Postdoc Fellowships for non-EU researchers

Final Report

Name	Kavitha Amalin
Selection	Postdoctorate from outside Europe 2010
Host institution	University of Liege
Supervisor	Prof. C. Jérôme
Period(s) covered by this report	from .01/05/2011 to 01/03/2012 from .01/03/2013 to 30/11/2013
Title	Nanoscale ordering of nanoparticles in diblock copolymers prepared by reactive processing

1. Objectives of the Fellowship

This project aimed at developing new methods to promote the selective localization of nanoparticles within a given phase or at the interface of nanostructured block copolymers, using the **melt blending technique** as a dispersion process and **reactive processing** for the ***in situ* formation of diblock nanostructures** and **NPs selective localization**.

To reach this main objective, the use of two kinds of inorganic fillers were envisioned, on one side gold nanoparticles for optical properties and on the other side graphene sheets for barrier and conductivity properties. To reach this goal, these particles have first to be coated efficiently with reactive groups that constitutes the first two challenges of the research. Indeed, since melt processing is envisioned, the coating has to resist to the thermal treatment required by the reactive processing. The study and development of appropriate surface modification chemistries is thus the first step of this research.

A second target to reach reactive processing, is the preparation of functional polymer able to quickly react with the coated particles. The synthesis of functional polymers by controlled radical polymerization techniques is thus a second goal. Particularly, functionalities evolving click chemistry are targeted to afford efficient and quick reactions without side-products.

When both, the coated inorganic filler and the functional polymers would be obtained, the reactive processing in the molten state and possible annealing, will be studied. The resulting morphologies will be observed by transmission electron microscopy and the relevant properties (optical properties for gold nanocomposites and electrical, mechanical, thermal, gas barrier and fire retardant properties for graphene sheets) of the resulting materials will be measured.

2. Methodology in a nutshell

1. *Preparation of heat-stable, reactive NPs.*

The thiol/maleimide has been proposed as thiol-ene click-reaction. There is thus a need to link one of these reactive moieties to the inorganic nanofillers via a thermostable way. Two strategies were proposed to achieve the preparation of heat stable reactive nanoparticles depending on their nature. For gold nanoparticles, the use of a cross-linked polymer shell obtained by ATRP as described by Matyjaszewski et al (J. Am. Chem. Soc., (2008) 130, 12852-12853) that would trap the gold particle in such dense coating appears interesting. The reactive moiety (maleimide, thiol) can be introduced as end-group of the polymer grown by ATRP. Besides, the formation of a thin silica interlayer is proposed to anchor the organic groups at the nanoparticles surface through silane chemistry. In case of graphene sheet, functionalization of exfoliated graphite oxide followed by reduction in graphene is envisioned.

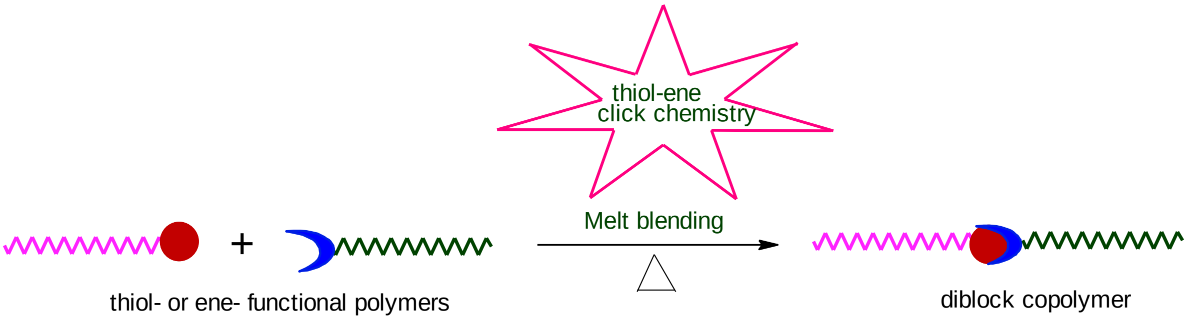
2. *Preparation of nano-organized nanocomposites*

In a first step, the synthesis of nanostructured block copolymers by reactive processing will be studied by coupling, during a melt blending experiment, homopolymers bearing complementary reactive end-groups (maleimide and thiol). These homopolymers (from (meth)acrylate or styrenic monomers) will be prepared by adequate controlled radical polymerizations (ATRP, NMP or RAFT) either starting from reactive functional initiators (cyclic anhydride, amine, protected maleimide) or by post-modification of the terminal end-group (for example, thiol coming from the aminolysis of the radical addition fragmentation transfer (RAFT) polymerization control agent). The chosen click reaction of the functional polymer will then be tested in conditions of reactive melt blending experiments by using a twin-screw micro-compounder. The effectiveness of the coupling reaction will be investigated by SEC, NMR, FTIR, and TEM. Melt blending conditions and annealing of the resulting materials will be optimized to obtain the best nanostructuration of the block copolymers.

Finally, in order to selectively localize the nanoparticles either within a given phase of the block copolymers prepared by reactive blending or at the interface between the blocks, the prepared heat stable reactive nanoparticles will be processed together with the set of reactive homopolymers.

