

SURFACE FUNCTIONALIZATION OF VAPOR-GROWN CARBON NANOTUBE AND IN-SITU POLYMERIZATION OF 3-PHENOXYBENZOIC ACID WITH VAPOR-GROWN CARBON NANOTUBE

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Introduction

Extensive researches have been performed on CNT or vapor-grown carbon nanotube (VGCNT) and reported their reinforcement in various thermoplastics and thermoset matrices [1-3]. However, despite of the extraordinary thermal, mechanical, and electrical properties predicted for carbon nanotubes (CNT) [4], the properties of CNT/polymer nanocomposites are not as good as expected. There would be two main reasons. One is that the difficulty in homogeneous dispersion of CNT into polymer solution or polymer matrix due to the strong static interaction between CNTs. The other would be lack of physical interaction between CNT and polymer due to smooth surface of CNTs. To make good dispersion and to increase surface roughness of CNT, surface modification of CNTs to enhance their chemical compatibility and dissolution properties for CNT/polymer nanocomposites is necessary. As a means to achieve a homogeneous dispersion of single wall carbon nanotube (SWNT) in viscous reaction medium such as polyphosphoric acid (PPA) at 190°C, in-situ polymerization of polybenzoxazole (PBO) with SWNT has been reported recently [5]. However, the stability of SWNT in such harsh conditions is questionable. On the other hand, VGCNT is relatively stable. Although the diameter of VGCNT is 10~100 times bigger than SWNT, their cost and stability make it more attractive for uses in polymer reinforcement.

Polyetherketones (PEKs) are a class of high-performance engineering plastics because of their unique mechanical and thermal properties [6]. Both aromatic electrophilic substitution reactions (Friedel-Crafts acylation reaction) and aromatic nucleophilic substitution reactions are versatile methods to synthesize PEKs. We reported the use of PPA/P₂O₅ as a non-toxic, non-volatile, and relatively less corrosive media to yield high molecular weight PEKs [7-8].

As an approach to impart covalent adhesion between a thermoplastic matrix and reinforcing CNT or VGCNT, we investigate the possibility of functionalizing VGCNT by a

model reaction of C₆₀ with an acylium precursor in PPA/P₂O₅ and in-situ polymerization of PEK with various amount of VGCNT. The results on the characterization of the PEK/VGCNT composites are presented.

Experimental

Model reaction with C₆₀. Into a 100 mL resin flask equipped with a high torque mechanical stirrer, nitrogen inlet and outlet, and pressure regulator, 4-(2,4,6-trimethylphenoxy)benzoic acid (0.27g, 1.05 mmol), C₆₀ (Strem Chemicals, 99.9% purity; 0.11g, 0.15 mmol), and PPA (83% assay, 20g) were placed and stirred with dried nitrogen purging at 100°C for 3h and P₂O₅ (5.00g) was then added. The mixture was heated at 130°C for 48h. At the end of the reaction, water was added into the flask. The resulting gray powder was collected by suction filtration, washed with diluted ammonium hydroxide, and then Soxhlet extracted for 72h under the nitrogen, and finally dried under phosphorous pentoxide under reduced pressure (0.05 mmHg) at room temperature for 12h to yield 0.31g of crude gray solid: mp 205-230°C. Anal. Calcd. for C₁₅₆H₉₀O₁₂: C, 86.89%; H, 4.21%. Found: C, 85.19%; H, 4.40%.

