

AN ABSTRACT OF THE THESIS OF

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Nanocomposites

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Metal/polymer nanocomposites are of increasing importance with their tunable properties being used in catalysis and sensors. Previous studies have focused on the effects of metal content, molecular weight of polymer and reaction conditions on the structure-property relationship of the metal/polymer nanocomposites. This thesis focuses on the effect of two synthetic routes, *ex situ* and *in situ*, on the structure and properties of palladium/polycarbonate (Pd/PC) nanocomposites. Discrete and agglomerated nanoclusters were obtained from *ex situ* and *in situ* methods, respectively. The effects of the varied morphology on the optical, thermal and electrical properties of the nanocomposites were studied. Dependence of the thermal stability of the nanocomposites on the heating rates, Pd content and synthetic methods was also investigated. The *ex situ* nanocomposites exhibited better optical transmission and thermal stability, while the *in situ* nanocomposites showed higher electrical conductivity. These

observations lay the foundation for developing new synthetic strategies for designing new materials by varying the size, shape, concentration and distribution of metal nanoclusters in various polymer matrices. Such materials will be investigated for sensor and catalyst applications.

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Synthesis and Characterization of Palladium/Polycarbonate Nanocomposites

by

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Valmikanathan P. Onbattuvelli, Author

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To my parents, Mr. Panchapakesan & Mrs. Girija Panchapakesan.

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Chapter 1

Introduction

Nanoparticles are thought to hold some keys for solving many present and future technological demands [1]. However, direct applications of these nanoparticles are limited due to their size and stability. They aggregate easily because of their high surface energy, and are quickly oxidized as well. To overcome the aggregation and stability problems, these nanoparticles are incorporated in a dielectric matrix thereby forming a nanocomposite. Polymers, when used as a dielectric matrix result in a wide range of useful characteristics in the nanocomposites [2].

Metal/polymer nanocomposites are usually synthesized by two different approaches: *ex situ* and *in situ*. The *ex situ* methods generally involve simple addition of metal nanoparticles to the polymer matrix [3-5]. The *in situ* methods on the other hand, comprise of the preparation of nanoparticles in the presence of a polymer [6-9]. It can be evidenced from the prior studies that, both incorporation methods offer a greater possibility of developing nanocomposites with useful thermal [5, 10-11], optical [12-13] and electrical properties [14-15].

The different *ex situ* and *in situ* methods available for synthesizing metal/polymer nanocomposites, the procedures followed, the polymers used, and the properties of the nanocomposites are reviewed in the following sections. The morphology of the nanoclusters in the metal/polymer nanocomposites are found to be controlled by various factors [3-9]. These morphologies in turn are found to control the thermal, optical and electrical properties of the nanocomposites produced [6-9]. Thus, it is possible to employ an available

procedure with proper metal, polymer combinations under preferred reaction conditions to obtain metal/polymer nanocomposites with desired properties.

1.1 Synthesis of metal/polymer nanocomposites

Nanocomposite synthesis techniques consist of highly specific approaches, which can be classified as *ex situ* and *in situ* methods. The *ex situ* method generally involves a homogenous mixing of chemically pre-synthesized nanoparticles with pre-synthesized polymer matrix [3-6]. The steps followed in the synthesis of nanocomposites by the *ex situ* and *in situ* methods are given in Figure 1.1. An understanding of how to synthesize the nanoparticles chemically is important for further discussion of this topic. The following section details the chemical methods available for synthesizing the nanoparticles.

1.1.1 Synthesis of Metal Nanoclusters

When chemically synthesized, nanoparticles represent clusters of metastabilized nanoparticles or nanoclusters. These nanoclusters tend to agglomerate forming macro-sized metal powders. Thus when chemically synthesized, stabilization of the nanoclusters against agglomeration becomes the primary goal. This may be accomplished by protecting the nanoclusters with electrostatically-bound ions like citrates [16-17] or by molecular ligands like thiols and amines [18-20], or even by polymer matrices like polymethyl methacrylate (PMMA) and polystyrene (PS) [6-9].

Synthesis of these nanoclusters involves one of the following routes: a) a “bi-phasic” approach where the phase transfer of metal nanoclusters into organic phase takes place after reduction, b) a “mono-phasic” approach where the metal salt forms a complex with the organic ligands and then gets reduced, c) the organic ligand acting as both reducing and capping agent. The synthetic strategies employed to produce monolayer protected metal nanoclusters are listed in Table 1.1 along with the associated pros and cons [17-19, 21].

1.1.2 *Ex situ* methods for synthesizing metal/polymer nanocomposites

The nanoclusters prepared as described above are dispersed in solvents like water, toluene ($C_6H_5-CH_3$) and dichloromethane (CH_2Cl_2). Hence a homogenous mixture of the nanoclusters with the polymer solution can be easily obtained. The steps followed in the synthesis of nanocomposites by the *ex situ* method are given in Figure 1.1. The resulting nanocomposites can remain either as dispersion, film, powder, or flakes. Various *ex situ* methods have been reported for the preparation of metal/polymer nanocomposites. Some of them are given in Table 1.2 along with their limitations [3-5].

1.1.3 *In situ* methods for synthesizing metal/polymer nanocomposites

The *in situ* method is newer and involves the synthesis of nanoclusters in the presence of a polymer or polymerization in the presence of nanoclusters (with the monomers being the capping agent) [6-9]. In the *in situ* methods the polymer that serves as the dielectric matrix also acts as the capping agent,

unlike the *ex situ* methods that use separate capping agents like thiols and amines. The steps followed in the synthesis of nanocomposites by the *in situ* method are given in Figure 1.1. The advantage of the *in situ* method is the absence of surfactants and the lack of intermediate purification steps, thereby resulting in a higher nanocluster yield [22]. However, this results in the poor size distribution of the nanoclusters in the nanocomposites. Various *in situ* methods have been reported for the preparation of metal/polymer nanocomposites. Some of them are tabulated in Table 1.3 along with the associated pros and cons [6-9].

1.2 Characterization of the Metal/Polymer Nanocomposites

1.2.1 Morphology of metal/polymer nanocomposites

The microstructural characterization of the nanocomposites is performed mainly by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). These three techniques are very effective in determining the particle morphology, structure, composition, particle size and size distribution. Of these techniques, TEM has proven to be the most useful. The technique is currently used to probe the internal morphology of the nanoclusters in the nanocomposites. High-quality images can be obtained because of the presence of regions in the sample that do not allow high voltage electron beam passage (metallic domains) and regions perfectly transparent to the electron beam (polymer matrix). High resolution transmission electron microscopy (HRTEM) allows morphological investigations with

resolution of 0.1 nm and thus this technique makes it possible to accurately image the size and shape of the nanoclusters.

1.2.1.1 Size of the nanoclusters in the nanocomposites

The size of the nanoclusters in the nanocomposites determines their electronic, thermal and optical properties [23]. In small nanoclusters, the electronic energy levels are discrete unlike in the bulk materials, where continuous energy bands are observed. This is due to the confinement of the electron wave function to the physical dimensions of the nanoclusters. This phenomenon is known as quantum confinement; therefore nanoclusters are also called as quantum dots [24]. Agglomerated nanoclusters never exhibit this quantum confinement. Hence, it is essential to control the size and discreteness of the metal nanoclusters during the synthesis of the nanocomposites. The diameters of the nanoclusters in the nanocomposites produced via different methods are given in Tables 1.2 and 1.3. It can be inferred that the *ex situ* nanocomposites show better control over the size than the *in situ* nanocomposites.

The discussion about the morphology of the nanocomposites requires, an understanding of the three steps involved in the nanocluster formation: nucleation, growth and termination [25-26]. These steps are schematically shown in Figure 1.2. Wang et al (2005) [27] suggested that in order to obtain nanocomposites with discrete nanoclusters, the rate of adsorption of organic ligands (thiols, amines or polymers) on the surface of nanoclusters (step 3)

should equal the rate of nanocluster formation (step 1). From Tables 1.1-1.3, it can be concluded that the above mentioned steps are controlled by the factors such as the synthesis methods, metal salt concentrations and the capping agents used (organic ligands in *ex situ* and polymers in *in situ*).

1.2.1.2 Size distribution of the nanoclusters in the nanocomposites

Typically, the size distribution of nanoclusters in nanocomposites is normal with a standard deviation of 10% [26]. Given that the nanocomposites exhibit size-dependent properties, it is important to minimize the size-distribution. This can be accomplished to a limited extent by size-selective precipitation or through centrifugation. For example, Au nanoclusters (produced using the sodium citrate method) used in *ex situ* nanocomposites are generally centrifuged to exclude the larger nanoclusters [17]. It can also be done by using a miscible solvent-non-solvent liquid mixture to precipitate them. For example, Liu et al [7] use water/methanol mixture in the *in situ* synthesis of Au/PMMA.

1.2.1.3 Factors affecting the morphology of the nanocomposites

The size of nanoclusters in the nanocomposites is found to be controlled by the synthesis methods and the reaction conditions. For example, the size of nanoclusters used in the *ex situ* nanocomposites, when synthesized by Brust and Schmidt method, are generally controlled by the rate of reduction, reaction temperature, addition of surfactants, and capping action of organic ligands over the metal particles [18-19].

The rate of capping by organic ligands depends on the nature of the capping agent. For example, Hutchison et al [19] dispersed the Au nanoclusters capped by triphenylphosphine into the thiol solutions and found ligand exchange from triphenylphosphine to thiols. Brown and Hutchison [28] also found that triphenylphosphine can be ligand exchanged with 1-pentadecylamine. Thus, it can be inferred that for nanoclusters used in the *ex situ* nanocomposites, the preferable capping agents can be ranked as: Thiols, Amines and Phosphines. For the *in situ* nanocomposites, the ranking will be based on the end/functional groups of the polymers and will be: Thiols, Amines and Acids.

However, just by being a thiol or amine, an organic ligand or a functional group in polymer cannot stabilize the metal nanoclusters. Jia et al [29] and Zhu et al [30] studied the effect of the chain length of the capping agents on the morphology of the nanoclusters produced. Jia et al found that with thiols, as the chain length increases, the nanoparticle size decreases. They found that, generally ligands with the chain length containing more than six carbons have been found effective for capping. However, when the chain length exceeded certain limit (C_{18} in this case) the capping action of thiols was once again slowed down. Thus, it can be inferred that even though the capping action of the organic ligands increases with the chain length, long chain ligands show poor capping action. Also for capping action, we can conclude that, the alkyl/aryl chains are better than the polymers and *ex situ* nanocomposites with

organic ligands as capping agents have better morphology over the *in situ* nanocomposites with polymers as the capping agents.

In the *ex situ* methods, the nanoclusters are capped by low molecular weight compounds like dodecanethiol [3-6] while in the *in situ* methods, the nanoclusters are capped by the polymer itself whose molecular weight generally exceeds 10,000 [6-9]. Earlier reports by Jewrajka and Chatterjee [31], Tamilselvan et al [32] and Corbierre et al [33] suggest that rate of capping decreases with increase in the molecular weight of the capping agents. Aymonier et al [8] once again found that while polymers possessed favorable capping nature, their long chain length and high molecular weight disable their ability to terminate the growth of nanoclusters more swiftly thereby leading to agglomeration. Thus, it can be inferred that the *ex situ* nanocomposites can have discrete nanoclusters and agglomerated nanoclusters are more common in the *in situ* nanocomposites.

Liu et al [7] studied the effect of changing the metal salt to capping agent ratio. They found that as the ratio increases, the size of the nanoclusters decreases and no change is noted when there is a decrease in the ratio. This is due to the fact that when the metal salt content increases, the amount of the reduced metal to be capped by the capping agent increases. However, due to the unavailability of the capping agents, the termination process slows which in turn results in the increase in the size of the nanoclusters. On the contrary, when the capping agent in the reaction mixture is increased, only the required amount will be utilized for capping while the remaining gets washed off.

1.2.2 Chemical interactions in the metal/polymer nanocomposites

When exposed to the electromagnetic radiation from the Fourier transform infra-red spectrometer (FTIR), the nanocomposites tend to absorb from the radiation. The energy of the radiation is varied from $500\text{-}3000\text{ cm}^{-1}$ and the response is plotted as a function of radiation energy (or frequency). At certain frequencies nanocomposite samples absorb the radiation resulting in a series of peaks in the spectrum, which can then be used to identify the sample.

Studies were conducted to check the effect of changing the chain length of the same capping agent over the chemical interactions. Laibinis et al [34] found that the intensity of the CH_2 symmetric stretching peak at 2853 cm^{-1} decreases with increase in the chain length of the thiols. King and Codella [35] showed that the intensity and width of the carbonyl peak at 1770 cm^{-1} vary by changing the testing conditions (increasing the process temperature).

Thus, it can be inferred that in the *ex situ* nanocomposites, the chemical interaction is between the organic ligands and the nanoclusters. On the other hand, in the *in situ* nanocomposites, the interaction is observed between the nanoclusters and the polymer. Chain length of the capping agents and the testing conditions were also found to affect the chemical interaction.

1.2.3 Optical properties of metal/polymer nanocomposites

Metal nanoclusters always involve oscillation of their electrons when induced by the electromagnetic field. Each metal absorbs electromagnetic radiations at certain wavelengths. The characteristics of this absorption are

related to the size and structure of the metal cluster system and are determined by UV-Vis spectroscopy.

Metals like gold and silver show characteristic absorption peaks at 530 and 420 nm respectively [36]. Generally shift in these peak positions and changes in the peak intensities are noted with changes in particle concentration, size, size distribution and film thickness. For example, Balamurugan et al [37] noted red shift in the peak positions of Au nanoparticles with the increase in the particle size. Gao et al [38] found that the Plasmon absorption maxima of Au nanoclusters decrease with increase in the chain length of the capping agent. Gole and Murphy [39] and Carotenuto et al [4] found that the plasmon absorption maxima of nanoclusters decrease with increase in the thickness of the coating.

UV-Vis spectroscopic technique is also used for determining %Transmittance (optical filtering) of light through the sample. Prior reports by Aymonier et al [8], Akamatsu et al [40], and Nemamcha et al [41] have shown that the transmittance of light in the UV-Vis region decreased with increase in the nanocluster concentration. Thus, it can be inferred that it is possible to determine and control the optical filtering abilities of nanocomposites by controlling the synthesis methods, nanocluster size, nanocluster content and also thickness of the final nanocomposites (in the case of films).

1.2.4 Thermal Properties of metal/polymer nanocomposites

1.2.4.1 *Differential Scanning Calorimetry*

Phase transitions, glass transition temperatures (T_g) of the nanocomposites are generally determined by the differential scanning calorimetry (DSC). It is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of the sample and reference are measured as a function of temperature.

Earlier works by Liu et al [7] on Au/PMMA and Hsu et al [11] on Au/Polyurethane state that the T_g of the polymer matrix decreases by incorporating metal nanoclusters. Prior studies by Merkel et al [42], Ash et al [43] indicate an increase in the free volume between the polymer chains by incorporating metal nanoclusters in them. The increase in the free volume softens the polymer chains thereby decreasing the T_g . However, increase in T_g is also noted by Ash et al on Alumina/PMMA [44]. On summary, the T_g of the nanocomposites depend on the factors like metal content, surrounding atmosphere (air/inert atmosphere).

