Graphene Nanocomposites with High Molecular Weight Poly(ε-caprolactone) Grafts: Controlled Synthesis and Accelerated Crystallization

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Supporting Information

ABSTRACT: Grafting of high molecular weight polymers to graphitic nanoplatelets is a critical step toward the development of high performance graphene nanocomposites. However, designing such a grafting route has remained a major impediment. Herein, we report a "grafting to" synthetic pathway by which high molecular weight polymer, poly(ε-caprolactone) (PCL), is tethered, at high grafting density, to highly anisotropic graphitic nanoplatelets. The efficacy of this tethering route and the resultant structural arrangements within the composite are confirmed by neutron and X-ray scattering measurements in the melt and solution phase. In the semicrystalline state, X-ray analysis indicates that chain tethering onto the graphitic nanoplatelets results in conformational changes of the polymer chains, which enhance the nucleation process and aid formation of PCL crystallites. This is corroborated by the superior thermal properties of the composite, manifested in accelerated crystallization kinetics and a significant increase in the thermal degradation temperature. In principle, this synthesis route can be extended to a variety of high molecular weight polymers, which can open new avenues to solution-based processing of graphitic nanomaterials and the fabrication of complex 3D patterned graphitic nanocomposites.

The development of high performance polymer nanocomposites by the incorporation of nanoparticles of different dimensions into polymer matrices is of significant interest for next-generation advanced polymeric materials. The prospect of achieving enhanced material properties such as high mechanical strength or better electrical conductivity with the addition of a small amount of nanoparticles has motivated a vast body of research.1−4 In such materials, anisotropic nanoparticles like graphene or expanded graphite are becoming increasingly attractive due to their low percolation threshold and potential multifunctional applications. For general applications, graphene is usually obtained through standard graphite-exfoliation methods that yield graphene oxide (GO). Despite its advantageous single- or few-layer structure, the hydrophilic nature of GO causes irreversible aggregation5 in organic solvents and polymer matrices and limits the versatility of approaches and media that can be used in graphene-based products. To date, the major impediment in advancing high-performance graphene nanocomposites is the difficulty in controlling the dispersion and the interaction of the graphitic phase within polymer matrices without sacrificing the inherent properties of the nanoplatelets.6 In fact, different strategies, like modification through covalent or noncovalent techniques, have been employed to optimize the dispersion and the interfacial interactions of graphitic nanoplatelets in nanocomposites.7,8 Other techniques like "grafting from" and "grafting to" have also gained widespread popularity over the past few years due to their intrinsic capability of allowing better control of interfaces and chain density. Materials synthesized by these techniques often result in better graphitic dispersion, especially at higher grafting densities.9 In such systems, polymer grafts with moderate to high molecular weights transition from sparse to dense brush regime at grafting densities of ≈0.05 chain/nm².10 For instance, grafting densities in the dense brush regime

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(0.07–0.4 chain/nm²) are commonly reported on modified graphitic sheets obtained by "grafting from" techniques and are associated with high graphitic dispersion in polymers and solutions. But, despite the effectiveness of the "grafting from" technique in growing polymers with low polydispersity and high grafting density, it is restricted to polymers whose initiators can be appended on the nanomaterials’ surface. In contrast, "grafting to" is a more versatile and easy approach for tethering a broad spectrum of polymers. However, the "grafting to" technique has been less frequently adopted on graphene due to the challenges of grafting high-molecular-weight polymer chains at high grafting densities and has thus been more commonly used with low molecular weight polymeric systems. Yet, even with low molecular weight polymers, "grafting to" approaches yield relatively low grafting densities (0.002–0.02 chain/nm²) on graphene, rendering most "grafted to" graphene systems in the mushroom or sparse-brush regime.