3. Results

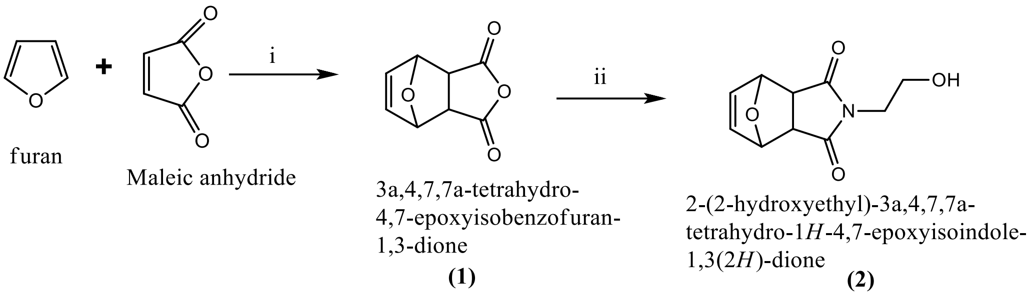
The first goal of the research is the synthesis of diblock copolymers by melt blending techniques using mini extruder (Scheme 1). For that purpose, the first objective was to prepare end-functional polystyrene (PS) and polymethymethacrylate (PMMA) with complementary functions able of click reaction. In order to compare the efficiency in reactive processing of two click reactions, we have selected the thiol-ene and the Diels-Alder click reactions. For that purpose, we have targeted the functionalization of PMMA with a maleimide moiety and PS with a thiol for thiol-ene reaction or anthracene for Diels-Alder reaction with the PMMA-maleimide.



Scheme 1: General Representation of Thiol-ene click reaction via melt blending

Preparation of Tailor-made Ene Terminated Polymer via ATRP:

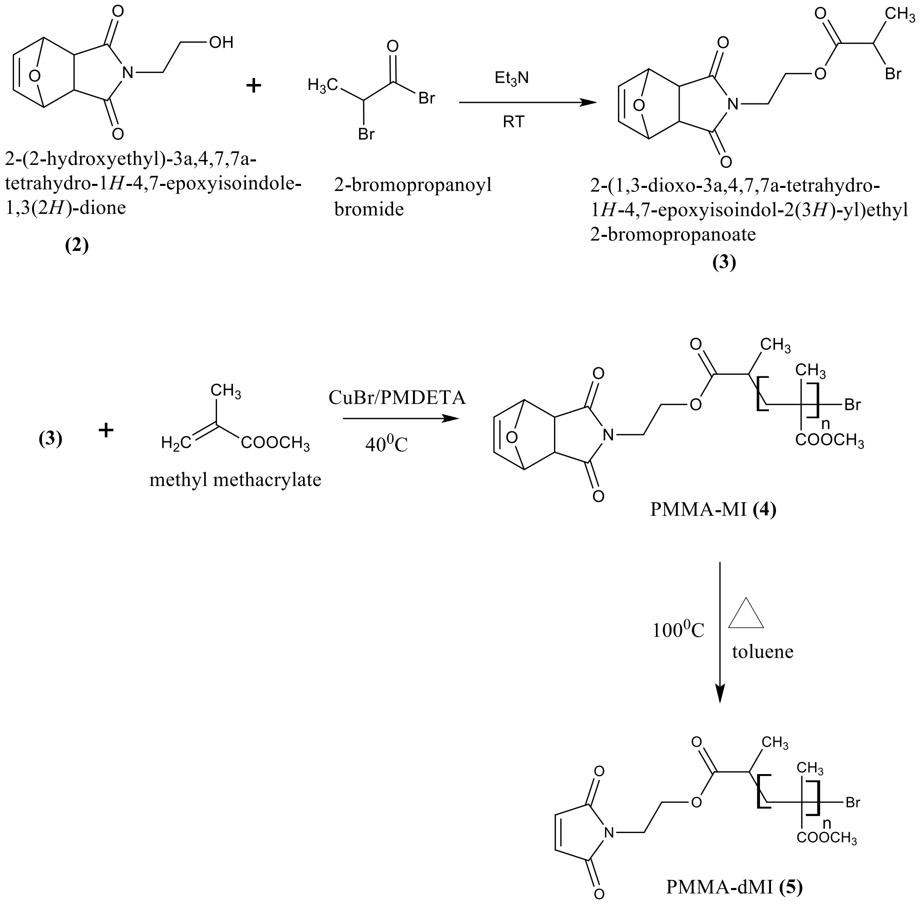
To prepare end-functional polymers we have used controlled radical polymerization starting with a functional initiator. Since maleimide would react during the polymerization, this group has been protected by the Diels-Alder adduct with furan (Scheme 1). We have synthesized 3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione (1) by reacting furan and maleic anhydride at 80°C. Then anhydride '**1**' was reacted with ethanolamine to get 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (**2**) as shown in Scheme 2. For preparing furan-protected maleimide bearing ATRP initiator (ene functionality), compound 2 was reacted with 2-bromopropanoyl bromide in presence of triethyl amine at room temperature for 12 h to get compound **3** in scheme 3. The chemical structure and the attachment of the functional groups to the initiator were confirmed by ^{1}H-NMR analysis. The peaks at 6.52 and 3.4 ppm are due to the CH_{vinyl} and >CH-Br of **3** respectively (NMR spectrums are in the supporting information).



(i) heated at 80^0C, toluene
(ii) ethanolamine, methanol

Scheme 2: synthesis of protected initiator precursor

Furan-protected maleimide-PMMA (PMMA-MI) (**4**) (scheme 3) was prepared by atom transfer radical polymerization techniques as described in Scheme 3. Methyl methacrylate (MMA) was polymerized by using functional initiator (**3**) and CuBr as a catalyst in combination with PMDETA as ligand. The polymerization temperature was deliberately kept low at 40 °C, so as to prevent possible deprotection of (**3**) during the polymerization. The maleimide conjugation site can be readily regenerated at elevated temperatures. Kinetic study of the polymerization was carried out at different time intervals, the sample was withdrawn under nitrogen atmosphere and a part of it was used for the gravimetric determination of monomer conversion. The linear dependence kinetic plot of [ln (1/1-x)] verses time shows the controlled nature of the polymerization. A very fast rate of polymerization (95% conversion in 15 min) was observed when acetone was used as solvent. This is due to the increasing polarity of the solvent which can affect the solubility of the catalyst. The polar nature of the solvent, can attributes to the homogeneity of the copper catalyst in the reaction medium. It is reported that, while using polar, dipolar, aprotic solvents and ionic liquids CuBr instantaneously disproportionate Cu(0) to Cu(II) species in the presence of N-containing ligand. This disproportionation promotes a faster ATRP, and leads to controlled nature of the polymerization. At such a faster polymerization rate with acetone as solvent, the polydispersity index of the final polymer was found to be low (1.23), suggesting a well controlled nature of the polymerization..