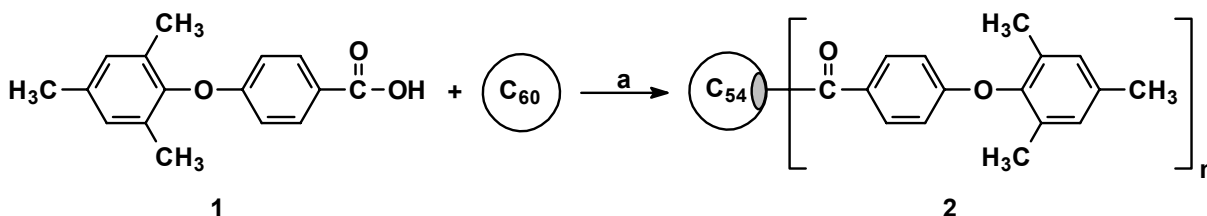
Model reaction with VGCNT. Into a 250 mL resin flask equipped with a high torque mechanical stirrer, and nitrogen inlet and outlet, 4-(2,4,6-trimethylphenoxy)benzoic acid (2) (0.50g, 1.95 mmol), and VGCNT (0.50g), and PPA (83% assay, 20g) was placed and stirred with dried nitrogen purging at 130°C for 3h. P₂O₅ (5.0g) was then added in one portion. The initially dark mixture became deep brown after 24h. The temperature was maintained 130°C for 80h. After cooling down to room temperature, water was added. The resulting precipitates were collected, washed with diluted ammonium hydroxide and Soxhlet extracted with water for three days and methanol for three days, and finally dried over phosphorous pentoxide under reduced pressure (0.05 mmHg) at 100°C for 72h to give 0.82g (85% yield) of dark brown solid: Anal. Calcd. for C_{21.58}H_{0.63}O_{1.43}: C, 91.68%; H, 0.22%; O, 8.10%. Found: C, 90.93%; H, 2.82%; O, 4.89%. [Calcd for VGCNT (C_∞): C, 100.00%; H, 0.00%; O, 0.00%. Found: C, 98.67%; H, 1.10%; O, <0.20% (less than detection limit)]. FT-IR (KBr, cm⁻¹): 1240, 1590, 1646, 2922, 3434.

General procedure for PEK polymerization with VGCNT. Into a 250 mL resin flask equipped with a high torque mechanical stirrer, nitrogen inlet and outlet, and pressure regulator, 3-phenoxybenzoic acid (2.7g, 12.6 mmol), and VGCNT (Applied Science Inc., Cedarville, OH; 0.3g), and PPA (83% assay, 60g) was placed and stirred with dried nitrogen purging at 130°C for 3h. P₂O₅ (15.0g) was then added in one portion. The initially dark mixture became lighter and viscous after 1h at 130°C and started to stick to stirring rod. The temperature was maintained 130°C for 48h. At the end of the reaction, water was added into the flask. The resulting purple polymer clusters were put into a Warring blender and the polymer bundles were chopped, collected by suction filtration, washed with diluted ammonium hydroxide and Soxhlet extracted with water for three days and with methanol for further three days, and finally dried under phosphorous pentoxide under reduced pressure (0.05 mmHg) at 140°C for 72h to give the polymer in

quantitative yield. Anal. Calcd. for $C_{14.76}H_8O_2$: C, 81.56%; H, 3.71%; O, 14.73%. Found: C, 81.40%; H, 3.61%; O, 13.16%.

Results and Discussion

Model reaction with C_{60} . 4-(2,4,6-trimethylphenoxy)benzoic acid, **1**, was synthesized via aromatic nucleophilic substitution reaction between 2,4,6-trimethylphenol and 4-fluorobenzonitrile followed by oxidation to give good overall yield. Although C_{60} is electron-deficient, its reactions with electrophilic NO_2^+ is known [9]. Thus, **1** was treated with C_{60} in PPA/ P_2O_5 to drive electrophilic substitution reaction (Scheme 1).



Scheme 1. Model reaction between **1** and C_{60} : a. PPA/ P_2O_5 , 130°C

MALDI-TOF-MS study. The polysubstituted product **2** was run in MALDI-TOF mass spectroscopy to determine the degree of substitution and stability of C_{60} under reaction conditions. The molecular mass of pure C_{60} is 720.66 Da, but MALDI-TOF spectrum indicates that the molecular mass of the all-carbon core is 643 Da, which is equal to 53.5 carbons (Figure 1), suggesting that an average of 6.5 carbons are missing during the reaction or work up. However, the major peak intervals are exactly 237-238 Da apart indicating that the possibility of attaching up to six of $C_{16}H_{14}O_2$ moieties (1- H_2O) to the “ C_{54} -core”. From this study, a preliminary conclusion could be drawn that single-wall carbon nanotubes (SWNT) may not remain intact under electrophilic substitution polymerization conditions in PPA/ P_2O_5 . Thus, we decided to use VGCNT for the in-situ polymerization study.

