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A Tertiary Amine in Two Competitive Processes: Reduction of Graphene Oxide vs Catalysis of Atom Transfer Radical Polymerization

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Electrically conductive graphene oxide/polystyrene hybrids (GO-PS) were prepared by reduction of graphene oxide (GO) in one step during covalent modification of graphene oxide surface using surface-initiated atom transfer radical polymerization (SI-ATRP) of styrene. The reduction of the GO surface was proven by Raman spectroscopy, electrical conductivity measurements, thermogravimetric analysis and X-ray photoelectron spectroscopy. Electrical conductivity of the synthesized GO-PS particles increased in eight orders of magnitude, depending on the polymerization period. Detailed studies were performed to determine that the tertiary amine, such as *N*,*N*,*N*',*N*',*N*''-pentamethyldiethylenetriamine (PMDETA), used in SI-ATRP as a ligand complexing copper catalyst, was responsible for the GO surface reduction. It was shown that due to participation of PMDETA in reduction of graphene oxide, the ATRP in the presence of GO can proceed only above a certain PMDETA/GO ratio.

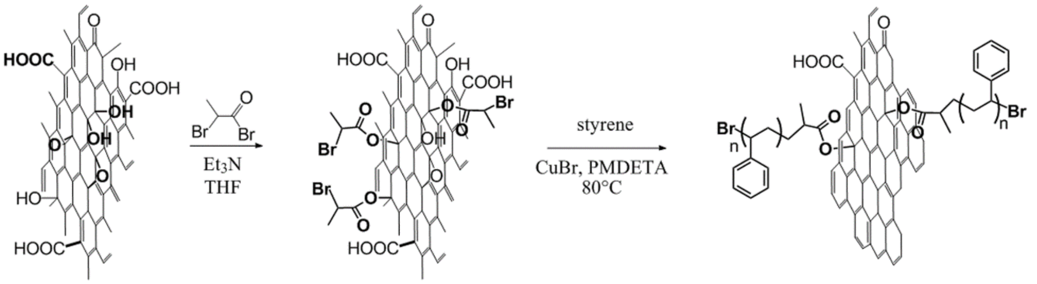
Introduction

Graphene has a two-dimensional (2D) atomic crystal structure consisting of carbon atoms arranged in a hexagonal lattice. It has a large surface area, large Young's modulus, high thermal conductivity and good electrical conductivity.[1] There are several methods used to prepare graphene, such as chemical vapor deposition,[2] micro-mechanical cleavage[3] and various chemical methods,[4] but the least expensive, and thus the most suitable method for industrial graphene production is doubtlessly using natural graphite as a precursor.[5] The shape and size of the filler as well as its dispersion in a matrix plays a key role in both the improvement of physical and mechanical properties of the resultant nanocomposite and formation of the conductive network with low percolation.[6] Therefore, several methods were developed to transform the graphite to separate graphene sheets. One of the most used methods is rapid thermal expansion in a furnace at temperatures above 600 °C to form expanded graphite**,** which can be readily mechanically exfoliated in polymer matrices.[7] Unprotected bulk graphene sheets, however, can spontaneously agglomerate and even restack to form graphite.[4] Moreover, neat graphene is insoluble and relatively inert. To increase its dispersibility in solvents, improve interactions with polymer matrices[7] and prevent agglomeration, a functionalization of the graphene surface is needed.[4] The oxidation of the graphene surface is very common by various methods and results in different degrees of graphene surface oxidation.[8]

Graphene oxide (GO) is hydrophilic, readily exfoliating into individual GO sheets in water, and forms stable dispersions in various solvents. The oxygen functional groups, namely, hydroxyl, epoxy, carbonyl and carboxy groups, present on the GO surface can be further chemically modified with appropriate organic groups to facilitate dispersion in composites.[4] During the oxidation, however, the regular graphitic structure is damaged; hence, the electrical conductivity of the graphene is lost in GO.[9] Therefore, at least partial reduction of graphene oxide is necessary to restore electrical conductivity. The GO surface can be reduced either thermally or chemically.[4] Although the mechanism for the reduction of GO is not completely understood, many reducing agents have been developed to date in order to reduce GO.[4,9-11] Among the reducing agents for GO, hydrazine is currently the most widely used due to its strong reductive effect.[9,12]

