

Polymeric Modification of Graphene through Esterification of Graphite Oxide and Poly(vinyl alcohol)

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Soluble graphene covalently functionalized with poly(vinyl alcohol) (PVA) has been synthesized by simple esterification reaction of carboxylic groups in graphite oxide using two different synthetic strategies.

Graphene has emerged to be a promising material due to its novel electrical transport properties.¹ However, the use of graphene is limited by the lack of an effective method for large-scale production. Several chemical methods have been explored to obtain soluble graphene including the reduction of graphite oxide (GO) in a stabilization medium² and covalent modification by amidation of the carboxylic groups,³ nucleophilic substitution to epoxy groups,⁴ and the diazonium salts coupling.⁵ These modified graphenes provide opportunities for researchers to employ them in designing new materials, such as polymer nanocomposites. In such materials, controlling the interfacial interaction between the filler and the polymer is crucial to control the properties. Although graphene-based polymeric nanocomposites have been developed,⁶ polymer chains have not been used to covalently modify graphene. Nevertheless, polymer-bounded carbon nanotubes (CNT)⁷ and fullerene (C₆₀)⁸ have been widely studied. PVA-functionalized CNTs have been obtained by esterification reaction⁹ and used as fillers in nanocomposites. In that sense, the presence of COOH in the edge planes of GO can be exploited to anchor PVA by using a similar way.

In this Communication, we report the covalent functionalization of graphene sheets with PVA (Scheme 1). We employed two synthetic strategies. The first one involves the direct esterification of GO, while the second one goes through its acyl chloride derivative (GOCl) (Supporting Information). The obtained products, named as GO-es-PVA and GOCl-es-PVA, are soluble in DMSO and water with the aid of heat, similar to PVA and PVA-CNT.⁹ In the present research a special interest has been paid to the isolation and characterization of the PVA-functionalized GO. First, an appropriate elimination of the no reacted GO was achieved by centrifugation, which completely removes the GO and leaves the PVA-functionalized GO (see Supporting Information). A comprehensive spectroscopic analysis was carried out to ensure that the esterification reactions were successfully completed.

The ¹H NMR spectrum of the soluble GO-es-PVA and GOCl-es-PVA in DMSO-*d*₆ are compared with that of neat PVA (Figure S2). The latter exhibits the polymer backbone signals at ~3.82 ppm (methine) and ~1.38 ppm (methylene) and the hydroxyl signals at 5–4 ppm, from which the stereoregularity of PVA is estimated as isotactic (*mm*):hetero (*mr*): syndiotactic (*rr*) of roughly 2:5:3.¹⁰ Upon the attachment to GO the PVA proton signals become a little wider but maintain similar chemical

shifts (Figure S2). The signals are less broadened than in PVA-CNT suggesting that, in principle, a lower degree of functionalization was achieved in our case.

It is interesting to pay special attention to the hydroxyl protons resonances which are resolvable in terms of configurational sequences (Figure 1). Several authors have concluded¹¹ that the hydrogen-bonding tendency, which is dominant for hydroxyl units in a meso configuration, predominantly determines the hydroxyl proton shielding. Since hydrogen bonding leads to downfield shifts, the chemical shifts of hydroxyl sequences resonances increase when passing from iso (4.7 ppm) to hetero (4.5 ppm) and from hetero to syndio (4.2 ppm) triad. On the other hand, it has been demonstrated that the reactivity of substituent groups along the polymer chain can be influenced by tactic sequence¹² where the substituent at *mm* sequence exhibited higher reactivity than those at the *rr* counterpart.

By a mere inspection of the evolution of the ¹H spectrum, we can easily observe an increase in the *rr* signal in detriment of the *mm* one for both GO-es-PVA and GOCl-es-PVA which suggests that esterification reaction occur at isotactic configuration. Surprisingly, as shown in Figure 1, a new signal at 4.2 ppm upfield, very closed to the *rr* triads of unmodified PVA, is clearly observed in spite of the low degree of esterification. This signal can be related to hydroxyl protons next to acetate groups as have been reported for esterification of PVA.^{13,14} By integration of this ¹H NMR signal we can evaluate, within the experimental uncertainties, the degree of functionalization, obtaining a modification of around 1.8%. Interestingly, this value is reasonably low due to the huge volume of graphitic laminates (GLs) and is in agreement with the decrease of *mm* triad content, as consequence of being less sterically hindered internally than those at syndiotactic counterpart, specifically in the incorporation of the GLs.

