Graphite Oxide as an Olefin Polymerization Carbocatalyst: Applications in Electrochemical Double Layer Capacitors

*Daniel R. Dreyer and Christopher W. Bielawski**

Graphite oxide (GO) is shown to be an efficient heterogeneous catalyst for the polymerization of various olefin monomers, including n-butyl vinyl ether, *N*-vinylcarbazole, styrene, and sodium 4-styrenesulfonate. The GO-catalyzed polymerization of n-butyl vinyl ether (0.1–5.0 wt% GO relative to monomer) proceeds rapidly under solvent-free conditions and affords polymers with moderate number average molecular weights and broad polydispersities. Analysis of the carbon recovered at the conclusion of the polymerization reactions reveals that the material's catalytic activity is retained and multiple polymerization cycles can be performed without regenerating the catalyst. GO also catalyzes the polymerization of *N*-vinylcarbazole and styrene, although only low molecular weight polymers are obtained. Sodium 4-styrenesulfonate polymerizes in the presence of GO to afford poly(sodium 4-styrenesulfonate) (PSS) composites. After thermal treatment, the composites can be fabricated into electrodes for use in electrochemical double layer capacitors (EDLCs). The devices display high specific capacitances (25–120 F g^{-1}) and low equivalent series resistances (14–27 Ω).

1. Introduction

The polymerization of olefins via cationic chain growth processes represents one of the most fundamental and widely utilized methods for synthesizing polyolefins.[1–4] Poly(vinyl ether) s, in particular, are an important class of polymers prepared via this method, and have found widespread use as lubricants,[5] adhesives,[6] and optical coatings,[7] among other applications. Polymerizations of the corresponding vinyl ether monomers are commonly performed using $AlEt_2Cl$, BF_3, mineral acids or other similarly strong Lewis or Brønsted acids.[8] The need to modulate these polymers' properties (e.g., for increased fire retardation,[9] enhanced viscoelasticity,[10] etc.) has led to interest in the incorporation of additives. For example, poly(vinyl ether) s and other cationically-prepared polyolefins may be blended with various carbon materials (e.g., carbon black) to produce composites with desirable viscoelastic, barrier, thermal, electronic, or pigmentation properties.[11,12] As in many composite materials, however, phase separation of these additives from the polyolefin matrices often challenges their preparation and practical utility.[13] In an effort to circumvent this problem and enhance the interfacial interactions between the carbon filler and these polymers, Tsubokawa and co-workers elegantly showed that carbon black, graphite, and carbon fibers may be functionalized with acylium moieties that serve as initiators for the cationic polymerization of vinyl ethers,[14,15] *N*-vinylcarbazole,[16] styrene,[17,18] and various cyclic monomers.[19–21] While effective in preventing the aforementioned phase separation of the carbon additive, this approach often requires extensive engineering of the carbon surface. Since many olefins polymerize in the presence of various strong acids, we reasoned that other well-known and inherently Lewis or Brønsted acidic carbon materials may exhibit similar reactivity while also avoiding phase separation from the polyolefin.

An example of one such acidic carbon material is graphite oxide (GO). Originally prepared over 150 years ago,[22] GO has enjoyed a fresh resurgence of interest as a result of its ability to facilitate access to graphene and related materials.[23] In addition to using various chemical reductants to facilitate its conversion to graphene-like materials, we have recently shown that GO is a strong chemical oxidant and may be harnessed for the productive synthesis of a wide range of small molecule species (e.g., aldehydes, ketones, sulfoxides, and disulfides).[24–26] Moreover, it has been shown that GO's surface functionalization renders the material acidic,[23] a feature that has been applied toward the formation of polymers.[27,28] Indeed, we recently showed that GO can be used to facilitate the dehydrative polymerization of benzyl alcohol (BnOH), resulting in the formation of poly(phenylene methylene) (PPM),[27] as well as initiate the ring opening polymerization of various lactones and lactams.[28] Moreover, the products obtained from the polymerization reactions were found to display a range of useful properties, such as high mechanical stiffness and thermal stability.

Building on these results, we envisioned using GO's acidity ($pK_a \sim 3$ in water)[28] to polymerize olefins via acid-initiated mechanisms. Herein, we show that GO catalyzes the polymerization of butyl vinyl ether,[29] as well as other olefinic monomers, such as N-vinylcarbazole, styrene, and sodium 4-styrenesulfonate. Moreover, composites comprising reduced GO (r-GO) (formed by the mild thermal deoxygenation of the GO) and poly(sodium 4-styrenesulfonate) (PSS) showed high conductivity (σ) and specific capacitance (C_{sp}) when fabricated into

---

D. R. Dreyer, Prof. C. W. Bielawski
Department of Chemistry and Biochemistry
The University of Texas at Austin
1 University Station, A1590, Austin, TX, 78712, USA
E-mail: bielawski@cm.utexas.edu

DOI: 10.1002/adfm.201103152

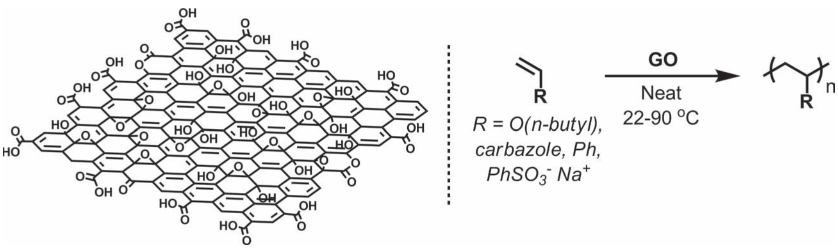

Figure 1. Graphite oxide (GO) (left) was used to catalyze the cationic polymerization of various olefins (right).

electrodes and tested in an electrochemical double layer capacitor (EDLC).