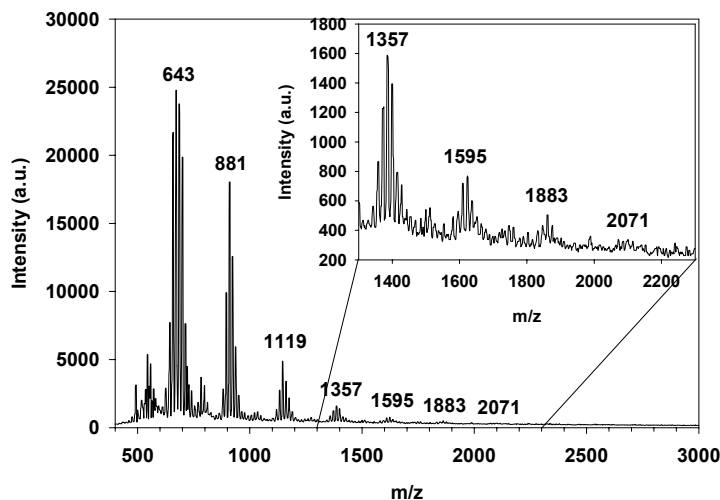
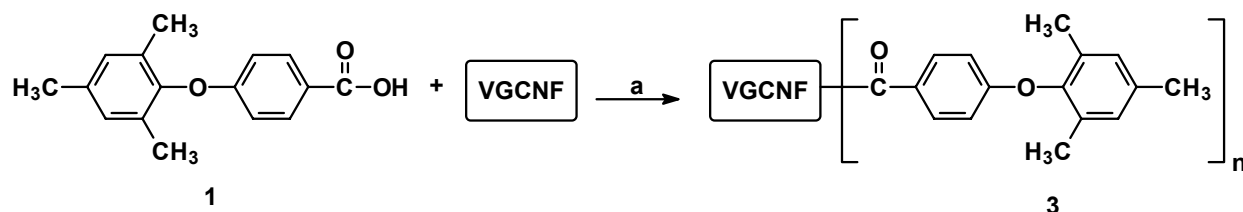


Figure 1. MALDI-TOF mass spectrum of substituted C_{60} **2**.

Model reaction with VGCNT. Since C₆₀ functionalization was successful, it is very worthwhile to do the same type of reaction on to VGVNT. The chemical natures of C₆₀ and VGCNT are similar. Thus, the compound **1** was also treated with VGCNT in PPA/P₂O₅ to afford substituted VGCNT **3** (Scheme 2).



Scheme 2. Model reaction between **1** and VGCNT: a. PPA/P₂O₅, 130°C

The products were fully worked up. For instance, after precipitated in water, washed, treated with ammonium hydroxide to neutralize with residual phosphoric acid, Soxhlet extracted with water for three days to completely remove residual phosphoric acid, and further Soxhlet extraction was conducted with methanol for three days to completely get rid of residual **1**, which is not reacted. The resulting products were dried under reduced pressure (1 mmHg) at 100°C for 72h to give 85% yield after complete work-up. The analytical data are summarized in Table 1. It is worthwhile to note that virgin C₆₀ and VGCNT are containing noticeable amount of hydrogen, although the source is not clear. However, almost all cases have good agreement when hydrogen content is taken into account.

Table 1. Elemental analysis data for functionalized C₆₀ **1** and VGCNT **3**

Sample	Elemental Analysis	C (%)	H (%)	O (%)	P (%)
C60	Calcd	100.00	0.00	0.00	0.00
	Found	99.40	1.05	< 0.20*	< 0.04*
Functionalized C60	Calcd ¹	86.89	4.21	8.90	0.00
	Found	85.19	4.40	9.01	< 0.08*
VGCNT	Calcd	100.00	0.00	0.00	0.00
	Found	98.87	1.10	< 0.20*	< 0.04*
Functionalized VGCNT	Calcd ²	91.68	0.22	8.10	0.00
	Found	90.93	2.82	4.89	< 0.08*

* Less than detection limit.

1. Calculated based on six substitution of compound **1** on to C₆₀.
2. Calculated based on 1:1 (by weight) ratio of VGCNT:compound **1** reaction.

TGA analysis of functionalized VGCNT. To ensure functionalization of compound **2** on to electron deficient VGCNT, TGA was used to monitor percent weight loss could be occurred at lower temperature because of substituents. Onset temperature of weight loss occurred at 381°C should be due to substituent and 62% of residue at 600 °C must be due to VGCNT, which remain constant up to 700 °C (Figure 2). Thus, the result is

strong indication of electrophilic substitution reaction indeed happened on to electron deficient VGCNT.