Besides the need for a facile synthetic route for tethering high molecular weight polymers onto graphene, a proper understanding of the molecular processes involved in controlling the properties of the nanocomposites is required. The caveat is that attaching nanoparticles to a polymer matrix can cause perturbations in the polymer chain conformations, which can alter the macroscopic material behavior. This is particularly important in semicrystalline polymers in which the structure and dynamics of the polymer chains are quite distinct in the crystalline and amorphous regions of the polymer. In such nanocomposites, it is crucial to understand the effect of the nanoparticles (topological barriers) and tethering-induced conformational (entropic) changes on the resultant nucleation and crystallization mechanisms. The topological effect of nanoparticles on polymer crystallization was thoroughly explored in a recent comparative study on graphene and carbon nanotube (CNT) poly(ε-lactide) (PLLA) blends. CNTs were found to be more effective in inducing highly ordered crystal structures due to the 1D distribution of the nucleating sites that they offer and their low hindrance to conformational adjustments of the polymer chains. Graphene sheets, on the other hand, provide a 2D landscape of nucleating sites for randomly oriented single crystals, which can impinge and suppress further crystal growth. In fact, there is increasing experimental and computational support for the hypothesis that graphene-induced crystal growth in blend composites strongly depends on lattice matching. These results emphasize that, for graphene to be an effective additive for the development of advanced semicrystalline polymer composites, precursor conformational order is required at the interface. One way of obtaining such order is through high-density chain grafting onto graphitic sheets. The impact of such precursor conformation was recently validated on highly grafted CNT–poly(ε-caprolactone) (PCL) composites, which showed significantly faster crystallization rates compared to their blend analogues. To the best of our knowledge, analogous studies on the crystallization behavior of grafted graphene platelets are lacking and are no doubt demanding. The crystallization behavior in such nanocomposites is of ultimate importance not only on a scientific level but also for applications because the crystal structure and morphology directly impact macroscopic material properties like mechanical strength. In fact, the need for such investigations is becoming more pressing, especially with the growing initiative of using semicrystalline polymer graphene nanocomposites as an environmentally friendly substitute for synthetic polymers. Thus far, high-density tethering of high molecular weight semicrystalline polymers onto graphene platelets (often difficult due to steric hindrance) is still in its nascent stage, and its utilization in enhanced-performance semicrystalline composites has not been explored. In this communication, we report a facile "grafting to" synthetic route for tethering high molecular weight polymer, in this case, poly(ε-caprolactone) (PCL), onto functionalized graphene platelets and demonstrate the effectiveness of this strategy in inducing superior thermal properties in the composite.

The synthesis route we report here utilizes the isocyanate group as the pendant unit for the anisotropic graphene platelets due to its linear structure, which minimizes steric hindrance and allows the polymer chains in the solution phase to reach the reactive site without significant barriers (Supporting Information, section 1). High molecular weight PCL with weight-average molecular weight $M_w \approx 80000$ g/mol, number-average molecular weight $M_n \approx 44000$ g/mol, and polydispersity index, PDI ($M_w/M_n$) \approx 1.8, was synthesized using techniques described elsewhere and was "grafted to" toluene diisocyanate (TDI) functionalized graphene nanoplatelets (CMG) in the sequence shown in Figure 1. Characterization of CMG, poly(ε-caprolactone) and polymer-grafted nanoplatelets (PCLG) is provided in the Supporting Information (Figures S2 and S3).

![Figure 1](https://example.com/image.png)

Figure 1. Schematic pathway for tethering high-$M_w$ PCL chains onto chemically modified graphene (CMG) nanoplatelets, as inferred from XPS spectra at each step of the synthesis procedure.

The mechanistic pathway of the reaction (Figure 1) was illustrated by high resolution X-ray photoelectron spectroscopy (XPS). Analysis of the XPS spectra on expanded graphite (EG), GO and CMG shows clear evidence of a predominant reaction of TDI with the hydroxyl groups of the GO surface, indicating the successful conversion of GO to CMG. After the completion of the reaction, the dispersion of PCL-grafted graphene platelets in tetrahydrofuran was centrifuged for 3 min at $\approx 210$ rad/s to remove the unreacted graphitic platelets. The supernatant solution was isolated and was reprecipitated from excess cold methanol in order to remove low molecular weight polymer chains. The procedure of redissolving the isolated product in tetrahydrofuran and reprecipitating in excess cold methanol was repeated five times. These two purification steps are critical for synthesizing a composite material free of ungrafted PCL chains and unreacted graphene nanoplatelets. The resultant composition is estimated to be $\approx 1\%$ graphene by