The reduction of GO is usually performed in a separate step either before or after the covalent modification of the GO surface.[4,13-16] Performing the reduction of GO before the covalent modification of GO surface can lead to restacking of the reduced GO sheets and various surfactants have to be used to stabilize the reduced GO suspensions.[17]

Surface-initiated polymerizations are a convenient "grafting from" techniques allowing the growing of polymer chains with controlled molar mass and dispersity from various substrate surfaces. So far, only a few works described using of surface initiated atom transfer radical polymerization (SI-ATRP) for grafting of various monomers, such as methyl methacrylate,[18,19] styrene,[18] 2-(dimethylamino)ethyl methacrylate,[20] *tert*-butyl acrylate[21] and sodium 4-styrenesulfonate,[22] from surface of either GO or reduced GO. In these works, either no reduction or only partial reduction of GO surface was observed during SI-ATRP, without any deeper studies of the reduction process.



Scheme 1. Modification of graphene oxide with ATRP initiator and subsequent simultaneous reduction of GO surface and grafting of styrene from GO surface using surface-initiated ATRP

Here, we showed for the first time that electrically conductive polystyrene-grafted GO can be prepared in one step during SI-ATRP from the surface of nonconductive GO (see Scheme 1). Eight orders increase in conductivity of GO was achieved during this polymerization process. More detailed investigation was carried out in order to find out which component was responsible for the *in situ* reduction of GO and how the GO reduction affected the kinetic of ATRP.

Experimental

Materials

Styrene was purchased from Aldrich and purified by passing through a basic alumina column to remove the inhibitor. 4-(2-Hydroxyethyl)nitrobenzene, 2-bromopropionyl bromide, methyl 2-bromopropionate (MBP), *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine (PMDETA) (all from Aldrich) were used as received. Triethylamine (Et$_3$N) was purchased from Fluka and was dried over sodium. The tetrahydrofuran (THF, POCH, Poland) was dried over sodium wires and freshly distilled before use. CuBr was purified according to the literature procedures.[23] The expanded graphite powder (ECOPHIT G; GFG 50 with size of 40-55 μm) from SGL Groups Carbon (Germany) was used. The expanded graphite was oxidized by Brodie method according to the literature procedure[8a] to obtain hydroxyl groups on the surface. The amount of oxygen-containing groups in graphene oxide (GO) estimated from TGA was 31 wt.%. All other reagents and solvents were purchased from Aldrich and used as received without further purification.

Graphene surface modifications

Synthesis of GO modified with 2-bromopropionyl groups (GO-Br). 1 g of GO was put into 500 mL three-neck round-bottom flask. The flask was evacuated and back filled with argon three times. The freshly distilled dry THF was added into the flask and the mixture was sonicated shortly (4 min). The triethyl amine (3.8 mL, 27 mmol), was added into the reaction flask followed by drop-wise addition of 2-bromopropionyl bromide (2.9 mL, 27 mmol). The mixture was stirred at room temperature overnight, and then it was refluxed at 80 °C for one hour. The product was purified by filtration over PTFE 0.2 μm membrane. The reaction mixture was filtered and washed with 100 mL acetone. Then it was dispersed in 200 mL DMF, shortly sonicated (2 min), filtered, and washed with acetone. This procedure was repeated three times (until the filtrate was clear). Finally the product was washed with diethyl ether and dried in oven at 60 °C and 100 mbar overnight.

