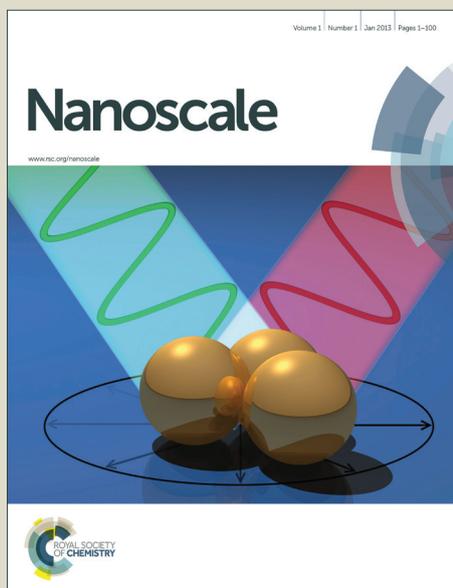


Nanoscale

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Designer Stabilizer for Preparation of Pristine Graphene/Polysiloxane Films and Networks

Dorsa Parviz, Ziniu Yu, Ronald C. Hedden,* Micah J. Green**

Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409, USA

+Current address: Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, USA

**corresponding author (polymer synthesis): ronald.hedden@ttu.edu*

***corresponding author (graphene nanomaterials): micah.green@tamu.edu*

Abstract

A conductive polymer film containing pristine graphene was prepared by designing a polysiloxane-based stabilizer for graphene. The stabilizer was prepared by grafting 1-ethynylpyrene to the backbone of a poly(dimethylsiloxane)-*co*-(methylhydrosiloxane) (PDMS-PHMS) random copolymer by Pt-catalyzed hydrosilylation with a SiH:ethynyl ratio of 1.0:1.3. The resulting copolymer was able to stabilize pristine graphene in chloroform solution via π - π interactions between the pyrene groups and graphene sheets. TEM and SEM images show a homogeneous distribution of the graphene in cast films deposited from chloroform. The conductivity of a graphene/PDMS film prepared from copolymer with a 1.7 vol. % graphene loading was measured as 220 S/m after the removal of unbound polymer by a simple separation technique. With a SiH:ethynyl ratio of 1.7:1.0, the copolymer self-crosslinked at 110 °C in the presence of adventitious moisture, providing a straightforward route to incorporate graphene into silicone elastomers. The crosslinking process (with and without added graphene) was characterized by FT-IR spectroscopy and by swelling and extraction of the obtained networks. Again, unbound polymer removal increases the conductivity of the composite.

Keywords: graphene, pyrene derivatives, designer stabilizer, poly(dimethylsiloxane), hydrosilylation

Electrically conductive polymer nanocomposites have received growing attention in recent years and conductive fillers such as carbon black¹⁻³ and carbon nanotubes (CNT) have been mixed into non-conductive polymer matrices to enhance electrical conductivity.⁴⁻⁷ However, the conductivity reported for these composites in the literature varies widely; precise determination of the percolation threshold for various composite systems has been controversial because of differences in sample preparation and microstructure. In particular, the quality of the dispersion of the filler within the polymer matrix is one of the main parameters that cause the inconsistency of the conductivity value reported in the literature. Therefore, new strategies that can improve filler-matrix compatibility and filler dispersion quality are crucial.

Graphene is a 2D carbon sheet with promising electrical, thermal and mechanical properties which make it attractive for nanocomposite applications.⁸⁻¹³ However, difficulties in exfoliation and dispersion have caused major obstacles for scalable graphene/polymer nanocomposite production.^{9,14-16} As a result, many prior attempts at preparing graphene/polymer nanocomposites have resulted instead in multilayer graphite nanoplatelet-filled polymers. One technique often used to overcome this issue is to produce graphene oxide (GO) for exfoliation and dispersion, followed by a reduction step aimed at removing oxygen-containing functional groups of GO.^{17,18} However, the potential to obtain nanocomposites of even higher electrical conductivity by using pristine graphene motivates the search for new dispersion and processing strategies that do not rely upon oxidation schemes.

Another promising technique involves stabilizing pristine graphene against restacking in solvents using stabilizer molecules such as surfactants and polymers.¹⁹⁻²² Additionally, polyaromatic molecules can display π - π interactions with graphene such that these species may act as a dispersant for graphene (as well as CNTs) in aqueous solutions.^{23,24} In our prior work, we investigated the behavior of pyrene derivatives with various functional groups as stabilizers for pristine graphene.²⁵ While the basal plane of the pyrene adsorbs onto the surface

of graphene via π - π stacking, attaching functional groups onto the pyrene allows for electrostatically stabilized colloidal graphene dispersion. These functional groups' interactions are solvent-dependent; thus, it is possible to vary functional groups on the pyrene and design pyrene-based stabilizers for use in specific media. For example, pyrene molecules have been grafted to the backbone of poly(glycidyl methacrylate) to stabilize graphene by π - π stacking in the epoxy matrix.²⁶ In another attempt to tailor graphene-polymer π - π interactions in nanocomposites, thermosensitive polyacrylamide-based nanocomposites have been prepared by attaching pyrene molecules to the polymer chain, using this new polymer as a graphene dispersant, followed by polymerization.²⁷ In this paper, we explore the use of pyrene as a side group for elastomeric silicone polymers and create the first-ever conductive dispersion of pristine graphene in a silicone matrix.

Polydimethylsiloxane (PDMS) is an organosiloxane polymer having a low glass transition temperature and good thermal stability, which is used in a wide range of applications such as elastomers, electronic materials, microfluidics, medical devices, and piezoresistive devices.²⁸ GO and reduced graphene oxide (RGO) can be added to elastomer matrices in order to enhance properties such as mechanical strength, electrical conductivity and barrier properties.²⁹ Due to the attractive possibilities of enhancing mechanical or electrical properties of silicones by addition of carbon nanomaterials, numerous studies have reported incorporation of graphite nanoplatelets, GO and RGO into PDMS. Kujawski *et al.* mixed exfoliated graphite into the PDMS and observed a percolation threshold at 3 wt. % loading of the filler, along with enhanced mechanical properties of the composite.³⁰ Chen *et al.* studied the piezoresistive behavior of PDMS composites filled with graphite nanosheets by wet-mixing.³¹ Raza *et al.* blended PDMS with graphite nanoplatelets through mechanical mixing and studied thermally conductive behavior at interfaces.³² Ozbas *et al.* mixed exfoliated, oxidized graphite sheets into PDMS, which led to a low percolation threshold at 0.8 wt. % loading of the filler and also a tenfold decrease in gas permeability through the composite.³³ Xu *et al.* shear-mixed RGO into PDMS

to enhance the mechanical properties.³⁴ However, the aggregation of nanosheets made it difficult to obtain a homogenous dispersion of the fillers in the polymer. To overcome this issue, several research groups tried methods other than conventional mixing of the filler into the polymer matrix. Guimont *et al.* grafted PDMS onto graphite oxide sheets via a hydrosilylation reaction and varied the grafting density to enhance the filler dispersion quality in the PDMS.³⁵ Gao *et al.* covalently attached the GO to PDMS, and they observed enhancement in mechanical properties.³⁶ Hou *et al.* functionalized GO to make its surface energy more compatible with PDMS.³⁷ Also, some groups have infused pre-made graphene or CNT aerogels (or other conductive monoliths) with PDMS, creating rigid composites.³⁸

In all prior studies, expanded graphite, GO or RGO were used as conventional nanofillers, with varying degrees of success in dispersion. Usage of GO and RGO can affect the conductivity because the reduction process cannot remove all the oxidized functional groups; some of them remain on the surface of the sheet and hinder electrical conductivity of the RGO compared to pristine graphene.^{39,40} Using pristine graphene, instead of GO and RGO, potentially helps to overcome these issues and improve the conductivity.

