask were added **11** (100 mg) and 2-methyl-2-oxazoline (3.57 g, 42.0 mmol). The flask was heated to 105 °C. The reaction was stopped after 12 h when the mixture was solidified. The solid was dissolved in chloroform (10 mL), and then the solution was precipitated into ethyl ether (200 mL). A slightly off-white polymer was obtained (931 mg, 25% with respect to utilized 2-methyl-2-oxazoline). IR (cm^{-1}): 672, 763, 777, 885, 969, 1026, 1115, 1244, 1300, 1361, 1411, 1422, 1488, 1635, 1652, 1732, 1771, 2913, 3241. ^{1}H NMR ($CDCl_3$): δ = 3.60−3.15 (br s), 2.40−2.20 (br s), 2.20−1.80 (br m). GPC: unable to determine. $M_n = 90 \times 10^4$ (estimated by weight). Quantum yield (in chloroform): 0.11.

Acknowledgment. The authors thank the National Science Foundation (CHE 0138-659, PI U.H.F.B.) for funding. U.H.F.B. is a Camille Dreyfus Teacher−Scholar (2000−2005).

Supporting Information Available: A .cif file containing details of crystallographic data of **6** (CCDC 233728). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (b) Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998. (c) Huber, C.; Bangerter, F.; Caseri, W. R.; Weder, C. *J. Am. Chem. Soc.* **2001**, *123*, 3857.

(2) Wilson, J. N.; Wang, Y.; Lavigne, J. J.; Bunz, U. H. F. *Chem. Commun.* **2003**, 1626.

(3) (a) Pinto, M. R.; Schanze, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *101*, 7505. (b) Pinto, M. R.; Schanze, K. S. *Synthesis* **2002**, 1293.

(4) (a) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864. (b) Kim, T. H.; Swager, T. M. *Angew. Chem.* **2003**, *42*, 4803.

(5) Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652.

(6) (a) Kim, J.; Swager, T. M. *Nature (London)* **2001**, *411,* 1030−1034. (b) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658.

(7) (a) Lavigne, J. J.; Broughton, D. L.; Wilson, J. N.; Erdogan, B.; Bunz, U. H. F. *Macromolecules* **2003**, *36*, 7409−7412. (b) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655.

(8) Swager, T. M.; Zhou, Q. *J. Am. Chem. Soc.* **1995**, *117*, 12593. Haskins-Glusac, K.; Pinto, M.; Tan, C.; Schanze, K. *J. Am. Chem. Soc.* **2004**, *126*, 14964.

(9) Kim, I.-B.; Erdogan, B.; Bunz, U. H. F. *Chem.—Eur. J.*, in press.

(10) Wagner, M.; Nuyken, O. *Macromolecules* **2003**, *36,* 6716.

(11) Wang, Y. Q.; Erdogan, B.; Wilson, J. N.; Bunz, U. H. F. *Chem. Commun.* **2003**, 1634.

(12) (a) Breen, C. A.; Deng, T.; Breiner, T.; Thomas, E. L.; Swager, T. M. *J. Am. Chem. Soc.*, **2003**, *125*, 9942. (b) Kuroda, K.; Swager, T. M. *Macromolecules* **2004**, *37*, 716.

(13) Gilbert, B. C.; Kalz, W.; Lindsay, C. I.; McGrail, P. T.; Parsons, A. F.; Whittaker, D. T. E. *Tetrahedron Lett.* **1999**, *40*, 6095.

(14) Crystal data for **6**: $C_{17}H_{25}I_2NO$, triclinic, $M = 513.18$ g cm^{-3}, space group = $P\bar{1}$. $T = 150(2)$ K, Mo Kα, $a = 8.0000(5)$ Å, $b = 11.5696(7)$ Å, $c = 11.8431(7)$ Å, $\alpha = 62.9210(10)°$, $\beta = 76.8720(10)°$, $\gamma = 76.0130(10)°$, $Z = 2$, $D = 1.816$ g cm^{-3}, $\mu = 3.351$ mm^{-1}, 7588 measured reflections, 3298 independent reflections, R (R_w) = 0.0225.

(15) Negishi, E.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979.

(16) (a) Beck, J. B.; Kokil, A.; Ray, D.; Rowan, S. J.; Weder, C. *Macromolecules* **2002**, *35*, 590. (b) Ricks, H. L.; Choudry, U. H.; Marshall, A. R.; Bunz, U. H. F. *Macromolecules* **2003**, *36*, 1424.

(17) (a) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901. (b) Greszta, D.; Matyjaszewski, K. *J. Polym. Sci., Part A* **1997**, *35*, 1857. (c) Patten, T. E.; Xia, J. H.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.

(18) (a) Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373. (b) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904. (c) Malmstrom, E.; Miller, R. D.; Hawker, C. J. *Tetrahedron* **2001**, *53*, 15225.

(19) A bimodal distribution was observed in **10b** with the second considerably smaller peak showing an M_n of 1.7×10^6. We attribute the second peak to aggregation of **10b.**

(20) (a) Inoue, S.; Aida, T. In *Ring opening polymerization* Brunelle, D. J., Ed.; Hanser Verlag: München, Germany, 1993; Chapter 6. (b) Saegusa, T.; Ikeda, H.; Fujii, H. *Polym, J.* **1973**, *4*, 87.

(21) Wang, Y.; Solntsev, K. M.; Tolbert, L M.; Bunz, U. H. F. *Macromolecules*, submitted for publication.

(22) Bässler, H. in Müllen, K.; Wegner, G., Eds.; *Electronic materials, the oligomer approach,* Wiley-VCH: Weinheim, Germany, 1998.

(23) Wang, S.; Gaylord, B. S.; Bazan, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 5446.

(24) (a) Imhof, J.; Bly, R. K.; Bangcuyo, C. G.; Bunz, U. H. F.; Vandenbout, D. A. *J. Am. Chem. Soc.,* submitted for publication. (b) Sluch, M. I.; Godt, A.; Bunz, U. H. F.; Berg, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 6447.

(25) Neher, D. *Adv. Mater.***1995**, *7*, 691.

(26) The experimental details for the determination of the quantum yields were obtained from: http://www.jobinyvon.com/usadivisions/Fluorescence/applications/quantumyieldstrad.pdf.

MA048308O