The FTIR spectra of GO-es-PVA and GOCl-es-PVA retained most of the bands of PVA, although some of them changed in intensity or even disappeared due to the modification, and show new bands (Figure 1). The development of the band at 1715 cm⁻¹ suggests the presence of new carbonyl species. This band is most often related to the C=O stretching motions of COOH groups situated at the edges of the GO lamellae¹⁵ and has low intensity due to high aspect ratio of GO which makes the relative amount of edge sites very small. Similarly, in our case the band at 1715 cm⁻¹ can be attributed to C=O stretching of ester groups. Indeed, this band was also observed in the esterification reaction of PVA and glycerol,¹⁶ suggesting that esterification is also taking place in our system. This is confirmed by the marked increase in the band around 1640 cm⁻¹, which appears weakly in PVA and has been assigned to adsorbed water.¹⁷ However, this is a strong band centered at 1628 cm⁻¹ in the spectrum of the GO (Figure S1), and although may also be due to adsorbed water, it contains a significant contribution from the skeletal vibration of nonoxidized graphitic domains.¹⁵ In addition, some interesting changes in the relative intensities of the characteristics bands of PVA in the 1200–1000 cm⁻¹ region can be observed. These bands are attributed to the C–O of doubly H-bonded OH in crystalline regions (1144 cm⁻¹) and C–O unbonded in amorphous zones (1096 cm⁻¹).¹⁸ The intensity ratio of these bands (*I*₁₁₄₄/*I*₁₀₉₆) diminishes markedly for the esterified products, suggesting a large decrease in the degree of crystallinity of the modified polymer.

Raman data further confirm the presence of GLs covalently bonded to PVA chains (Figure S3). The Raman spectra for

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GOCl-es-PVA product shows the most of the bands of PVA and two new broad bands at 1320 and 1596 cm^{-1} corresponding with the characteristics D and G bands of graphitic materials. In the case of GO-es-PVA, the spectrum shows only the typical D and G bands of GO on top of a broad fluorescent band¹⁹ while the bands of PVA become imperceptibles (Figure S3).

At this point, it is important to emphasize the special care taken in the purification of the products to ensure that no traces of nonreacted GO remained. Therefore, the observed D and G bands in Raman spectra correspond to graphitic layers covalently linked to PVA chains.

Regarding the changes in crystallinity suggested by FTIR results, some changes in the crystallization and crystalline parameters of the esterified products can be expected. Indeed, significant changes in the crystalline parameters have been observed in reduced GO/PVA (RGO-PVA) nanocomposites,²⁰ where an almost amorphous material was obtained for 10 wt % of filler.

Regarding the heating scan, it can be observed that T_m and the melting enthalpy (ΔH_m) are dramatically influenced by the presence of graphitic layers (GLs). In the modified products the melting peaks disappear, and the partially crystalline PVA ($X_c = 0.51$) became totally amorphous, supporting the existence of covalent linkage between the PVA and the GLs. Because of low content of GLs grafted from the PVA chains, we suppose that

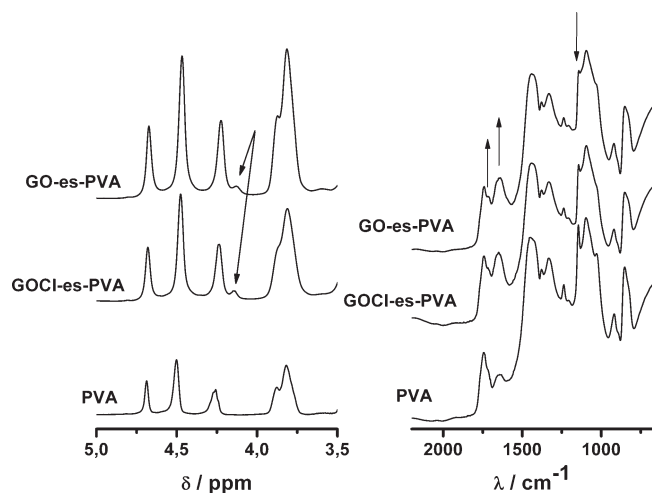


Figure 1. Spectroscopic characterization of PVA, GO-es-PVA, and GOCl-es-PVA: enlarged view of the hydroxyl signals in ^1H NMR, at room temperature in $\text{DMSO}-d_6$ (left) and FTIR spectra (right).