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mass. The isolated product was pelletized using a hydraulic press under vacuum at 80 °C for further characterization. The polymer grafting density (σ) was estimated from thermogravimetric analysis to be ≈0.2 chain/nm², which is substantially higher than literature values reported on “grafting to” techniques on graphene.9 The radius of gyration of the unperturbed PCL chain was calculated from the empirical relation, \( R_g = 0.031 \times M_w^{1/2} = 65 \text{ Å}, \) based on intrinsic viscosity measurements of linear PCL chains in a \( \theta \) solvent.19 This \( R_g \) value renders a reduced tether density, \( \Sigma = \sigma \pi R_g^2 = 26. \) Since \( \Sigma \gg 1 \), we surmise the grafted polymer chains fall in the dense brush regime and are thus highly stretched.10 This high-density chain grafting should prevent graphene aggregation and ensure a good dispersion of the graphitic nanoplatelets in the composite.

The efficacy of the polymer tethering and graphitic dispersion was confirmed by contrast variation small-angle neutron scattering (SANS) experiments on suspensions of the composite in deuterated and hydrogenated dimethylformamide (dDMF and hDMF, respectively; Figure 2). The neutron scattering length density for the polymer is similar to that of the protonated solvent, but is significantly different from that of the deuterated solvent (see Table S1). Hence, from a neutron scattering viewpoint, the polymer is almost invisible in the protonated solvent, but is significantly perturbed in the deuterated solvent.18 This contrasts verify that the graphene nanoplatelets can be inferred from the wide-angle X-ray scattering (WAXS) patterns on PCL and PCLG and the corresponding Gaussian fits. More insights into the local crystalline order and the dispersion of the graphene nanoplatelets can be inferred from the wide-angle X-ray scattering (WAXS). The absence of the peak due to graphene at low 2\( \theta \approx 10^\circ \) or at 2\( \theta \approx 26.5^\circ \) (\( \lambda = 1.54 \text{ Å} \)) indicates excellent dispersion of the graphene nanoplatelets in the PCL matrix. Neat PCL is known to adopt an orthorhombic structure with Miller indices of (110), (111), and (200), as demonstrated in Figure 3c. The ratio of the (110) peak to the (111) peak provides information about the orientation and/or the crystallization texture in the samples. Since the 2D WAXS scattering patterns (not shown here) show no sign of anisotropy on any of the measured samples in either the crystalline or the melt state, we attribute variations in the peak ratio to changes in crystallinity rather than to preferential alignment within the sample.21 Accordingly, the decrease in the peak ratio for PCLG compared to PCL (Figure 3c,d) indicates a perturbation in the crystalline morphology of the polymer. This is contrary to previous studies on “non-grafted” polymer crystals grown on graphene sheets22 in which no change in the crystalline polymer morphology was detected. However, it is analogous to earlier observations of significant changes in the crystalline morphology of nylon-6 crystals in layered-silicate
composites in the case of strong interactions between the silicate sheets and the polymer.\textsuperscript{23} This suggests that the observed changes in the crystal morphology of the graphene grafted PCL are due to enhanced “effective” interactions between the polymer and the graphitic platelets, herein caused by chain grafting. But unlike silicate/nylon-6 composites, the present system shows a slight increase in the percentage crystallinity compared to neat PCL with a crystallinity of 40 ± 0.5%. The reported errors represent ±1 standard deviation throughout the manuscript. Further analysis of the width of the (110) diffraction peaks shows a reduction in the crystallite size in PCLG compared to PCL (Supporting Information, section 4). This is further corroborated by earlier studies on graphene-induced crystallization in polyethylene and poly(\textit{l}-lactide).\textsuperscript{16,22} In this scenario, the increase in crystallinity is attributed to the increase in the number of nucleating sites on the graphitic nanoparticles within the composite and is in agreement with the transformation process in the composite, including nucleation and growth (section 5 of the Supporting Information). In the temperature window of the study, PCL took longer to crystallize compared to PCLG, which suggests that the graphene platelets act as heterogeneous nucleating agents. The resultant isothermal thermographs were analyzed using the Avrami equation:\textsuperscript{24}