2. Results and Discussion

GO (see **Figure 1**) was prepared using a modified Hummers method (see Supporting Information).[30] Briefly, natural flake graphite (-10 mesh) was reacted with $KMnO_4$ in concentrated H_2SO_4, and the reaction was quenched by dilution in deionized water and the addition of aqueous H_2O_2. The carbon product (also termed a "carbocatalyst"[31–33]) was isolated by filtration and purified by rinsing with aqueous HCl and deionized water.

In a preliminary reaction, excess n-butyl vinyl ether (1.0 g) was mixed with GO (25 mg, 2.5 wt%). Upon addition of the carbocatalyst to the monomer, the polymerization proceeded rapidly, as evidenced by a brief exotherm (T_{max} = 90 °C) and a noticeable increase in viscosity, which were consistent with autoacceleration behavior.[34,35] After 14 h, the mixture became a viscous gel with carbon particles heterogeneously dispersed throughout. The monomer exhibited complete conversion, as determined by ^1H NMR spectroscopy upon dissolution of the polymer in $CDCl_3$ and filtration of the insoluble carbon material.[36] The reaction afforded a polymer with a number average molecular weight (M_n) of 5200 Da and a polydispersity index (PDI) of 9.42, as determined by gel permeation chromatography (GPC) referenced to poly(styrene) standards in tetrahydrofuran (THF). Broad polydispersity is often observed in cationic polymerizations initiated by either Brønsted or Lewis acids due to the high reactivity of the propagating carbenium ions,[8] particularly when the initiator exhibits multiple active species such that initiation, propagation, and termination events of the polymerization occur at significantly different rates.[37–40]

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to characterize the thermal properties of the poly(vinyl ether) composite. The polymer exhibited a glass transition temperature (T_g) of –63 °C, consistent with previous reports on neat poly(butyl vinyl ether) (PBVE),[41,42] and the polymer-carbon composite was found to be highly stable, exhibiting a decomposition temperature (T_d) of 354 °C. No changes in the polymer's T_g or T_d were observed when the residual carbon catalyst was removed by trituration in THF.

In an effort to optimize the reaction time, 2.5 wt% GO was mixed with butyl vinyl ether at 22 °C. After 5 min, 97.8% of the monomer was converted to PBVE, as determined by ^1H NMR spectroscopy, and the polymer obtained at this reaction time exhibited nearly the same molecular weight (M_n = 5400) and polydispersity (PDI = 10.37) as the previously described product obtained after 14 h. After 4 h, no unreacted monomer was observed by ^1H NMR spectroscopy, indicating that the reaction had reached completion. Based on these results, all subsequent polymerization reactions involving butyl vinyl ether were performed for 4 h at 22 °C.

Further optimization efforts were directed toward minimizing the required GO loadings. No reaction was observed in the absence of GO, indicating that butyl vinyl ether did not self-polymerize under the conditions explored (see **Table 1**). Likewise, low monomer conversion (2.3%, determined gravimetrically) and molecular weight (700 Da versus 5700 Da) were observed when a very low loading (0.01 wt%) of GO was used. We reasoned that such a small quantity was unable to efficiently initiate the polymerization, leading to low conversion and the observed low molecular weight products. Monomer conversion increased with the GO loading although the molecular weight of the polymer produced decreased. For example, a polymer with a M_n of 8100 Da was obtained at 0.1 wt% GO, while a polymer with a M_n of 5000 Da was observed at 5.0 wt% GO, consistent with an increase in the number of propagating chains generated at higher initiator loadings.[43]

To test the catalyst's recyclability, the recovered carbon material was reused in the polymerization of butyl vinyl ether under the standard conditions employed (2.5 wt% catalyst, 22 °C, neat, 4 h) without further treatment or regeneration. As shown in Figure S1 (Supporting Information), monomer conversion dropped by only 9.2% after five use and recovery cycles.

To confirm that the observed polymerization behavior was due to GO's acidity, several control experiments were performed wherein other carbon materials were substituted for GO. Under conditions otherwise identical to the optimized

Table 1. Catalyst loading optimization for the polymerization of butyl vinyl ether initiated by GO.[a]

GO loading [wt%]	Monomer conversion [%][b]	Molecular weight (M_n) [Da][c]	PDI[c]
0	0.0	–	–
0.01	2.3[d]	700	1.45
0.1	92.5	8100	13.88
1.0	98.7	7700	10.88
2.5	100.0	5700	9.45
5.0	100.0	5000	10.35

[a] Polymers prepared by reacting butyl vinyl ether (1.0 g) with the indicated amount of GO under solvent-free conditions at 22 °C for 4 h; [b] Determined via ^1H NMR spectroscopy after dissolving the polymer in $CDCl_3$ and separating from the catalyst via filtration; [c] Number average molecular weights (M_n) and polydispersity indices (PDIs) were determined by GPC against poly(styrene) standards after dissolving the polymer in THF and separating from the carbon additive via filtration; [d] Determined by mass after removal of the unreacted monomer under reduced pressure; no polymer was observed by ^1H NMR spectroscopy.

conditions previously described (2.5 wt% catalyst, neat, 22 °C, 4 h), natural flake graphite, hydrazine-reduced graphene oxide (a derivative of GO whose oxygen functional groups have been removed via reaction with a strong reductant[44]), and basified GO (prepared by reacting as-prepared GO with aqueous K_2CO_3) were all unable to polymerize butyl vinyl ether, as determined by ^{1}H NMR spectroscopy and GPC. Collectively, these results indicated that the chemical potential intrinsic to GO was necessary to polymerize butyl vinyl ether.