hydrogen bonding between oxygenated groups in GO and PVA is also involved. However, the covalent bonds are the main contribution for altering the parameters, since in GOR-PVA was not achieved the same effect even with 10 wt % of filler.²⁰ In addition, the mobility of the polymer chains is strongly affected by the covalent linkage of graphitic species (Figure 2). It is especially conspicuous the dramatic shift in T_g of 35°C for the GO-es-PVA. This shift is similar to the best available data obtained for polymer composites using individuals functionalized graphene sheets (FGS) as filler in the same composition.^{6a} In these systems, the wrinkled single-sheet morphology of FGS and its surface oxygen and hydroxyl groups gave rise to intimate filler–polymer interactions. In our system the effect can be ascribed to the effective covalent attachment of the polymer to the graphitic layers that prevents the segmental motions of the polymer chains. Obviously, the presence of huge rigid graphitic structures in the polymer chains restricts the movement. In the case of GOCl-es-PVA, the shift is lower than in GO-es-PVA (12°C). The shift in T_g is more marked when graphite oxide is used since the GO laminates in a chain can interact with nearby chains by hydrogen bonding, limiting even more the mobility. Also, it is necessary to consider that in the case of GOCl-es-PVA the presence of big chlorine atoms which have not reacted may also increase the steric effect compared with GO-es-PVA. The dramatic effects on