1.2.4.2 *Thermogravimetric Analysis*

Other than X-ray diffraction (XRD) technique, composition of metal-polymer nanocomposites can once again be determined by thermogravimetric analysis (TGA). This technique involves three simultaneous steps: heating the sample, measuring the temperature, measuring the sample weight. The result can be gained as a plot of temperature ($^{\circ}\text{C}$) against remaining sample weight

(%). This plot helps in determining the onset temperature of thermal degradation of the nanocomposites (T_{onset}), end temperature of degradation (T_{end}) and metal content (wt %) in the nanocomposites.

Prior works state that the T_{onset} for any metal/polymer nanocomposites depends on the factors like heating rates, metal content and surrounding atmosphere. Peng et al [11] found that the T_{onset} of the metal/polymer nanocomposites increase with increase in the heating rates. The reason for such behavior can be explained by the fact that the polymer a natural insulator, tends to retain the heat. When such heating continues and exceeds the limit, the thermal degradation of polymer chains commences. The rate of degradation depends on the rate of heat absorption by polymer which once again depends on the heating rate. Additionally, Xia et al [5], Aymonier et al [8], and Hsu et al [10] show that the thermal stability of the nanocomposites increase with increase in the metal nanocluster content. The increment in the thermal stability is due to the increase in the metal-nanocluster interfacial area. Aymonier et al [8] also found that the T_{onset} of the nanocomposites is higher in the N_2 atmosphere than in the normal air.

A plot of differential thermal analysis (DTGA) can once again be obtained from TGA plot. DTGA plot help us in determining the temperature at which the maximum degradation (T_{max}) occurs for the sample. Hsu et al [10] and Aymonier et al [8] found that the T_{max} of the nanocomposites increases with increase in metal content.

Efforts were also made to study the kinetics of the thermal degradation of the nanocomposites by Kissinger method [45], Flynn-Wall-Osawa Method [46, 47]. Even though TGA and DTA plots help in determining the thermal stability of the nanocomposites, difficulty arises in referring to these plots in the case of varying working/exposure condition. A master decomposition curve [48, 49] is therefore required which results in an optimal time-temperature cycle for a given metal/polymer nanocomposites.

1.2.5 Electrical properties of metal/polymer nanocomposites

The electrical properties of the nanocomposites have stimulated significant interest due to possible applications in fluid sensors [50] and single electron transistors [51]. Prior reports by Sarma et al [14], Athawale et al [50] and Sadik et al [15] state that incorporation of metal nanoclusters into conducting polymer matrices resulted in enhancement in the electrical conductivity. They found that the conductivity increase with decrease in the particle size and increase in the nanoclusters content. However, most of the prior reports involve polymers that are generally semi-conducting in nature. Further research is required in developing an electrically conducting nanocomposite system using an insulating polymer.

1.3 Applications of metal/polymer nanocomposites

1.3.1 Electrical Applications

When individual nanoparticles are sandwiched between metal contacts, electrons can only be transferred one-by-one by quantum tunneling where the

probability of tunneling is controlled by an applied external voltage. This phenomenon, called single electron tunneling (SET), has been demonstrated for individual nanoparticles by Brousseau et al [52] and Houbertz et al [53] using scanning tunneling spectroscopy (STS).

Four-point probe conductivity measurements of Au nanoparticles embedded in polypyrrole [15] polyaniline [14] and polythiophene [54] demonstrate an increase of approximately two orders of magnitude compared to similar polymers without nanoparticles present. However, there has always been some difficulty in obtaining the information on the role of the metal particles in the films, due to problems which include: (1) random distribution of nanoparticles, (2) poor nanoparticles – polymer chains interactions and (3) it is feasible for charge transport to occur without involving the nanoparticle by charge percolation through the polymer alone [22]. Further research is required to find solutions to the above said problems. Currently, the electrical and sensing capabilities of the metal/polymer nanocomposites are utilized in developing fluid sensors and batteries.

1.3.1.1 Sensors

The unique properties of the metal/polymer nanocomposites have led to several possible applications. To date, the most extensively explored of these is their sensing properties. For example, Athawale et al [50] succeeded in developing a potential methanol sensor out of Pd/Polyaniline nanocomposites. Affinity of Pd towards methanol was utilized by Tang et al to solve methanol

cross over problem in direct methanol fuel cells [DMFCs] [55]. Tang et al laid Pd nanoclusters over carbon nanotubes and incorporated these nanotubes into the barrier films in the DMFCs. Ahn et al found that electrically conducting thiol capped Au nanoparticles can sense the vapors of organic solvents [56].

1.3.1.2 Batteries

Metal/polymer nanocomposites may also find utility as cathode materials. Park et al [57, 58] found that by embedding Ag or Pd nanoparticles in a polyaniline (PANI) matrix an increase in redox activity is noticed. This increase in redox activity has been attributed to electro-activity of the nanoparticles and improved conductivity of the nanocomposite. The improved redox activity results in charge–discharge performance potentially making these useful as cathode materials in improved lithium rechargeable batteries.

1.3.2 Catalytic Applications

Another important application includes the catalytic action of nanocomposites over certain chemical reactions. Prior work by Houdayer et al [59] indicated that the Pd nanoclusters supported on PANI behave as efficient heterogeneous catalysts in the Heck and Suzuki–Miyaura reactions of aryl iodides. Ciebien et al [60] found that the Pd nanoclusters protected by di-block copolymer can be used to catalyze the hydrogenation of ethylene and propylene.

1.4 Thesis Outline

In general, almost all prior works on the chemical synthesis of metal/polymer nanocomposites involved either of the *ex situ* and *in situ* methods discussed previously in this chapter. These works describe the synthesis, characterization and applications of the resulting nanocomposites. However, there have been very few prior reports pertaining to the comparison of the synthesis modes and thus discuss the effect of synthetic method on the structure and properties of the resulting metal/polymer nanocomposites. Also, very few prior works on the thermal stability of the nanocomposites along with the activation energy determination were found. This thesis details the synthesis and characterization of Palladium/Polycarbonate (Pd/PC) nanocomposites. Pd is selected as the metal of interest because of its better catalytic [59-60] properties. Pd also shows a great affinity towards H₂. It can absorb H₂ up to 900 times of its volume [60]. The fluid sensing properties of Pd are well known from the prior works [50, 55]. PC is selected as the dielectric matrix because of its enhanced mechanical, thermal and optical properties over other polymers like Polystyrene, polyethylene [61-63].

Synthesis of the Pd/PC nanocomposites is detailed in the following chapter. The Pd/PC nanocomposites synthesized in two different methods (*ex situ* and *in situ*) were characterized and their properties were compared. When synthesized in different approaches, the nanocomposites revealed a huge difference in their morphology. The morphology of the nanocomposites was

once again considered to be responsible for the differences in the optical, thermal and electrical properties of these nanocomposites.

In the third chapter, thermal stability of the Pd/PC nanocomposites was studied in detail. For this study, Pd/PC nanocomposites of different Pd content (i.e., 2 vol.% and 1 vol.%) were prepared via *ex situ* and *in situ* methods. TGA and DTGA for all four samples along with PC were performed at different heating rates (5, 10, 15 and 20 °C) under nitrogen atmosphere. T_{onset} , T_{end} , T_{max} and total degradation time for all samples were determined and the results were discussed. Efforts were made to determine the activation energies associated with the thermal degradation theoretically by Kissinger method. The master decomposition curves (MDC) for the nanocomposites has been formulated based on the activation energies calculated by Kissinger method.

Chapter four gives a brief conclusion for the works discussed in the chapters 2 and 3. Potential of applying the Pd/PC nanocomposites in developing NH_3 sensors is briefly discussed. The possible areas for future research are outlined in detail. The first stage of the work includes synthesizing semi-conducting Pd based polymer nanocomposites. Second stage of the work involves the exploration of the effect of changing the metal content, capping agents, synthetic routes, addition of surfactants, reaction conditions and surrounding atmosphere over the electrical conductivity. The third stage is planned to be employing these nanocomposites in the presence of NH_3 at different concentrations and check its conductivity. All the prior works referred for conducting this research are listed in appendix.

References

1. Feldheim D.L. and Keating C.D., *Chemical Society Review*, (1998), 21, 1.
2. Carolyn M., Sih B.C., Scott T.L. and Wolf M.O., *Journal of Materials Chemistry*, (2005), 15, 2433.
3. Huang H. and Yang X., *Colloids and Surfaces B: Biointerfaces*, (2004), 39, 31.
4. Carotenuto G., Nicolias L. and La peruta G., *Sensors and Actuators B*, (2006), 114, 1092.
5. Xia X., Cai S. and Xie C., *Materials Chemistry and Physics*, (2006), 95, 122.
6. Wang L. and Chen D., *Colloid Polymer Science*, (2006), 284, 449.
7. Liu F.K., Hsieh S.Y., Ko F.H. and Chu T.C., *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, (2002), 231, 31.
8. Aymonier C., Bortzmeyer D., Thomann R. and Mulhaupt R., *Chemical Materials*, (2003), 15, 4874.
9. Zhang Z., Wang F. Chen F., and Shi C., *Materials Letters*, (2006), 60, 1039.
10. Hsu S.H., Chou C.W. and Tseng S.M., *Macromolecular Materials and Engineering*, (2004), 289, 1096.
11. Peng Z., Kong L.X., Li S.D. and Spiridonov P., *Journal of Nanoscience and Nanotechnology*, (2006), 6, 3934.
12. Gole A. and Murphy C.J., *Chemistry of Materials*, (2005), 17, 1325.
13. Akamatsu K., Takei S., Mizuhata M., Kajinami A., Deki S., Takeoka S., Fuji M., Hayashi S. and Yamamoto K., *Thin Film Solids*, (2000), 359, 55.
14. Sarma T.K., Chowdhury D., Paul A. and Chattopadhyay A., *Chemical Communications*, (2002), 10, 1048.
15. Briemer M.A., Yevgeny G., Sy S. and Sadik O.A., *Nano Letters*, (2001), 1, 305.
16. Hayat M.A., *Colloidal Gold: Principles, Methods and Applications*, Academic Press, New York, (1989).

17. Kamat P.V. and Shanghavi B., *The Journal of Physical Chemistry B*, (1997), 101, 7675.
18. Walker B.M., Bethell M., Schiffrin D., and Whyman D.J., *Journal of Chemical Society and Chemical Communication*, (1994), 20, 801.
19. Weare W.W., Reed S.M., Warner M.G., and Hutchison J.E., *Journal of American Chemical Society*, (2000), 122, 12890.
20. Selvakannan P.R., Senthilkumar P., More A.S., Shingt R.D., Wadgoankar P.P., and Sastry M., *Langmuir*, (2004), 20, 295.
21. Sarathy K.V., Gargi R., Yadav R.T., Kulkarni G.U., and Rao C.N.R., *Journal of Physical Chemistry B*, (1997), 101, 9876.
22. Sih B.C., and Wolf M.O., *Chemical Communications*, (2005), 3375.
23. Rao C.N.R. and Cheetham A.K., *Journal of Materials Chemistry*, (2001), 11, 2887.
24. Edwards P.P., Johnston R.L., and Rao C.N.R., *Metal clusters in Chemistry*, Wiley-VCH, Weinham, (1999).
25. Schmid G., *Clusters and Colloids: From Theory to Application*, Wiley-VCH, Weinham, (1994).
26. Kirkland A.I., Jefferson D.E., Duff D.G., Edwards P.P., Gameson I., Johnson B.F.U., and Smith D.J., *Process Royal Society London A*, (1993), 440, 589.
27. Wang H., Qiao X., Chen J., and Ding S., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, (2005), 256, 111.
28. Brown L.O., and Hutchison J.E., *Journal of American Chemical Society*, (1998), 121, 882.
29. Jia W., Mc Lachlan J., Xu J., Tadayyon S.M., Norton P.R., and Eichhorn S.H., *Canadian Journal of Chemistry*, (2006), 84, 998.
30. Zhu H., Tao C., Zheng S., Wu S., Li J., *Colloids and Surface A: Physiochemical and Engineering Aspects*, (2005), 256, 17.
31. Jewrajka S.K., and Chatterjee U., *Journal of Polymer Science Part A: Polymer Chemistry*, (2006), 44, 1841.

32. Tamilselvan S., Hayakawa T., Nogami M., Kobayashi Y, Marzan L., Hamanaka Y. and Nakamura A., *Journal of physical chemistry*, (2002), 106, 10157.
33. Corbierre M.K, Cameron N.S, Sutton M, Laaziri K. and Lennox R.B, *Langmuir*, (2005), 21, 6063.
34. Laibinis P.E., Whitesides G.M., Allara D.L., Tao Y.T., Parikh A.N. and Nuzzo R.G., *Journal of the American Chemical Society*, (1991), 113, 7152.
35. King J.A. and Codella P.J., *Macromolecules*, (1990), 23, 345.
36. Kamat P.V., *Journal of Physical Chemistry B*, (2002), 106, 7729.
37. Balamurugan B. and Maruyama T., *Applied Physics Letters*, (2005), 87, 143105.
38. Gao J., Bender C.M. and Murphy C.J., *Langmuir*, (2003), 19, 9065.
39. Gole A. and Murphy C.J., *Chemistry of Materials*, (2005), 17, 1325.
40. Akamatsu K., Takei S., Mizuhata M., Kajinami A., Deki S., Takeoka S., Fujii M., Hayashi S. and Yamamoto K., *Thin Film Solids*, (2000), 359, 55.
41. Nemamcha A., Rehsrpringer J.L. and Khatmi D., *Journal of Physical Chemistry B*, (2006), 110, 383.
42. Merkel T. C., He Z. and Pinnau I., *Macromolecules*, (2003), 36, 6844.
43. Ash B.J., Schadler L.S. and Siegel R.W., *Journal of Polymer Science Part B: Polymer Physics*, (2004), 42, 4371.
44. Ash B.J., Schadler L.S. and Siegel R.W., *Materials Letters*, (2002), 55, 83.
45. Kissinger H.E., *Analytical Chemistry* (1957), 29, 1702.
46. Flynn J. H., Wall L. A., *Polymer Letters*, (1966), 4, 323.
47. Ozawa T., *Journal of Thermal Analysis*, (1970), 2, 301.
48. DiAntonio C.B., Ewsuk K.G. and Bencoe D., *Journal of American Ceramic Society*, (2005), 88, 10, 2722.
49. Aggarwal, G., Park, S. J., Smid, I., and German R. M., *TMS Annual Meeting, MPMD 7th Global Innovation Process: Trends in Materials R and D for Sensor Manufacturing Technologies*, (2006), 29.