Having optimized the polymerization of a vinyl ether using GO as the initiator, we next sought to expand the reactivity of GO toward other olefins that are commonly polymerized via cationic pathways. Two monomers (*N*-vinylcarbazole and styrene) known[8] to be amenable to cationic polymerizations were selected for this purpose. *N*-vinylcarbazole, dissolved in a minimum of chloroform, polymerized rapidly and exothermically when GO (2.5 wt%) was added, similar to the reaction of butyl vinyl ether with GO (see above).[45] After 4 h, no unreacted monomer was visible by ^{1}H NMR spectroscopy and GPC analysis of the polymer revealed that the material possessed a molecular weight (M_n) of 1900 Da and broad polydispersity.[46] Polydisperse polymers and composites such as those described herein can exhibit useful properties, such as high processability in extruders or other similar apparatus.[47] Though more widely studied than *N*-vinylcarbazole or butyl vinyl ether, styrene is comparatively more challenging to polymerize under acidic conditions.[8] Indeed, under the conditions explored (2.5 wt% GO, neat, 25 °C, 4 h), only low molecular weight oligomers of poly(styrene) were formed (M_n = 400 Da), even at high monomer conversion (91.2%). Increased reaction temperatures (50–100 °C) led to self-polymerization of the monomer.[48]

In addition to the properties of the polymeric materials and composites produced in the aforementioned polymerizations, we were also interested in the chemical and physical characteristics of the carbon catalyst in order to understand the changes the catalyst underwent during the reactions. The nature and extent of GO's surface functionalization was studied both qualitatively and quantitatively using FT-IR spectroscopy and elemental analysis. As-prepared GO exhibited strong absorbances in its FT-IR spectrum (**Figure 2**) associated with hydroxyl (3430 cm^{-1}), carbonyl (1740 and 1625 cm^{-1}), and ethereal (1075 cm^{-1}) functional groups, consistent with the extensive surface modifications introduced during the oxidation process. Moreover, the high degree of oxygenation was confirmed by elemental analysis which revealed a carbon-to-oxygen (C:O) ratio of 1.60:1.

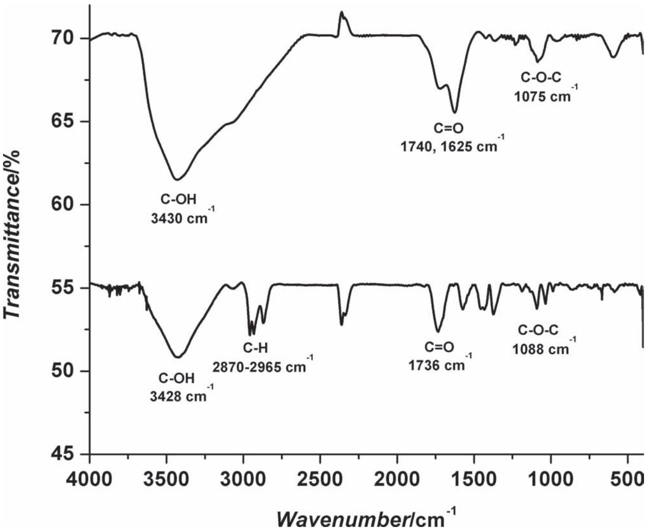

Figure 2. FT-IR spectra (KBr) for graphite oxide (top) and the carbon recovered after reaction of butyl vinyl ether with GO (2.5 wt%) (bottom).

At the conclusion of the reaction between GO and butyl vinyl ether (2.5 wt% GO, 22 °C, neat, 4 h), the heterogeneously blended carbon and polymer were separated from one another by trituration of the composite material in THF followed by vacuum filtration. The recovered carbon retained many of the diagnostic FT-IR spectral features (Figure 2), including resonances at 3428, 1736, 1572, and 1088 cm^{-1} associated with various C=O and C–O containing oxygen functional groups. These spectroscopic data indicated that a significant portion of the surface functionality was retained following the polymerization reaction. Additionally, a series of strong absorbances appeared in the range of 2870–2965 cm^{-1}, consistent with C–H stretching frequencies. As graphite, GO, graphene, and other similar carbon nanomaterials do not possess a significant number of C–H bonds, we surmised that these absorbances were due to functionalization of the carbon material's surface with PBVE. Gravimetric analysis of the recovered carbon, after extensive rinsing with THF and drying of the material under vacuum, indicated a 12.8% increase in mass, relative to the amount of GO used in the starting mixture. To estimate the amount of polymer attached to the surface, we reasoned that under these reaction conditions GO was minimally deoxygenated. Although GO can be thermally stripped of its functionality,[49] the temperatures required for this process to occur efficiently are typically much higher (usually ranging from 500–900 °C,[50,51] or more) than the short exotherm ($t < 5$ min, T_{max} ~ 90 °C) observed during the polymerization of butyl vinyl ether. Thus, we assumed that the GO experienced no mass loss during the reaction. Indeed, heating GO under solvent-free conditions to 90 °C for 5 min resulted in no measurable mass loss. Therefore, the 12.8% mass increase observed in the post-polymerization product was attributed to functionalization of the GO surface by poly(butyl vinyl ether) (PBVE) (1.29×10^{-3} moles of monomer equivalent per gram of recovered GO).