One possibility which has not been explored is to incorporate pristine graphene into linear PDMS or its copolymers in order to produce a conductive, liquid-phase nanocomposite that is well above its glass transition temperature at ambient temperature. In the absence of solvent, such a material does not have any vapor pressure, which is potentially favorable for conductive fluid applications. For example, this conductive melt can be cast onto a patterned substrate to fabricate stretchable electronic devices. In order to disperse pristine graphene in a solvent-free polymer, graphene sheets should interact strongly with the surrounding polymer matrix. Here we introduce a new strategy for combining pristine graphene with a siloxane-based matrix using a designer stabilizer that utilizes graphene-pyrene π - π interactions. Pyrene side groups are grafted to a PDMS backbone to design a copolymer that can act both as the matrix and the graphene stabilizer. This approach allows one to use pristine graphene as filler by

enhancing the compatibility of the filler and matrix. The product is a two-component system which does not have functional groups covalently bonded to the graphene, leaving the conjugation of the graphene rings intact. This strategy leads to the first pristine graphene/PDMS nanocomposites, which can be cast as solvent-free films. The combination of high conductivity and liquid-phase processability is a key feature of this work and is likely to inspire novel fabrication techniques for sensors, actuators and soft-matter devices based on simple casting methods. The PDMS/graphene copolymers can also be crosslinked readily by simply changing the stoichiometry of the hydrosilylation reaction, producing the first example of a silicone elastomer containing pristine graphene.

Experimental

Materials: Poly(dimethylsiloxane)-*co*-(methylhydrosiloxane) copolymer (HMS-064, 5-7 mole % PMHS) was purchased from Gelest Inc (USA). Cis-dichlorobis(diethyl sulfide) Pt (II) catalyst was purchased from Strem Chemicals (USA). 1-ethynylpyrene, chloroform (HPLC grade), toluene and methanol were purchased from Sigma-Aldrich (USA). Expanded graphite was provided by Asbury Carbons (CAS# 7782-42-5, Grade 3806, USA). All the chemicals were used as received.

Synthesis of poly(dimethylsiloxane)-co-(methyl(vinylpyrenyl)siloxane) linear copolymers (PMPyS): 5.0 g of HMS-064 copolymer was dissolved in 52.8 g of chloroform. 30 mol % excess (1.2 g, 5.3 mmol) of 1-ethynylpyrene was added to the solution, which was homogenized by stirring and heated to 44 °C. 847 μl of a toluene solution of cis-dichlorobis(diethyl sulfide) Pt (II) (2.66×10^{-3} g/g toluene) was added to initiate the hydrosilylation reaction. This grafting reaction was allowed to proceed at 44 °C for 3 d in solution. The reaction product was purified and separated into fractions of comparatively narrow molar mass distribution by fractional precipitation from chloroform (a good solvent) by incremental addition of methanol (a poor

solvent). Initial polymer concentration was approximately 10 g/L in chloroform. The residual liquid phase was discarded.

Preparation of Graphene Dispersions in PMPyS linear copolymers (PMPyS-G): In a typical preparation, a specific amount of a fractionated PMPyS polymer was dissolved in chloroform to obtain 1.0 mg/ml of pyrene in the final solution. Expanded graphite (EG) was subsequently added to the solution (30 mg/ml) and was tip sonicated (Misonix sonicator, XL 2000) for 1 h. During the sonication, an ice bath was used to maintain the sample at room temperature to avoid any chloroform evaporation and to maximize the efficiency of the exfoliation process. All dispersions were centrifuged (Centrifuge 225, Fischer Scientific) at 5000 rpm for 4 h in order to remove graphitic aggregates. The supernatant of the centrifuged samples was collected and used for further processing and characterization. Also, the original unfractionated polymer was used to disperse graphene through a similar procedure.

Synthesis of poly(dimethylsiloxane)-co-(methyl(vinylpyrenyl)siloxane) networks (PMPyS-N): A crosslinked network of PMPyS was obtained by reacting poly(dimethylsiloxane)-co-(methylhydrosiloxane) with an amount of 1-ethynylpyrene that was insufficient to convert all of the silane groups of the copolymer to vinylpyrene groups. An initial mole ratio of silane:alkyne groups of 1.7:1 was chosen. 1.84 g of HMS-064 copolymer was dissolved in 6.2 g of chloroform. 0.20 g (0.88 mmol) of 1-ethynylpyrene was added to the solution, which was homogenized by stirring and subsequently heated to 44 °C. 110 µl of a solution (2.66×10^{-3} g/g toluene) of cis-dichlorobis(diethyl sulfide) Pt (II) was added to initiate the hydrosilylation reaction between the alkyne group of the 1-ethynylpyrene and the silane groups of the polymer backbone. The grafting reaction was allowed to proceed at 44 °C for 3 d without stirring. The reaction product was poured into an open PTFE container and chloroform was allowed to evaporate at 22 °C for 4 h until a viscous, bronze-colored film was obtained. The temperature was increased to 110 °C and the film was allowed to cure for 7 d in air. No precautions were taken to prevent ambient

moisture from entering the film, and the relative humidity was approximately 40-50 % at the ambient temperature of 22 °C.

The resulting network was swelled to equilibrium in excess chloroform at 22 °C for 3 d, during which time the chloroform was changed twice. The extractable mass fraction of the network was determined after de-swelling the network by gradual addition of methanol, vacuum-drying the material, and recording its mass.

Synthesis of PMPyS network with Included Graphene (PMPyS-NG): A crosslinked network containing pristine graphene flakes was prepared by a similar procedure. After 3 d reaction between HMS-064 and 1-ethynylpyrene in chloroform, the resulting polymer solution (with solids concentration of 20 mg/ml) was sonicated in the presence of expanded graphite (30 mg/ml). The resulting suspension was centrifuged to remove excess graphite, leaving a black solution of polymer-stabilized graphene in the supernatant. The concentration of graphene was measured using the absorbance of the dispersion at 660 nm. This solution was deposited into the PTFE container and cured in air using the same temperature and humidity profile used for PMPyS-N.

FT-IR (Fourier Transform Infrared Spectroscopy): The expected product structure of linear PMPyS was confirmed by FT-IR analysis of the purified fractions using a Thermo Nicolet Nexus 470 spectrometer. In addition, the crosslinking reaction was monitored by FT-IR spectroscopy. A thin film of the reaction mixture was deposited onto a KBr disk and cured with the same temperature program used to prepare bulk samples, while spectra were recorded periodically.

GPC (Gel Permeation Chromatography): The PMPyS fractions obtained were characterized by GPC using tetrahydrofuran as mobile phase and four Phenomenex Phenogel columns ($5\mu\text{m}-10^6 \text{ \AA}$, $5\mu\text{m}-10^5 \text{ \AA}$, $5\mu\text{m}-10^4 \text{ \AA}$, $5\mu\text{m}-10^3 \text{ \AA}$) in series covering a molar mass range of 1 kg mol^{-1} to $10,000 \text{ kg mol}^{-1}$, which were calibrated by poly(methyl methacrylate) (PMMA)

standards. All molar masses reported are relative to PMMA. Elution of the polymer was detected by a Varian 380-LC mass-evaporative detector, and elution of the pyrene groups was detected by a KNAUER V2.8 ultraviolet-visible detector at a wavelength of 348 nm.

UV-Vis Spectroscopy: UV-Vis spectroscopy was performed on a Shimadzu 2550 spectrophotometer on fractionated PMPyS solutions in chloroform to measure the pyrene content of each fraction. All fractions of PMPyS were dissolved in chloroform with a polymer concentration of 1 mg/ml. Samples were scanned from wavelength 200 nm to 800 nm with pure chloroform as a reference. Also, the absorbance was measured on all PMPyS-G samples at 660 nm to measure the concentration of graphene in dispersions. The absorbance of the PMPyS copolymer was negligible at this wavelength. In this case, a solution of PMPyS in chloroform with the same concentration was used as the reference. The extinction coefficient for graphene in presence of the polymers in chloroform was calculated through the vacuum filtration method.

HR-TEM (High Resolution Transmission Electron Microscopy): The dispersions of PMPyS-G and the dispersion prepared with unfractionated polymer in chloroform were deposited on lacey carbon TEM grids and dried in the air for 1 min. A voltage of 75 kV on a Hitachi H8100 was used to image the samples.

SEM (Scanning Electron Microscopy): An accelerating voltage of 2 kV was used to image the samples on a Hitachi S4300 SE/N. The PMPyS-G sample was cast on a filtration membrane (PTFE, 0.2 μm , Omnipore Membrane Filters) for imaging. Samples were mounted on double face carbon tape.

Conductivity measurements: The electrical resistance of the samples was measured using the four-point probe method. The four-point probe head (Signatone, SP4-40045TBY) was mounted on a resistivity measurement stand (Signatone, Model 302). The current was supplied by a high impedance current source (Keithley 2400) through the outer two probes. A voltmeter (Keithley 2000) was used to measure the voltage across the inner two probes.