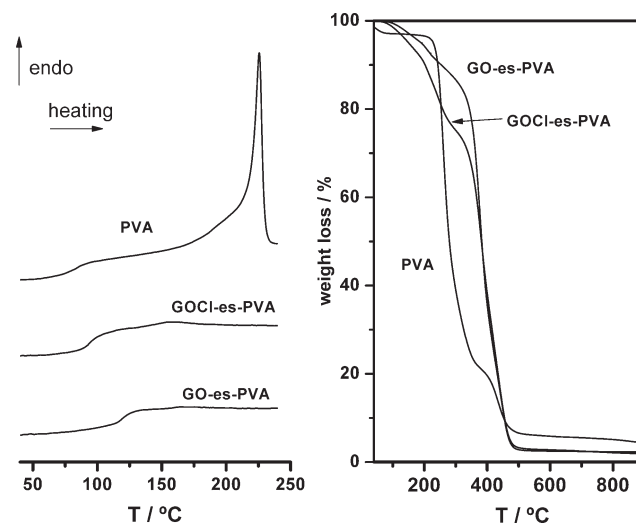
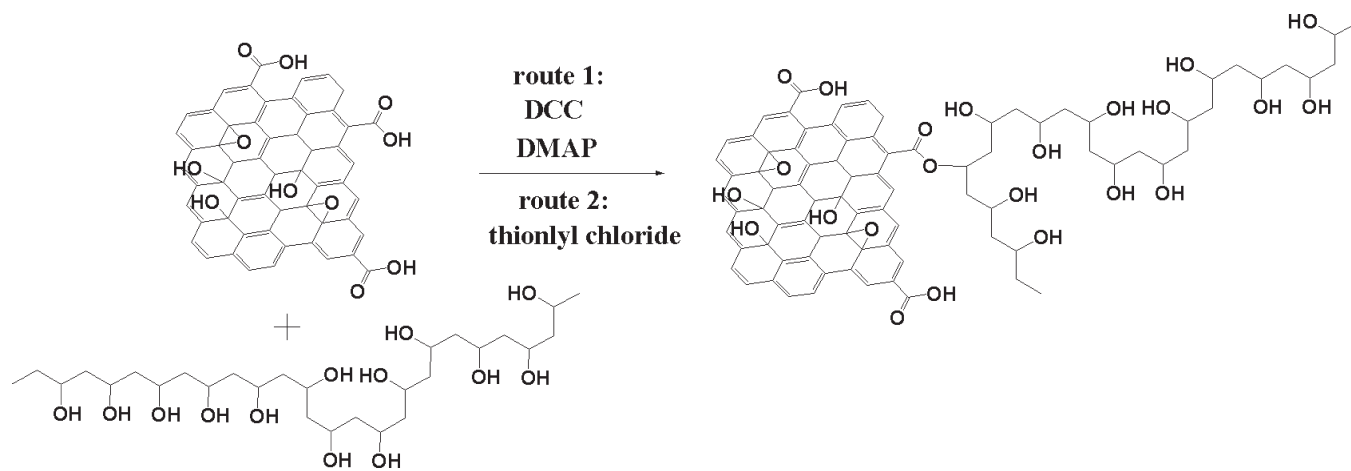
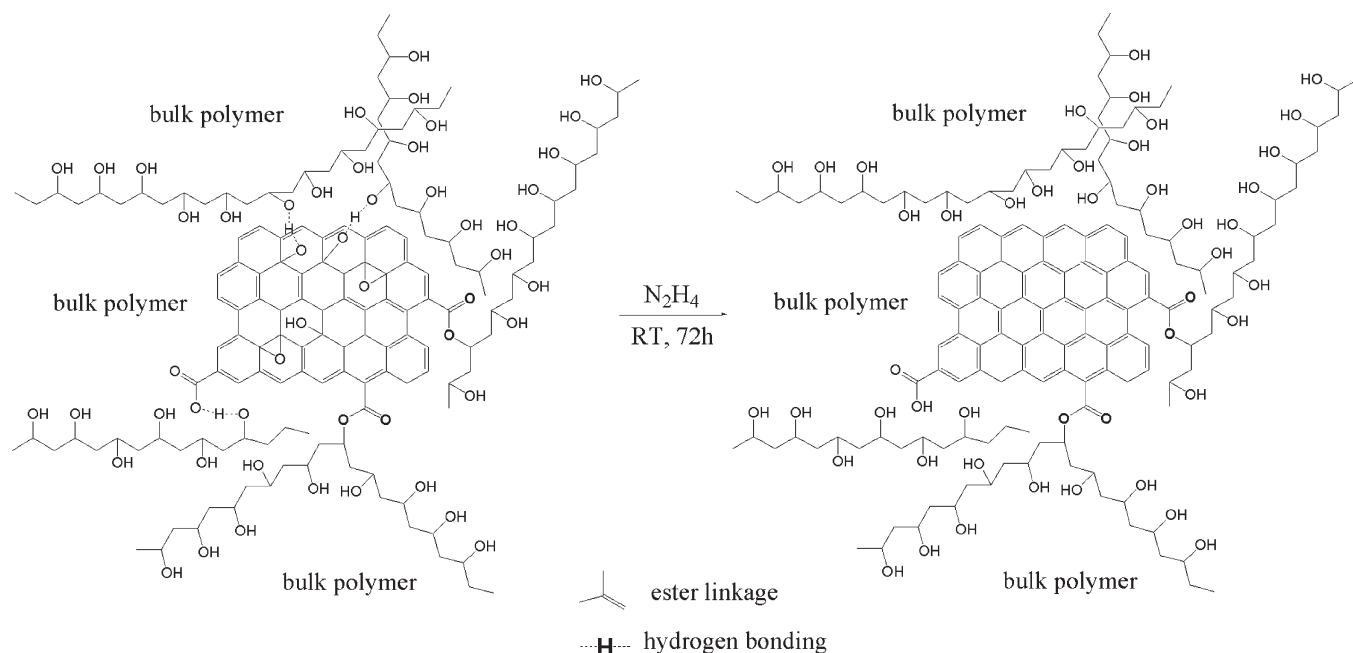


Figure 2. Thermal behavior of PVA, GO-es-PVA, and GOCl-es-PVA: DSC heating scans at $10^\circ\text{C min}^{-1}$ (left) and thermogravimetric curves (right).

Scheme 1. Schematic Illustration of the Esterification of Graphite Oxide with PVA



Scheme 2. Schematic Illustration of the Reduction of GO-es-PVA with Hydrazine



the thermal parameters are mainly due to the covalent bonds between GLs and PVA. Moreover, in the case of GO-es-PVA, the hydrogen bonding represents an additional factor that contributes to affect the polymer dynamics.

In order to investigate the effects of the GLs on the thermal stability of the polymer matrix, thermogravimetric analysis was performed (Figure 2b). TGA curves for both products suggest that just very small amounts of GLs improve remarkably the thermal stability of the nanocomposites. The temperature of maximum degradation rate for the nanocomposites increases more than 100 °C as occurred with PVA intercalated in GO²¹ and GOR/PVA nanocomposites (Figure S4).²⁰ Figure 2b also shows that despite a weight loss is observed around 200 °C common in these systems; the onset of decomposition for GO-es-PVA and GOCl-es-PVA is retarded. This noticeable effect in the thermal properties can be attributed to the high aspect ratio of the GLs laminates linked to PVA.