The physical structure and morphology of the as-prepared GO and recovered carbon were studied using powder X-ray diffraction (PXRD), Raman spectroscopy, surface analysis and powder conductivity methods. While as-prepared GO exhibited an interlayer spacing of 7.6 Å (compared to 3.3 Å in the starting graphite material) (see Figure S3, Supporting Information),[52] the carbon recovered from the polymerizations was amorphous; no discernible peaks were observed in the diffraction pattern. The lack of regular interlayer spacing was consistent with the disruption of the carbon's lamellar structure by the polymer. However, as determined by measurements performed on the powdered materials, the recovered carbon exhibited a decreased conductivity (σ = 3.02×10^{-4} S m^{-1}) compared to the starting GO (σ = 4.68×10^{-3} S m^{-1}). While this result was not consistent with the conversion of GO to highly conductive graphite- or graphene-like materials, functionalization of the carbon with PBVE (see above) could disrupt the π-conjugated network responsible for those materials' conductive properties. Raman spectroscopic analysis of GO ($I_D/I_G = 0.96{:}1$) and the recovered carbon ($I_D/I_G = 0.96{:}1$) indicated a high degree of disorder in both materials, confirming the PXRD results.[53,54] Collectively, the analyses of the carbon materials involved in the polymerization of butyl vinyl ether indicated that a small portion of the polymer grafted to the carbon's surface, as determined by FT-IR spectroscopy and PXRD, which contributed to the observed low conductivity and high morphological disorder.

Building on these results, we next sought to merge graphene's remarkable electronic and charge storing capabilities[55,56] with the ability to form polyolefin composites. Composites of reduced graphene oxide (r-GO) and polyelectrolytes (e.g., poly(vinylimidazolium)s) have previously been shown to be excellent materials for use as electrodes in EDLCs.[57,58] Indeed, polyelectrolyte-coated electrodes have shown marked improvement in specific capacitance (C_{sp}), relative to uncoated electrodes, likely as a result of the polymer's ability to facilitate wetting of the hydrophobic carbon surface by the electrolyte.[59,60] We reasoned that composites comprising poly(sodium 4-styrenesulfonate) (PSS), prepared from the corresponding sulfonated styrene monomer, and r-GO would exhibit similar behavior, and as a result, improve the C_{sp}. PSS has been previously shown to interact strongly with r-GO to the extent that stable aqueous dispersions may be prepared when the two materials are blended,[61,62] though to the best of our knowledge GO has never been used to directly polymerize the sulfonated monomer, and the EDLC properties of these composites have not been investigated.

We began by exploring the reactivity of GO with sodium 4-styrenesulfonate. In a preliminary reaction, a saturated aqueous solution of sodium 4-styrenesulfonate was prepared (approximately 180 mg mL^{-1}). A 0.1 mL aliquot of this solution was then mixed with 0.9 mL of deionized water and 50 mg of GO (approximately 280 wt%, relative to the dissolved monomer), and heated at 100 °C for 12 h in a sealed vessel to catalyze the polymerization. The reaction mixture was then diluted to 8 mL with methanol after which the composite was recovered by vacuum filtration and washed with excess methanol (50 mL) to remove unreacted monomer. Under these reaction conditions, it is possible that the GO underwent partial hydrothermal deoxygenation, as has previously been reported.[63] However, this may be beneficial as removal of GO's oxygen functionality is typically desirable for EDLC applications.[64] Carbon materials with extensive π-conjugated networks typically exhibit higher conductivities and better capacitive properties than materials whose conjugation is disrupted.[65] In order to facilitate deoxygenation of the GO in the composite, we subjected the recovered PSS-GO composite to thermal treatment by heating under vacuum at 175 °C for 24 h.[49,66] The resulting composite was found to be conductive ($\sigma = 1.93 \times 10^2$ S m^{-1}) (see Figure S16, Supporting Information), indicating that efficient deoxygenation of the carbon had taken place. For comparison, highly reduced graphene-like materials prepared from GO typically exhibit conductivities on the order of 500–2000 S m^{-1},[23] while a conductivity of only 2.59×10^{-3} S m^{-1} was observed for a similar PSS:r-GO composite that was not subjected to thermal treatment, prepared under otherwise identical conditions.

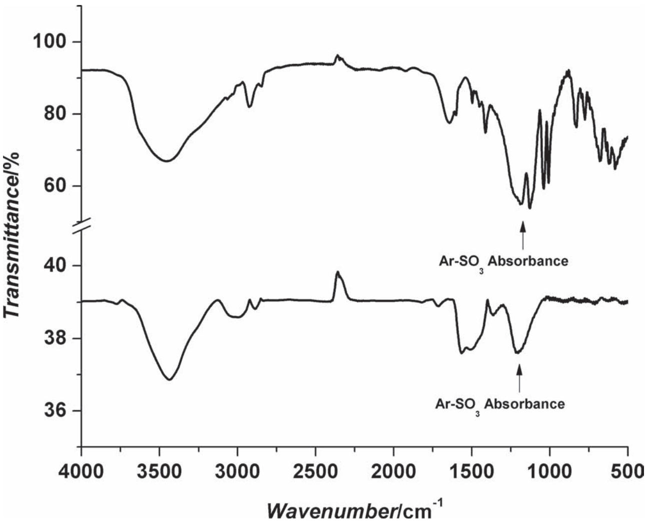

Figure 3. FT-IR spectra of an authentic PSS sample obtained commercially (top) and a PSS:r-GO composite prepared by reacting sodium 4-styrenesulfonate with GO (bottom).