DSC (Differential Scanning Calorimetry): The thermal behavior of the polymers before and after graphene loading was characterized by DSC (TA Instruments, Model Q-20-1848). Approximately 5 mg of each sample was sealed in an aluminum pan and heating traces were recorded under a nitrogen atmosphere. The heating rate for all the samples was 10 °C min⁻¹ and samples were heated from -80 °C to 90 °C.

Results & Discussion

Designer stabilizer for graphene

Our goal is to design a unique molecule which adsorbs on the pristine graphene sheets and simultaneously acts as a silicon-based polymer matrix. Our prior work shows that pyrene molecules can adsorb on the surface of graphene sheet through π - π interactions; if proper functional groups are attached to the pyrene, the pyrene derivative can stabilize pristine graphene sheets within specific solvents.²⁵ This functional group may be grafted to a polymer; hence, the designer pyrene-polymer molecule stabilizes the graphene sheets and prevents aggregation even after the solvent removal. To synthesize such a stabilizer, pyrene groups of 1-ethynylpyrene were grafted to the backbone of a silicon-based copolymer through hydrosilylation reaction. Figure 1 shows the proposed mechanism of reaction between the alkyne group of the 1-ethynylpyrene and the silane groups of the polymer backbone. The Si-H groups of PHMS covalently bond to the ethynyl groups through hydrosilylation, forming a substituted alkene. Further reaction of the alkene with an additional Si-H is unlikely due to both steric hindrance and due to conjugation with the adjacent pyrene ring. The percentage of Si-H groups bonding to pyrenes through this reaction depends on the initial mole ratio of ethynyl and Si-H groups present in the reaction medium. If the ratio of SiH:ethynyl is higher than 1.0, then excess Si-H groups remain intact after the alkynes are exhausted. These remaining Si-H groups self-crosslink later and form networks. However, if this ratio is lower than one, then most or all of the Si-H groups undergo the hydrosilylation reaction and the product is a linear copolymer. We

studied 1.7:1.0 and 1.0:1.3 as SiH:alkyne ratios to illustrate the dramatic differences in the product resulting from reaction stoichiometry.

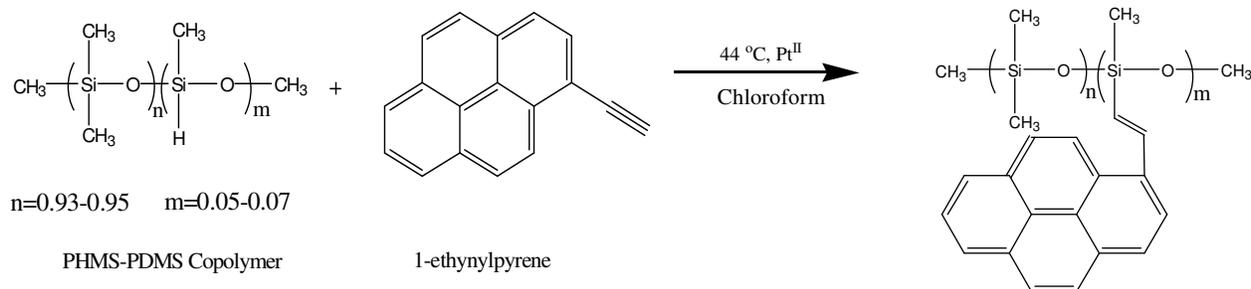


Figure 1. Grafting of 1-ethynylpyrene to PDMS-PHMS copolymer via Pt-catalyzed hydrosilylation in chloroform.

Linear Copolymers (PMPyS) and Graphene-Copolymer Films (PMPyS-G)

The reaction with the SiH:ethynyl ratio of 1.0:1.3 produces a linear copolymer having a broad chain length distribution. Therefore, we separated the sample into seven fractions of narrower molar mass distribution, with M_w ranging from 49 kg mol⁻¹ to 262 kg mol⁻¹, by fractional precipitation. The goal was to create well-defined polymeric stabilizers that were free of low molar mass species, in order to evaluate their effectiveness as graphene dispersants. The fractionation procedure not only narrows the molar mass distribution, but also removes the majority of low molar mass by-products and oligomers. Average molar mass characteristics of the fractions are summarized in Table 1. Molar mass decreases by an order of magnitude in going from fraction 1 to fraction 7. GPC results (Fig. 2) show the fractionated samples with polydispersity index (PDI, M_w/M_n) much less than 2.0 and containing a minimum amount of oligomeric impurities.

Table 1. Molar masses of the PMPyS fractions obtained from GPC analysis.

	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6	Fraction 7
M_w (kg/mol)	262	143	135	92	77	57	49
M_n (kg/mol)	170	82	124	78	66	56	43
M_w/M_n	1.55	1.74	1.09	1.18	1.17	1.02	1.13

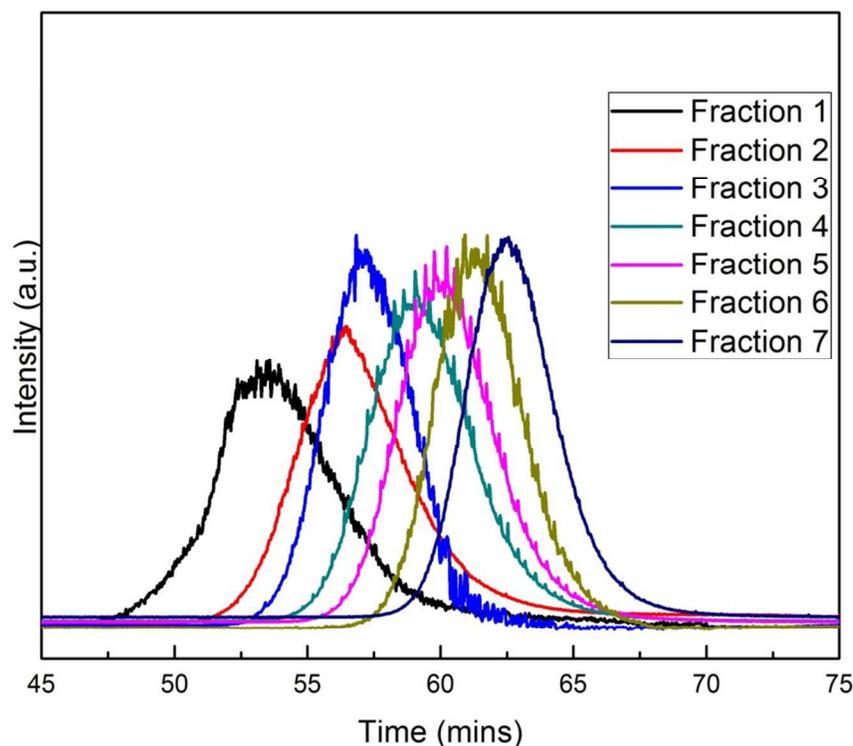


Figure 2. Elution profiles of different PMPyS fractions from GPC.

The expected structure of the PMPyS copolymer was confirmed by FT-IR analysis of the purified fractions (Fig. S1, Supporting Information). Absence of the alkyne band at 3294 cm^{-1} in the PMPyS copolymers indicated a lack of free 1-ethynylpyrene, and appearance of both a C=C stretch band at 1596 cm^{-1} and a second band at 1508 cm^{-1} is indicative of a C=C:Pt complex formed after grafting of pyrene groups to the polymer chains.^{41,42} Attachment of the pyrene groups to the polymer backbone was also confirmed by GPC analysis with multiple detections.

Simultaneous elution of pyrene groups and polymer chains confirmed that grafting of pyrene groups to the backbone was successful (Fig. 3). A minimal amount of free pyrene groups elutes with the residual impurity peak around $t = 80-95$ min, indicating that a majority of the original pyrene groups were successfully grafted to the polymer backbone.

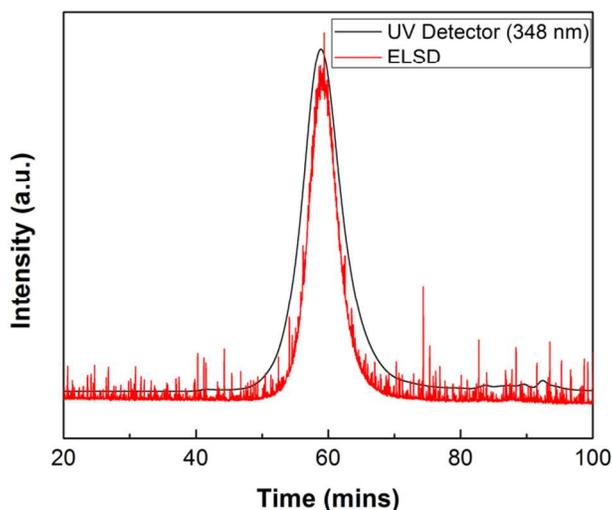


Figure 3. GPC analysis of a fractionated PMPyS sample (fraction 4), confirming attachment of vinylpyrene groups to the polymer backbone.