50. Athawale A.A., Bhagwat S.V., and Katre P.P., *Sensors and Actuators B*, (2006), 114, 263.
51. Simon U., *Advanced Materials*, (1998), 10, 1487.
52. Brousseau L. C., Zhao Q., Shultz D. A. and Feldheim D. L., *Journal of American Chemical Society*, (1998), 120, 7645.
53. Houbertz R., Feigenspan T., Mielke F., Memmert U., Hartmann U., U. Simon U., Schoen G. and Schmid G., *European physics Letters*, (1994), 28, 641.
54. Zhai L and McCullough R. D., *J. Mater. Chem.*, (2004), 14, 141.
55. Tang H.L., Pan M., Jiang S. P. and Yuan R. Z., *Materials Letters*, (2005), 59, 3766.
56. Ahn H., Chandekar A., Kang B., Sung C. and Whitten J.E., *Chemistry of Materials*, (2004), 16, 3274.
57. Park J.E., Kim S., Mihashi S., Hatozaki O. and Oyama N., *Macromolecules Symposia*, (2002), 186, 35.
58. Park J. E., Park S. G., Koukitu A., Hatozaki O. and Oyama N., *Synthesis of Materials.*, (2004), 140, 121.
59. Houdayer A., Schneider R., Billaud D., Ghanbaja J. and Lambert J., *Applied Organometallic Chemistry*, (2005), 19, 1239.
60. Ciebien J.F., Cohen R.E. and Duran A., *Supramolecular Science*, (1998), 5, 31.
61. Li X., Hristov H.A. and Yee A.F., *Polymer*, (1995), 36, 4, 759.
62. Choi Y.K., Sugimoto K.I., Song S.M. and Endo M., *Materials Letters*, (2005), 59, 3514.
63. Checchetto R., Miotello A. and Chayahara A., *Journal of Physics: Condensation Matter* (2000), 12, 9215.

Figures

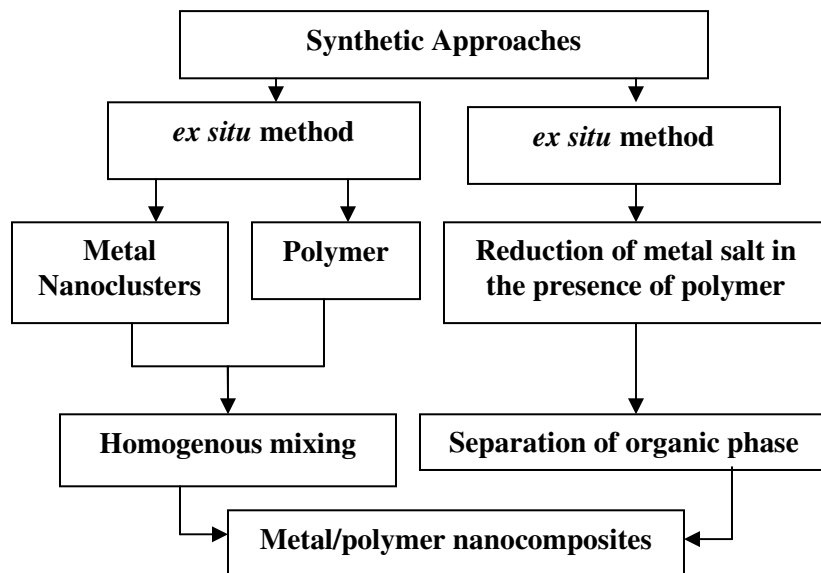


Figure 1.1: Schematic representation of *ex situ* and *in situ* methods for synthesizing metal/polymer nanocomposites.

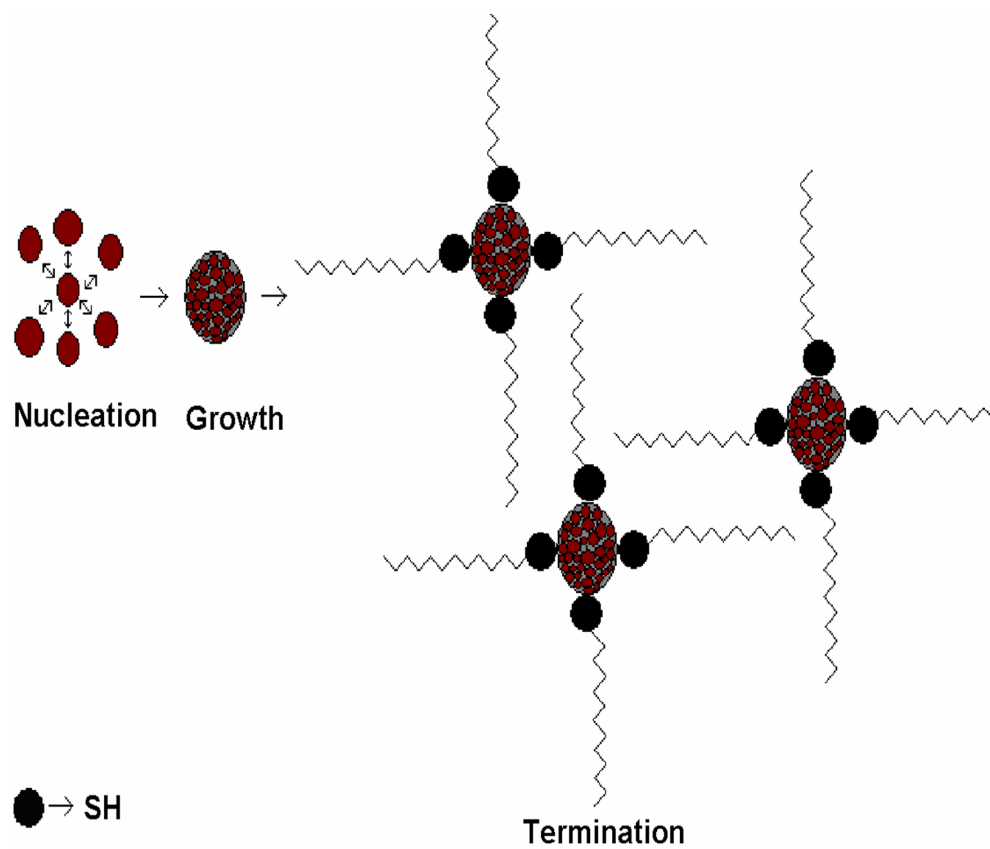


Figure 1.2: Schematic representation of control over nanoclusters size by monolayer protection (by dodecanethiol).

Tables

Table 1.1: Reaction conditions and reactants for different methods to produce long chain organic ligand protected metal nanoclusters.

Conditions followed	Brust Method [18]	Schmidt Method [19]	Sodium citrate Method [17]	Acid Facilitated Transfer method [21]
Phase	Biphasic	Biphasic	Monophasic	Biphasic
Capping Agent	Dodecanethiol	Triphenyl-phosphine	Sodium Citrate	Dodecanethiol
Reducing agent	NaBH ₄	NaBH ₄	Sodium Citrate	phosphonium chloride +NaOH
Reaction temp.	2 ⁰ C	Room temperature	100 ⁰ C	Room temperature
Surfactant	Tetraoctyl-ammonium bromide	Tetraoctyl-ammonium bromide	---	---
Addition of reducing agent	Drop wise	Vigorous	Drop wise	Vigorous
Post-synthesis processes	organic phase is vacuum distilled, washed with acetone to remove excess dodecanethiol	organic phase is washed with methanol/water mixture	Citrate capped metal nanoclusters are ultra-centrifuged	Organic phase is washed with water and washed with ethanol to remove excess dodecanethiol
size	2-5 nm	2 nm	10 nm	1-5 nm
Pros	Control over the size distribution, easy separation of nanoclusters from the reaction mixture, higher shell life of the nanoclusters, high Purity nanoclusters obtained	Faster reaction time, smaller particle size and size distribution, high purity nanoclusters are obtained.	Simple reaction, sodium citrate acts as both capping and reducing agent, can be dispersed in polar solvents.	No surfactant is added, Faster reaction time, desired size and shape of the particles are obtained, size of particles α metal salt content.
Cons	Complexity of the reaction, greater reaction time (>3 hours), nanocluster disperse only in organic solvents like benzene, toluene, washing of excess organic ligands, surfactant reduces the yield.	Nanoclusters disperse only in organic solvents, washing of excess organic ligands, surfactant reduces the yield. High precaution during reduction is advocated.	Nanoclusters formed remain stable only for a week or two; nanoclusters formed tend to have larger size.	Washing of excess organic ligands, surfactant reduces the yield.

Table 1.2: Metal/polymer nanocomposites synthesized via different *ex situ* methods.

Metal/polymer System	Au/Chitosan [3]	Ag/PS [4]	Cu/LDPE [5]
mode of addition or incorporation	Sodium salt of chitosan acts as both reducing and the capping agent for Au nanoclusters.	Ag nanoclusters are homogenously mixed with PS in chloroform and coated on the glass substrate.	Pre-synthesized Cu nanoclusters are extruded with LDPE.
Solvent used	Water + Acetic acid	Chloroform	-----
Metal content	2 wt%	5 to 15 wt%	2 to 17 wt%
Post-mixing processes	Ultra-centrifugation of reaction mixture to settle down the nanocomposites produced.	The coating is thermally annealed at 200 ⁰ C for 30 to 180 seconds.	Nanoclusters are dispersed in the molten LDPE and then extruded and/or injection molded
Size and morphology	--- and discrete	1.9 to 3.2 nm and discrete	--- and discrete
Pros	Better control over shape of the nanoclusters in the nanocomposites produced, can be extended to other metals very easily	Control over the metal content and film thickness is possible leading to wide range of properties and final applications.	Faster reaction time, direct application as injection molded/extruded nanocomposites.
Cons	Structure of chitosan is distorted disabling it from the final applications	Adhesion of PS to the glass surface is highly questionable, annealing defects are also to be considered.	Reproducibility in the application cannot be expected due to improper dispersion, molding defects are also to be considered.

Table 1.3: Metal/polymer nanocomposites synthesized via different *in situ* methods.

Metal/polymer system	Ag/PMMA[6]	Au/PMMA [7]	Pd/PMMA[8]	Au/polythiophene [9]
mode of synthesis or incorporation	Reduction of AgNO ₃ in the presence of emulsified MMA monomer followed by subsequent polymerization.	Reduction of HAuCl ₄ in the presence of PMMA.	MMA are polymerized in the presence of Pd(OAc) ₂ followed by thermal reduction of Pd(OAc) ₂	Au nanoclusters protected by thiophene are prepared followed by polymerization of thiophene
Mol.wt of polymer	---	---	10,000g/mol	----
Solvent used	Water/mercaptoethanol mixture	methanol/water mixture	Toluene	Dichloromethane
Metal content	----	10 vol.%	0.01 vol.%	8 wt%
Post-mixing processes	----	Excess PMMA is washed away with Ethanol/Water Mixture.	Excess polymerization initiator is removed by washing with water	Excess dichloromethane is evaporated by heating in vacuum for 2 hours
Size and morphology	70nm and discrete	2.2-3.1nm and discrete	2.5 nm and discrete	6-8 nm and both discrete & agglomerated
Pros	Simple reaction, No surfactant added, metal salt: mercaptoethanol ratio can be controlled to obtain desired nanocluster size.	No surfactant is added, direct application as nanocomposite films, coatings is possible.	Control over the reaction rate, superior dispersion of metal salt in the monomer, reproducibility is possible	Can be extended to other metals very easily, ability of the capping agent to get polymerized renders promising morphology.
Cons	Control over MMA emulsification and polymerization is not discussed, proper effect of mercaptoethanol on Ag nanoclusters is unknown.	Reproducibility cannot be expected, nanocomposites formed tend to have larger size, PMMA generally shows poor solubility with alcohols.	Control over the thermal decomposition of Pd(OAc) ₂ to Pd is difficult, improper removal of polymerization initiator will lead to PMMA cross-linking.	Complexity of the reaction, nanocomposites formed tend to get agglomerated.

Chapter 2

The Effect of Synthesis Procedures on The Structure and Properties of Palladium/Polycarbonate Nanocomposites

2.1 Abstract

We report the synthesis of palladium (Pd)/polycarbonate (PC) nanocomposites as well as their morphological, optical, thermal and electrical properties. Pd nanoclusters were produced by the reduction of palladium chloride using a variation of the Brust's method. Isolated Pd nanoclusters were formed in the absence of PC in the reaction mixture (*ex situ* method) while agglomeration of Pd nanoclusters was noticed in the presence of PC in the reaction mixture (*in situ* method). Fourier transform infrared spectroscopy (FTIR) suggests nanoparticle-polymer interactions and polymer conformational changes in the *in situ* nanocomposite films. Even after having same Pd content, the *ex situ* nanocomposites films were found to transmit more light than the *in situ* ones. The glass transition temperature (T_g), decreased by $\sim 15^\circ\text{C}$ for both the *ex situ* and *in situ* samples. Thermogravimetric analysis (TGA) indicated that the presence of Pd nanoclusters significantly improved the thermal stability of the nanocomposites, as evidenced by the enhanced onset of degradation by $\sim 20^\circ\text{C}$ and $\sim 40^\circ\text{C}$ for the *in situ* and *ex situ* nanocomposites, respectively. The electrical conductivity shows a dramatic difference between these nanocomposites revealing a semi-conducting nature for the *in situ* sample (resistivity = $17 \times 10^3 \Omega \text{ cm}$) and an insulating nature (resistivity = $2.24 \times 10^{10} \Omega \text{ cm}$) for the *ex situ* sample.

Key Words: nanoclusters; nanocomposites; morphology; transmittance; glass transition temperature; electrical conductivity.

2.2 Introduction

In the past few years, nanoclusters protected by polymers (1, 2) and organic ligands (3-5) have gained increased attention in materials research as they offer immense opportunities to design materials with tunable properties. For example, these nanoclusters showed variations in optical, thermal, electrical and electrochemical properties based on their size. Many of these properties were found to be controlled by the selection of the polymer as well as the distribution of the nanoclusters within the polymer matrix (6, 7).

Generally, polymer-protected nanoclusters can be prepared by two different synthetic methods. In the *ex situ* method, organic ligand-protected nanoclusters are initially prepared followed by homogenous mixing with a polymer solution. In contrast, the *in situ* method, involves the preparation of nanoclusters in the presence of a polymer. This method generally involves no additional organic ligands as protecting agents other than the polymer. The resulting solutions from either method can subsequently be cast into films.

Several variants of the *ex situ* method have been reported for the preparation of metal/polymer nanocomposites. For example, dodecanethiol protected gold (Au) nanoclusters were added to styrene or methyl methacrylate monomer and subsequently polymerized (8). Multilayer films were prepared from Au nanoclusters and chitosan solution (9). Sputtering of Au nanoclusters on a polystyrene (PS) film has also been reported (10). Variations of the *in situ* method have also been reported previously. For example, thermo-labile metallic precursors such as Palladium acetate ($\text{Pd}(\text{OAc})_2$) have been added to a solution

of polymethyl methacrylate (PMMA), in toluene followed by thermolysis to form polymer-protected metallic nanoclusters (11). Films have been obtained by reducing $\text{Pd}(\text{OAc})_2$ in the presence of aniline followed by polymerization to form Pd/polyaniline nanocomposites (12). Monophasic reduction of gold chloride (HAuCl_4) in the presence of PMMA was also used to produce polymer/metal nanocomposites (13).

From the earlier works (14-23), it can be inferred that the morphology of the resulting nanoclusters depends on several factors such as molecular weight of the protecting agent; metal salt: protecting agent ratio; functional groups in the protecting agents; temperature of the reaction; reducing agent; and reduction rate. However, there have been few prior reports pertaining to the effect of synthetic method on the structure and properties of the resulting metal/polymer nanocomposite films.