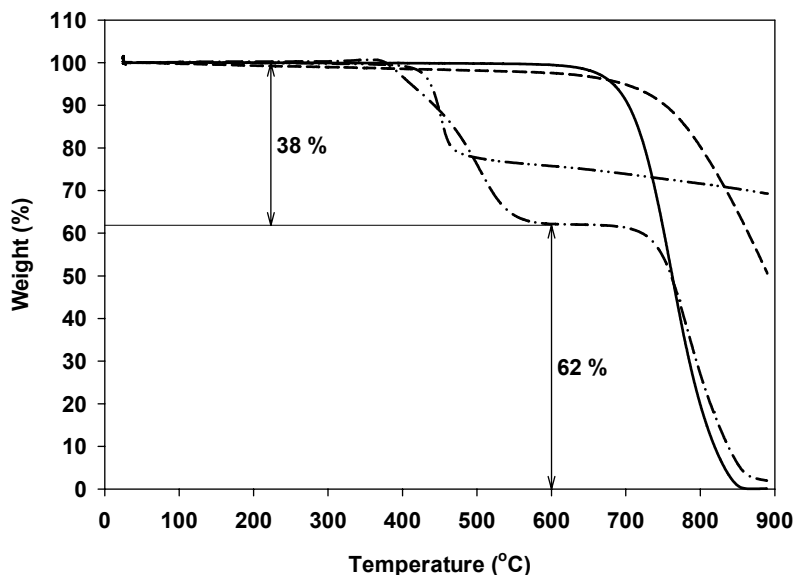
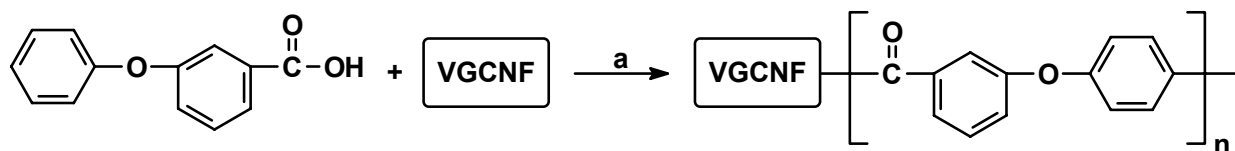


Figure 2. TGA thermograms with heating rate of 10°C/min: VGCNT in air (solid), VGCNT in helium (dash), functionalized VGCNT in air (dash-dot-dash), functionalized VGCNT in helium (dash-dot-dot-dash.)

In-situ polymerization. Various polymerizations were carried out with different ratios of monomer and VGCNT as shown in Scheme 2 (Table 2). As the amount of VGCNT increased, reaction time was generally longer because of the mixture's viscosity. In all cases, the dopes stuck to the stirring rod indicating that high MW polymers were synthesized. In lower VGCNT contents, an insoluble gel was formed, when reaction time is longer than 6h. Thus, the reaction was stopped at certain time by judging visually its viscosity.



Scheme 2. In-situ polymerization of PEK with VGCNT: a. PPA/P₂O₅, 130°C

Solution Properties. PEKs containing VGCNT from 10-30 wt% were cloudy in MSA solution, but the solutions were homogeneous enough to cast good quality films. The polymers containing VGCNT from 1-5 wt% formed clear and homogeneous MSA solutions and after filtration, were used to measure the intrinsic viscosities (1.00-1.73 dL/g at 30 ± 0.1°C). The weight percentage of carbon from elemental analysis are in a good agreement with theoretical values for all compositions. The results are summarized in Table 2.