The pyrene content of each PMPyS fraction was estimated by comparing its UV absorbance spectrum to that of 1-ethynylpyrene (Fig. S2, Table S1). 1-ethynylpyrene exhibits two absorbance bands near 350 and 330 nm, as do the PMPyS fractions; these bands are absent in the PDMS-PMHS copolymer as obtained from the supplier. The pyrene content in each PMPyS fraction was therefore estimated from these bands by comparison to a 1-ethynylpyrene solution of known concentration. The results show that the pyrene content of the PMPyS fractions is independent of the M_w within the limits of uncertainty of the experiment. There is no discernable trend in the pyrene content of the PMPyS chains with increasing molar mass.

The basic procedure for preparing dispersions of stabilized pristine graphene involves exfoliation of the graphene using tip sonication in a given solvent with the stabilizer pre-dissolved in the solvent; this step is followed by centrifugation to remove non-exfoliated graphitic material. The stable colloidal graphene remains in the supernatant with a concentration measured by UV-vis absorbance at 660 nm. We first checked whether 1-ethynylpyrene itself can act as a stabilizer in chloroform, but the resulting concentration of dispersed graphene was zero. This observation is consistent with our prior work;²⁵ regardless of π - π interactions between the graphene and pyrene, this particular functional group on the pyrene cannot provide enough electrostatic or steric repulsion to prevent aggregation of graphene sheets. In contrast, we successfully dispersed the graphene via the fractionated PMPyS samples in chloroform. Adsorption of the PMPyS to the surface of the graphene sheets not only hinders aggregation of the sheets, but provides a mechanism for the sheets to remain suspended in solution indefinitely due to the favorable free energy of mixing between the macromolecular stabilizers and the solvent.

The average extinction coefficient (at 660 nm) for graphene in presence of the polymer in chloroform was $2200 \text{ L g}^{-1}\text{m}^{-1}$, which was measured by the typical procedure of vacuum filtration. The graphene concentration after centrifugation was between 0.1- 0.7 mg/ml for various fractions (Fig. 4). In prior work on pristine graphene dispersions, the graphene concentration showed a clear trend with stabilizer concentration.^{21,25} The dependence of graphene concentration on stabilizer concentration is somewhat complex in the current case since the fractions vary in both molar mass and pyrene content. For simplicity, pyrene concentration was held constant for each fraction in the graphene dispersion experiments. With pyrene concentration held constant, the other quantities that vary from one fraction to another are the total polymer concentration and the molar mass. No trend in graphene concentration is seen at constant pyrene content. All PMPyS fractions are clearly capable of dispersing graphene in chloroform solution, regardless of molar mass. Thus, it appears that the overall

concentration of the pyrene groups, rather than chain length, may be the key factor that governs the maximum achievable concentration of dispersed graphene.

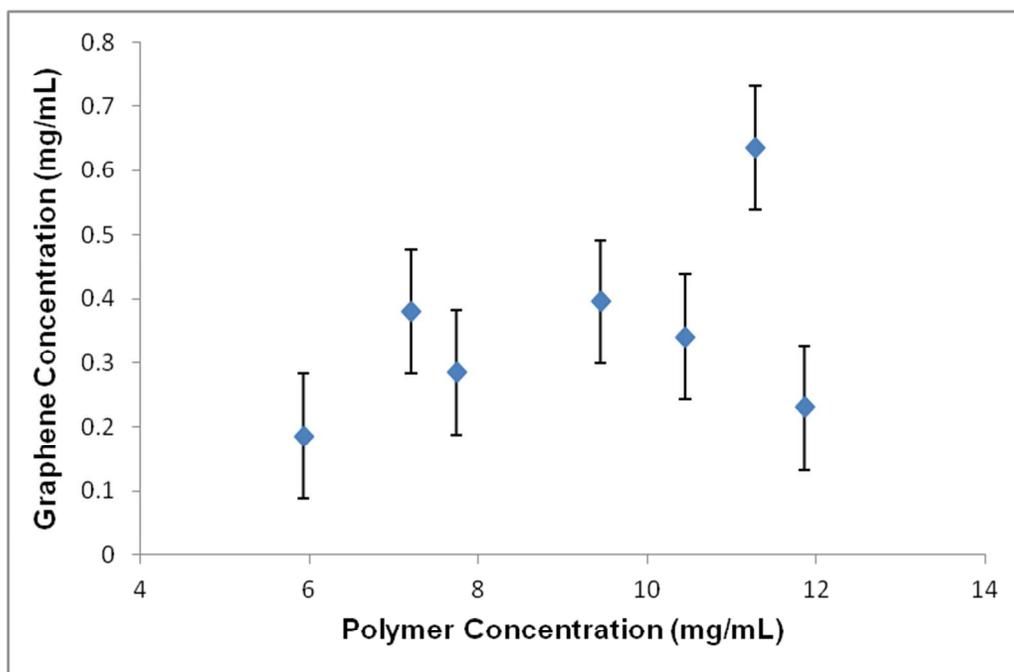


Figure 4. Graphene concentration variation vs. PMPyS fractions concentration; the pyrene content in the dispersions of all fractions was held constant at 1 mg/mL.

TEM images (Fig. 5, Fig. S3) show representative graphene sheets deposited from the dispersions onto a grid. The typical sheet sizes are 1 μm . The edge count for several samples shows that sheets typically consist of 3-4 layers. This edge count is typical for tip-sonicated pristine graphene dispersions enabled by a stabilizer.^{43,44}

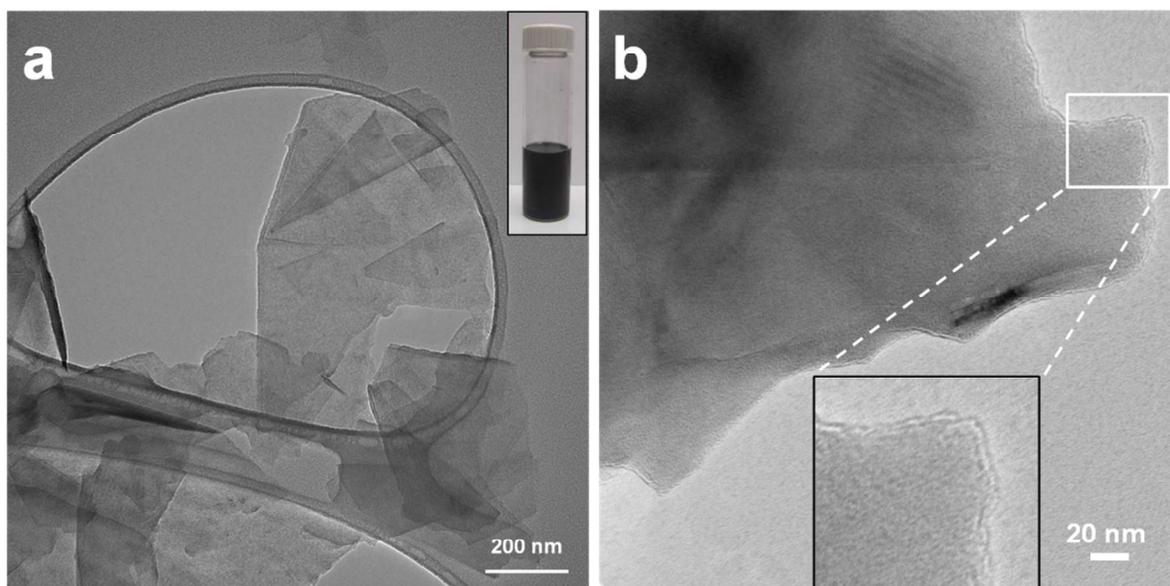


Figure 5. TEM images of (a) graphene sheets in the dispersion prepared by unfractionated polymer in chloroform; the inset is the graphene dispersion obtained from unfractionated polymer and (b) graphene sheets in the dispersion prepared by fraction 4 of the PMPyS polymers; the inset shows the edge of the same graphene sheet. The edge count of the sample shows the few-layer nature of the graphene in the dispersion.