Here we report an *in situ* method for preparing nanocomposite films by reducing PdCl_2 in the presence of polycarbonate (PC) dissolved in dichloromethane. We also synthesized Pd/PC nanocomposite films by an *ex situ* method involving the dispersion of dodecanethiol-protected Pd nanoclusters in a solution of PC in dichloromethane. These nanocomposite films were characterized by transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), UV-Vis spectroscopy, and thermal analysis [thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)]. It was found that the synthesis method had a significant impact on the

morphological characteristics and the corresponding optical, thermal and electrical properties of the nanocomposite films.

2.3 Experimental Section

2.3.1 Materials

Palladium chloride (PdCl_2), conc. hydrochloric acid (HCl), and dichloromethane (CH_2Cl_2) were purchased from Merck, India. Sodium borohydride (NaBH_4) and dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$) were purchased from Aldrich, USA. Polycarbonate (Caliber T303, (Mw: 160,000)) was obtained from Dow Chemicals, USA. Deionized water with a resistivity of $18 \times 10^6 \Omega\text{-cm}$ was obtained from a Millipore unit.

2.3.2 Synthesis of Pd/PC nanocomposite films

A schematic representation of Pd/PC nanocomposite synthesis is shown in Figure 2.1. In the *ex situ* method, $\text{C}_{12}\text{H}_{25}\text{SH}$ -protected Pd nanoclusters were prepared using Brust method (24). The Pd nanoclusters were then homogenously mixed with a solution of 40 mg of PC in 20 ml of CH_2Cl_2 ($1.6 \mu\text{M}$) followed by film casting at room temperature. In the case of the *in situ* method, PC (40 mg) was dissolved in CH_2Cl_2 (20 ml) ($1.6 \mu\text{M}$). 15 mg of PdCl_2 was first dissolved in 2ml of conc. HCl so as to form a complex $[\text{PdCl}_4]^{2-}$, and was further dissolved in 48 ml water to form a 1mM solution. This biphasic mixture was stirred continuously using a magnetic stirrer for 30 minutes. A freshly prepared solution of NaBH_4 in 20 ml water (0.1M) was added drop-wise to the mixture. The color of the reaction mixture changed rapidly from golden

yellow to black, indicating the formation of Pd nanoclusters. After stirring for 3 hours, the organic phase was separated, washed with water and was directly cast into film at room temperature. Soon after the reduction nearly all of the reduced Pd nanoclusters get themselves shifted from aqueous phase to organic phase.

2.3.3 Characterization of Pd/PC nanocomposite films

TEM micrographs were taken on a JEOL model 1200 EX instrument operated at an accelerating voltage of 120 kV. Samples for TEM analysis were prepared by casting nanocomposites from dichloromethane dispersion on a carbon coated Cu grid (400 meshes) and dried slowly at room temperature. FTIR spectroscopic measurements of the nanocomposite films were carried out on a Perkin-Elmer FTIR 1760X spectrometer operating at a resolution of 4 cm^{-1} in the range of 300 to 4000 cm^{-1} . Thermogravimetric analysis was performed using Perkin-Elmer TGA-7 thermal analysis system, operated under nitrogen flow in the temperature range of 50 to 700°C with a heating rate of $20^{\circ}\text{C}/\text{minute}$. The calorimetric measurements were carried out using a DSC-7 (Pyris 1, Perkin-Elmer) unit over a temperature range of 20 to 200°C . The samples were heated at the rate of $20^{\circ}\text{C}/\text{minute}$ under nitrogen atmosphere. UV-visible spectra of samples were taken with an Ocean Optics USB 400 spectrometer with an operating range from 300 to 1000 nm. Electrical conductivity measurements were made on the nanocomposite films by using a lab-developed, four-point probe conductivity tester where first and last probes were connected to a voltmeter while the second and third were connected to an ammeter. The voltage was applied on the film and the current was measured.

2.4 Results and Discussion

2.4.1 Morphology of Pd/PC nanocomposites

The TEM image of the *ex situ* nanocomposite with 2 vol.% Pd (on a stoichiometric basis) revealed dispersed Pd nanoclusters of ~15 nm embedded in PC (mol. wt. 1600,000) matrix (Figure 2.2a). Based on earlier reports on the synthesis and morphology of n-alkanethiol-protected Pd nanoclusters (15, 20), the presence of dodecanethiol on the surface of the Pd nanoclusters in the present study is likely to ensure the separation of the nanoclusters even after mixing with PC.

However, the average particle size of the Pd nanoclusters in previous studies was found to be ~ 5nm size; using the Brust method (24). Although identical metal salt: thiol ratio and reducing agent were used in the present study, an increase in the size of the nanoclusters was found. This may be due to the absence of the surfactant, tetraoctyl ammonium bromide, in the reaction mixture which helps in phase transfer of reduced Pd nanoclusters. The effect of increased temperature of the reaction mixture from ice-cold condition in the earlier studies in comparison to the reaction room temperature may have also contributed to the increased size of the nanoclusters (25). A difference in the concentration of reducing agent may have also contributed to the increase in the average size of nanoclusters.

In contrast to the above system, *in situ* nanocomposites of Pd nanoclusters (2 vol.% on a stoichiometric basis) in PC (mol. wt. 160,000) showed significant agglomeration (Figure 2.2b). Similar observations on agglomeration were

reported by Chen et al using Pd/ mercapto-poly(ethylene glycol) (19), Chatterjee et al with Au/poly(dimethylamino ethyl metacrylate-*b*-methyl methacrylate) copolymers (mol.wt: 50,000) (21), and Coiberre et al using Au/thiol terminated polystyrene (mol.wt: 80,000) (22). However, discrete nanoclusters were also noted by Tamilselvan et al in Au/ poly(styrene-*b*-vinyl pyrrolidone) copolymer systems (mol.wt: 30,000)(cluster size: ~ 9nm) (26), and Khanna et al (27) in Ag/poly(vinyl alcohol) systems (mol.wt: 125,000)(cluster size: ~10nm). Thus, morphological changes in nanocomposites appear to be strongly dependent on the specific polymer system and reaction conditions.

Wang et al have suggested that in order to obtain discrete nanoclusters, the rate of adsorption of organic ligands on the surface of nanoclusters should equal the rate of nanocluster formation (18). Accordingly, organic ligands with lower molecular weight have generally been found to be more effective in limiting the nanoclusters size (15, 28). The wide-ranging behavior of agglomeration in nanocomposites prepared by the *in situ* methods may be due to the differences in conformation of the polymer chain in the different systems. These differences can arise from variations in molecular weight, solvent, and temperature. Consequently, the mobility of the polymer during adsorption on the nanocluster surface can be affected, thereby limiting the agglomeration of the nanoclusters. In addition, the nature of interactions between the polymer and the surface of the nanoclusters may also play a role in determining the morphology of the resulting nanocomposites. Further studies are needed to better understand the differences in morphologies observed between the *in situ*

and *ex situ* nanocomposites. The following sections examine the consequences of the differences in morphology on the resulting properties of the nanocomposites.

2.4.2 Chemical interactions in the Pd/PC nanocomposites

The FTIR spectra for PC, the *ex situ* and *in situ* Pd/PC nanocomposites are shown in the Figure 2.3a. All peak positions of PC and the nanocomposites were assigned and tabulated in the Table 2.1 along with references from the prior works (29-36). From Figure 2.3a, we can confirm that at high wavenumber region ($2600\text{-}3200\text{ cm}^{-1}$), there is no big difference noted between PC and the *in situ* nanocomposites. However, with the *ex situ* nanocomposites new peaks at 2922 cm^{-1} and 2851 cm^{-1} were seen. From the assignments, it can be said that the appearance of these peaks may be due to the presence of alkyl chains (from dodecanethiol) in the *ex situ* nanocomposites.

In the wavenumber region of $1350\text{-}1950\text{ cm}^{-1}$, no big difference is noticed between PC and the *ex situ* nanocomposites. However, the -C=O peak showed a red shift to 1778 cm^{-1} for the *in situ* nanocomposites. The shift was also accompanied with a broadening of peak from 39 cm^{-1} to 64 cm^{-1} (bandwidth at half maximum) as shown in Table 2.2. This may be due to the conformational changes in the PC as shown in Figure 2.3b or the chemical interactions between the -C=O of PC and the Pd nanoclusters or the variations in the film thickness.

Additionally, a minor change in the peak position at 1598 cm^{-1} was noted for the *in situ* nanocomposites. The change was also accompanied with the

increase in the peak intensity. Similar to the prior explanation by Heymans et al (31) this may once again be due to the conformational changes of the PC.

Two new peaks at 1249 and 1214 cm^{-1} were noticed for the *in situ* nanocomposites. From the assignments in Table 1, we can infer that there is a possibility of conformational change of the PC chains when they interact directly with Pd nanoclusters. Further research is required to sufficiently explain the reasons for the appearance of these peaks. Also, more light should be thrown on the reduction in the peak intensities at 1164, 1082 cm^{-1} (Table 2.3) and broadening of peak at 1012 cm^{-1} for the *in situ* nanocomposites.

2.4.3 Optical Properties

Transmittance spectra of the *ex situ* and *in situ* Pd/PC nanocomposite films (2 vol. % Pd on a stoichiometric basis) in the UV-Vis-IR region (200-1000 nm) are shown in Figure 2.4. It can be observed that the transmittance of the *ex situ* nanocomposite film was higher than that observed for the *in situ* nanocomposite film at any wavelength in the investigated UV-Vis-IR region. In particular, the *in situ* nanocomposite film were found to completely filter light till 564 nm while the *ex situ* nanocomposite film was only able to filter light till 501 nm.

However, Checchetto et al (37) found that the % transmittance of light by PC remains nearly constant at 87% from 400 nm through 800nm. Early reports studied the influence of concentration, size, shape, particle size distribution and also molecular weight of protecting agent on the optical properties of the nanocomposites. For example, Aymonier et al (11) with Pd/PMMA, Akamatsu

et al (38) with Ag/Nylon, and Nemamcha et al (39) with Pd/ poly (vinyl pyrrolidone) have shown that the transmittance of light in the UV-Vis region decreased with increase in the metal nanoparticle concentration. Chang et al (40) in his work on Au nanorods state that the absorption peaks shift towards red as the mean aspect ratio of the particle increases. Balamurugan et al (41) noted red shift in the peak positions with the increase in the particle size. The work of Xiang et al (42) on the synthesis of Au nanorods explains the influence of shapes like cube, sphere and unshaped particles on the absorption spectra of Au nanoparticles. Gao et al (43) found that the Plasmon absorption maxima (inversely proportional to transmittance) of Au nanoparticles decrease with increase in the size of the capping agent, alkyltrimethylammonium bromide. Gole et al (44) found that in the case of Au nanorods coated with polyelectrolyte, the Plasmon absorption maxima of Au decreases with increase in the thickness of the coating. In compliment to the above mentioned reports, we in our work tried to study the influence of nanocomposite film morphology on the transmittance of light in the UV-Vis-IR region. Further studies are required for understanding the optical properties of these nanocomposites in a detailed manner.

2.4.4 Thermal Properties

A comparison of the DSC profiles of the nanocomposites is displayed in Figure 2.5. It was found that the T_g of both *ex situ* and *in situ* nanocomposites (with 2 vol.% Pd on a stoichiometric basis) decreased by 16 °C (from 146 °C to 130 °C). Aymonier et al (11) observed ~ 9 °C decrease in T_g for Pd / PMMA

nanocomposites synthesized by a different route. Differences in concentration (≤ 0.1 wt. %) and nanocluster size (~ 2 nm) between their work and the present study may account for differences in the magnitude of the change in T_g . Earlier studies by Liu et al (13) using Au/PMMA and Hsu et al (45) with Au/polyurethane also showed a decrease in T_g by 20 °C and 5 °C respectively. Prior studies with fumed silica-based poly(4-methyl-2-pentyne) and poly(1-trimethylsilyl-1-propyne) nanocomposites indicated a substantial rise in gas permeability compared to the unfilled polymers suggesting an increase in free volume between the polymer chains (46, 47). In a similar manner, the Pd nanoclusters embedded may have increased the free volume between the PC chains, thereby reducing the T_g of the nanocomposites.

However, an increase in T_g by 7 °C was also noted by Ash et al (48) in alumina/PMMA nanocomposites. The presence of strong interactions between the carbonyl groups of PMMA and alumina is well-known (49). Consequently, the polymer chains will be strongly pinned to the surface of the metal oxide, thereby increasing T_g . In contrast, relatively weak interactions exist in the Pd/PC nanocomposites as evidenced by the FTIR data. Similarly, relatively weak interactions between the filler and polymer are likely to exist in the fumed silica and Au-based nanocomposites, resulting in an increase in free volume and a corresponding decrease in T_g .

Thermogravimetric analysis performed under nitrogen (Figure 2.6) indicated that the incorporation of Pd nanoclusters in PC for the *ex situ* nanocomposites increased the thermal stability of the PC matrix from ~ 430 to

~470°C. In comparison, in the *in situ* nanocomposites an improvement in thermal stability to ~450°C was observed.

A similar increase in thermal stability was noted in earlier reports by Huang et al (50) for Au/poly(methyl styrene) (particle size: 3.5 nm), Aymonier et al (11) for Pd/PMMA (particle size: 2.5 nm), and Hsu et al (45) for Au/polyurethane (particle size: 5 nm). Aymonier et al (11) and Hsu et al (37) observed that the thermal stability of the nanocomposites increase with increase in metal concentration and with decrease in particle size and agglomeration. These results are based on changes in area of the polymer-nanocluster interface and are in close agreement with the present study.

2.4.5 Electrical Conductivity

The influence of Pd nanoclusters on the electrical behavior of Pd/PC nanocomposites are shown in Figure 2.7. PC is electrically insulating in nature with a resistivity of about 10^{17} Ω cm. The *ex situ* nanocomposite films (with 2 vol.% Pd (on a stoichiometric basis)) also revealed a similar insulating nature both in the air and argon atmospheres. However, the *in situ* nanocomposite films having 2 vol.% Pd (on a stoichiometric basis) showed a linear increase in the current with the voltage indicating a constant resistance of about 13.5 K Ω . However, the *in situ* nanocomposites with lesser Pd concentration were again found to be insulating in nature. Further, no significant difference is observed when the conductivity is measured for the *in situ* nanocomposites in the argon atmosphere.

Similar results were seen in earlier works by Athawale et al (51) on Pd/polyaniline nanocomposites and Rao et al (52) on Pd/polypyrrole nanocomposites. However, these works generally involved conducting polymers for electrical conductivity studies on nanocomposites. Our work involves an electrically insulating polymer (PC) rather than a conducting polymer.

The insulating nature of the *ex situ* nanocomposites might be because of the presence of discrete Pd nanoclusters. Here, the nanoclusters were separated from each other by dodecanethiol and were embedded in the PC matrix. However, in the *in situ* nanocomposites, the agglomerated Pd nanoclusters might form continuous segments. This in turn might facilitate the electron transfer from one Pd cluster to another Pd cluster leading to a continuous electrical conductivity. Further research should be carried out so as to utilize these nanocomposites for their applications in sensors.