\[ 1 - X_i = \frac{\Delta H_i \equiv \Delta H_i}{\Delta H_{i=\infty} - \Delta H_{i=0}} = e^{-k \times c^n} \]  

where $X_i$ is the relative crystallinity at time $t$, $\Delta H_{i=\infty}$, $\Delta H_i$, and $\Delta H_{i=0}$ are the crystallization enthalpies at complete crystallization at time $t$ and at $t = 0$, respectively. The parameters $k$ and $n$ represent the crystallization rate constant and the Avrami exponent, respectively. PCL registered an average Avrami exponent of $2.3 \pm 0.05$, whereas $n$ increased to $2.6 \pm 0.05$ in PCLG. The similarity of the Avrami exponents suggests that the chain grafting did not alter the growth dimensionality of individual spherulites. Moreover, an Avrami exponent of $2.5-3$ indicates three-dimensional growth of polymer spherulites in either case. Nonetheless, a significant acceleration in the crystal growth in the case of tethered graphene nanoplatelets is evident from the half-crystallization time $t_{1/2}$ defined as the crystallization time at $X_i = 0.5$. The composite shows more than 50% decrease in $t_{1/2}$ compared to neat PCL, indicating effective graphene-induced nucleation (Figure 4). Temperature-dependent temporal evolution of the relative crystallinity data are shown in Figure S12.

![Figure 4](image)

Beside the changes in the crystallization behavior, we also observed remarkable enhancement in the thermal stability of the polymer. For the composite, a significant increase of $80 \pm 2$ °C was detected in the thermal degradation temperature, $T_d$. This is in stark contrast with previous findings on covalently linked graphene–PCL composites\textsuperscript{25} or PCL–grafted clay composites,\textsuperscript{26} which show almost no change in the thermal degradation compared to neat PCL. However, similar significant changes in $T_d$ were recently observed in polyethylene/reduced-graphene-oxide composites prepared via controlled solution crystallization,\textsuperscript{22} but with much higher graphene content. This improved thermal degradation behavior can be ascribed to the efficiency of the graphitic nanoplatelets in capturing or scavenging free radicals.\textsuperscript{27} In the present composite, the significant delay in thermal degradation with such a low graphitic content emphasizes the high efficiency of the present grafting approach in reducing the free radicals in the matrix and promoting the thermal stability of the composite (Figure S14). Indeed, analysis of the activation energy ($E_a$) associated with the degradation process, using the Freeman–Carroll technique,\textsuperscript{28,29} renders $E_a$ values of $180 \pm 20$ kJ/mol for PCLG and $128 \pm 23$ kJ/mol for PCL, clearly indicating that chain tethering raised the energy barrier associated with thermal degradation and imparted higher thermal stability to the composite (section 7 of Supporting Information).

In conclusion, we present a facile synthesis route for grafting high molecular weight polymer onto anisotropic graphitic nanoplatelets, facilitated by the design of the functional group attached to the graphene surface. The grafting-induced alterations in chain conformation (indirectly inferred) and the presence of nanoplatelets result in superior thermal properties of the composite compared to the neat PCL. The complementary structural and thermal characterization we applied in this work support the conclusion that polymer tethering to graphene sheets enhances conformational order of the polymer chains and aid superstructure formation of PCL crystallites. Not only do the grafted-graphene sheets act as nucleating sites for the polymer crystals, they also result in enhanced thermal stability of the polymer. We anticipate that the present grafted system is more thermally stable than an analogous blend, where only space confinement is effective. Such property enhancements are of great value for applications requiring advanced semicrystalline polymer nanocomposites. However, it would also be interesting to investigate how the properties of the present composite would change with different graphene content upon blending with bulk polymer,
given the previously observed dependence of composite properties on graphitic loading.\(^{30,31}\) Finally, we emphasize the observation that our highly grafted graphene platelets demonstrate good dispersibility in DMF over several months, which begins to offer new possibilities for solution-phase engineering of a broad range of graphene-based materials, from graphene suspensions for energy-harnessing applications\(^32\) to solution-processed 3D-patterned graphene nanocomposites\(^{33}\) with virtually infinite choices of polymer matrices.

**ASSOCIATED CONTENT**

Supporting Information

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Experimental details, model fitting, and supplementary experimental evidence (PDF).

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