To evaluate the properties of the graphene/copolymer system in the absence of the solvent, a sample with an initial concentration of 1.7 vol. % graphene was cast onto a non-porous polypropylene substrate to form a film. The sample was kept at room temperature for a day to ensure that the chloroform was completely removed. The electrical conductivity of this film was 2.6×10^{-5} S/m, and no increase in conductivity was observed within a few weeks afterward. We hypothesized that removal of the unbound polymer chains which are not adsorbed on the graphene may enhance the electrical conductivity of the sample. In order to substantiate this hypothesis, a simple technique was applied to remove the free polymer chains from the sample. The same dispersion was cast onto the PTFE membrane with 0.2 μm pore size to yield a film with initial 1.7 vol. % graphene content (Fig. 6). This film was not crosslinked or glassy, so the free PMPyS chains were absorbed into the pores of the membrane, leaving a

concentrated film of graphene and bound PMPyS on the surface. The lateral dimensions of the graphene sheet are large enough to prevent sheets from entering the pores. SEM images show no large graphene aggregates and the film morphology has a uniform appearance (Fig. 6).

The electrical conductivity of the sample on the membrane was ~ 4 S/m after being kept at ambient temperature for 2 d. The drastic increase in the electrical conductivity of the sample verifies the removal of unbound polymer chains, increasing the graphene concentration. Furthermore, the electrical conductivity of the same sample was measured after 3 months, at which point the conductivity had increased to 220 S/m. Such a considerable increase can be attributed to gradual leaching of unbound PMPyS chains into the membrane, leaving a concentrated film of polymer-stabilized graphene on the surface. As the PMPyS linear copolymers are well above their T_g at room temperature and can be considered to be a melt, leaching of unbound chains from the film into the pores is likely. The capillary effect induced by the porous structure of the membrane drives the migration of the free polymer chains into the membrane, while the graphene-bound chains remain on top of the membrane. The conductivity value of 220 S/m is significantly higher than what has been reported for polymeric films in the pristine graphene nanocomposite literature. To achieve such conductivity values using conventional nanofillers such as carbon black would require extremely high (20-30 vol %) loadings.⁴⁵ Comparable conductivity values have been achieved using CNTs as nanofiller in other polymer matrices;⁴⁶ however, the prospect of achieving similar conductivity using low-cost, graphite-derived graphene at low loadings in polymers is highly intriguing for broad-scale industrial use. Furthermore, removal of unbound polymer using a porous substrate can be considered as a useful post-processing technique to increase graphene content and composite conductivity that may be useful in the broader field of polymer nanocomposite processing.

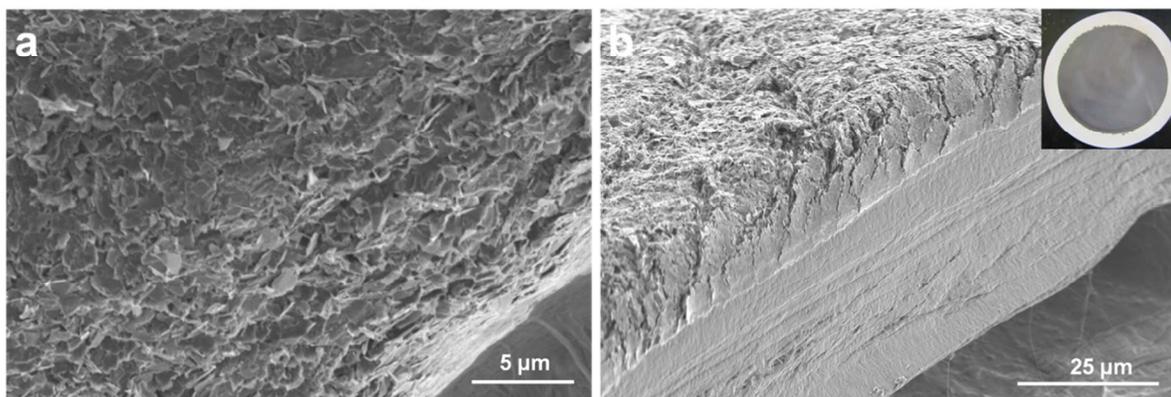


Figure 6. SEM images of (a) the top surface of the graphene/PDMS film (fraction 4) cast on the membrane and (b) cross section of the film on the membrane (inset shows digital image of the cast film). The average thickness of the sample is $\sim 10 \mu\text{m}$. This film has an electrical conductivity of 220 S/m.

The thermal behavior of the PMPyS and PMPyS-G was also investigated using DSC. The T_g of the PMPyS is lower than $-95 \text{ }^\circ\text{C}$ and could not be observed in our setup. As shown in Figure S4, an endotherm due to crystallization was observed at about $-50 \text{ }^\circ\text{C}$ for the fraction of higher molar mass (fraction 2). The appearance of a polymer crystallization peak likely indicates that the sequence distribution in the PMPyS copolymers has some blocky character. The crystallization is probably dominated by a population of chains having long, uninterrupted runs of PDMS repeat units. The bulky pyrene groups are unlikely to participate in crystallization, especially if they are adsorbed to the surface of graphene sheets. For fractions of higher M_w , the addition of graphene does not change the crystallization temperature, further suggesting that pyrene groups do not participate in crystallization. For PMPyS copolymers of lower M_w , crystallization was weak or not observed at all, probably due to the influence of numerous chain ends.

Graphene/Polymer Self-Crosslinking Networks (PMPyS-N & PMPyS-NG)

The fractionated PMPyS samples did not crosslink at high temperatures due to replacement of nearly all SiH groups with pendant pyrene groups. In contrast, the polymer with SiH:ethynyl ratio of 1.7:1.0 was able to undergo a slow self-crosslinking reaction due to the presence of excess SiH groups. This polymer was cured in chloroform solution for 3 d as before, and a film of this polymer was then cast from chloroform solution and heated to 110 °C in air at 40-50 % relative humidity for an additional 4 d. The reaction progress was observed by FT-IR (Fig. 7). After 3 d in chloroform, absence of bands characteristic of alkynes and the presence of C=C (1596 cm⁻¹) bands confirmed that the grafting of 1-ethynylpyrene to the polymer backbone (Fig. 8a) was essentially complete. The band at approximately 2160 cm⁻¹ is associated with Si-H groups, which are consumed during the grafting reaction, but are still present in significant excess after 60 h. After 7 d at 110 °C, the sample had become a firm, rubber-like network. In the presence of the Pt catalyst, excess Si-H groups are able to react with adventitious moisture (Fig. 8a). Disappearance of the band at 2160 cm⁻¹ and appearance of a weak, broad band at approximately 3200 to 3500 cm⁻¹ confirms that silanol (SiOH) groups play a role in the crosslinking. Condensation of silanol groups 110 °C produces Si-O-Si linkages, which are not easily detected spectroscopically due to the presence of a large number of such bonds in the starting material. No new bands are detected except the C=C:Pt band at 1508 cm⁻¹. Pt catalyst residues associate with a portion of the C=C bonds generated during the grafting reaction. This association does not play a role in the crosslinking, as this band was also present in the spectra of the linear PMPyS copolymers, which did not crosslink when heated to 110 °C.