Synthesis of polystyrene-modified GO (GO-PS) [Table 1, Entries 3 and 4]. 410 mg of GO-Br (approximately 1x10^{-4} mol of Br, as determined from XPS) was put into 100 mL Schlenk flask. The flask was evacuated and back filled with argon three times. The anisole (24.6 mL) was purged with argon and added into Schlenk flask. The PMDETA (0.29 mL, 1.4x10^{-3} mol), and initiator MBP (0.31 mL, 2.8 mmol) were added and the reaction mixture was shortly sonicated in ultrasonic bath (10 min). The styrene (24.6 mL, 0.224 mol) was purged with argon and added into Schlenk flask. The four freeze-pump-thaw cycles were then performed. The CuBr (0.2 g, 1.4x10^{-3} mol) was put into frozen reaction mixture under argon flow. One more freeze-pump-thaw cycle was performed. The polymerization was performed at 80 °C, and stopped after 46 h by opening the flask and dissolving the mixture in 15 mL of anisole. The monomer conversion was 20 % according to the ^{1}HNMR spectra. Since the amount of sacrificial initiator was approximately 20 times higher than the amount of initiator attached on GO surface, the amount of polymer grown from GO surface had a small impact on determination of monomer conversion from ^{1}HNMR spectra. The molar mass and dispersity (*Đ)* determined by GPC was 1,600 g/mol and 1.07, respectively. In order to separate GO-PS hybrids from free PS chains, the reaction mixture was filtered using PTFE 0.2 μm membrane and washed with 100 mL acetone. Then it was dispersed in 200 mL DMF, shortly sonicated (2 min), filtered, and washed with acetone. This procedure was repeated three times. Finally the product was washed with diethyl ether and dried in oven at 70 °C and 100 mbar overnight. The amount of the GO-PS was 0.440 g.

The synthesis of GO-PS was performed twice under the same conditions. The second polymerization was stopped after 108 h, when the monomer conversion was 44 % according to the ^{1}H NMR spectra. The molar mass and *Đ* was 2,900 g/mol and 1.09, respectively.

The same procedure was used for further polymerizations except polymerizations where different ratios of components was used as desribed in Table S1 [Entries 13-16].

General procedure for reduction of graphene oxide with CuBr/PMDETA [Table 1, Entries 5-8]. 200 mg of GO was put into a 50 mL Schlenk flask, evacuated and back filled with argon (three times). Then 12 mL of argon purged anisole was added followed by addition of PMDETA (0.15 mL, 7x10^{-4} mol). Three freeze-pump-thaw cycles were performed and then CuBr (0.1g, 7x10^{-4} mol) was put into the reaction mixture under argon flow. Then the flask was evacuated. One more freeze-pump-thaw cycle was done before the mixture was put into oil bath pre-heated to 80 °C. The reaction was done four times and stopped after one, two, four and eight days. The graphene

Table 1 Conductivity and ratio of intensity of D and G peaks from Raman spectra for graphene oxide (GO) and graphene oxide modified with ATRP initiator (GO-Br) before and after treatment with various catalytic systems.

Entry	Type of GO[a]	Catalyst[a]	Solvent[a]	reduction time	Conductivity σ (S/cm)	I_D/I_G
1	GO	-	-	-	$4.6x10^{-8}$	0.96
2	GO-Br	-	-	-	$1.1x10^{-8}$	NA
3[b]	GO-Br	CuBr:PMDETA 1:1	anisole/styrene	46 h	$1.7x10^{-3}$	1.09
4[b]	GO-Br	CuBr:PMDETA 1:1	anisole/styrene	108 h	$1.1x10^{1}$	1.23
5	GO	CuBr:PMDETA 1:1	anisole	24 h	$6.8x10^{-8}$	0.97
6	GO	CuBr:PMDETA 1:1	anisole	48 h	$4.9x10^{-7}$	0.98
7	GO	CuBr:PMDETA 1:1	anisole	96 h	$5.3x10^{-4}$	1.05
8	GO	CuBr:PMDETA 1:1	anisole	192 h	$1.7x10^{0}$	1.06
9	GO	-	anisole	192 h	$2.0x10^{-8}$	NA
10	GO	CuBr	anisole	192 h	$2.9x10^{-8}$	NA
11	GO	PMDETA	anisole	48 h	$8.4x10^{-1}$	NA
12	GO	PMDETA	anisole	192 h	$6.1x10^{0}$	1.16
13[b]	GO-Br	CuBr:PMDETA 1:4	anisole/styrene	75 h	$1.2x10^{1}$	1.27
14[b]	GO-Br	CuBr:PMDETA 1:1	anisole/styrene	48 h	$1.9x10^{-6}$	NA
15[b]	GO	CuBr:PMDETA 1:4	anisole/styrene	55 h	$5.8x10^{0}$	1.08