Incorporation of PSS into the composite was qualitatively confirmed by FT-IR spectroscopy (**Figure 3**), which revealed a diagnostic absorbance at 1203 cm^{-1}, attributable to the presence of sulfonate groups. In order to determine the amount of sodium 4-styrenesulfonate that was polymerized and deposited onto the carbon surface, the thermally treated composite was analyzed by elemental combustion analysis and found to contain 1.09 wt% sulfur (see Table S1, Supporting Information). Assuming all of the sulfur in the composite was from the PSS fraction, we calculated that the composite contained 6.8 wt% PSS and 93.2 wt% r-GO. Moreover, by subtracting the oxygen content attributable to the PSS portion of the composite and assigning the remaining oxygen content to the r-GO, the deoxygenated carbon material was calculated to have a C:O ratio of 3.98:1. Comparatively, GO exhibited a C:O ratio of 1.60:1, which further indicated that the thermal treatment was effective in removing the oxygen functional groups from GO. Efforts to separate the water-soluble polymer from the carbon material by triturating in D_2O proved unsuccessful, even under prolonged sonication (2 h) and heating (90 °C), as indicated by the lack of ^{1}H NMR resonances attributable to either the polymer or unreacted monomer. Additionally, no phase separation between the components was observed, as indicated by the lack of graphitic peaks in the material's X-ray diffraction pattern. Such inseparability could be the result of covalent attachment of the polymer to the carbon surface, as observed in the GO-mediated polymerization of butyl vinyl ether, or of strong, non-covalent interactions with the carbon surface (e.g., Coulombic effects) as a result of the polymer's ionic character.

The material recovered after thermal treatment (surface area = 4.37 m^2 g^{-1}) was then fabricated into electrodes suitable for use in EDLCs and soaked in 6 M aqueous potassium hydroxide (a commonly utilized electrolyte[67]) for 12 h. The electrolyte-soaked electrodes were then assembled into

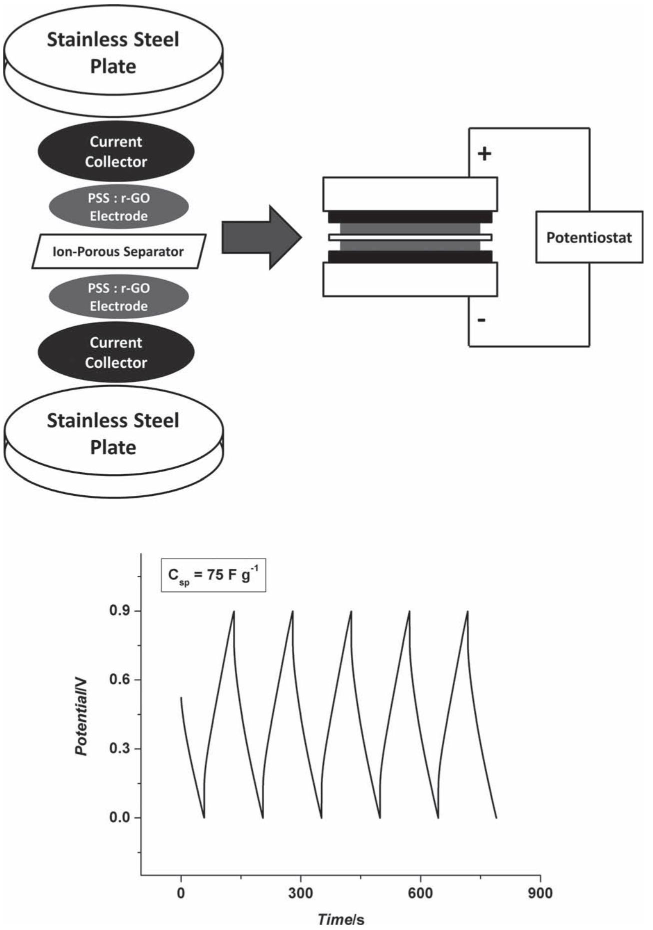

Figure 4. Test cell configuration (top) and galvanostatic charge-discharge plot ($I = 5$ mA) (bottom) for EDLCs fabricated from a PSS:r-GO composite (starting mixture: 50 mg GO, 0.1 mL saturated solution of sodium 4-styrene sulfonate, and 0.9 mL deionized water) using potassium hydroxide (6 M aq.) as the supporting electrolyte.

Table 2. EDLC properties of PSS:r-GO composites as a function of varying monomer-to-GO ratios.[a)]

Ratio of sodium 4-styrenesulfonate (saturated aqueous solution) to deionized water [v/v]	Analysis method[b)]	Specific capacitance (C_{sp}) [F g^{-1}][c)]	Equivalent series resistance [Ω][d)]	RC time constant (τ) [s][d)]
0.0:1.0	CV; 50 mV s^{-1}	25	52	32.0
	CV; 10 mV s^{-1}	50		
	CC; 500 mA g^{-1}	15		
	CC; 250 mA g^{-1}	40		
0.1:0.9	CV; 50 mV s^{-1}	75	27	47.1
	CV; 10 mV s^{-1}	120		
	CC; 500 mA g^{-1}	50		
	CC; 250 mA g^{-1}	75		
0.5:0.5	CV; 50 mV s^{-1}	55	15	23.5
	CV; 10 mV s^{-1}	85		
	CC; 500 mA g^{-1}	60		
	CC; 250 mA g^{-1}	75		
1.0:0.0	CV; 50 mV s^{-1}	40	14	15.2
	CV; 10 mV s^{-1}	70		
	CC; 500mA g^{-1}	25		
	CC; 250 mA g^{-1}	45		

[a)] Composites prepared by reacting GO (50 mg) with an aqueous solution of sodium 4-styrenesulfonate (1.0 mL) at the indicated ratio of sodium 4-styrenesulfonate (satd. aq. soln.)-to-deionized water at 100 °C for 12 h, followed by thermal treatment of the recovered composite at 175 °C for 24 h; [b)] EDLC analyses performed using the two-electrode cell described in the ESI (see Figure S19, Supporting Information). CV = cyclic voltammetry; CC = constant current or galvanostatic charge-discharge; [c)] CV specific capacitances (C_{sp}) determined by averaging the discharge current (I) on the fifth charge-discharge cycle and applying the average current to Eq. S3; CC specific capacitances (C_{sp}) determined by calculating the rate in voltage decrease (dv/dt) on the fifth charge-discharge cycle and applying the resulting dv/dt value to Eq. S3; [d)] Determined from the discharge phase of the galvanostatic charge-discharge plot (current density = 250 mA g^{-1}) (see ESI).