Table 2. Properties of PEK's containing VGCNT

Product		VGCNT (TGA-wt%)	[η] (dL/g)	Elemental Analysis			
VGCNT (wt%)	mPEK (wt%)				C (%)	H (%)	O (%)
31.9	68.1	32.03	--	Calc	84.52	3.12	12.36
				Expl	84.14	3.21	9.79
21.5	78.5	22.22	--	Calc	83.20	3.38	13.42
				Expl	83.64	3.19	11.88
10.8	89.2	11.04	--	Calc	81.56	3.71	14.73
				Expl	81.40	3.61	13.16
5.4	94.6	5.64	1.73	Calc	80.63	3.90	15.47
				Expl	80.21	4.19	14.48
2.2	97.8	2.0	1.00	Calc	80.02	4.02	15.96
				Expl	80.06	4.17	15.07
1.1	98.9	1.2	1.42	Calc	79.80	4.07	16.13
				Expl	79.91	4.25	15.11

Thermal Properties. The T_g 's of PEK's containing VGCNT were determined by DSC. The DSC scans were run on the powder samples after they had been heated to 200°C in the DSC chamber and allowed to cool to ambient temperature under nitrogen purge. The T_g was taken as the mid-point of the maximum baseline shift from the second run. As shown in Table 2, PEK without VGCNT displayed a T_g at 136.6°C. As the amount of VGCNT content increased, polymer T_g 's were gradually increased to 138.2 °C with VGCNT 10 wt% and to 144.0 °C with VGCNT 20%. The TGA experiments on the powder sample of pure VGCNT indicated that the temperatures at which a 5% weight loss ($T_{d5\%}$) occurred at 682.7 °C in air (Figure 3) and 696.8 °C in helium. All other PEK's with and without VGCNT displayed higher $T_{d5\%}$ in the range of 408-448 °C in air than 365-409 °C in helium. Char percents at 650 °C in air are in excellent agreement with the amounts of VGCNT present during PEK polymerization.

Table 2. Thermal properties of PEK's and VGCNT

Product		Tg		TGA			
VGCNT (wt%)	mPEK (wt%)	DSC (°C)	TMA (°C)	In Air		In Helium	
				$T_{d5\%}$ (°C)	Char At 650°C (%)	$T_{d5\%}$ (°C)	Char At 650°C (%)
100.0	0.0	ND	ND	682.7	98.2	696.8	96.7
31.9	68.1	157.6	164.2	448.2	31.7	409.0	68.6
21.5	78.5	151.8	153.9	408.6	20.5	388.6	63.1
10.8	89.2	143.7	145.4	430.5	11.4	406.8	55.3
5.4	94.6	143.7	141.2	492.4	5.6	479.9	61.9
2.2	97.8	141.0	138.5	485.7	2.0	478.0	53.7
1.1	98.9	142.5	141.5	477.5	1.2	463.1	54.6
0.0	100.0	136.6	137.1	414.2	0.8	365.6	48.3

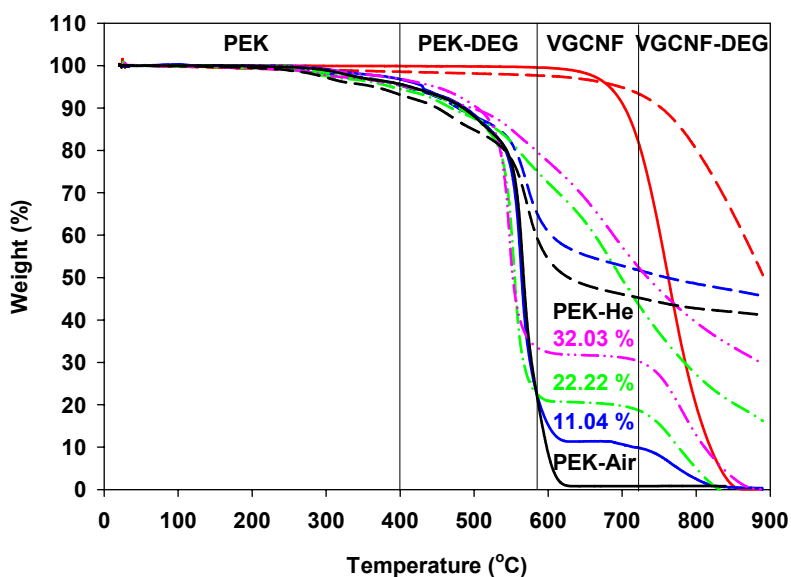


Figure 3. TGA thermograms of PEK containing VGCNT (10 °C /min.)

TEM and SEM Studies. The TEM images of a selected sample (PEK with 30wt% VGCNT; powder) showed that the VGCNT in the PEK matrix still has the diameter of 100-200 nm and wall thickness of 30-40 nm, suggesting its relative stability under the polymerization conditions (Figure 3a). The SEM image of functionalized VGCNT displayed that m-PEK was heavily coated on the surface of VGCNT (Figure 4b).