2.5 Conclusions

Pd/PC nanocomposites prepared by the *ex situ* and *in situ* methods exhibited marked differences in their morphology. The Pd nanoclusters produced by the *ex situ* method were well-dispersed while the Pd nanoclusters produced by the *in situ* method were agglomerated. In the absence of any capping agent such as thiol or polymer, stable Pd nanoclusters could not be obtained due to inadequate stabilization. FTIR of the PC and the nanocomposites were thoroughly studied. Changes in the peak positions for the *in situ* nanocomposites suggest possible conformational changes in the PC

chains. The nanocomposites exhibited a strong dependence of optical, thermal and electrical properties on their morphology. The *in situ* nanocomposites filter light up to 564 nm than the *ex situ* nanocomposites which filters light only up to 501 nm. The T_g of both the nanocomposites were lower than PC by 15°C. In addition, the onset of thermal degradation of the *ex situ* and *in situ* nanocomposites were higher than PC by 40°C and 20°C, respectively. The electrical properties of these nanocomposites suggest that *in situ* method is best suited to make electrically conducting metal-polymer nanocomposites.

References

1. Ziolo, R. F. Giannelis, E. P.; Weinstein, B. A.; O'Horo, M. P.; Ganguly, B. N.; Mehrotra, V.; Russell, M. W. and Huffman, D. R. *Science* (1992), 257, 219.
2. Wuelfing, W. P., Gross, S. M.; Miles, D. T. and Murray, R. W. *Journal of American Chemical Society* (1998), 120, 12696.
3. Aslam M; Mulla I.S., and Vijayamohanan K., *Langmuir* (2001), 17, 7487.
4. Aslam M; Mulla I.S. and Vijayamohanan K, *Applied Physics Letter* (2001), 79, 689.
5. Aslam M; Gopakumar G., Shoba T.L., Mulla I.S.; Vijayamohanan K, Kulkarni S.K., Urban J., and Vogel W., *Journal of Colloid and Interface Science* (2002), 255, 79.
6. Liu F.K., Hsieh S.Y., Ko F.H., and Chu T.C., *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (2002), 231, 31.
7. Whetten R.L., Khoury J.T., Alvarez N.M., Murthy S., Vezmar I., Wang Z.L., Stephens P.W., Cleaveland C.L., and Landman U., *Advanced Materials* (1996), 8, 248.
8. Gonsalves K.E., Carlson G., Chen X., Gayen S.K., Perez R., and Yacaman M.J., *NanoStructured Materials* (1996), 7, 293.
9. Huang H., and Yang X., *Colloids and Surfaces B: Biointerfaces* (2004), 39, 31.
10. Chattopadhyay S, and Datta A., *Synthetic Metals*, (2005), 155, 365.
11. Aymonier C., Bortzmeyer D., Thomann R., and Mulhaupt R., *Chemical Materials* (2003), 15, 4874.
12. Houdayer A., Schneider R., Billaud D., Ghanbaja J. and Lambert J., *Applied Organometallic Chemistry* (2005), 19, 1239.
13. Liu F.K., Hsieh S.Y., Ko F.H., and Chu T.C., *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (2002), 231, 31.
14. Sondi I., Goia D.V. and Matijevc E., *Journal of Colloid and Interface Science* (2003), 260, 75.
15. Zamborini F.P., Gross S.M., and Murray R.W., *Langmuir* (2001), 17, 481.

16. Henglein A., and Giersig M., *Journal of physical Chemistry:B* (1999), 103, 9533.
17. Ramirez E, Jansat S, Philippot K, Lecante P, Gomez M, Bulto A.M.M., and Chaudret B., *Journal of organometallic chemistry* (2004), 689, 4601.
18. Wang H., Qiao X., Chen J., and Ding S., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2005), 256, 111.
19. Chen M., Falkner J., Guo W.H., Zhang J.Y., Sayes C., and Colvin V.L., *Journal of Colloid and Interface Science* (2005), 287, 146–151.
20. Sun Y, Frenkel A.I., Isseroff R, Shonbrun C., Forman M., Shin K, Koga T, White H, Zhang L., Zhu Y., Rafailovich M.H., and Sokolov J.C., *Langmuir* (2006), 22, 807.
21. Jewrajka S.K., and Chatterjee U., *Journal of Polymer Science Part A: Polymer Chemistry* (2006), 44, 1841.
22. Corbierre M.K, Cameron N.S, Sutton M, Laaziri K., and Lennox R.B, *Langmuir* (2005), 21, 6063.
23. Ronga M, Zhanga M., Liua H., and Zenga H., *Polymer* (1999), 40, 6169.
24. Walker B.M., Bethell M., Schiffrin D., and Whyman D.J., *Journal of Chemical Society and Chemical Communication* (1994), 20, 801.
25. Koga K., Ikeshoji T., and Sugawara K., *Physical review letters* (2004), 92, 11507-1.
26. Tamilselvan S., Hayakawa T., Nogami M., Kobayashi Y., Marzan L., Hamanaka Y. and Nakamura A., *Journal of physical chemistry* (2002), 106, 10157.
27. Khanna P.K., Singh N., Charan S., Subbarao V.V.V.S, Gokhale R., and Mulik U.P., *Materials Chemistry and Physics* (2005), 93, 117.
28. Yukihide S., and Naoki T., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2000), 169, 59.
29. Wang J., Montville D. and Gonsalves K.E., *Journal of Applied Polymer Science*, (1999), 72, 1851.
30. Laibinis P.E., Whitesides G.M., Allara D.L., Tao Y. T, Parikh A. N., and Nuzzo R.G., *Journal of the American Chemical Society* (1991), 113, 7152.

31. Heymans N. and Rossum S.V., *Journal of Material Scienc*, (2002), 37, 4273.
32. Hopfe I., Pompe G., and Eichhorn K.J., *Polymer* (1997), 38, 10, 2321.
33. Ning P. and Ko T.M., *Polymer Engineering and Science* (1997), 37, 7, 1226.
34. Liu C. K., Hu C.T. and Lee S., *Polymer Engineering and Science* (2005), 45, 5, 687.
35. Dehaye F., Balanzat E., Ferain E., and Legras R., *Nuclear Instruments and Methods in Physics Research B* (2003), 209, 103.
36. Wang Y., Jin Y., Zhu Z., Liu C., Sun Y., Wang Z., Hou M., Chen X., Zhang C., Liu J., Li B., *Nuclear Instruments and Methods in Physics Research B* (2000), 164-165, 420.
37. Checchetto R., Miotello A. and Chayahara A., *Journal of Physics: Condensation Matter* (2000), 12, 9215.
38. Akamatsu K., Takei S., Mizuhata M., Kajinami A., Deki S., Takeoka S., Fujii M., Hayashi S., and Yamamoto K., *Thin Film Solids* (2000), 359, 55.
39. Nemamcha A., Rehsrpringer J.L., and Khatmi D., *Journal of Physical Chemistry B* (2006), 110, 383.
40. Chang S.S., Shih C.W., Chen C.D., Lai W.C., and Wang C.R.C., *Langmuir* (1999), 15, 701.
41. Balamurugan B., and Maruyama T., *Applied Physics Letters* (2005), 87, 143105.
42. Xiang X.C., Brioude A., and Pileni M.P., *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (2006), 277, 201.
43. Gao J., Bender C.M., and Murphy C.J., *Langmiur* (2003), 19, 9065.
44. Gole A. and Murphy C.J., *Chemistry of Materials* (2005), 17, 1325.
45. Hsu S.H., Chou C.W., and Tseng S.M., *Macromolecular Materials and Engineering* (2004), 289, 1096.
46. Merkel T. C., He Z., and Pinnau I., *Macromolecules* (2003), 36, 6844.
47. Ash B.J., Schadler L.S., and Siegel R.W., *Journal of Polymer Science Part B: Polymer Physics* (2004), 42, 4371.

48. Ash B.J., Schadler L.S., and Siegel R.W., *Materials Letters* (2002), 55, 83.
49. Tirrell M., Tannenbaum R., King S., Lecy J., and Potts L., *Langmuir* (2004), 20, 4507.
50. Huang H.M., Chang C.Y., Liu I.C., Tsai H.C., Lai M.K., and Tsiang C.C.R., *Journal of Polymer Science: Part A: Polymer Chemistry* (2005), 43, 4710.
51. Athawale A.A., Bhagwat S.V., and Katre P.P., *Sensors and Actuators B* (2006), 114, 263.
52. Rao C.R.K., and Trivedi D.C., *Catalysis Communications* (2006), 7, 662.

Figures

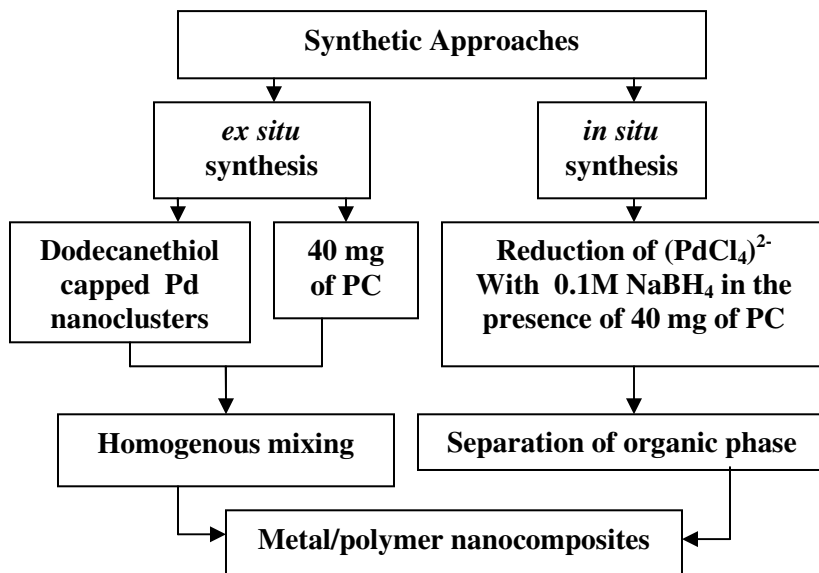


Figure 2.1: Schematic representation of synthetic approaches for preparing *in situ* and *ex situ* Pd/PC nanocomposites.

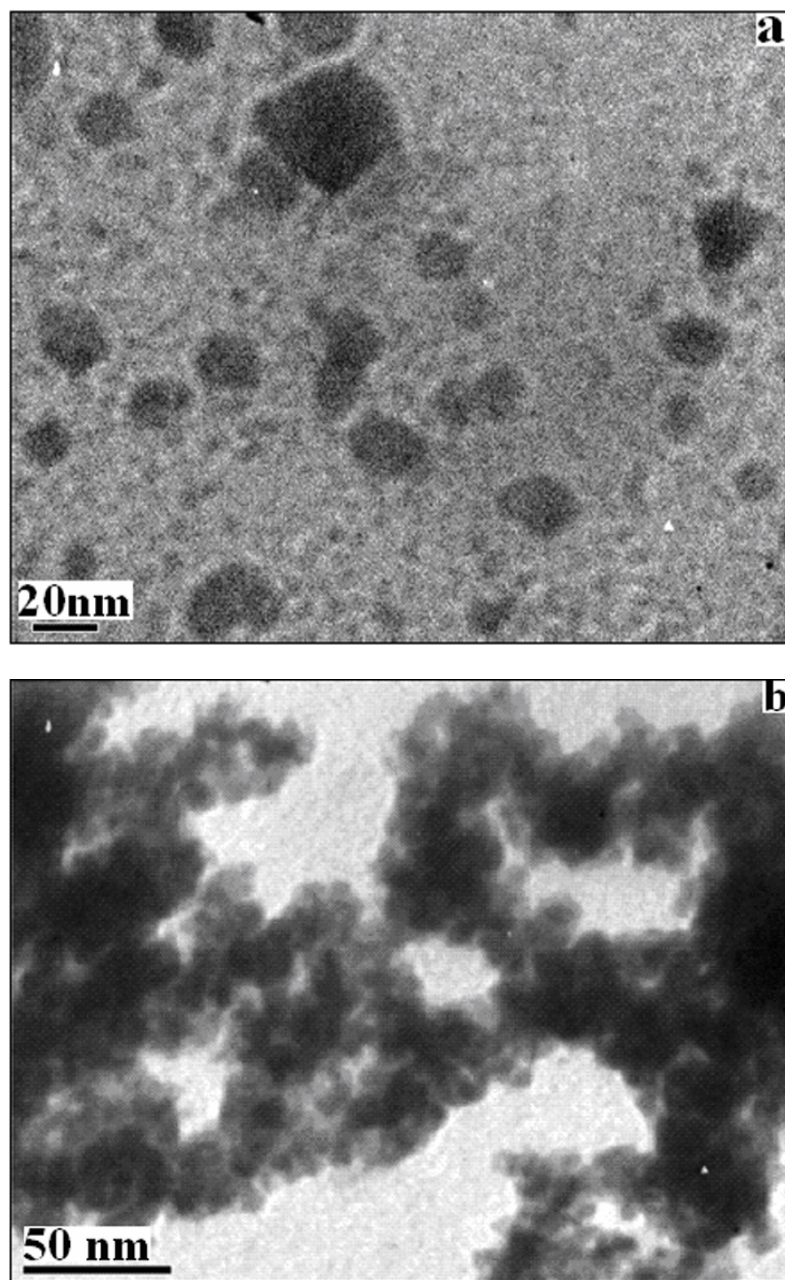


Figure 2.2: TEM image of the *ex situ* and *in situ* Pd/PC nanocomposites showing (a) dispersed Pd nanoclusters, and (b) agglomerated Pd nanoclusters, respectively.