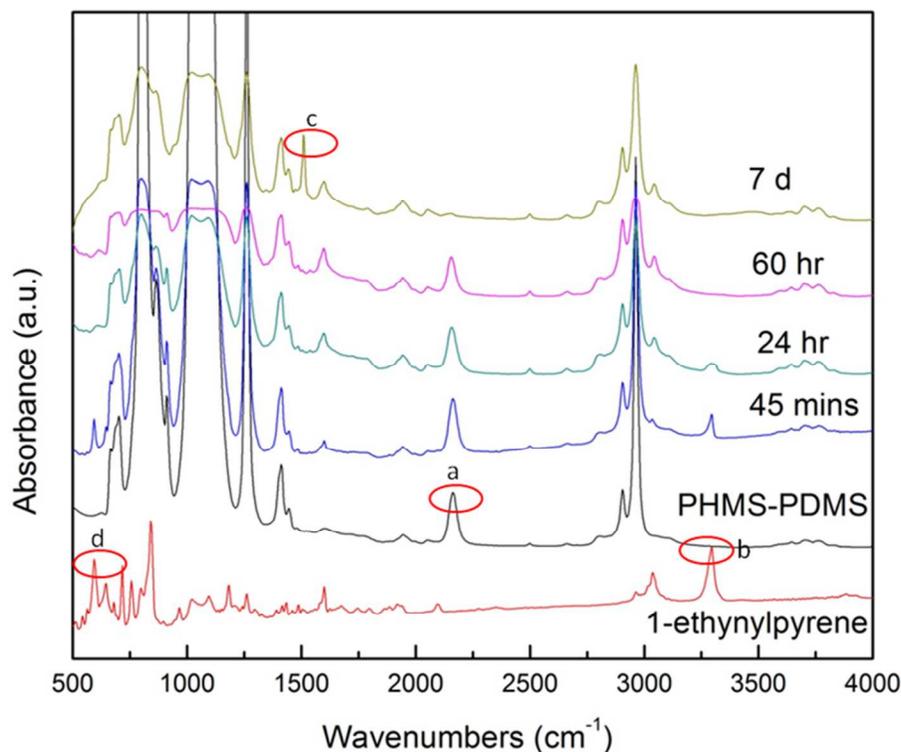


Figure 7. FT-IR spectra of starting materials and reaction products for preparation of PMPyS-N. (a) SiH peak, these peaks were present during the reaction and disappeared only after 7 days, (b) alkyne band peak, absence of this peak at 3294 cm⁻¹ in the PMPyS copolymers indicated a lack of free 1-ethynylpyrene in the product, (c) a second band at 1508 cm⁻¹ is indicative of a C=C: Pt complex formed after grafting of pyrene groups to the polymer chains and (d) -C≡C-H peak which disappeared after the reaction.

This polymer (PMPyS-N) was then used as a stabilizer for graphene as described previously. The polymer concentration was 20 mg/mL and the resulting stable graphene concentration after centrifugation was 0.3 mg/mL as measured by absorbance. The chloroform in these dispersions was evaporated at room temperature to yield a film with 0.6 vol. % graphene. The neat copolymer was heated to 110 °C in humid air, as with the PMPyS-N sample, and underwent a crosslinking reaction according to (Fig. 8a). After 14 d, the PMPyS-

NG sample was removed from the heat and characterized. The PMPyS-NG and PMPyS-N samples are shown in Figure 8b and the inset of 8c. The PMPyS-N sample appeared to reach the gel point more quickly than the graphene-loaded sample, which may be due to the ability of nanofillers to hinder the mobility of the reactive species (e.g. water) during crosslinking. SEM (Fig. 8c) shows a smooth, uniform surface with some areas of roughness. Cross-sections of PMPyS-NG show a similar appearance.

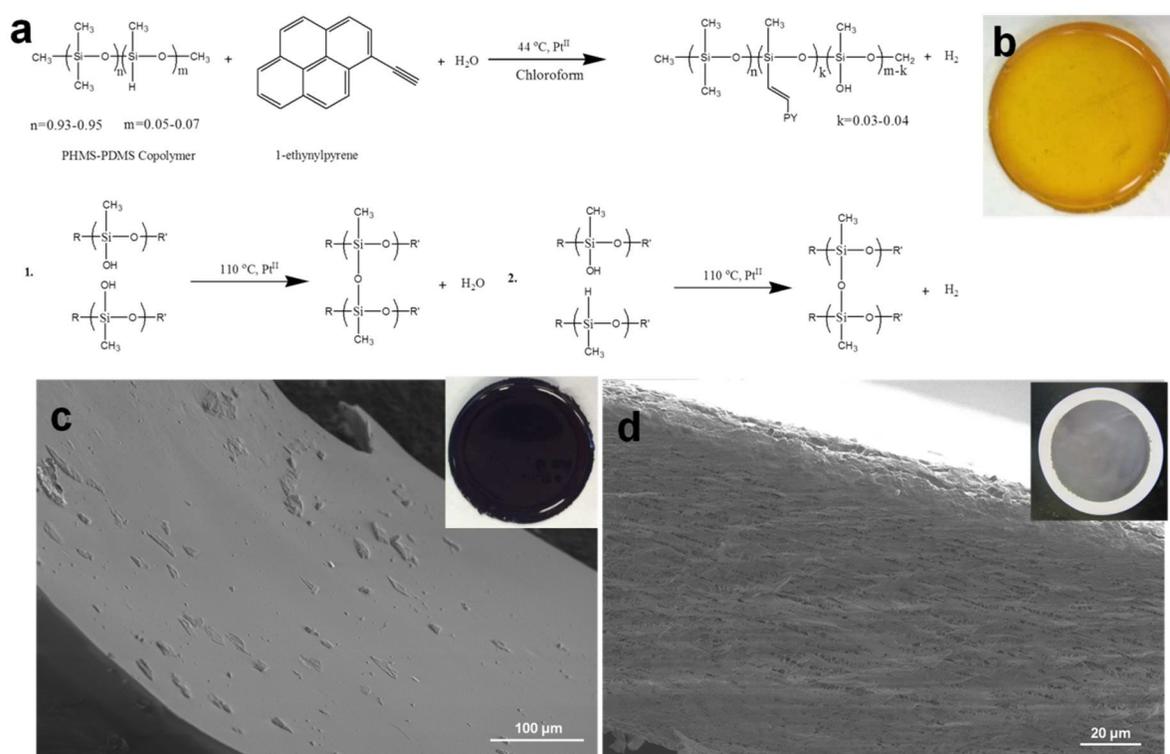


Figure 8. (a) Proposed mechanism of crosslinking; (b) Crosslinked film of PMPyS-N; (c) SEM image of the PMPyS-NG (digital image of the sample is shown in the inset) and (d) SEM image of the cross section of the crosslinked PMPyS-NG cast on the membrane. The average thickness of the sample is $\sim 10 \mu\text{m}$ (digital image of the sample is shown in the inset).

The graphene-loaded sample (PMPyS-NG) had a conductivity of $4.28 \times 10^{-6} \text{ S/m}$. We used the membrane deposition technique as before to remove some of the unbound polymer chains via leaching to enhance the electrical conductivity of the crosslinked composite. A 0.6

vol. % PMPyS-NG film was cast onto the PTFE membrane (as shown in Fig. 8d). The conductivity of this sample immediately after chloroform removal was $\sim 10^{-3}$ S/m. Improvement of the electrical conductivity in this case was not as drastic as in the case of the linear PMPyS-G sample. The most likely explanation is that fewer unbound polymer chains leached into the membrane due to the onset of crosslinking, so the increase in the graphene concentration was not as pronounced in the crosslinked film as in the melt. In addition, the precursor solution for PMPyS-NG contained fewer pyrene units per chain, so the initial amount of graphene stabilized was lower. Also, the conductivity of the crosslinked composite on the membrane did not change after several months, which verifies that completion of crosslinking inhibits further leaching of the unbound polymer chains.

To illustrate that the sample was fully crosslinked, the sample was swelled in chloroform (Fig. 9). The sample did not dissolve, and after deswelling in methanol (a poor solvent for PDMS), the mass decreased from 0.60 g to 0.51 g. The removed mass corresponds to uncrosslinked polymer and any other low molar mass species present. The conductivity of the sample after swelling and deswelling was approximately the same. The conductivity of this sample is typical for pristine graphene/polymer composites reported in the literature, although some rGO/polymer composites have reported substantially higher values.^{14,47-49}

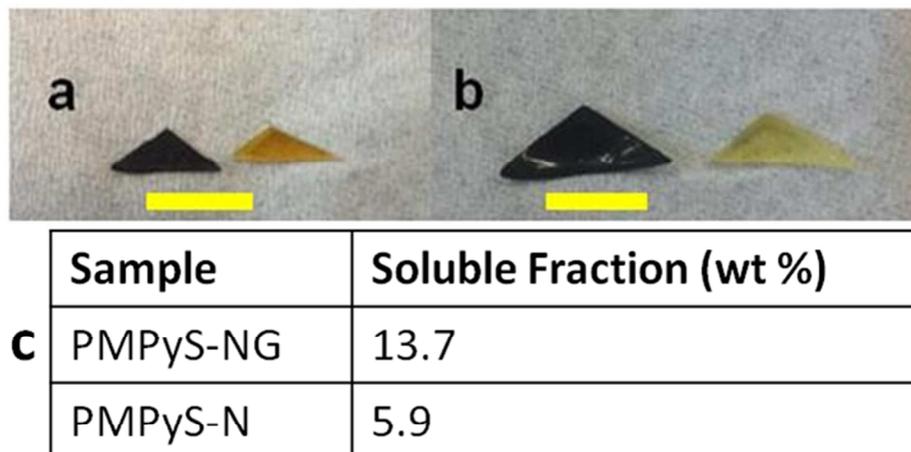


Figure 9. (a) PDMS gel with and without graphene (0.6 vol. %) before swelling; (b) PDMS gel with and without graphene after swelling in chloroform. Scale bars are ~ 1 cm; (c) Soluble fraction of gel as measured from swelling study.