Because of water solubility of the esterified systems, highly transparent films can be prepared (Figure S5). In addition, this material can be used as filler for nanocomposites with PVA and PVA-miscible polymers such as poly(*N*-vinyl-2-pyrrolidone)²² and polyaniline (PANI).²³ Furthermore, solubility allows us for subsequent modifications of GO-es-PVA getting higher yields than in heterogeneous phase. It is widely known that GO became graphene when treated with reducing agents, and it aggregates giving graphite when no stabilizing agents are added. Taking into account that the reduction of GO in the presence of PVA prevents the aggregation,²⁰ we attempt the reduction of PVA-functionalized GO to produce PVA-functionalized graphene (Scheme 2). The obtained product (named RGO-es-PVA) had a blackish color, different from the original slightly brown for GO-es-PVA (Figure S5), suggesting that the oxygenated groups are eliminated during the reduction. RGO-es-PVA retains the solubility in water exhibited by GO-es-PVA, giving transparent films as well (Figure S5). Because of the low yield of esterification, the concentration of GLs in GO-es-PVA and so in RGO-es-PVA is very low. Therefore, the structural changes produced by the reduction of the graphite sheets are difficult to detect and quantify by spectroscopic techniques used in this work. However, the Raman spectrum of RGO-es-PVA is better defined than the obtained

for GO-es-PVA because of the broad fluorescence band disappearance (Figure S3). This result indicates that there is a reduction of GO to graphene as it has been shown that solid GO emits photoluminescence (PL), and the PL is altered by chemical reduction with hydrazine.¹⁹ These changes have been attributed to the generation/elimination of electronic band gap for single graphene sheets caused by the disruption/regeneration of the π -network.¹⁹

Although graphene has a high aspect ratio, no measurable conductivity values were obtained for RGO-es-PVA due again to its very low GLs concentration. Anyway, is not the aim of this Communication to study a particular property, but to show that graphene laminates can be covalently modified with polymers by using the above-described esterification reaction. In addition, the procedure could be extended to other polymers bearing pendant hydroxyl and amino groups. In fact, we are studying the esterification of poly(ethylene glycol) using similar procedures. Whereas the number of carboxylic groups in GO is high under the conditions employed in its synthesis (and thus the number of reactive sites), the degree of esterification is mainly governed by the tacticity of PVA.

In summary, we have successfully modified graphene laminates by esterification using the carboxylic groups in GO and the hydroxyl groups in PVA. We have demonstrated that the reaction depends on the tacticity of the polymer and that the covalent linkages between the GLs and the PVA are responsible for remarkably altering the crystallinity and thermal stability