[a] Concentration of GO or GO-Br was maintained at approximately 8.13 g/L and $3.5x10^{-4}$ mol of CuBr and PMDETA per 100 mg of GO or GO-Br was used in most of the experiments (for exceptions, see the Experimental section and Table 2); [b] methyl 2-bromopropionate was also used as a sacrificial initiator, and 50 vol% of anisole was used; NA – not analyzed.

particles were purified according to the same procedure as described above.

Reduction of graphene oxide with CuBr [Table 1, Entry 10]. 100 mg of graphene oxide was put into a 25 mL Schlenk flask, evacuated and back filled with argon (three times). Three freeze-pump-thaw cycles were performed, then CuBr (0.05 g, $3.5x10^{-4}$ mol) was put into the reaction mixture under argon flow. The flask was then evacuated. One more freeze-pump-thaw cycle was done before the mixture was put into oil bath pre-heated to 80 °C. The reaction was running for eight days. The graphene particles were purified according to the same procedure as described above.

General procedure for reduction of graphene oxide with PMDETA [Table 1, Entry 11]. 100 mg of graphene oxide was put into 25 mL Schlenk flask, evacuated and back filled with argon three times. Then 6.15 mL of anisole purged with argon was added, followed by addition of PMDETA ($3.5x10^{-4}$ mol, 72.5 μL). The four freeze-pump-thaw cycles were performed to remove air from reaction flask. The reaction mixture was put into oil bath preheated to 80 °C and the reaction was stopped after eight days (192 hour). The graphene oxide was filtered over 0.22 μm PTFE filter membrane, and washed with acetone (200 mL). The GO particles were dispersed in DMF (200 mL), filtered and washed with acetone again. This procedure was repeated three times. Finally the product was washed with diethyl ether and put into oven heated to 60 °C overnight. The same procedure was used for control experiment [Table 1, Entry 9], but in the absence of PMDETA.

Characterization

The molar mass and *Đ* of the PS chains grown from the free (sacrificial) initiator were determined by gel permeation chromatography (GPC), consisted of a Waters 515 pump, two PPS SDV 5 μm columns (d = 8 mm, l = 300 mm; 500 Å + 105 Å) and a Waters 410 differential refractive index detector, with THF as an eluent at flow rate of 1.0 mL/min. The polystyrene was used as a standard and anisole as an internal standard.

Monomer conversions were determined by ^{1}H NMR on a 400 MHz VNMRS Varian NMR spectrometer equipped with 5mm 1H-19F/15N-31P PFG AutoX DB NB probe at 25 °C in deuterated chloroform as a solvent.

The amount of attached organics substances was determined by thermogravimetric analysis (Mettler Toledo, Switzerland), heating rate 10 K/min, in nitrogen atmosphere. The weight percentages of oxygen-containing groups were calculated after deduction of water at 100 °C and where applicable also polymer.

The morphology of GO samples before and after modifcation with polymer chains was investigated using a scanning electron microscope (SEM, Vega II LMU, Tescan, Czech Republic).