Conclusion

A conductive, silicone-stabilized graphene film was synthesized for the first time using a copolymeric designer stabilizer as the polymer matrix. A pyrene group was grafted to a PDMS backbone via hydrosilylation reaction with a SiH:ethynyl ratio of 1.0:1.3. The resulting polymer was able to stabilize pristine graphene in chloroform through π - π interactions between the pyrene groups and graphene sheets. Graphene/polysiloxane films were obtained by casting the dispersion on different substrates. At 1.7 vol. % loading of the graphene, sample was cast onto a polypropylene substrate and the conductivity of this film was 1.6×10^{-5} S/m. When cast onto a filtration membrane, the same sample had an electrical conductivity as high as 220 S/m. Such a drastic increase in the conductivity was attributed to the removal of unbound polymer which led to higher graphene concentration. SEM images showed a homogeneous distribution of the graphene sheets in the film. Changing the SiH:ethynyl ratio in the hydrosilylation reaction to 1.7:1.0 leaves some unreacted SiH groups in the polymer chain which self-crosslink at higher

temperatures in the presence of adventitious water. The crosslinked graphene/PDMS composite containing 0.6 vol. % graphene had an electrical conductivity of 4.28×10^{-6} S/m, which is typical for pristine graphene/polymer composites reported in the literature. When the same sample was cast onto the porous membrane, the conductivity increased to $\sim 10^{-3}$ S/m due to the removal of unbound polymer. This work holds promise for the synthesis of polymers with graphene-binding pendant groups as a new framework for graphene/polymer nanocomposite design.

Acknowledgements. The authors would like to acknowledge Sriya Das and Fahmida Irin of TTU for helpful insights on this project. We acknowledge Colin Young and Prof. Matteo Pasquali of Rice University for their help with Raman measurements. We also acknowledge Dr. Sinee Simon of Texas Tech University for her equipment for FT-IR measurements. We thank Dr. Brandon Weeks of TTU for his equipment for DSC measurements. We also acknowledge the TTU Imaging Center (funded by NSF MRI 04-511) for the electron microscopy images. Funding was provided by the U.S. National Science Foundation (NSF) under CAREER award CMMI-1253085 and by the Air Force Office of Scientific Research Young Investigator Program (AFOSR FA9550-11-1-0027).

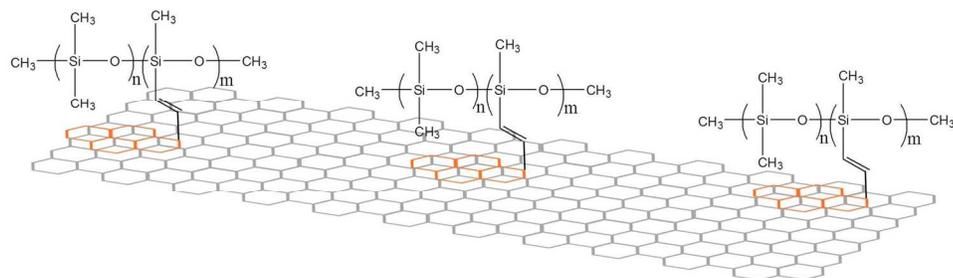
References

- (1) Flandin, L.; Chang, A.; Nazarenko, S.; Hiltner, A.; Baer, E.: Effect of strain on the properties of an ethylene-octene elastomer with conductive carbon fillers. *Journal of Applied Polymer Science* **2000**, *76*, 894-905.
- (2) Mather, P. J.; Thomas, K. M.: Carbon black high density polyethylene conducting composite materials .2. The relationship between the positive temperature coefficient and the volume resistivity. *Journal of Materials Science* **1997**, *32*, 1711-1715.
- (3) Mather, P. J.; Thomas, K. M.: Carbon black/high density polyethylene conducting composite materials .1. Structural modification of a carbon black by gasification in carbon dioxide and the effect on the electrical and mechanical properties of the composite. *Journal of Materials Science* **1997**, *32*, 401-407.
- (4) Tchoul, M. N.; Ford, W. T.; Ha, M. L. P.; Chavez-Sumarriva, I.; Grady, B. P.; Lolli, G.; Resasco, D. E.; Arepalli, S.: Composites of single-walled carbon nanotubes and polystyrene: Preparation and electrical conductivity. *Chemistry of Materials* **2008**, *20*, 3120-3126.

- (5) Das, N. C.; Liu, Y.; Yang, K.; Peng, W.; Maiti, S.; Wang, H.: Single-Walled Carbon Nanotube/Poly(methyl methacrylate) Composites for Electromagnetic Interference Shielding. *Polymer Engineering and Science* **2009**, *49*, 1627-1634.
- (6) Bao, H.-D.; Guo, Z.-X.; Yu, J.: Effect of electrically inert particulate filler on electrical resistivity of polymer/multi-walled carbon nanotube composites. *Polymer* **2008**, *49*, 3826-3831.
- (7) Chang, L.; Friedrich, K.; Ye, L.; Toro, P.: Evaluation and visualization of the percolating networks in multi-wall carbon nanotube/epoxy composites. *Journal of Materials Science* **2009**, *44*, 4003-4012.
- (8) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K.: Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences of the United States of America* **2005**, *102*, 10451-10453.
- (9) Geim, A. K.; Novoselov, K. S.: The rise of graphene. *Nature Materials* **2007**, *6*, 183-191.
- (10) Zhao, X.; Zhang, Q.; Chen, D.; Lu, P.: Enhanced Mechanical Properties of Graphene-Based Poly(vinyl alcohol) Composites. *Macromolecules* **2010**, *43*, 2357-2363.
- (11) Goncalves, G.; Marques, P. A. A. P.; Barros-Timmons, A.; Bdkin, I.; Singh, M. K.; Emami, N.; Gracio, J.: Graphene oxide modified with PMMA via ATRP as a reinforcement filler. *Journal of Materials Chemistry* **2010**, *20*, 9927-9934.
- (12) Gomez, H.; Ram, M. K.; Alvi, F.; Villalba, P.; Stefanakos, E.; Kumar, A.: Graphene-conducting polymer nanocomposite as novel electrode for supercapacitors. *Journal of Power Sources* **2011**, *196*, 4102-4108.
- (13) Shahil, K. M. F.; Balandin, A. A.: Graphene-Multilayer Graphene Nanocomposites as Highly Efficient Thermal Interface Materials. *Nano Letters* **2012**, *12*, 861-867.
- (14) 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.: Graphene-based composite materials. *Nature* **2006**, *442*, 282-286.
- (15) Sekitani, T.; Noguchi, Y.; Hata, K.; Fukushima, T.; Aida, T.; Someya, T.: A rubberlike stretchable active matrix using elastic conductors. *Science* **2008**, *321*, 1468-1472.
- (16) Watcharotone, S.; Dikin, D. A.; Stankovich, S.; Piner, R.; Jung, I.; Dommett, G. H. B.; Evmenenko, G.; Wu, S.-E.; Chen, S.-F.; Liu, C.-P.; Nguyen, S. T.; Ruoff, R. S.: Graphene-silica composite thin films as transparent conductors. *Nano Letters* **2007**, *7*, 1888-1892.
- (17) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S.: Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* **2007**, *45*, 1558-1565.
- (18) Park, S.; An, J.; Jung, I.; Piner, R. D.; An, S. J.; Li, X.; Velamakanni, A.; Ruoff, R. S.: Colloidal Suspensions of Highly Reduced Graphene Oxide in a Wide Variety of Organic Solvents. *Nano Letters* **2009**, *9*, 1593-1597.
- (19) Green, A. A.; Hersam, M. C.: Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation. *Nano Letters* **2009**, *9*, 4031-4036.
- (20) Lotya, M.; King, P. J.; Khan, U.; De, S.; Coleman, J. N.: High-Concentration, Surfactant-Stabilized Graphene Dispersions. *Acs Nano* **2010**, *4*.
- (21) Wajid, A. S.; Das, S.; Irin, F.; Ahmed, H. S. T.; Shelburne, J. L.; Parviz, D.; Fullerton, R. J.; Jankowski, A. F.; Hedden, R. C.; Green, M. J.: Polymer-stabilized graphene dispersions at high concentrations in organic solvents for composite production. *Carbon* **2012**, *50*, 526-534.
- (22) Das, S.; Kin, F.; Ahmed, H. S. T.; Cortinas, A. B.; Wajid, A. S.; Parviz, D.; Jankowski, A. F.; Kato, M.; Green, M. J.: Non-covalent functionalization of pristine few-layer graphene using triphenylene derivatives for conductive poly (vinyl alcohol) composites. *Polymer* **2012**, *53*, 2485-2494.
- (23) Fujigaya, T.; Nakashima, N.: Methodology for homogeneous dispersion of single-walled carbon nanotubes by physical modification. *Polymer Journal* **2008**, *40*, 577-589.