a two-electrode test cell (**Figure 4**) and analyzed by cyclic voltammetry (CV), galvanostatic charge-discharge (also referred to as constant current (CC) charge-discharge), and impedance spectroscopy to characterize the device's capacitive and electronic properties. As shown in **Table 2**, the C_{sp} of the device ranged from 50 to 120 F g^{-1}, depending on the measurement technique. The equivalent series resistance of the cell, determined from the galvanostatic charge-discharge plot, was found to be low (R_{ESR} = 27 Ω). After an initial rapid drop in C_{sp} of approximately 7.5%, possibly due to partial pseudocapacitive behavior,[68] slow degradation of the C_{sp} was observed over 1000 successive charge-discharge cycles (see Figure S24, Supporting Information) and eventually decreased 22.5%, relative to the the initial capacitance. As shown in Table 2, increased monomer loadings in the starting mixture led to EDLCs with uniformly decreased C_{sp} values (≤70 F g^{-1}). We reasoned that this was due to inhibition of charge buildup on the carbon electrode by the polymer. As has been previously reported,[69,70] obstruction of the carbon electrodes' surface can impede access by the electrolyte and lead to long charge and discharge times. Slow ion migrations were also supported by the relatively long RC time constants (>15 s) for electrodes containing varying amounts of the monomer in the starting mixture (see Table 2).

To determine if the one-step approach to preparing the composite was advantageous to adding pre-formed poly(sodium 4-styrenesulfonate) (PSS) to pre-formed r-GO, a commercial PSS sample (MW = 70 kDa) was mixed with r-GO (prepared by a hydrazine-mediated reduction of GO) by stirring in a minimum of deionized water at room temperature for 4 h to form an analogous PSS:r-GO composite. The resulting carbon material was collected, fabricated into EDLC electrodes, and analyzed by cyclic voltammetry, galvanostatic charge-discharge, and impedance spectroscopy. A maximum C_{sp} of 85 F g^{-1} was measured, suggesting the one-step approach described above is preferable to the multi-step approach incorporating pre-formed components.

Finally, to demonstrate that the inclusion of PSS in the electrode composite was operative in improving the C_{sp} of the device, a sample of r-GO was prepared in the absence of sodium 4-styrenesulfonate under otherwise identical conditions (1.0 mL of deionized water, 100 °C, 12 h, followed by annealing at 175 °C for 24 h). The resulting PSS-free material (surface area = 9.96 m^2 g^{-1}) exhibited C_{sp} values ranging from 15 to 50 F g^{-1} using the same analysis techniques described above. The diminished C_{sp} of the carbon material, relative to the previously described PSS:r-GO composites, suggested to us that the incorporation of the polyelectrolyte improved the electrodes' wettability by the supporting electrolyte and, ultimately, afforded a EDLC with increased capacitance.

3. Conclusions

In summary, we have shown that GO may be used as a solid state acid catalyst for the polymerization of various olefins. The polymerization of butyl vinyl ether under solvent-free conditions was rapid (>97% conversion after 5 min) and afforded PBVE of moderate molecular weight (M_n = 5000–8100 Da). Moreover, catalyst loadings as low as 0.1 wt% (relative to the monomer) were found to be effective for the formation of polymer. FT-IR and PXRD analyses indicated that a small amount (approximately 12.8%, as determined by mass balance) of the PBVE formed was grafted to the carbon material's surface. Sodium 4-styrenesulfonate was also polymerized using GO. After thermal treatment, the resulting PSS:r-GO composite was successfully employed as an electrode material for use in EDLCs. Indeed, the composite's high conductivity ($\sigma = 1.93 \times 10^2$ S m^{-1}) and specific capacitance (C_{sp} up to 120 F g^{-1}) allowed the devices to outperform those prepared from PSS-free r-GO. The devices containing these composite materials exhibited a 200–300% improvement over electrodes formed from PSS-free r-GO, similar to other previously reported graphene-based electrode materials.[56]

The results described herein indicate that GO and other similar carbon materials (e.g., activated carbon[71]) may be used as solid state initiators for a broad range of acid-catalyzed polymerizations, or as co-catalysts for use in the presence of other compatible acid initiators. The low cost, ease of preparation, and simplicity of removal (if desired) from the target products make carbon catalysts practical choices for the facile formation of a range of commercially and technologically useful polymer materials. Moreover, when retained within the as-produced polymer, catalysts derived from GO may enhance the electronic properties of a broad range of graphene-enhanced composites. Indeed, the ability to retain the catalyst within the polymer matrix represents a key advantage over other acidic polymerization catalysts (e.g., mineral acids), allowing for the single-step formation of highly conductive and capacitive polymer composites.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors gratefully acknowledge support for this work provided by the National Science Foundation (grant No. DMR-0907324) and the Robert A. Welch Foundation (grant No. F-1621).