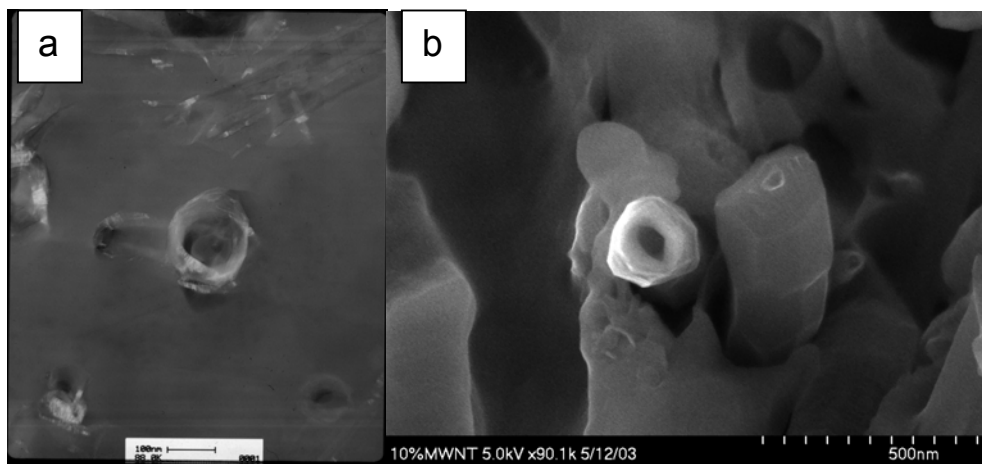


Figure 4. (a) TEM and (b) SEM images obtained from powder sample containing 30 wt% of VGCNT.

Conclusions

MALDI-TOF-MS result is indicative of multiple acylation reactions of 4-(2,4,6-trimethylphenoxy)benzoic acid and C₆₀ in PPA/P₂O₅ at 130°C. It also suggested that

C₆₀ was not chemically inert under the reaction conditions to preserve its original structure with an average of six and half carbons missing. TGA result of functionalized VGCNT confirmed that the reaction medium was strong enough to facilitate efficient functionalization of VGCNT. Based on successful functionalizations onto C₆₀ and VGCNT, polymerizations of 3-phenoxybenzoic acid onto the surface of VGCNT were carried out in PPA/P₂O₅ medium and high MW PEK's containing various amounts of VGCNT were afforded. According to the various analysis such as elemental analysis, TGA, TEM, and SEM of resulting polymers, VGCNT remained structurally intact under the reaction medium, PPA/P₂O₅, which is strong enough to drive efficient electrophilic substitution reaction onto electron deficient C₆₀ and VGCNT.

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References

- [1] Kumar, S.; Doshi, H.; Srinivasrao, M.; Park, J. O.; Schiraldi, D. A. *Polymer* **2002**, *43*, 1701.
- [2] Quin, D.; Dickey, E. C.; Andrews, R.; Rantell, T. *Appl. Phys. Lett.* **2000**, *76*, 20.
- [3] Andrews, R.; Jacques, D.; Rao, A. M.; Rantell, T. Derbyshire, F.; Chen, Y.; Chen, J.; Haddon, R. C. *Appl. Phys. Lett.* **1999**, *75*, 1329.
- [4] Treacy, M. M. J.; Ebbesen, T. W.; Gibson, J. M. *Nature* **1996**, *381*, 678.
- [5] Kumar, S.; Dang, T.; Arnold, F. E.; Bhattacharyya, A. R.; Min, B. G.; Zhang, X.; Vaia, R. A.; Park, C.; Adams, W. W.; Hauge, R. H.; Smalley, R. E.; Ramesh, S.; Willis, P. A. *Macromolecules* **2002**, *35*, 9039.
- [6] Bonner, W. H. *US Patent 3 065 205*, **1962**.
- [7] Baek, J.-B.; Tan, L.-S. *Polym. Prepr.* **2002**, *43(1)*, 533.
- [8] Baek, J.-B.; Tan, L.-S. *Polymer* **2003**, *44*, 4135.
- [9] Chiang, L. Y.; Upasani, R. B.; Swirczewski, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 10154.