- (24) An, X.; Simmons, T. J.; Shah, R.; Wolfe, C.; Lewis, K. M.; Washington, M.; Nayak, S. K.; Talapatra, S.; Kar, S.: Stable Aqueous Dispersions of Noncovalently Functionalized Graphene from Graphite and their Multifunctional High-Performance Applications. *Nano Letters* **2010**, *10*, 4295-4301.
- (25) Parviz, D.; Das, S.; Ahmed, H. S. T.; Irin, F.; Bhattacharia, S.; Green, M. J.: Dispersions of Non-Covalently Functionalized Graphene with Minimal Stabilizer. *ACS Nano* **2012**, *6*, 8857-8867.
- (26) Teng, C.-C.; Ma, C.-C. M.; Lu, C.-H.; Yang, S.-Y.; Lee, S.-H.; Hsiao, M.-C.; Yen, M.-Y.; Chiou, K.-C.; Lee, T.-M.: Thermal conductivity and structure of non-covalent functionalized graphene/epoxy composites. *Carbon* **2011**, *49*, 5107-5116.
- (27) Liu, J.; Yang, W.; Tao, L.; Li, D.; Boyer, C.; Davis, T. P.: Thermosensitive Graphene Nanocomposites Formed Using Pyrene-Terminal Polymers Made by RAFT Polymerization. *Journal of Polymer Science Part a-Polymer Chemistry* **2010**, *48*, 425-433.
- (28) Luo, C.; Zuo, X.; Wang, L.; Wang, E.; Song, S.; Wang, J.; Wang, J.; Fan, C.; Cao, Y.: Flexible Carbon Nanotube-Polymer Composite Films with High Conductivity and Superhydrophobicity Made by Solution Process. *Nano Letters* **2008**, *8*, 4454-4458.
- (29) Kim, H.; Miura, Y.; Macosko, C. W.: Graphene/Polyurethane Nanocomposites for Improved Gas Barrier and Electrical Conductivity. *Chemistry of Materials* **2010**, *22*, 3441-3450.
- (30) Kujawski, M.; Pearse, J. D.; Smela, E.: Elastomers filled with exfoliated graphite as compliant electrodes. *Carbon* **2010**, *48*, 2409-2417.
- (31) Chen, L.; Chen, G.; Lu, L.: Piezoresistive behavior study on finger-sensing silicone rubber/graphite nanosheet nanocomposites. *Advanced Functional Materials* **2007**, *17*, 898-904.
- (32) Raza, M. A.; Westwood, A.; Brown, A.; Hondow, N.; Stirling, C.: Characterisation of graphite nanoplatelets and the physical properties of graphite nanoplatelet/silicone composites for thermal interface applications. *Carbon* **2011**, *49*, 4269-4279.
- (33) Ozbaz, B.; O'Neill, C. D.; Register, R. A.; Aksay, I. A.; Prud'homme, R. K.; Adamson, D. H.: Multifunctional elastomer nanocomposites with functionalized graphene single sheets. *Journal of Polymer Science Part B-Polymer Physics* **2012**, *50*, 910-916.
- (34) Xu, P.; Loomis, J.; Bradshaw, R. D.; Panchapakesan, B.: Load transfer and mechanical properties of chemically reduced graphene reinforcements in polymer composites. *Nanotechnology* **2012**, *23*.
- (35) Guimont, A.; Beyou, E.; Alcouffe, P.; Martin, G.; Sonntag, P.; Cassagnau, P.: Synthesis and characterization of PDMS-grafted graphite oxide sheets. *Polymer* **2013**, *54*, 4830-4837.
- (36) Gao, J.; Shen, K.; Bao, F.; Yin, J.; Wang, D.; Ma, R.; Yan, C.; Chen, T.; Wang, G.; Liu, X.; Zhang, X.; Zhang, D.: Preparation and Characterization of a Graphene Oxide Film Modified by the Covalent Attachment of Polysiloxane. *Polymer-Plastics Technology and Engineering* **2013**, *52*, 553-557.
- (37) Hou, Y.; Wang, D.; Zhang, X.-M.; Zhao, H.; Zha, J.-W.; Dang, Z.-M.: Positive piezoresistive behavior of electrically conductive alkyl-functionalized graphene/polydimethylsilicone nanocomposites. *Journal of Materials Chemistry C* **2013**, *1*, 515-521.
- (38) Chen, M.; Tao, T.; Zhang, L.; Gao, W.; Li, C.: Highly conductive and stretchable polymer composites based on graphene/MWCNT network. *Chemical Communications* **2013**, *49*, 1612-1614.
- (39) Li, D.; Mueller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G.: Processable aqueous dispersions of graphene nanosheets. *Nature Nanotechnology* **2008**, *3*, 101-105.
- (40) Tung, V. C.; Allen, M. J.; Yang, Y.; Kaner, R. B.: High-throughput solution processing of large-scale graphene. *Nature Nanotechnology* **2009**, *4*, 25-29.
- (41) Powell, D. B.; Sheppard, N.: Nuclear magnetic resonance and infrared spectroscopic evidence for the structure of some metal-olefin complexes. *Journal of the Chemical Society* **1960**, 2519-2521.
- (42) Wertz, D.W.; Bouian, D. F.; Hazouri, M. J. . *Spectrochimica Acta* **1973**, *29 A*, 1439-1449.

- (43) Bourlinos, A. B.; Georgakilas, V.; Zboril, R.; Steriotis, T. A.; Stubos, A. K.; Trapalis, C.: Aqueous-phase exfoliation of graphite in the presence of polyvinylpyrrolidone for the production of water-soluble graphenes. *Solid State Communications* **2009**, *149*, 2172-2176.
- (44) Behabtu, N.; Lomeda, J. R.; Green, M. J.; Higginbotham, A. L.; Sinitskii, A.; Kosynkin, D. V.; Tsentelovich, D.; Parra-Vasquez, A. N. G.; Schmidt, J.; Kesselman, E.; Cohen, Y.; Talmon, Y.; Tour, J. M.; Pasquali, M.: Spontaneous high-concentration dispersions and liquid crystals of graphene. *Nature Nanotechnology* **2010**, *5*.
- (45) Grunlan, J. C.; Gerberich, W. W.; Francis, L. F.: Electrical and mechanical property transitions in carbon-filled poly(vinylpyrrolidone). *Journal of Materials Research* **1999**, *14*, 4132-4135.
- (46) Grady, B. P.: *Carbon nanotube - polymer composites*; Wiley: Hoboken, N.J., 2011.
- (47) Zaman, I.; Kuan, H.-C.; Meng, Q.; Michelmore, A.; Kawashima, N.; Pitt, T.; Zhang, L.; Gouda, S.; Luong, L.; Ma, J.: A Facile Approach to Chemically Modified Graphene and its Polymer Nanocomposites. *Advanced Functional Materials* **2012**, *22*, 2735-2743.
- (48) Martin-Gallego, M.; Hernandez, M.; Lorenzo, V.; Verdejo, R.; Lopez-Manchado, M. A.; Sangermano, M.: Cationic photocured epoxy nanocomposites filled with different carbon fillers. *Polymer* **2012**, *53*, 1831-1838.
- (49) Mao, C.; Zhu, Y.; Jiang, W.: Design of Electrical Conductive Composites: Tuning the Morphology to Improve the Electrical Properties of Graphene Filled Immiscible Polymer Blends. *ACS Applied Materials & Interfaces* **2012**, *4*, 5281-5286.



Structure of graphene non-covalently stabilized by PDMS-pyrene polymers
324x88mm (150 x 150 DPI)