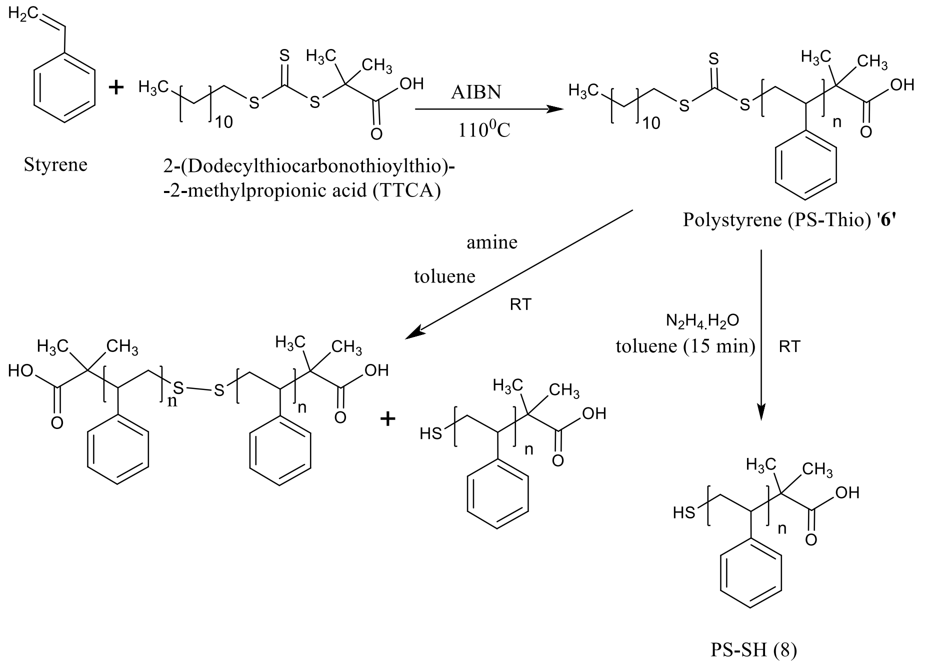


Scheme 3: Synthesis of PMMA-dMI by ATRP

Theoretical molecular weight of PMMA-MI (**4**) was calculated by using the following equation: Mn,theo = ($[M]_0/[I]_0$) X conversion % X molecular weight of monomer + molecular weight of **3**. $M\text{n},_{\text{NMR}}$ of PMMA-MI was determined from the ratio of integrated signals at 3.60 ppm (-OCH_3 protons of MMA) and 6.82 ppm (vinyl end protons). $M\text{n},_{\text{GPC}}$, $M\text{n},_{\text{theo}}$ and $M\text{n},_{\text{NMR}}$ values of PMMA-MI were calculated as 30999, 30444 and 30320, respectively. The dispersity (D) of the polymer was 1.23, which indicates the polymerizations are controlled with well-defined end group. Deprotection of PMMA-MI (**4**) (retro-DA reaction) proceeds via releasing of furan to give the deprotected maleimide functionality (**5**) (PMMA-dMI) upon reflux in toluene (Scheme 3). Molecular weight and polydispersity index of the PMMA-dMI (**5**) was 30857 and 1.23 respectively. The active end group was analyzed by ^{1}H-NMR spectroscopy. The resonance at 6.82 ppm is attributed to the –CH=CH- of maleimide proton. It clearly confirmed that PMMA polymers had a vinyl end group. This vinyl group is useful for click reaction.

Synthesis of Thiol- terminated polymer prepared by RAFT:

Well-defined linear polystyrene was polymerized in toluene in the presence of AIBN as the free radical initiator and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid **(**TTCA) as RAFT reagent at 100°C under nitrogen atmosphere. Polymers with different molecular weights were prepared at 100°C with the reaction time depending on the molecular weight targeted. In all cases, gel permeation chromatography (GPC) analyses revealed mono modal molecular weight distributions with a polydispersity index (PDI) of 1.2. The molecular weight and polydispersity index shows that polymerizations are controlled with well-defined end groups. Structures of all polymers were characterized by ^{1}H-NMR spectroscopy. A small resonance at 3.7 ppm is attributed to the proton of –CH_2-S- that is the thio group containing polystyrene. It indicates the presence of sulphur atom in the macromolecular chains. The presence of thiocarbonylthio end groups in polymer **6** was confirmed by ^{1}H-NMR spectroscopy.



Scheme 4: synthesis of thiol-PS by RAFT

End group removal is an important issue as residual RAFT agent functionality in polymers can be a problem due to their inherent reactivity and the possibility of decomposition of the thiocarbonylthio end group. There are a number of methods available to cleave thiocarbonylthio end groups from the RAFT polymer. According to the existing literature, dithioesters are expected to undergo fast reactions with amine leading to their reduction to thiols. In this work, thiocarbonylthio end groups were reduced to thiols via aminolysis at room temperature in the presence of primary amines as well as hydrazine (Scheme 4). It is reported that during aminolysis the polymeric solution with a high concentration favours intermolecular disulfide-bridge formation, whereas solutions with more diluted leads to the cyclization of the polymeric chains through the formation of

S-S bond. To avoid these unwanted reaction we used a polymeric solution with a concentration of 2.5 x 10^{-2} mol/L. Polymer **6** (PS-Thio) was reacted with slight excess of primary amine under nitrogen atmosphere for 1 hr at room temperature after which it was precipitated into methanol. The aminolysis reaction was followed by UV-vis spectroscopy as well as GPC analysis. In UV-vis absorbance spectra of RAFT polymer before and after aminolysis were recorded as well. The broad absorption band around 300 - 320 nm observed for the polymer before aminolysis, due to the dithioester group, after aminolysis it was disappeared illustrating that all the dithioester end groups were reduced to thiol.