The conductivity of the pellets was measured by four-point van der Pauw method (Keithley 6517B, USA) at room temperature. The pellets of 13 mm diameter and 0.5–0.7 mm thickness were prepared by compression at 400 MPa with a manual hydraulic press. The value of the conductivity is the average value from 3 different pellets when each pellet was measured five times.

Raman spectra were recorded using two equipments, a portable i-Raman plus (BWTEK inc., Newark Delaware, USA) and DXR Raman microscope (Thermo Scientific, USA). In portable i-Raman the laser intensities with excitation at 532 nm were kept low (10-40 %) to avoid any laser induced damage. Raman spectra were also excited at room temperature through Olympus TH4-200 microscope. An excitation wavelength of 532 nm was used with 3 mW power on sample. Each spectrum was collected in 20 exposition of 10 s with 50 μm spectrograf aperture.

XPS signals were recorded using a Thermo Scientific KAlpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al Ka x-ray source (1486.6 eV). An x-ray beam measuring 400 mm in size was used at 6 mA and 12 kV. Spectra were acquired in the constant analyzer energy mode with pass energy of 200 eV for the survey. Narrow regions were collected with a pass energy of 20 eV. Charge compensation was achieved using the system flood gun, which provides low-energy electrons (0 eV) and low-energy argon ions (20 eV) from a single source. The argon partial pressure was $2\text{x}10^{-7}$ mbar in the analysis chamber. Thermo Scientific Avantage software, version 4.84 (Thermo Fisher Scientific), was used for digital acquisition and data processing. Spectral calibration was performed using the automated calibration routine and the internal Au, Ag and Cu standards supplied with the K-Alpha system. The surface compositions (in atomic%) were determined by considering the integrated peak areas of detected atoms and the respective sensitivity factors. The fractional concentration of a particular element A was computed as follows:

$$\%A = \frac{I_A / S_A}{\sum I_n / S_n} \times 100\% \qquad (1)$$

where I_n and S_n are the integrated peak areas and the Scofield sensitivity factors corrected for the analyzer transmission, respectively.

Results and discussion

GO was prepared from expanded graphite by oxidation using the Brodie method,[8a] and the content of oxygen-functional groups on the graphene surface was determined by TGA to be approximately 31 wt% (see Figure 1). For surface-initiated ATRP (SI-ATRP), the hydroxyl groups on the GO surface were first modified by reaction with 2-bromopropionyl bromide to attach the ATRP initiator to the GO surface. The SI-ATRP of styrene was then performed using CuBr with *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine (PMDETA) as the catalyst complex in anisole as the solvent. An excess of the sacrificial initiator methyl 2-bromopropionate was also used, in addition to the initiator attached on the GO surface, to enable control of styrene conversion and the molar mass of the formed polystyrene (PS). Polymerization was stopped after 46 and 108 hours at 20 and 44 % of monomer conversions, respectively. The narrow dispersities and pre-determinable molar masses of the PS chains (see Table 2) confirm that the polymerization proceeded with good control.

The color of the polymerization mixture changed from brown to black during the polymerization, indicating some structural changes in the GO structure. SEM images of separated GO-PS hybrids did not show any significant change in the morphology of the particles in comparison with untreated GO (see Figure S1). On the other hand, thermogravimetric analysis (TGA) of separated GO-PS hybrids confirmed the decrease of oxygen-containing functional groups in the GO after SI-ATRP (see Figure 1). In GO, most of the oxygen-containing groups decomposed between 250 and 300 °C. After modification with the ATRP initiator, decomposition started at 140 °C, while the organic content increased from 31 wt% to 33 wt%. The amount of oxygen-containing functional groups that decomposed in the 140 to 250 °C temperature range decreased to 27 wt% (GO-PS, M_n of PS = 1,600 g/mol) and to 15 wt % (GO-PS, M_n of PS = 2,900 g/mol) after 46 and 108 hours of polymerization respectively. Although the decomposition of some oxygen-containing functional groups could overlap with the decomposition of grafted polystyrene, which continued to decompose until temperatures reached 400°C, the decrease in the total content of cleavable groups on the GO surface with respect to duration of polymerization was clear. Moreover, from the TGA results and molar masses of the PS chains, it could be calculated that the reduction during prolonged polymerization from 46 to 108 hours led to almost half of the PS chains being cleaved from the GO surface. To prove the cleavage, isolated GO-PS was again dispersed in anisole and treated under the same conditions, i.e., in the presence of CuBr/PMDETA, but without free initiator and monomer, for 6 days. Subsequently, cleaved PS chains with the same molar mass were detected in solution by gel permeation chromatography (GPC).