Received: December 27, 2011
Revised: March 6, 2012

---

[1] M. Sawamoto, *Prog. Polym. Sci.* **1991**, *16*, 111.
[2] K. Matyjaszewski, *New Polym. Mater.* **1990**, *2*, 115.
[3] M. Sawamoto, K. Kitano, M. Kamigaito, *Polym. Mater. Sci. Eng.* **1995**, *72*, 176.
[4] F. C. Whitmore, *Ind. Eng. Chem.* **1934**, *26*, 94.
[5] R. G. Larsen, A. Bondi, *Ind. Eng. Chem.* **1950**, *42*, 2421.
[6] C. E. Schildknecht, A. O. Zoss, C. McKinley, *Ind. Eng. Chem.* **1947**, *39*, 180.
[7] T. Namikoshi, T. Hashimoto, M. Urushisaki, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4389.
[8] K. Matyjaszewski, *Cationic Polymerizations: Mechanisms, Synthesis, and Applications*, Marcel Dekker, Inc., New York **1996**.
[9] E. Kandare, G. Chigwada, D. Wang, C. A. Wilkie, J. M. Hossenlopp, *Polym. Degrad. Stab.* **2006**, *91*, 1209.
[10] Z. S. Nurkeeva, G. A. Mun, V. V. Khutoryanskiy, A. D. Sergaziev, *Eur. Polym. J.* **2001**, *37*, 1233.
[11] A. S. Crasto, S. H. Own, R. V. Subramanian, *Polym. Compos.* **1988**, *9*, 78.
[12] T. Yamamoto, H. Sugimoto, M. Hishinuma, *J. Mater. Sci.* **1986**, *21*, 604.
[13] J. R. Potts, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff, *Polymer* **2011**, *52*, 5.
[14] N. Tsubokawa, N. Takeda, T. Iwasa, *Polym. J.* **1981**, *13*, 1093.
[15] N. Tsubokawa, N. Takeda, K. Kudoh, *Carbon* **1980**, *18*, 163.
[16] K. Ohkita, N. Tsubokawa, M. Noda, M. Uchiyama, *Carbon* **1977**, *15*, 194.
[17] N. Tsubokawa, *J. Polym. Sci: Polym. Lett.* **1983**, *21*, 705.
[18] N. Tsubokawa, *J. Polym. Sci: Polym. Chem.* **1984**, *22*, 1515.
[19] N. Tsubokawa, I. Asano, Y. Sone, *Polym. Bull.* **1987**, *18*, 377.
[20] N. Tsubokawa, S. Ohshima, Y. Sone, T. Endo *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 4413.
[21] N. Tsubokawa, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2115.
[22] B. C. Brodie, *Philos. Trans. R. Soc. Lon.* **1859**, *149*, 249.
[23] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228.
[24] D. R. Dreyer, H.-P. Jia, A. D. Todd, J. Geng, C. W. Bielawski, *Org. Biomol. Chem.* **2011**, *9*, 7292.
[25] D. R. Dreyer, H.-P. Jia, C. W. Bielawski, *Angew. Chem. Int. Ed.* **2010**, *49*, 6813.
[26] H.-P. Jia, D. R. Dreyer, C. W. Bielawski, *Adv. Syn. Catal.* **2011**, *353*, 528.
[27] D. R. Dreyer, K. A. Jarvis, P. J. Ferreira, C. W. Bielawski, *Macromolecules* **2011**, *44*, 7659.
[28] D. R. Dreyer, K. A. Jarvis, P. J. Ferreira, C. W. Bielawski, *Polym. Chem.* **2012**, *3*, 757.
[29] G. Allen, J. C. Bevington, *Comprehensive Polymer Science: The Synthesis, Characterization, Reactions & Applications of Polymers*, Pergamon Press, Oxford **1989**.
[30] W. S. Hummers Jr., R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339.
[31] D. R. Dreyer, C. W. Bielawski, *Chem. Sci.* **2011**, *2*, 1233.
[32] Y. Pan, S. Wang, C. W. Kee, E. Dubuisson, Y. Yang, K. P. Loh, C.-H. Tan, *Green Chem.* **2011**, *13*, 3341.