GPC traces of PS-Thio (6) before and after aminolysis show a shoulder at the higher molecular weight side for the aminolysis product using primary amine, which is ascribed to the oxidation of thiol end groups into disulfides of twice molecular weight. This unwanted formation is due to the oxidative coupling of thiols, which results in the formation of a disulfide bridge (S-S bond) between the two polymer chains. Previous literatures reported this coupling of the thiols could be suppressed by the addition of antioxidant. However, we did aminolysis in presence of antioxidant (aqueous solution of sodium bisulfite ($Na_2S_2O_4$)) using primary amine, observed that the coupling reaction was less compared to that of without antioxidant. It was evident from GPC analysis. However the synthesis of high molar mass polymers with thiol end group from the RAFT polymers, free of disulfide formations represent a great challenge because of the thiol group inherent reactivity towards disulfide formation.

It was our interest to develop a simple methods to produce thiol end group polymer with free of disulfide formation in a highly efficient chemical methods. Our focus was drawn to use nucleophile and reductant such as hydrazine. Hydrazine is a stronger nucleophile compared to primary alkyl amines due to the 'α' effect. Recently it has been reported that the use of hydrazine as a nucleophile is advantageous both in giving rapid rate of reaction and suppressed disulfide formation even when the process is carried out in air. The aminolysis of PS-Thio (6) by using hydrazine monohydrate in different solvents under nitrogen atmosphere at room temperature was tested (Scheme 4). When using DMF as solvent, the colour change (from yellow color to colourless) of the solution appeared within 5 min and it was immediately precipitated into hexane. It was observed that hexane was the good non solvent for precipitating PS-SH (**7**) (thiol polymer) when compared to methanol. GPC curve of this polymer shows the slight formation of disulfide-bridged PS. But this disulfide formation was less compared to propylamine. Aminolysis carried out with hydrazine in toluene as solvent lead to colour change occurring within 15 min. The resulting polymer solution was precipitated into hexane. Interestingly, the GPC curve shows the formation of PS-SH (7) completely free of disulfide contamination. The absence of disulfides in the aminolysis of RAFT high molecular weight polymers using hydrazine has important implications.

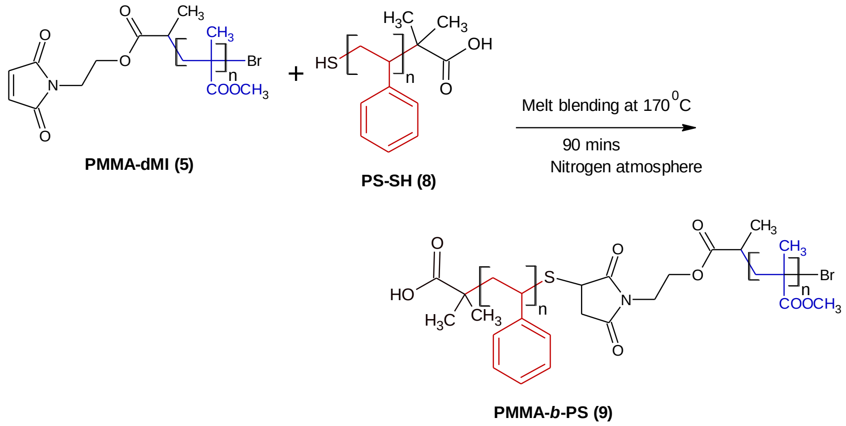
The kinetic study was performed by using UV-Vis spectroscopy to established hydrazine as a strong nucleophile compare to that of primary amine. At predetermined period an aliquot of the reaction mixture was taken and analyzed by UV. Interestingly, when hydrazine was used, markedly faster aminolysis of the polymer (Mw 31678 g/mol and PDI 1.21) than primary amine (Figure 6). While using hydrazine the reaction was completed within 15 mins and it took 90 min using primary amines. This may be due to that hydrazine is better nucleophile (neuclophilicity parameter (N) = 12.45) and strong antioxidant than primary alkyl amine. The formation of thiol-terminated polystyrene (PS-SH) (8) was further confirmed by ^{1}H-NMR analysis. The disappearance of $-S-CH_2-$ peak at 3.7 ppm in the ^{1}H-NMR spectrum clearly confirmed the cleavage of thio group in the RAFT polymer. This simple method using a single reagent for the efficient preparation of thiol end group polymer from RAFT polymer with free of side reactions will promote their use in a number of technologies such as thiol-ene click chemistry.
based initiator **4** and polymer grafted Au-NPs **5** were thermally stable.

Synthesis of anthracene end-group bearing polystyrene by RAFT:

On the same general scheme, the synthesis of well-defined anthracene end capped polystyrene (PS-anthracene) was targeted. By working in toluene as solvent, AIBN as the free radical initiator and anthracen-9-ylmethyl 2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoate as RAFT reagent at 100°C under nitrogen atmosphere, such functional homopolymer was successfully achieved. The kinetic study, molecular weight and PDI of the polymers shows the polymerizations are controlled. ^{1}HNMR analysis revealed that the peaks between 7.3 to 8.5 ppm are due to the aromatic protons of anthracene present at the chain end. UV spectra showed a broad absorbance at 300 to 340 nm, due to anthracene moieties. SEC-UV studies clearly confirmed the polymer **8** had anthracene end group.

Thiol–Ene Click Reactions:

Once both PS and PMMA partners obtained, we have tested the possibility to prepare block copolymer by reactive mixing of the two homopolymers as illustrated below (scheme 5).