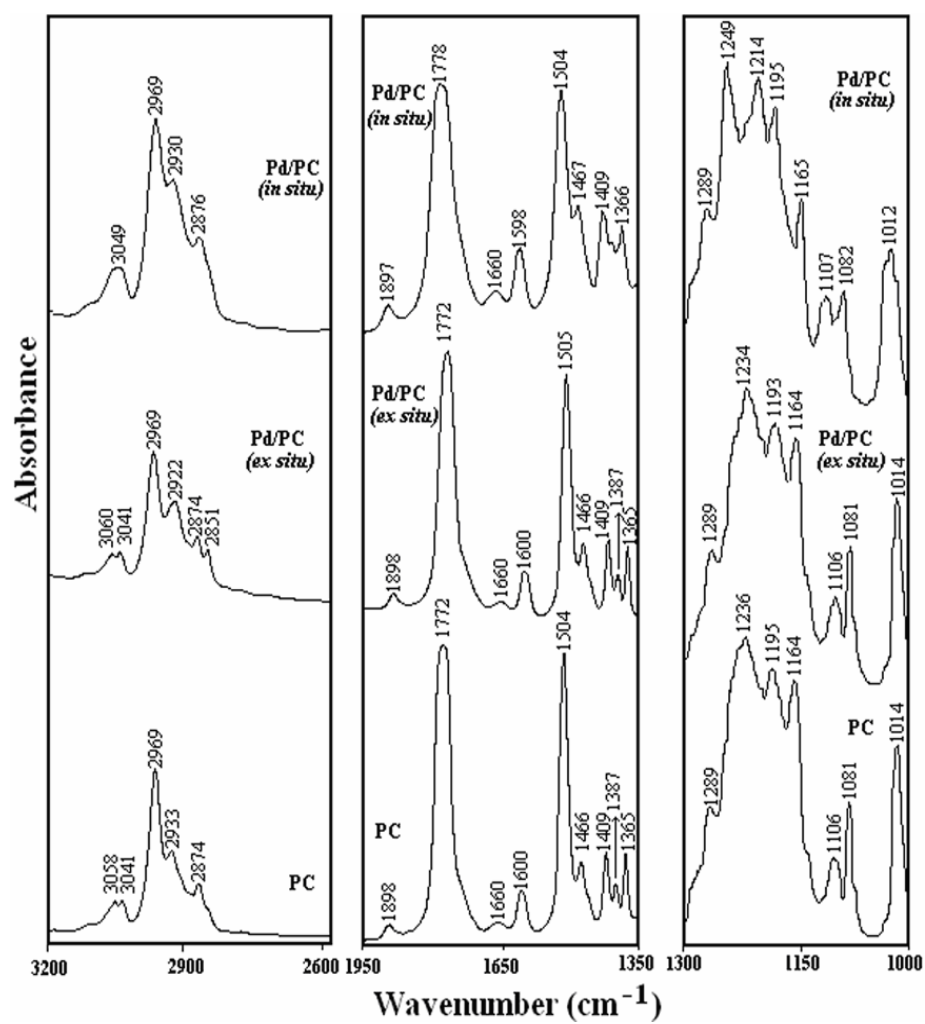


Figure 2.3a: FTIR spectra of PC and Pd/PC nanocomposites

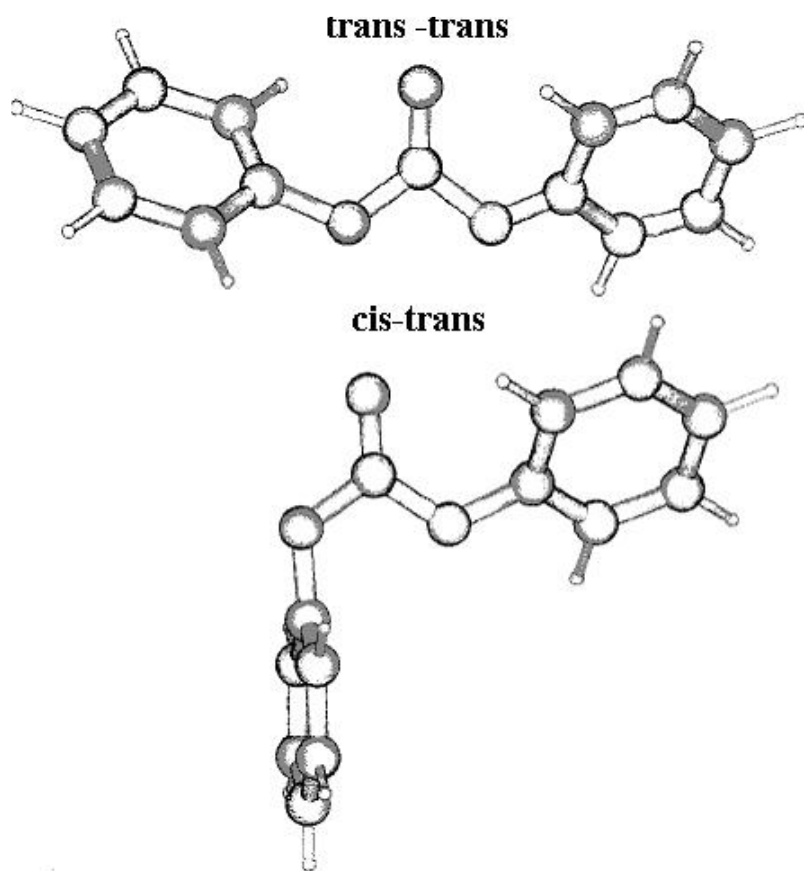


Figure 2.3b: Conformational Changes in the PC chains.

(Dybal J., Schimdt P., Baldrian J. and Kratochvil J., *Macromolecules*, (1998), 31, 6611)

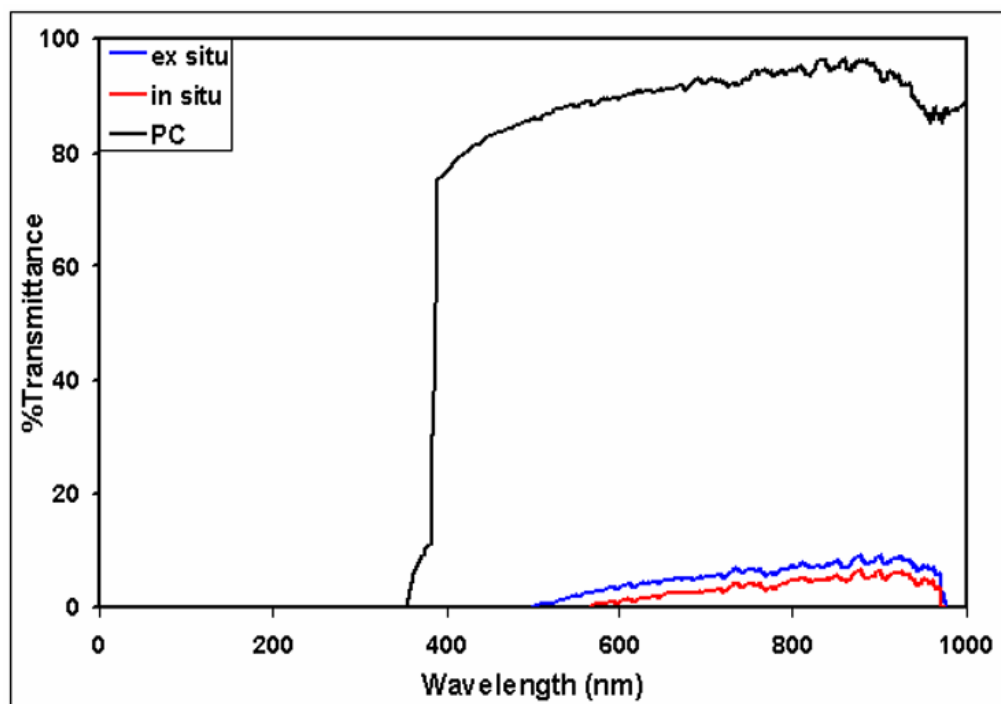


Figure 2.4: Comparison of transmission spectra of PC, and Pd/PC nanocomposites with 2 vol.% Pd content.

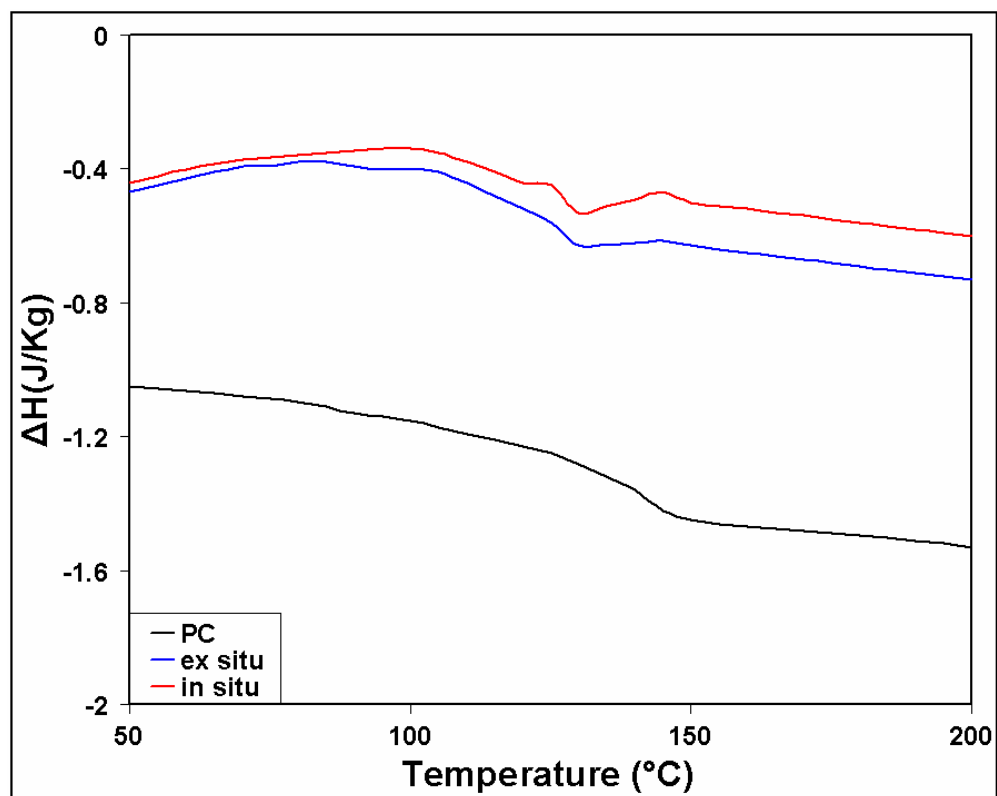


Figure 2.5: DSC measurements showing reduction in the T_g of *ex situ* and *in situ* Pd/PC nanocomposites when compared to free PC.

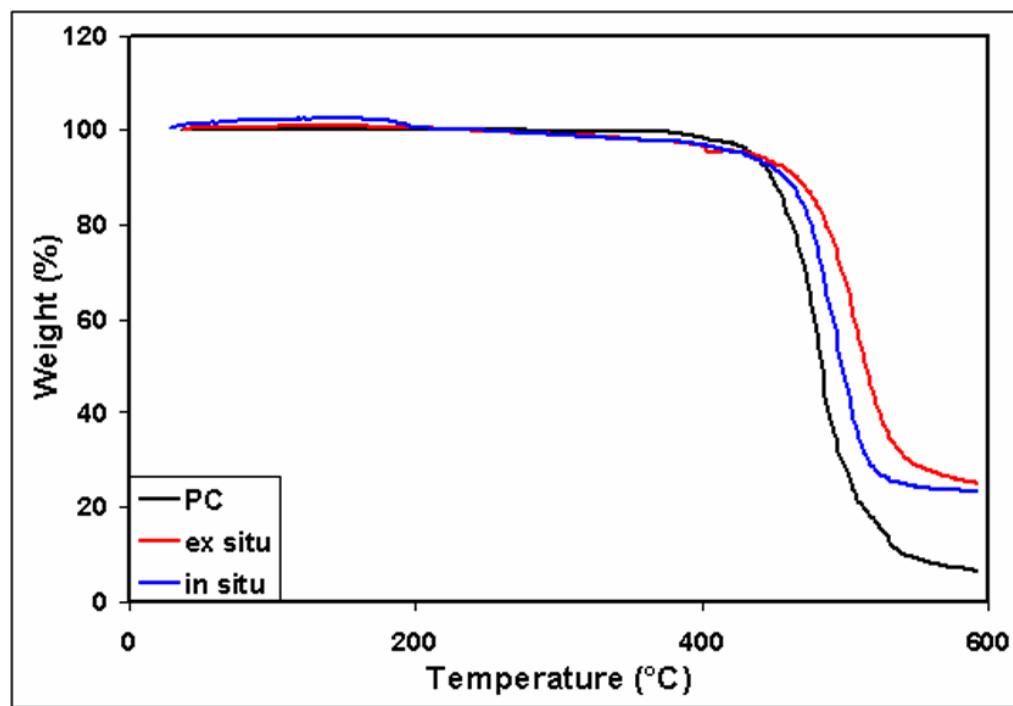


Figure 2.6: Thermogravimetric analysis of PC and Pd/PC nanocomposites.

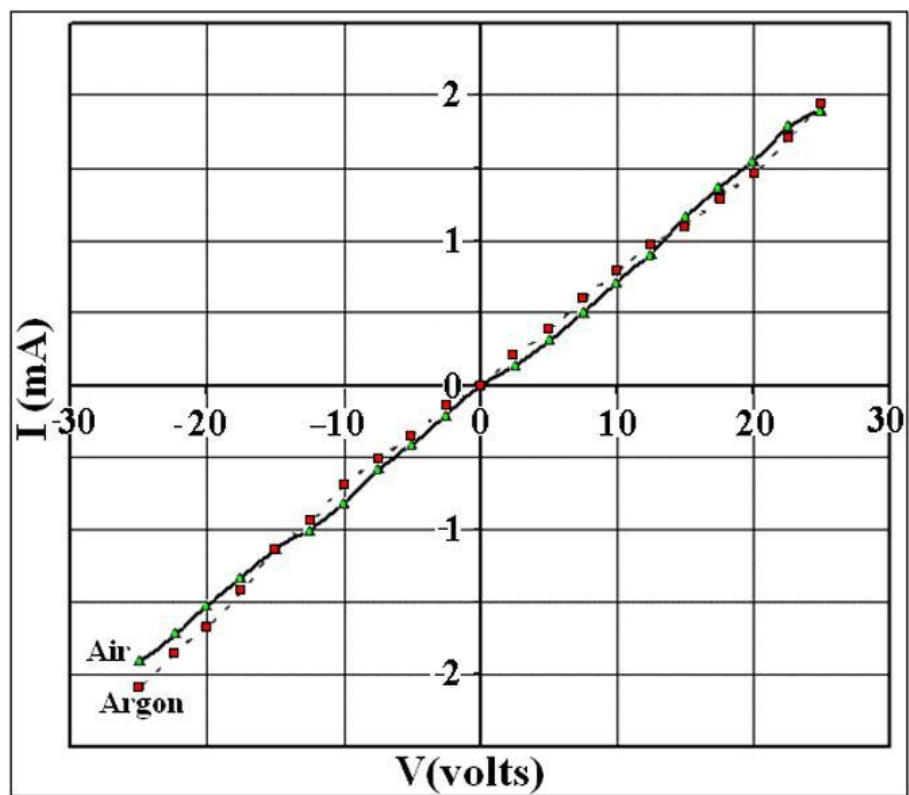


Figure 2.7: I-V measurements of *in situ* prepared Pd/PC nanocomposites confirming its semi-conducting nature.

Tables

Table 2.1: FTIR peaks for PC and Pd/PC nanocomposites.

PC	Pd/PC (<i>ex situ</i>)	Pd/PC (<i>in situ</i>)	Description for the bands observed	Ref.
3058	3060	---	C-H stretching for phenyl	(29)
---	---	3049	C-H stretching for phenyl	
3041	3041	---	C-H stretching for phenyl	
2969	2969	2969	C-H asym. stretching for $-\text{CH}_3$	(30)
2933	---	2930	C-H sym stretching for CH_3 (Fermi)	
---	2922	---	C-H asym. stretching for CH_2	
2874	2874	2876	C-H sym stretching for CH_3	
---	2851	---	C-H sym stretching for CH_2	(31)
1772	1772	1778	C=O stretching vibration (1785 cm^{-1} cis-trans; 1767 cm^{-1} trans-trans)	
1660	1660	1660	C=C stretching in the phenyl	
1600	1600	1598	C-C in-plane stretching for phenyl (1604 cm^{-1} cis-trans; 1594 cm^{-1} trans-trans)	
1504	1505	1504	phenyl C-C in-plane stretching	(32) (33) (34)
1409	1409	1409	C-C sym in-plane stretching for phenyl	(32) (33)
1387	1387	---	C-H asym. bending vibration of CH_3	(35)
1365	1365	1366	C-H sym. bending vibration of CH_3	
---	---	1249	C-O-C asym. stretching (trans-trans)	(31)
1236	1234	---	C-O-C asym. stretching	
---	---	1214	C-O-C asym. stretching (cis-trans)	
1195	1193	1195	C-O-H	(29)
1165	1164	1164	C-O-C sym stretching	
1106	1106	1107	C-H in plane bending for o,p- substituted benzenes	
1081	1081	1082	C-C-C bend for phenyl	(31) (33) (36)
1014	1014	1012	C-C-C in plane bend C-O stretching for aryl-O-C	

Table 2.2: Bandwidth at half maximum for PC and Pd/PC nanocomposites.