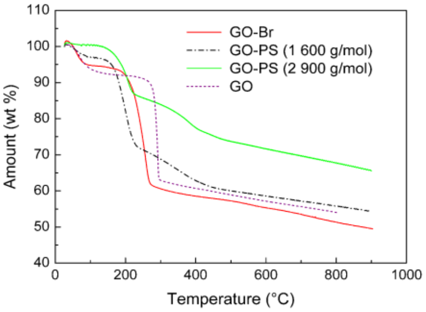


Fig. 1 Thermogravimetric analysis of graphene oxide (GO), initiator-modified graphene oxide (GO-Br), and graphene oxide modified with polystyrene with molar mass of 1,600 and 2,900 g/mol (GO-PS). Analysis was performed under nitrogen atmosphere at a heating rate of 10 K/min.

To confirm the reduction of GO surface, Raman spectroscopy was used. Three prominent peaks (G, D and 2D) could be recognized in the Raman spectra (see Figure 2). Surface reduction is commonly expressed as an increase in the ratio of D (1355 cm^{-1}) to G (1575 cm^{-1}) band intensities

Table 2. Molar ratio of reactants in SI ATRP and ATRP of St and characterization of prepared polymers. All polymerizations were performed with [St] = 4.5 mol/L and 50 vol% of anisole.

Entry	Styrene	GO	MBP	CuBr/PMDETA	Time [hr]	Conv.[a] [%]	$M_{n,\ exp.}$[b] [g/mol]	$Đ$[b]
3[c]	80	GO-Br	1	0.5/0.5	46	20	1600	1.07
4[c]	80	GO-Br	1	0.5/0.5	108	44	2900	1.09
13[d]	80	GO-Br	1	0.5/2	75	64	6500	1.07
14[e]	33	GO-Br	1	0.5/2	48	0	-	-
15[d]	80	GO	1	0.5/2	55	80	7000	1.06
16	80	-	1	0.5/0.5	68.5	80	6250	1.14

[a] based on ^{1}H NMR spectra, [b] based on GPC using PS standards, [c] $3.5\text{x}10^{-4}$ mol of PMDETA was used per 100 mg of GO-Br, [d] $1.4\text{x}10^{-3}$ mol of PMDETA was used per 100 mg of GO-Br or GO, [e] $9.6\text{x}10^{-5}$ mol of PMDETA was used per 100 mg of GO-Br

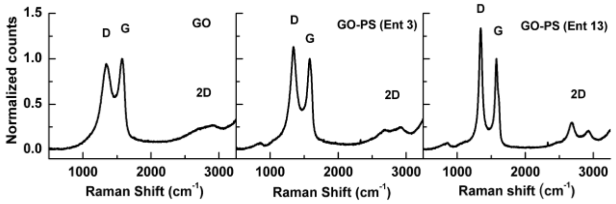


Fig. 2 Raman spectra of unmodified GO (a), GO grafted by PS (Entry 3 in Table 1) (b) and GO grafted by PS in the excess of PMDETA (Entry 13 in Table 1) (c); spectra are normalized to peak G.