[33] S. Verma, H. P. Mungse, N. Kumar, S. Choudhary, S. L. Jain, B. Sain, O. P. Khatri, *Chem. Commun.* **2011**, *47*, 12673.
[34] P. R. Dvornić, M. S. Jaćović, *Polym. Eng. Sci.* **1981**, *21*, 792.
[35] The reaction exotherm was controlled through the addition of solvent. At an initial concentration of 1.0 M, butyl vinyl ether was polymerized to a molecular weight (M_n) of 3900 Da (PDI = 2.40) in dioxane or chloroform. Monomer conversion reached 78.3%, as determined by mass balance, after a reaction time of 4 h. No temperature increase was observed.
[36] Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated approximately 3-5% hydrolysis of the vinyl ether monomer to the corresponding aldehyde (acetaldehyde) and acetal (dibutylacetal), consistent with previous reports on the reactivity of alkyl vinyl ethers in acidic media. See: D. M. Jones, N. F. Wood, *J. Chem. Soc.* **1964**, 5400.
[37] C. H. Lin, J. S. Xiang, K. Matyjaszewski, *Macromolecules* **1993**, *26*, 2785.
[38] H. Everland, J. Kops, A. Nielsen, B. Iván, *Polym. Bull.* **1993**, *31*, 159.
[39] K. Matyjaszewski, *Makromol. Chem. - M. Symp.* **1992**, *60*, 107.
[40] K. Matyjaszewski, C.-H. Lin, *Makromol. Chem. - M. Symp.* **1991**, *47*, 221.
[41] J. Lal, G. S. Trick, *J. Polym. Sci., Part A: Polym. Chem.* **1964**, *2*, 4559.
[42] T. Sagane, Y. Abe, A. Mizuno, *Polym. Bull.* **1992**, *28*, 259.
[43] N. M. B. Smeets, R. W. K. Lam, R. P. Moraes, T. F. L. McKenna, *Polym. Chem.* **2012**, *3*, 514.
[44] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* **2007**, *45*, 1558.
[45] Although the polymerization was performed in the melt (m.p. of N-vinylcarbazole = 66 °C), the reaction mixture was highly viscous, resulting in low monomer conversion (< 50%) and low molecular weight polymers (< 1000 Da).
[46] In order to determine if the exotherm generated during the polymerizations enhanced the polymers' formation or altered the products' properties, the reaction with N-vinylcarbazole as well as the other olefins was performed again at 90 °C. The conversion of N-vinylcarbazole to poly(N-vinylcarbazole) (PVK) remained quantitative, but only a slightly higher molecular weight was achieved (M_n = 2800 Da).
[47] D. Nichetti, I. Manas-Zloczower, *Polym. Eng. Sci.* **1999**, *39*, 887.
[48] K. S. Khuong, W. H. Jones, W. A. Pryor, K. N. Houk, *J. Am. Chem. Soc.* **2005**, *127*, 1265.
[49] C.-J. Kim, W. Khan, S.-Y. Park, *Chem. Phys. Lett.* **2011**, *511*, 110.
[50] X. Gao, J. Jang, S. Nagase, *J. Phys. Chem. C* **2010**, *114*, 832.
[51] R. Larciprete, S. Fabris, T. Sun, P. Lacovig, A. Baraldi, S. Lizzit, *J. Am. Chem. Soc.* **2011**, *133*, 17315.
[52] The GO catalyst prepared from -10 mesh flake graphite exhibited diffraction peaks in addition to a primary peak at 2θ = 11.65°. A broad peak spanning approximately 2θ = 18-41° suggested to us that the graphite starting material did not undergo complete oxidation to GO, possibly a result of its very large particle size.
[53] The specific surface areas of both the GO catalyst and recovered carbon remained low (1.80 m^2 g^{-1} and 4.81 m^2 g^{-1}, respectively).
[54] A slight red shift in the peak position of the D band (from 1365 cm^{-1} to 1353 cm^{-1}) was observed in the Raman spectra of the carbon recovered after reaction of butyl vinyl ether with GO (2.5 wt%) relative to the as-prepared GO catalyst. Natural flake graphite exhibited a D band peak position of 1356 cm^{-1}, suggesting the red shift in the recovered carbon's peak position may be a result of partial restoration of graphitic character in the carbon product. While no shift was observed in the G band peak position of either GO or the recovered carbon (ν = 1590 cm^{-1}), both were blue shifted with respect to the starting graphite (ν = 1581 cm^{-1}), consistent with previous reports on GO and similarly functionalized carbon materials. See: K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'homme, I. A. Aksay, R. Car, *Nano Lett.* **2008**, *8*, 36.
[55] Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, R. S. Ruoff, *Science* **2011**, *332*, 1537.
[56] M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff, *Nano Lett.* **2008**, *8*, 3498.
[57] T. Y. Kim, H. W. Lee, M. Stoller, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff, K. S. Su, *ACS Nano* **2011**, *5*, 436.
[58] S. Murali, D. R. Dreyer, P. Valle-Vigón, M. D. Stoller, Y. Zhu, C. Morales, A. B. Fuertes, C. W. Bielawski, R. S. Ruoff, *Phys. Chem. Chem. Phys.* **2011**, *13*, 2652.
[59] Y. Sun, Q. Wu, G. Shi, *Phys. Chem. Chem. Phys.* **2011**, *13*, 17249.
[60] C. Schmitt, H. Pröbstle, J. Fricke, *J. Non-Cryst. Solids* **2001**, *285*, 277.
[61] S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen, R. S. Ruoff, *J. Mater. Chem.* **2006**, *16*, 155.
[62] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* **2006**, *442*, 282.
[63] K.-H. Liao, A. Mittal, S. Bose, C. Leighton, K. A. Mkhoyan, C. W. Macosko, *ACS Nano* **2011**, *5*, 1253.
[64] W. Deng, X. Ji, M. Gómez-Mingot, F. Lu, Q. Chen, C. E. Banks, *Chem. Commun.* **2012**, *48*, 2770.
[65] Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen, Y. Chen, *J. Phys. Chem. C* **2009**, *113*, 13103.
[66] Though higher temperatures have been shown to be more effective in the thermal deoxygenation of GO, a lower temperature was selected in order to ensure that the poly(sodium 4-styrenesulfonate) (PSS) would not undergo decomposition or other side reactions during thermal treatment. To confirm that PSS is stable under these conditions, a commercial sample of the polymer (M_w = 70 kDa) was heated at 175 °C for 24 h in a thermogravimetric analyzer. No mass loss was observed. A ^{1}H NMR spectrum collected from this thermally treated sample also showed no differences from that of an untreated, authentic PSS sample, further indicating the polymer's stability under these annealing conditions.
[67] M. D. Stoller, R. S. Ruoff, *Energy Environ. Sci.* **2010**, *3*, 1294.
[68] C.-M. Wu, C.-Y. Fan, I.-W. Sun, W.-T. Tsai, J.-K. Chang, *J. Power Sources* **2011**, *196*, 7828.
[69] K. Zhang, L. L. Zhang, X. S. Zhao, J. Wu, *Chem. Mater.* **2010**, *22*, 1392.
[70] E.-H. El Brouji, O. Briat, J.-M. Vinassa, N. Bertrand, E. Woirgard, *IEEE Trans. Veh. Technol.* **2009**, *58*, 3917.
[71] E. Humeres, R. F. P. M. Moreira, M. d. G. B. Peruch, *Carbon* **2002**, *40*, 751.