Sample	Peak Position (cm⁻¹)	Bandwidth at half maximum (cm⁻¹)
PC	1772	39
Pd/PC (<i>ex situ</i>)	1772	42
Pd/PC (<i>in situ</i>)	1778	64
PC	1012	16
Pd/PC (<i>ex situ</i>)	1012	16
Pd/PC (<i>in situ</i>)	1014	26

Table 2.3: Ratio of intensities of the peaks for PC and Pd/PC nanocomposites.

Sample	Peaks compared (cm⁻¹)	Ratio of the intensities
PC	1014 & 1081	1.38
Pd/PC (<i>ex situ</i>)	1014 & 1081	1.34
Pd/PC (<i>in situ</i>)	1012 & 1082	1.34
PC	1014 & 1106	2.3
Pd/PC (<i>ex situ</i>)	1014 & 1106	2.07
Pd/PC (<i>in situ</i>)	1012 & 1107	1.42
PC	1081 & 1106	1.47
Pd/PC (<i>ex situ</i>)	1081 & 1106	1.55
Pd/PC (<i>in situ</i>)	1082 & 1107	1.06
PC	1504 & 1600	8.8
Pd/PC (<i>ex situ</i>)	1505 & 1600	7.4
Pd/PC (<i>in situ</i>)	1504 & 1598	5.9

Chapter 3

Studies on the Thermal Stability of Palladium/Polycarbonate Nanocomposites

3.1 Abstract

Palladium/polycarbonate (Pd/PC) nanocomposites were synthesized using two different techniques, *ex situ* and *in situ* methods. The influence of the heating rate, Pd content, and method of synthesis on the thermal stability of the Pd/PC nanocomposites was investigated using thermogravimetric analysis (TGA). It was noticed that the *ex situ* Pd/PC nanocomposites showed a higher T_{onset} for thermal degradation than *in situ* ones and PC. In both the nanocomposites when the Pd content and heating rates were increased, T_{onset} of the nanocomposites were found to be increase. From the differential thermal analysis (DTA), it is found that the T_{max} of the given nanocomposite increased with the increase in the heating rates. The kinetics of degradation was studied and the activation energies of the nanocomposites were determined by using the Kissinger method. The Master Decomposition Curve (MDC) was determined from the obtained activation energies to describe the time-temperature dependence of the nanocomposite pyrolysis. The normalized weight–time–temperature plots for the Pd/PC nanocomposites were constructed.

Keywords: ex situ, in situ, nanocomposites, T_{onset} , T_{max} , Master Decomposition Curve.

3.2 Introduction

Direct applications of the metal nanoclusters are limited due to their size and stability. They are easily aggregated because of their high surface energy, and get easily oxidized too. Incorporating these metal nanoclusters into some dielectric matrices is commonly followed to solve these problems. Using polymers as an incorporating medium can render a wide range of useful characteristics to the nanocomposites developed [1]. For example, palladium nanoparticles dispersed in polymers find useful applications as sensors and catalysts. In these applications, it is important to understand the thermal stability of the polymer nanocomposites in order to recognize their useful operating temperature limits.

Metal/polymer nanocomposites were synthesized by two different approaches: *in situ* and *ex situ*. The *ex situ* methods generally involve the addition of already synthesized metal nanoclusters to the polymer matrix [2-3]. The *in situ* methods on the other hand, involve the preparation of nanoclusters in the presence of a polymer or polymerization in the presence of nanoclusters [4-5]. It can be evidenced from the prior works that such incorporations offers a greater possibility of developing nanocomposites with useful thermal [2, 6-7], optical [8-9] and electrical properties [10-11].

In this study, the *ex situ* and *in situ* Pd/PC nanocomposites with 2 different Pd content (1 and 2 vol.%) are prepared. The degradation behavior of PC and the Pd/PC nanocomposites were studied using thermogravimetric analysis under nitrogen atmosphere. Focus is given on the influences of the heating rates, the

Pd content and the modes of synthesis on the degradation temperatures. Activation energies associated with the thermal degradation of these nanocomposites were theoretically calculated using Kissinger method. The master decomposition curves (MDC) for the nanocomposites has been formulated based on the activation energies calculated by Kissinger method.

3.3 Experimental Section

3.3.1 Materials

Palladium chloride (PdCl_2), conc. hydrochloric acid (HCl), and dichloromethane (CH_2Cl_2) were purchased from Merck, India. Sodium borohydride (NaBH_4) and dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$) were purchased from Aldrich, USA. Polycarbonate (Caliber T303, (M_w : 160,000)) was obtained from Dow Chemicals, USA. Deionized water with a resistivity of $18 \times 10^6 \Omega\text{-cm}$ was obtained from a Millipore unit.

3.3.2 Synthesis of Pd/PC nanocomposite Films

A schematic representation of Pd/PC nanocomposite synthesis is shown in Figure 3.1. In the *ex situ* method, $\text{C}_{12}\text{H}_{25}\text{SH}$ -protected Pd nanoclusters were prepared using the Brust method [12]. The Pd nanoclusters were then homogenously mixed with a solution of 40 mg of PC in 20 ml of CH_2Cl_2 (1.6 μM) followed by film casting at room temperature. In the case of the *in situ* method, PC (40 mg) was dissolved in CH_2Cl_2 (20 ml) (1.6 μM). 15 mg (for 2 vol.%) / 7.5 mg (for 1 vol.%) of PdCl_2 was first dissolved in 2ml of conc. HCl so as to form a complex $[\text{PdCl}_4]^{2-}$, and was further dissolved in 48 ml water to

form a 1mM solution. This biphasic mixture was stirred continuously using a magnetic stirrer for 30 minutes. A freshly prepared solution of NaBH₄ in 20 ml water (0.1M) was added drop-wise to the mixture. The color of the reaction mixture changed rapidly from golden yellow to black, indicating the formation of Pd nanoclusters. After stirring for 3 hours, the organic phase was separated, washed with water and was directly cast into film at room temperature. Soon after the reduction nearly all of the reduced Pd nanoparticles get themselves shifted from aqueous phase to organic phase.

3.3.3 Characterization of Pd/PC nanocomposite films

TEM micrographs were taken on a JEOL model 1200 EX instrument operated at an accelerating voltage of 120 kV. Samples for TEM analysis were prepared by casting nanocomposites from CH₂Cl₂ dispersion on a carbon coated Cu grid (400 meshes) and dried slowly at room temperature. Thermogravimetric analysis was performed using TA instruments thermal analysis system. The instrument operated under nitrogen atmosphere at a purge rate of 50 ml/min. All TGA were carried out in the temperature range of room temperature (~25 °C) to 600°C with four different heating rates of 5, 10, 15 and 20°C/min.

3.4 Results and Discussion

3.4.1 Morphology of Pd/PC nanocomposite films

The TEM image of the *ex situ* nanocomposite with 2 vol.% Pd, revealed dispersed Pd nanoclusters of ~15 nm embedded in PC (mol. wt. 160,000) matrix (Figure 3.2a). Based on earlier reports on the synthesis and morphology of n-alkanethiol-protected Pd nanoclusters, the presence of dodecanethiol on the

surface of the Pd nanoclusters in the present study is likely to ensure the separation of the nanoclusters even after mixing with PC.

In contrast to the results of the present study, the average particle size of the Pd nanoclusters in previous studies was found to be ~ 5nm size; using the Brust's biphasic method [12]. Although identical metal salt: thiol ratio and reducing agent were used in the present study, an increase in the size of the nanoclusters was found. This may be due to the absence of the surfactant, tetraoctyl ammonium bromide, in the reaction mixture which helps in phase transfer of reduced Pd nanoclusters. The effect of increased temperature of the reaction mixture from ice-cold condition in the earlier studies in comparison to the reaction room temperature may have also contributed to the increased size of the nanoclusters. A difference in the concentration of reducing agent may have also contributed to the increase in the average size of nanoclusters.

In contrast to the above system, *in situ* nanocomposites of Pd nanoclusters (2 vol.% on a stoichiometric basis) in PC showed significant agglomeration (Figure 3.2b). Similar observations on agglomeration were reported by Chen et al using Pd/ mercapto-poly(ethylene glycol) [13], and Chatterjee et al with Au/poly(dimethylamino ethyl methacrylate-*b*-methyl methacrylate) copolymers [14]. However, discrete nanoclusters were noted by Aymonier et al in Pd/ PMMA [4] and Liu et al [5] in Au/PMMA systems. Thus, morphological changes in nanocomposites appear to be strongly dependent on the specific polymers system and reaction conditions.

Wang et al have suggested that in order to obtain discrete nanoclusters, the rate of adsorption of organic ligands on the surface of nanoclusters should equal the rate of nanocluster formation [15]. Accordingly, organic ligands with lower molecular weight have generally been found to be more effective in limiting the nanoclusters size [16]. In addition, the nature of interactions between the polymer and the surface of the nanoclusters may also play a role in determining the morphology of the resulting nanocomposites. The following sections examine the consequences of the differences in morphology on the resulting thermal stability of the nanocomposites.

3.4.2 Thermal Stability

The thermogravimetric (TGA) curves for the Pd/PC nanocomposites and PC at different heating rates are shown in Figures 3.3. For each sample, the corresponding DTA plots in Figure 3.4 revealed the temperature at which the maximum rate of weight loss ($T_{\max}$) occurs. The DTA plots are represented with normalized weight Ψ (%) which can be expressed as,

$$\Psi = \left[\frac{W_i - W_{\text{end}}}{W_0 - W_{\text{end}}} \right] * 100$$

Where, W_i is the weight (%) of the sample at the given temperature, W_0 is the weight (%) at the starting of TGA experiment and W_{end} is the weight (%) at the ending of TGA experiment.

The onset temperature of degradation (T_{onset}) and the end temperature of degradation (T_{end}) can be obtained from the TGA. Their difference ΔT thus, represents the temperature range for thermal degradation of a given sample. The

ratio of ΔT with the heating rates (r) gives the overall degradation time of the sample. The $T_{\max}$, T_{onset} , T_{end} , ΔT and $\Delta T/r$ of the *in situ* and the *ex situ* nanocomposites with different Pd Content (1 and 2 vol.%) are listed in Table 3.1. The following subsections discuss in detail the effect of various factors like heating rate, Pd content, mode of synthesis on the thermal stability of the Pd/PC nanocomposites.

3.4.2.1 *Effect of heating rates on the thermal degradation of the nanocomposites*

From Figures 3.3-3.4 and Table 3.1, it can be seen that the thermal stability of PC and the nanocomposites increases with increase in the heating rates. The results are supported by the shifts in the values of T_{onset} and $T_{\max}$ to the higher range with increase in the heating rates. Also, the overall degradation time ($\Delta T/r$) for the sample decreases with increase in the heating rates. Similar results were obtained by Peng et al [7] for silica/poly(vinyl alcohol) nanocomposites.

3.4.2.2 *Effect of Pd content on the thermal degradation of the nanocomposites*

It is clear from the Table 3.1 as well as Figures 3.5-3.6, that the values of T_{onset} and $T_{\max}$ increase as the Pd content in the nanocomposites increases. Similar results were obtained by Aymonier et al [4] for Pd/PMMA, Xia et al [2] for Cu/LDPE, and Hsu et al [6] for Au/polyurethane. The increase in the thermal stability may possibly be due to the increase in the polymer-nanocluster interfacial area. Further research is required to find the percolation limit of Pd

above which the thermal stability of the nanocomposites may remain unaffected.

3.4.2.3 Effect of the mode of synthesis on the thermal degradation of the nanocomposites

From the Figure 3.3, it can be seen that the *ex situ* nanocomposites showed more thermal stability than the *in situ* nanocomposites irrespective of the heating rates and the Pd content. A similar increase in the thermal stability was noted in earlier reports by Huang et al [17] for Au/poly(methyl styrene) and Sui et al [18] for Agcl/ polyaniline. These results may be due to the changes in the total area of the polymer-nanocluster interface and are in close agreement with the morphology of the nanocomposites that are currently being studied. Aymonier et al and Hsu et al also observed that the thermal stability of the nanocomposites decrease with decrease in particle size and agglomeration. Further research is required on the effect of particle sizes on the thermal stability.

3.4.3 Kinetic Studies

3.4.3.1 Kissinger Method

With a single filler like Pd nanoclusters, both the *ex situ* and *in situ* Pd/PC nanocomposites follow first order reaction kinetics for their thermal degradation. The remaining weight fraction (α) of a sample in a TGA experiment, can be expressed as:

$$\frac{d\alpha}{dt} = -K\alpha \quad (1)$$

where, t is the time and K is the rate constant for thermal degradation which follows the Arrhenius equation:

$$K = k_0 \exp\left[-\frac{Q}{RT}\right] \quad (2)$$

$$\Rightarrow \frac{d\alpha}{dt} = -\alpha k_0 \exp\left[-\frac{Q}{RT}\right] \quad (3)$$

The activation energy for the nanocomposites degradation can be determined from TGA data in a method developed by Kissinger [19]. The Kissinger method utilizes the temperature $T_{\max}$ at various heating rates as follows:

$$\frac{d}{dt}\left(\frac{-d\alpha}{dt}\right) = 0 \text{ at } T = T_{\max} \quad (4)$$

Now, in a given TGA both the weight (%) (α) and temperature (T) depends on the time (t) and thus with the equation 2, the above differentiation can be expressed as,

$$\begin{aligned} -k_0^2 \alpha [\exp(-Q/RT_{\max})]^2 + Q/RT_{\max}^2 \alpha k_0 \left[\frac{dT}{dt}\right] [\exp(-Q/RT_{\max})] &= 0 \\ \Rightarrow Q/RT_{\max}^2 \left[\frac{dT}{dt}\right] &= k_0 \exp(-Q/RT_{\max}) \end{aligned} \quad (5)$$

Under the condition of constant heating rate r , that is $dT/dt = r$, the above equation can be expressed as:

$$\begin{aligned} \frac{rQ}{RT_{\max}^2} &= k_0 \exp[-Q/RT_{\max}] \quad \text{or} \\ \ln\left[\frac{r}{T_{\max}^2}\right] &= Q[-1/(R \cdot T_{\max})] - \ln[Q/k_0 R] \end{aligned} \quad (6)$$

Thus, from the above equation, a graph between $\ln[r/(T_{\max})^2]$ and $-1/RT_{\max}$ for $T_{\max}$ from several different heating rates can be plotted. The slope of this plot gives the apparent activation energy, Q as shown in Figure 3.7. The values of Q and k_0 are tabulated in the Table 3.2. The value of activation energy obtained for the nanocomposites are plotted against the Pd content (vol.%) in Figure 3.8. It is found that the activation energy of the nanocomposites increase with the Pd content. Further research is required to dig up the reason for such behavior of the nanocomposites.