(I_D/I_G).[24] While the GO exhibited a I_D/I_G ratio of 0.96, the I_D/I_G ratio increased to 1.09 and 1.23 after 46 and 108 hours of SI-ATRP, respectively (see Figure 2 and Table 1). The reduction of the GO surface was further confirmed by an increase in electrical conductivity, σ, measured by the four point method, according to van der Pauw.[1c] The results are shown in Table 1. While introduction of the initiator onto the GO surface did not lead to a change in electrical conductivity, the electrical conductivity increased by several orders of magnitude from $4.6x10^{-8}$ originally to $1.7x10^{-3}$ and $1.1x10^{1}$ S/cm after 46 and 108 hours of polymerization, respectively.

Expecting that the GO reduction was caused by the ATRP catalytic system or by one of its components, the GO was stirred only in the presence of the CuBr/PMDETA catalytic system in anisole under the same experimental conditions as used for polymerization, but in the absence of any initiator and monomer. The changes in Raman spectra and conductivity of the treated GO were followed after 24, 48, 96 and 192 hours of reaction (see Table 1, Entries 5-8). The I_D/I_G in Raman spectra progressively increased during the treatment of GO with CuBr/PMDETA from the original value of 0.96 up to 1.06 after 192 hours. Similarly, a progressive increase in conductivity with duration of treatment of GO with CuBr/PMDETA from $4.6x10^{-8}$ S/cm originally to 1.7 S/cm after 192 hours.

To investigate the atomic composition changes, X-ray photoelectron spectroscopy (XPS) of GO before and after treatment with CuBr/PMDETA in the ratio of 1/1 in anisole for 48 and 192 hours was performed (see Table 3 and Figure S2). Apparently, the amount of oxygen-containing groups present, mainly hydroxyl and epoxy groups, as well as the amount of sp3 hybridized carbon decreased with duration of treatment. This decrease was accompanied with an increase in the amount of sp2 hybridized carbon and the carbon/oxygen ratio, suggesting that the conjugated graphene structure was partially recovered by reducing GO. Similar to the previously mentioned analysis, XPS confirmed the presence of copper in reduced GO samples (see Table 3 and Figure S3). In addition, approximately 2 atomic % of nitrogen was detected in all samples. The nitrogen can originate from PMDETA complexing the copper compounds and/or from the nucleophilic attack of epoxy or hydroxyl groups on the GO surface by PMDETA (nitrogen in the form of N+ was found using XPS, see Figure S4) and/or from complexes of carbonyl compounds with PMDETA.[25]

To further understand which component of the catalytic system was responsible for the reduction of GO, the effect of individual components was investigated. A control experiment of GO in anisole without any other compound did not lead to any change in electrical conductivity (see Table 1, Entry 9). Similarly, no change in conductivity was obtained after mixing GO with CuBr alone (see Table 1, Entry 10). On the contrary, when GO was treated with PMDETA alone, an increase in conductivity to $8.4x10^{-1}$ and 6.1 S/cm was observed after 48 and 192 hours, respectively (see Table 1, Entry 11 and 12, respectively). Treatment of GO with PMDETA only led to faster reduction compared to treatment with CuBr/PMDETA ($\sigma = 8.4x10^{-1}$ and $4.9x10^{-7}$ S/cm after 48 hours of treatment with PMDETA and CuBr/PMDETA, respectively), suggesting that preferentially free PMDETA is responsible for this reduction. The reduction of GO by PMDETA was confirmed by XPS (see Entry 12 in Table 3 and Figure S2 and S4).

It is worth mentioning that a large difference was observed in the polymerization rate between ATRP of styrene in the presence and absence of GO-Br (see Figure 3 and Table 2, Entry 4 and 16). Due to the participation of PMDETA in the reduction of GO, one can expect a lower extent of participation in catalysis of ATRP in the form of complexation with CuBr. Thus, decreasing the ATRP catalyst concentration could lead to lower rates of polymerization. To prove this, SI-ATRP in the presence of GO-Br was performed with a 4-times-higher PMDETA concentration.