Scheme 5: synthesis of diblock by reactive processing using thiol-ene click reaction

Thiol-Ene click reaction was performed by reactive processing using melt blending techniques under nitrogen atmosphere at 170^{0}C for 90 mins (Scheme 5). The kinetics of the thiol-ene click reaction between PMMA-dMI (**5**) (M.wt 30857 g/mol and PDI 1.23) and PS-SH (**8**) (M.wt 31678 g/mol and PDI 1.21) was followed by monitoring the molecular weight traces as obtained by GPC on aliquots extruded at different time intervals. Figure 7 shows the GPC traces of resulting materials (starting materials + formed diblock copolymer) at different time intervals. It shows the appearance of new peak at a high molecular weight range indicates the formation of diblock copolymer (**9**). When increasing reaction time, the diblock copolymer formation also increased. After 90 mins of reactive processing under the used reaction conditions, around 80 % of diblock copolymer was formed. ^{1}H-NMR of diblock at different reaction time confirms the resonances at 6.2 to 7.0 and 3.6 ppm attributed to the aromatic proton of polystyrene and –OCH$_3$ of PMMA respectively. It indicates the corresponding diblock copolymers (PMMA-*b*-PS) had polystyrene and PMMA block.

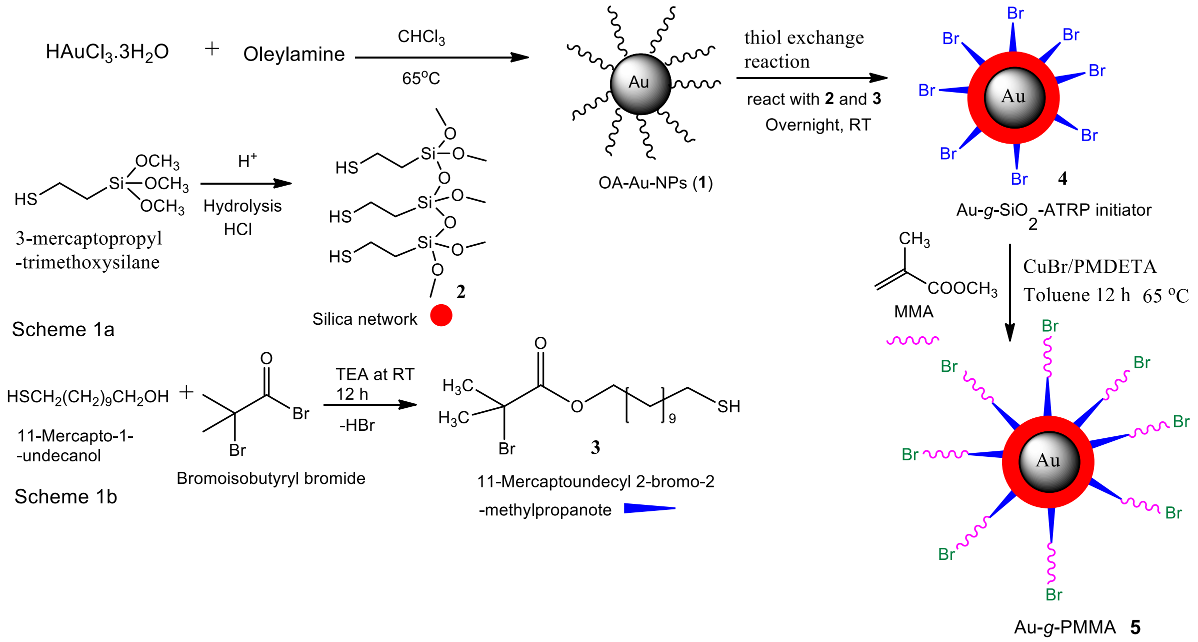
The SEC kinetics of the formation of diblock copolymer via melt blending technique at 170°C shows the expected increasing of the molecular weight with time. When the initial polymer of PMMA-dMI (5) and PS-SH (8) each of molecular weight of ~50000 and ~30000 is used under nitrogen atmosphere, the prominent increase in the molecular weight of diblock copolymer is observed. It is evident from the higher slopes of the linear fit curve. This is also can be due to the absence of unfavourable side reactions of the reactive end group as the reaction is carried out under an inert atmosphere. Considering the diblock copolymerization without N$_2$ atmosphere as given as curve 3 a lower slope of the linear fit curve is observed owing to the slow pace of reaction. This is attributed to the possible side reaction within the active end groups of the polymers. In case of the reaction which is carried out at 200°C, a much lower molecular weight is observed during the initial period of the reaction. But as the reaction progresses the molecular weight suddenly increases resulting in the deviation from the linearity in the reaction kinetics. The initial region of lower molecular weight can be attributed to the possible thermolytic chain scission due to higher reaction temperature. As the reaction time progresses the homogeneity in the reaction mix plays a role in the increased viscosity of the melt and thereby the increase in molecular weight in the later stage. Considering the kinetics, the favourable condition for melt blending is suggested as 170°C under nitrogen atmosphere.

Morphology of the diblock copolymer (PMMA-*b*-PS) (**9**) was characterized by TEM analysis of the polymer blend containing the diblock copolymer at different reaction time. These TEM images show a drastic decrease in the domain size which occurs after 90 min of reaction time. This supports the formation of significant amount of diblock copolymer in the blend.

Synthesis of Thermally Stable Gold Nanoparticles (Au-NPs) functionalized for ATRP:

The two general strategies proposed in the methodology have been tested but were found unsuccessful to get well dispersed and functional gold nanoparticles that resist heat treatment. We thus looked for a novel pathway to achieve our goal. We successfully prepared thermally stable Au-NPs based ATRP initiator by the following process depicted in the scheme 6 below, that we imagined, developed and optimized.