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Supporting Information Available: Experimental procedures and equipments; characterization by XRD and XPS of the GO employed in the work; ¹H NMR and Raman characterization and enlarged view of the *T_g* region of PVA and esterified products; photographs of powders and transparent films of the esterified products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Geim, A. K.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183–191. (b) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666–669. (c) Wu, J.; Pisula, W.; Mullen, K. *Chem. Rev.* **2007**, *107*, 718–747.
- (2) (a) Park, S.; An, J.; Poner, R. D.; Jung, I.; Yang, D.; Velamakanni, A.; Nguyen, S. T.; Ruoff, R. S. *Chem. Mater.* **2008**, *20*, 6592–6594. (b) Li, D.; Muller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. *Nat. Nanotechnol.* **2008**, *3*, 101–105.
- (3) (a) Stankovich, S.; Poner, R. D.; Nguyen, N. T.; Ruoff, R. S. *Carbon* **2006**, *44*, 3342–3347. (b) Nigoyi, S.; Bekyarova, E.; Itkis, M. E.; MacWilliams, J. L.; Hamon, M. K.; Haddon, R. C. *J. Am. Chem. Soc.* **2006**, *128*, 7720–7721.
- (4) Bourlino, A. B.; Gournis, D.; Petridis, D.; Szabó, T.; Szeri, A.; Dékány, I. *Langmuir* **2003**, *19*, 6050–6055.
- (5) (a) Si, Y.; Samulski, E. T. *Nano Lett.* **2008**, *6*, 1679–1682. (b) Bekyarova, E.; Itkis, M. E.; Ramesh, P.; Berger, C.; Sprinkle, M.; de Heer, W. A.; Haddon, R. C. *J. Am. Chem. Soc.* **2009**, *131*, 1336–1337.
- (6) (a) Ramanathan, T.; Abdala, A. A.; Stankovich, S.; Dikin, D. A.; Herrera-Alonso, M.; Piner, R. D.; Adamson, D. H.; Schniepp, H. C.; Chen, X.; Ruoff, R. S.; Nguyen, S. T.; Askay, I. A.; Prud'homme, R. K.; Brinson, L. C. *Nat. Nanotechnol.* **2008**, *3*, 327–331. (b) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2006**, *442*, 282–286.
- (7) (a) Jeon, I.-Y.; Tan, L.-S.; Baek, J.-B. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3471–348. (b) Sakellariou, G.; Ji, H.; Mays, J. W.; Baskaran, D. *Chem. Mater.* **2008**, *20*, 6217–6230. (c) Baskaran, D.; Mays, J. W.; Bratcher, M. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2138–2142. (d) Song, W.; Zheng, Z.; Tang, Wang, X. *Polymer* **2007**, *48*, 3658–3663.
- (8) (a) Martínez, G.; Gómez, M. A.; Gómez, R.; Segura, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5408–5419. (b) Martínez, G.; Gomez, M. A.; Marco, C.; Ellis, G.; Gómez, R.; Segura, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6722–6733. (c) Tang, B. Z.; Peng, H.; Leung, S. M.; Au, C. F.; Poon, W. H.; Chen, H.; Wu, X.; Fok, M. W.; Yu, N. T.; Hiraoka, H.; Song, C.; Fu, J.; Ge, W.; Wong, G. K. L.; Monde, T.; Nemoto, F.; Su, K. C. *Macromolecules* **1998**, *31*, 103–108.
- (9) Lin, Y.; Zhou, B.; Fernando, K. A. S.; Liu, P.; Allard, L. F.; Sun, Y.-P. *Macromolecules* **2003**, *36*, 7199–7204.
- (10) (a) Moritani, T.; Kuruma, I.; Shibata, K.; Fujiwara, Y. *Macromolecules* **1972**, *5*, 577–580. (b) Wu, T. K.; Ovenall, D. W. *Macromolecules* **1973**, *6*, 582–584.
- (11) (a) Wu, T. K. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 343–352. (b) Wu, T. K.; Ovenall, D. W. *Macromolecules* **1974**, *7*, 776–779.
- (12) (a) Jameison, F. A.; Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1986**, *19*, 2168–2173. (b) Imai, K.; Shiomi, T.; Tezuka, Y.; Tsukahara, T. *Polym. J.* **1991**, *23*, 1105–1109. (c) Martínez, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2476–2486.
- (13) Wang, Y.; Ono, H.; Ikeda, A.; Hori, N.; Takemura, A.; Yamada, T.; Tsukatani, T. *Polymer* **2006**, *47*, 7827–7834.
- (14) Fernández, M. D.; Fernández, M. J. *J. Appl. Polym. Sci.* **2008**, *107*, 2509–2519.
- (15) Szabo, T.; Berkesi, O.; Dekany, I. *Carbon* **2005**, *43*, 3186–3189.
- (16) Yang, S.-Y.; Huang, C.-Y. *J. Appl. Polym. Sci.* **2008**, *109*, 2452–2459.
- (17) *Polyvinyl Alcohol Developments*; Finch, C. A., Ed.; John Wiley & Sons: Chichester, 1992.
- (18) Mallapragada, S. K.; Peppas, N. A. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1339–1346.
- (19) Luo, Z.; Vora, P. M.; Mele, E. J.; Johnson, A. T. C.; Kikkawa, J. M. *Appl. Phys. Lett.* **2009**, *94*, 111909.
- (20) Salavagione, H. J.; Martínez, G.; Gómez, M. A. *J. Mater. Chem.* **2009**, *19*, 5027–5032.
- (21) Matsuo, Y.; Hatase, H.; Sugie, Y. *Chem. Mater.* **1998**, *10*, 2266–2269.
- (22) Thyagarajan, G.; Janarthanan, V. *Polymer* **1989**, *30*, 1797–1799.
- (23) Naidu, B. V. K.; Sairam, M.; Raju, K. V. S. N.; Aminabhavi, T. M. *J. Membr. Sci.* **2005**, *260*, 142–155.