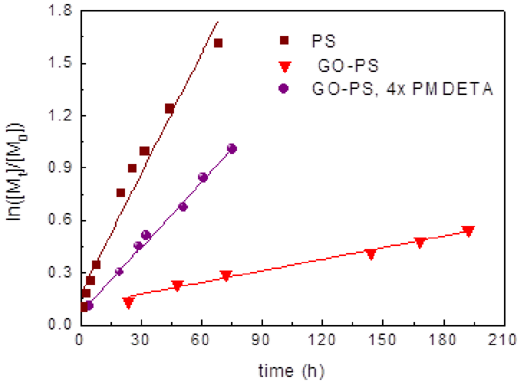


Fig. 3 Kinetics plot of neat PS, PS grafted from GO-Br (GO-PS) and PS grafted from GO-Br in the excess of PMDETA (GO-PS, 4xPMDETA).

Table 3 The surface atomic composition of graphene oxide (entry 1) and graphene oxide reduced either by CuBr/PMDETA complex for 48 and 192 hours (Entry 6 and 8, respectively) or by PMDETA for 192 hours (Entry 12), determined by XPS.

Entry	Surface composition (atomic %)									C1s/O1s
	C1s	O1s	N1s	Cusp3	C1s sp2 + C1s π-π*	C1s sp3	C1s C-O	C1s C=O	C1s O-C=O	
1	72.2	27.4	0.4	-	11.7	31.8	48.0	6.5	2.0	2.6
6	73.9	21.5	2.3	0.4	13.2	38.3	43.4	3.4	1.7	3.4
8	82.3	14.3	2.1	0.4	41.7	20.1	33.6	2.7	1.9	5.8
12	83.1	12.1	3.0	-	39.9	27.1	25.6	5.5	1.9	6.9

As shown in Figure 3 and Entry 13 in Table 2, a higher amount of PMDETA significantly accelerated the polymerization of styrene, while significant reduction of the GO surface was attained, as confirmed by high conductivity and increased I_D/I_G ratio (see Table 1, Entry 13). On the contrary, the four-fold increase in the GO-Br/PMDETA ratio led to no polymerization, and only reduction of the GO surface accompanied by an increase in conductivity by two orders of magnitude was observed (see Entry 14 in Table 1 and 2).

Finally, ATRP polymerization of styrene was performed in the presence of GO without the initiator bonded to its surface. As expected, PS composite with reduced GO was obtained after 55 hours of polymerization (see Entry 15 in Table 1 and 2).

Conclusions

In summary, it was shown that GO can be reduced *in situ* during ATRP to partially restore the conductive graphene structure. Thus, the GO can be reduced and modified using SI-ATRP in one step to obtain conductive hybrids/composites without the need to reduce the GO surface in a separate step after surface modification. It was proven that tertiary amine, such as PMDETA, commonly used in ATRP as a ligand in the copper catalyst system, is responsible for the reduction of GO during ATRP. Thus, it is involved in two separate competitive processes - catalysis of the polymerization and GO reduction. The presented results also show the importance of using sufficient amounts of a ligand such as PMDETA to perform ATRP in the presence of GO. Using excess PMDETA, compared to CuBr, can increase both the rate of polymerization and the reduction of GO. Although the reduction effect of another amine-containing compound, such as hydrazine, is well known, further studies are needed in order to understand the mechanism of reduction of GO by tertiary amine, such as PMDETA.

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† Electronic Supplementary Information (ESI) available: XPS analysis - Table S1 and Figure S1-S3. See DOI: 10.1039/b000000x/

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A Tertiary Amine in Two Competitive Processes: Reduction of Graphene Oxide vs Catalysis of Atom Transfer Radical Polymerization

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Graphene oxide can be reduced by tertiary amine in one step during ATRP to directly obtain conductive hybrids and/or composites.