In the first step, oleylamine capped Au-NPs (**1**) (OA-Au-NPs) were synthesized using oleylamine and $HAuCl_4.3H_2O$ in chloroform as solvent at 65°C for 12 h. Particle purification was accomplished by repeated centrifugation of the resultant solution. The reaction mixture was first washed with ethanol in a 50/50 volume ratio and then acetone. This process was repeated three times and redissolved in chloroform. The OA-Au-NPs **1** were characterized by NMR and TGA studies. The NMR spectrum, showing a peak at 5.4 ppm due to the CHvinyl showed that the generated gold nanoparticles were mainly coated with oleylamine. The weight loss of 4.65 wt% was observed in OA-Au-NPs by TGA studies. TEM images of the OA-Au-NPs show uniform spherical nanoparticles of about 8 to 9 nm diameters. Thiol terminated silica network **2** was prepared by the hydrolysis of 3-mercaptopropyl-trimethoxy silane as shown in Scheme 6a. 11-mercaptoundecyl 2-bromo-2-methylpropanote **3** was synthesized from 1:1 ratio of 11-mercapto 1-undecanol and α-bromoisobutyryl bromide (Scheme 6b). Finally, Au-*g*-SiO_2-ATRP initiator (**4**) was synthesized by dropwise addition of compound **1** to the 1:1 equivalence mixture of **2** and **3** at room temperature for 12 h (Scheme 6). The final particles were purified by repeatedly washed with 50/50 volume ratio of ethanol. Purified particles were redissolved in chloroform and cast on a TEM grid for size analysis. A representative TEM image of the nanoparticles shows uniform size distribution, and an average diameter of 8 to 9 nm. Histogram of **4** shows the average size of the Au-NPs at ~8.5 nm. The uniform sizes of resultant Au-NPs were also supported by dynamic light scattering (DLS), which showed a similarly narrow particle-size distribution. The grafting density of the initiator moiety on the gold surface is 0.45 chain/nm^2 as determined from TGA.



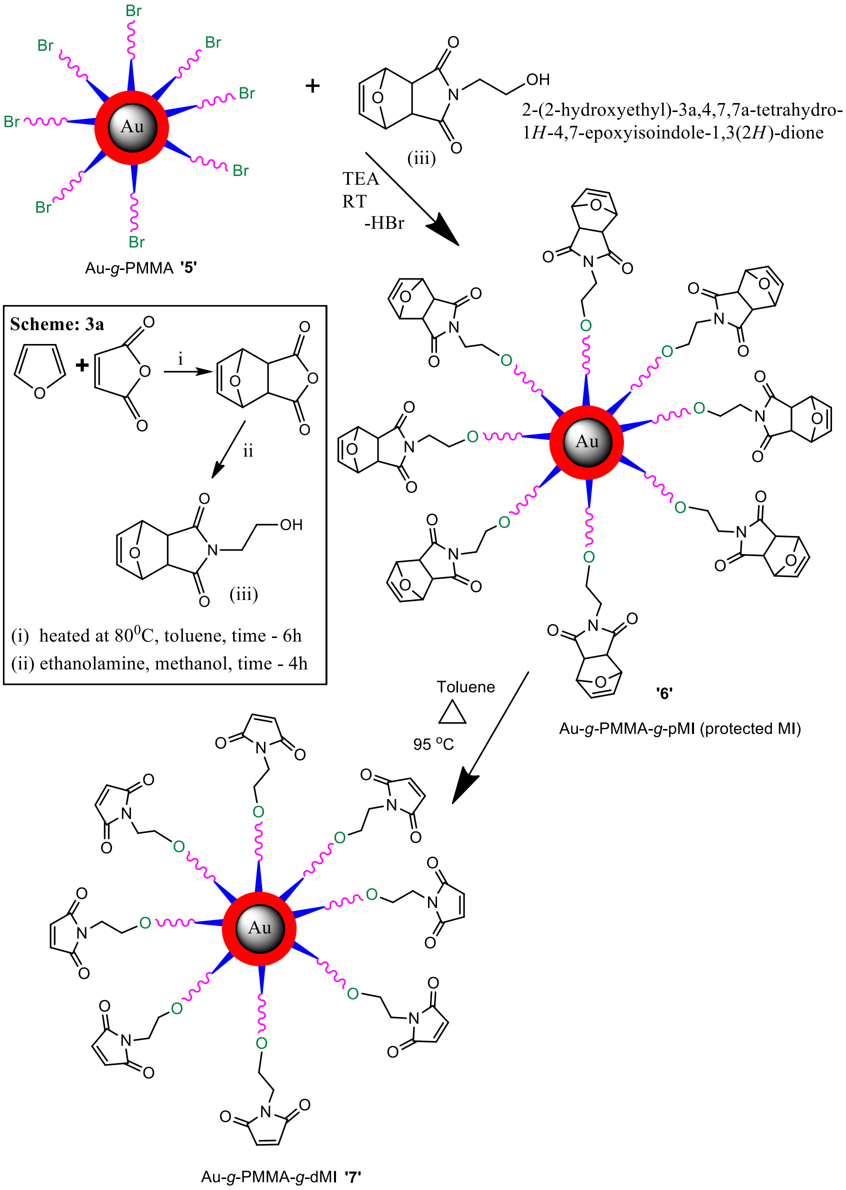
Scheme 6: Synthesis of Thermally stable Gold Nanoparticle

Synthesis of Thermally Stable Gold Nanoparticles (Au-NPs) coated by alkene-PMMA for reactive blending by Diels-Alder click reaction:

The main objective of the functionalization is to prepare alkene-terminated PMMA grafted on the Au-NPs surfaces (see scheme 7), to ensure the functionality required for the click reaction during reactive blending. According to the existing literature, grafting functional polymers on Au-NPs using the cycloaddition reaction suffered from low yield and/or NPs aggregation mainly because of the different solubility of the different reagents including the polymers, the Au-NPs, the catalyst and the functional groups, so as leads to the lowering the grafting density of the polymer shell on the Au-NPs and limits the usefulness of the cycloaddition reaction on the nanoparticles. To overcome these issues, first we prepared Au-*g*-PMMA '**5**' by ATRP using '**4**' as initiator, the resultant polymer was free of alkene functional group. The polymerization of MMA was carried out in an oxygen-free environment using compound **4** as ATRP initiator, CuBr as catalyst, and PMDETA was used as ligand (Scheme 6, step 4=>5). The molecular weight (M*n*) and polydispersity index (PDI) of Au-g-

PMMA ‘**5**’ were found to be 36,000 g/mol and 1.14 respectively. The compound **5** gives a narrow distribution as well showing that the single polymer chains undergo controlled growth also on the Au surface. The monomodal distribution of SEC trace can be regarded as proof for the interpretation that the free polymer chain in **5** and the Au-NPs remain unchanged in size and size distribution. Finally, the grafting density was determined by TGA studies, the weight loss allows evaluating the grafting density. The determined grafting density of PMMA chains on the gold nanoparticle surface is 0.47 chains/nm^2. ^{1}HNMR studies shows the resultant polymer had no a free vinyl end group at this stage.

The maleimide functional group could not be directly introduced at the surface of the Au-NPs because a strong reducing reagent is present during the reduction of Au(I) to Au(0). A place-exchange reaction is also impractical because maleimide is a good thiol scavenger and the maleimide-tethered thiol undergoes a Michael addition reaction with itself. To circumvent these problems, a furan-protected maleimide (i) (2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione) was synthesized, for use in the post-polymerization reaction with the Au-*g*-PMMA. The maleimide conjugation site can be readily regenerated at elevated temperatures. Scheme 7 depicts the syntheses of the Au-*g*-PMMA-pMI (**6**). Deprotection of **6** proceeds via., releasing of furan to give the deprotected maleimide functionality (**7**) (Au-*g*-PMMA-dMI) in toluene at 95°C for 6h (Scheme 7). To monitor the maleimide functional groups, the compound **7** was characterized by ^{1}HNMR studies. The resonance at 6.82 ppm attributed to the –CH=CH- of maleimide protons clearly confirmed that PMMA polymers had a vinyl end group. This vinyl group is useful for click reaction during the next step, i.e. the reactive processing. The size distribution of the Au-NPs was unaffected by the grafting process and the average diameter is about 8.5 nm.

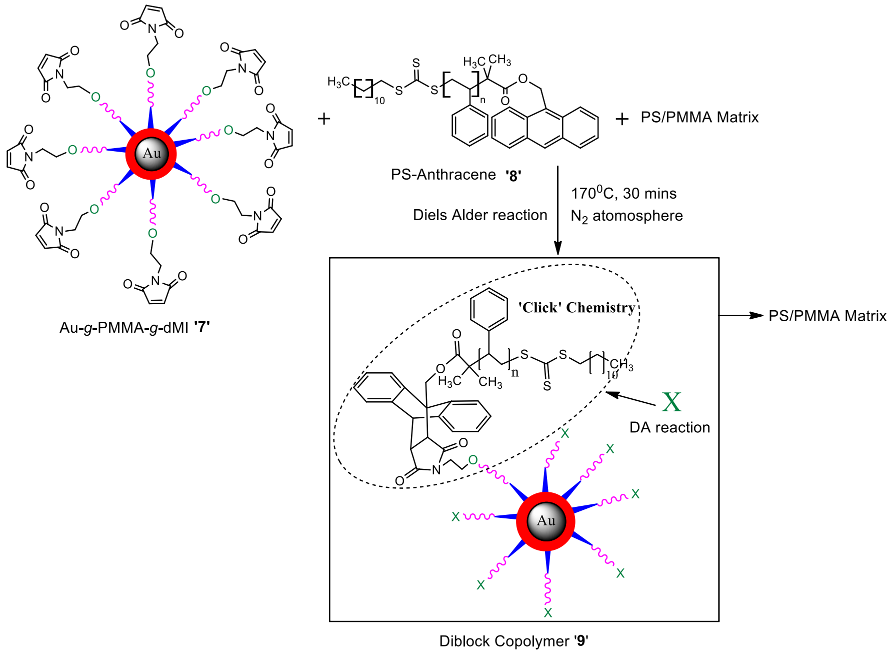


Scheme 7: Post-functionalization of gold nanoparticles with maleimide moieties

Thermal stability: Thermal stability of the compound **4** and **5** were studied by using toluene at 200°C for 3 days. The UV-vis spectra of both **4** and **5** exhibited a distinct absorption band at ~ 540 nm. After heating, initiator **4** was centrifuged with ethanol and it was re-dissolved in toluene, the UV shows the same observation at ~540 nm. The compound **5** was re-precipitated into methanol and re-dissolved in toluene and the UV shows the same observation. The colour appearance in the both cases was not affected before and after heating. The similar observation was found at 100°C for 3 days. TEM observation shows that the size distribution of the Au-NPs in the ‘**4**’ and ‘**5**’ was unaffected after heating proving the thermal stability. Indeed,it was shown that thermal instability observed for Au-S bonds at 90 °C for 6 h, resulted in aggregation and growth of the nanoparticles. Shell-crosslinked Au-Pt nanoparticles were stable in organic solvents up to 130°C·· We observed high thermal stability of the Au-NPs at higher temperatures for long time. As the Au-NPs are embedded in the silica, no growth of Au-NPs takes place during high temperature treatments. It clearly confirmed the Au-NPs

Au-NPs nanocomposite in PS-PMMA blends by reactive processing:

Scheme 8 illustrates the Diels Alder reaction (DA) expected between the Au-NPs-PMMA-MI and PS-anthracene when blended at 170°C using miniextruder under nitrogen atmosphere for 30 mins. For this study, we used commercially available immiscible polystyrene and poly(methyl methacrylate) polymers as a templating matrix and try to compatibilize the blend by adding the reactive Au-PMMA-MI and PS-anthracene to form in situ the block copolymer at the surface of the particles. Different sets of reactions were studied the details. The kinetics of the DA reaction was followed by monitoring the UV studies at different time intervals. In the UV measurements, the characteristic broad absorbance of PS-anthracene was observed at 300 to 340 nm. While increasing the reaction time this characteristic peak disappeared, due to DA reaction between polymers ‘**7**’ and ‘**8**’. A complete disappearance was observed at 30 min of reaction time. Overall UV measurements clearly pointed out a quantitative DA reaction between anthracene and maleimide moieties.



Scheme 8: nanocomposites PS-PMMA by reactive compatibilization by Diels-Alder reaction

Comparing TEM micrographs PS/PMMA blends with Au-PMMA and Au-PMMA-MI, it is clearly obvious that in absence of reaction (Au particles without maleimide moieties), the particles are located in the PMMA phase, while they go to the interface or in the PS phase when the Diels-Alder reaction can occur. (after mixing at 170°C for 30 min (Table 1, entry 1 and 2). This delocalization of the Au-NPs from the PMMA domains to PS domains due to the DA reaction between maleimide and anthracene functional groups demonstrated the concept proposed in the initial research program. In addition, the Au-NPs are well dispersed in the polymer matrix with free of Au-Au particles aggregations.

We have compared these results with OA-capped Au-NPs **1** and SiO_2 grafted NPs **4** at 170°C for 30 min. At this temperature OA-capped Au-NPs **1** was aggregated and the colour of Au-NPs are shifted from pink to blue colour. In case of SiO_2 grafted NPs **4,** particles were not aggregated and the colour of the Au-NPs was unaffected, but it is not well dispersed in the polymer matrix in contrast to our PMMA modified Au-NPs. Unchanged Au-NPs diameter were observed, the Au-NPs were randomly dispersed with no preference for either the PS or PMMA domains. These results are also supporting that the NPs are highly thermally stable and Au-*g*-PMMAs are easy to disperse in the polymer matrix compare to that of OA-capped NP as well as SiO_2 grafted NP. DLS study also supported the particles were uniform in size.

Conclusions:

Thiol-ene reaction was successfully carried out between end groups bearing PMMA-dMI and PS-SH via melt blending techniques. The linear end functional polymers such as PMMA and PS were synthesized by controlled radical polymerization techniques. The controlled nature and structure of the polymers were characterized by GPC and NMR. Diblock copolymer was synthesized by melt blending method at 170°C for 90 mins under N_2 atmosphere. The kinetic study was performed by the formation of diblock copolymers by GPC analysis.

Maleimide functional group bearing polymethyl methacrylate grafted gold nanoparticles (Au-*g*-PMMA-dMI) with a mean diameter of ~8.5 nm were synthesized by atom transfer radical polymerization. Thermal stability of the grafted Au-NPs was confirmed by UV and TEM studies. TGA studies showed that grafting density of PMMA in the Au-NPs ~ 0.45 chain/nm^2.

Using PS/PMMA as a templating matrix, the Au-*g*-PMMA-dMI was dispersed in the polymer matrix at 170°C at 30 mins in nitrogen atmosphere. The TEM image showed the locations of the Au-NPs are in the PMMA domains, these due to the Au-NPs are grafted with PMMA. In case of mixture of PS-anthracene, Au-*g*-PMMA-dMI in the polymer matrix at 170°C the maleimide and anthracene groups were joined via diels alder reaction (DA). After DA reaction, Au-NPs were found in the PS domains or the edge of PMMA domains. DA reaction joins the PS-anthracene in to the Au-NPs grafted PMMA, as leads to more PS content around the Au-NPs. In the TEM images showed the Au-NPs migrated from the PMMA domains to PS domains this due to the increase in the aromaticity (PS) around the Au-NPs. Interestingly, PMMA grafted Au-NPs are well dispersed in the PS/PMMA matrix. This opens novel applications in the field of optical materials.

4. Perspectives for future collaboration between units

The stay in Liege allows me to acquire a first postdoctoral research in Europe. In order to pursue my academic career, it is mandatory for me to get at least two postdoctoral positions abroad. With this first experience in Liege, in Belgium, I can reach one important step in that perspective I am thus currently looking for performing a second research stay abroad to go on my professional ambitions to get an academic permanent position in India.

However, it is for me also very important to keep the initiated collaboration living and it is a wish to try getting common grants to support collaborative projects between CERM, Belgian labs and the Indian Institute of Technology of Kharagpur in India. Prof. Jérôme and myself, will keep aware of the possible opportunities of applications to such program and go further in developing common research.

5. Valorisation/Diffusion (including Publications, Conferences, Seminars, Missions abroad...)

Publications:

- ***Synthesis of diblock copolymers via "Click Reactions" by Melt Blending in Twin screw extruders using reactive functional polymers***, Amalin Kavitha, Jean-Michel Thomassin, Michaël Alexandre and Christine Jérôme, see annexe 1

- ***Nanoscale ordering of Au nanoparticles in diblock copolymers prepared by reactive processing,*** Amalin Kavitha, Jean-Michel Thomassin, Michaël Alexandre and Christine Jérôme, see annexe 2

Poster presentation:

IAP annual meeting, poster presentation, ***Nanoscale ordering of Au nanoparticles in diblock copolymers prepared by reactive processing,*** Amalin Kavitha; Jean-Michel Thomassin, Michaël Alexandre and Christine Jérôme 18/09/13, Ghent

6. Skills/Added value transferred to home institution abroad

The stay at CERM allowed me to acquaint novel expertise in the following fields:

- Controlled radical polymerization by ATRP and RAFT
- Chemical analysis of functional polymers by up to date equipments (SEC triple detection)
- Surface chemistry of gold nanoparticles
- Characterization of nanoparticles (TEM, DLS, TGA, UV) in terms of size and surface chemistry
- Preparation of nanocomposite and block copolymers by reactive processing
- Characterization of nanocomposites (microtome, TEM)

Besides, I could practice my English, participate to group meetings and learn about another management and lab organization. I could also take part to the meetings of the IAP program and be in touch with some other labs of the consortium also active in nanocomposites, functional polymers and reactive blending.

Last but not least, in order to achieve a permanent position in my home institution, two postdoctoral studies are mandatory. This first experience of 18 months spent in Liege (Belgium) in the framework of the fellowship was thus a great opportunity for me and a first determinant step for my personal career. I am currently looking for a second stay abroad and pursue collaborations with CERM and Belgium.