3.4.3.2 Master Decomposition Curve

Generally the TGA and DTA plots can be referred to determine the thermal stability of the nanocomposites. However, difficulty arises in referring to these plots in the case of varying working condition. Consequently, thermal pyrolysis cycles of the polymeric materials continue to typically be based on “trial-and-error” methods until an optimal time-temperature cycle is achieved.

Master decomposition curve (MDC) is generally used to construct an optimized time-temperature cycle for a given polymeric material. Unlike master sintering curve [20], these MDC curves are formulated based on the intrinsic kinetics of polymer pyrolysis based on the method of DiAntonio et al [21]. To start with, the onset temperature $[T_{\text{onset}}]$ and end temperature $[T_{\text{end}}]$ of the thermal degradation of nanocomposites are noted down from the TGA plots. Using these data, the work of decomposition (θ) is calculated as follows,

$$\frac{d\alpha}{dt} = -\alpha k_0 \exp\left[\frac{Q}{RT}\right]$$

$$\Rightarrow -\int \frac{d\alpha}{\alpha} = -\ln \alpha = \int_0^t k_0 \exp\left[\frac{Q}{RT}\right] dt = k_0 \theta \quad (7)$$

$$\theta = \int_0^t \exp(-Q/RT) dt \quad (8)$$

where, Q is the activation energy obtained from the Kissinger method (KJ/mol), R is the gas constant, T is the Temperature (K) and t is the time (s). Time T can be back calculated from the temperature T and heating rate (r). Now, a graph of Ψ (%) vs $\ln \theta$ for a sample all four heating rates are plotted. It can be seen from Figure 3.9 that the decomposition curves at all four heating rates are merged down into one thereby developing the master decomposition curve. The MDC for the PC and the Pd/PC nanocomposites are given in Figure 3.9. Similar MDCs were developed by DiAntonio et al [21] and Aggarwal et al [22]. The normalized weight Ψ (%) used in our MDC curves is assumed to involve W_{end} (= stoichiometric weight of Pd nanoclusters (which is 9% for 1 vol.% and 18.4% for 2 vol.% Pd content)). This assumption is included to reduce the effect of the possible PdO_x formation (which is not uniform with different heating rates) on the nature of the MDC curves. Our assumption might get validated by further researching on the effect of isothermal heating on the thermal stability of the nanocomposites samples. The isothermal condition should be reached via faster heating rates so as to avoid any prior thermal degradation. Studying the effect of oxygen atmosphere on the thermal stability of the nanocomposites is another future research as it may lead to a completely new set of MDC curves.

Now in a given time (t) at a temperature (T), the weight (%) (α) can be back-calculated using the formulae:

$$-\int \frac{d\alpha}{\alpha} = -\ln \alpha = \int_0^t k_0 \exp\left[\frac{Q}{RT}\right] dt = k_0 \exp\left[\frac{Q}{RT}\right] t \quad (9)$$

For a nanocomposites sample, k_0 and Q are known through the Kissinger method. A weight–time-temperature plot for the nanocomposites is thus constructed and is shown in the Figure 3.10. This plot helps in determining the allowable working conditions (time and/or temperature of exposure) for a given nanocomposites sample.

3.5 Conclusions

Pd/PC nanocomposites were synthesized in two different techniques, *ex situ* and *in situ* methods. The influence of heating rate, Pd content, and method of synthesis on the thermal stability of the Pd/PC nanocomposites were investigated. It was found that increase in the Pd content have a positive impact over the thermal stability of the nanocomposites. The *ex situ* nanocomposites were found more thermally stable than the *in situ* ones. Activation energies for the nanocomposites were determined by using the Kissinger method and subsequently, the master decomposition curves (MDC) were developed for the Pd/PC nanocomposites.

References

1. Carolyn M., Sih B.C., Scott T.L. and Wolf M.O., *Journal of Materials Chemistry*, (2005), 15, 25, 2433.
2. Xia X., Cai S. and Xie C., *Materials Chemistry and Physics*, (2006), 95, 1, 122.
3. Chattopadhyay S., and Datta A., *Synthetic Metals*, (2005), 155, 2, 365.
4. Aymonier C., Bortzmeyer D., Thomann R., and Mulhaupt R., *Chemical Materials* (2003), 15, 4874.
5. Liu F.K., Hsieh S.Y., Ko F.H., and Chu T.C., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2002), 231, 31.
6. Hsu S.H., Chou C.W., and Tseng S.M., *Macromolecular Materials and Engineering*, (2004), 289, 12, 1096.
7. Peng Z., Kong X., Li S.D., and Spiridonov P., *Journal of Nanoscience and Nanotechnology*, (2006), 6, 12, 3934.
8. Gole A. and Murphy C.J., *Chemistry of Materials* (2005), 17, 1325.
9. Akamatsu K., Takei S., Mizuhata M., Kajinami A., Deki S., Takeoka S., Fujii M., Hayashi S., and Yamamoto K., *Thin Film Solids* (2000), 359, 55.
10. Sarma T.K., Chowdhury D., Paul A., and Chattopadhyay A., *Chemical Communications*, (2002), 10, 1048.
11. Briemer M.A., Yevgeny G., Sy S., and Sadik O.A., "Incorporation of *Nano Letters*, (2001), 1, 6, 305.
12. Walker B.M., Bethell M., Schiffrin D., and Whyman D.J., *Journal of Chemical Society and Chemical Communication* (1994), 20, 801.
13. Chen M., Falkner J., Guo W.H., Zhang J.Y., Sayes C., and Colvin V.L., *Journal of Colloid and Interface Science* (2005), 287, 146.
14. Jewrajka S.K., and Chatterjee U., *Journal of Polymer Science Part A: Polymer Chemistry*, (2006), 44, 6, 1841.
15. Wang H., Qiao X., Chen J., and Ding S., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, (2005), 256, 2-3, 111.

16. Yukihide S., and Naoki T., *Colliods and Surfaces A: Physiochemical and Engineering Aspects* (2000), 169, 59.
17. Huang H.M., Chang C.Y., Liu I.C., Tsai H.C., Lai M.K., and Tsiang C.C.R., *Journal of Polymer Science: Part A: Polymer Chemistry*, (2005), 43, 20, 4710.
18. Sui X., Chu Y., Xing S., and Liu C., *Materials Letters*, 2004, 58, 7-8, 1255.
19. Kissinger H.E., *Analytical Chemistry*, (1957), 29, 1702.
20. Liu C., Yu J., Sun X., Zhang J. and He J., *Polymer Degradation and Stability*, (2003), 81, 197.
21. DiAntonio C.B., Ewsuk K.G. and Bencoe D., *Journal of American Ceramic Society*, (2005), 88, 10, 2722.
22. Aggarwal, G., Park, S. J., Smid, I., and German R. M., *TMS Annual Meeting, MPMD 7th Global Innovation Process: Trends in Materials R and D for Sensor Manufacturing Technologies*, (2006), 29.

Figures

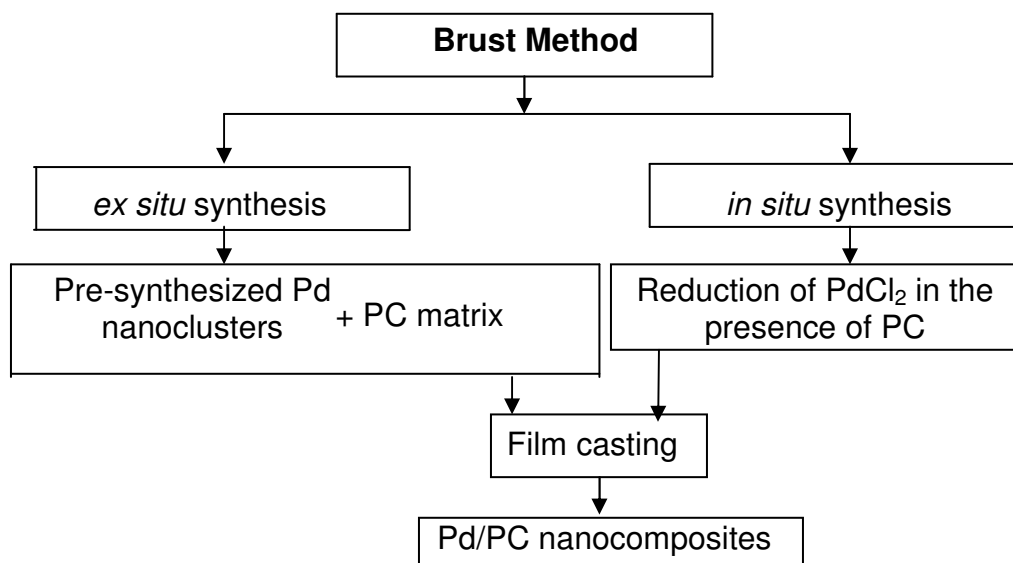


Figure 3.1: Schematic representation of synthesis of Pd/PC nanocomposites

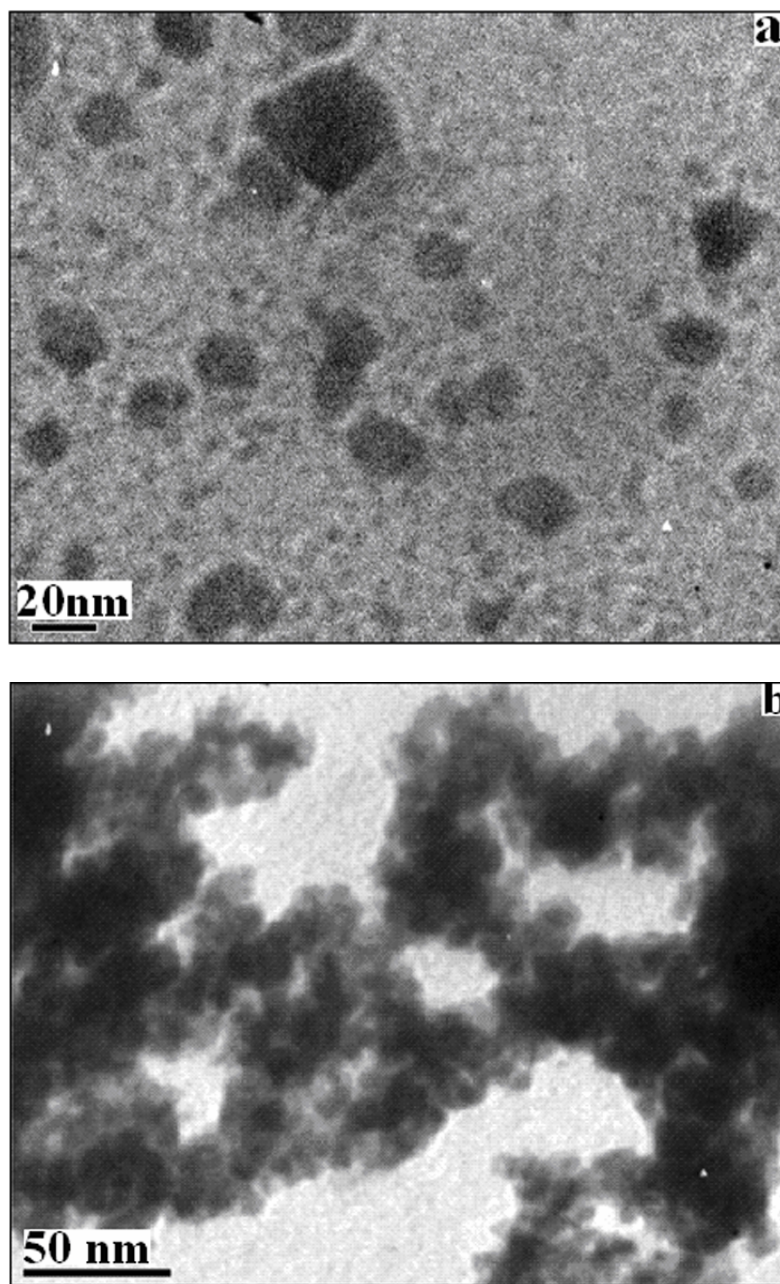


Figure 3.2: TEM image of the *ex situ* and *in situ* Pd/PC nanocomposites showing (a) dispersed Pd nanoclusters and (b) agglomerated Pd nanoclusters, respectively.

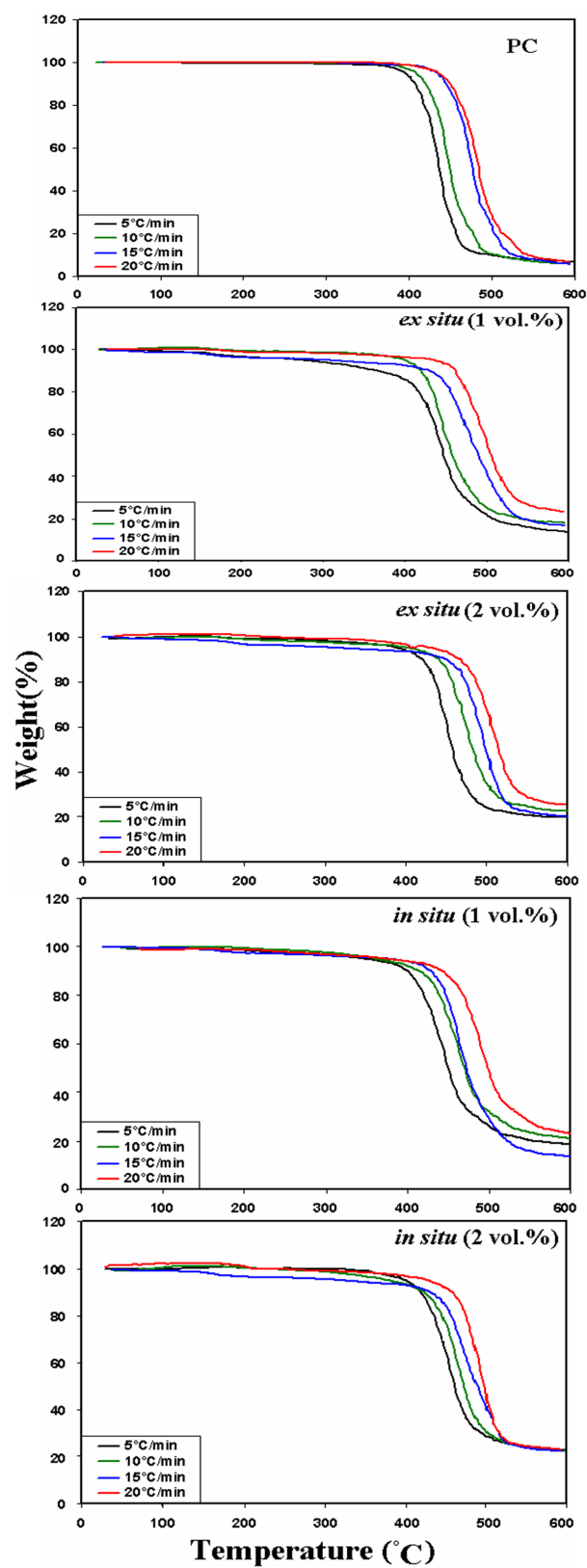


Figure 3.3: TGA for PC and Pd/PC nanocomposites with two different Pd content (1 and 2 vol.%) at different heating rates (5, 10, 15 and 20 °C/min).

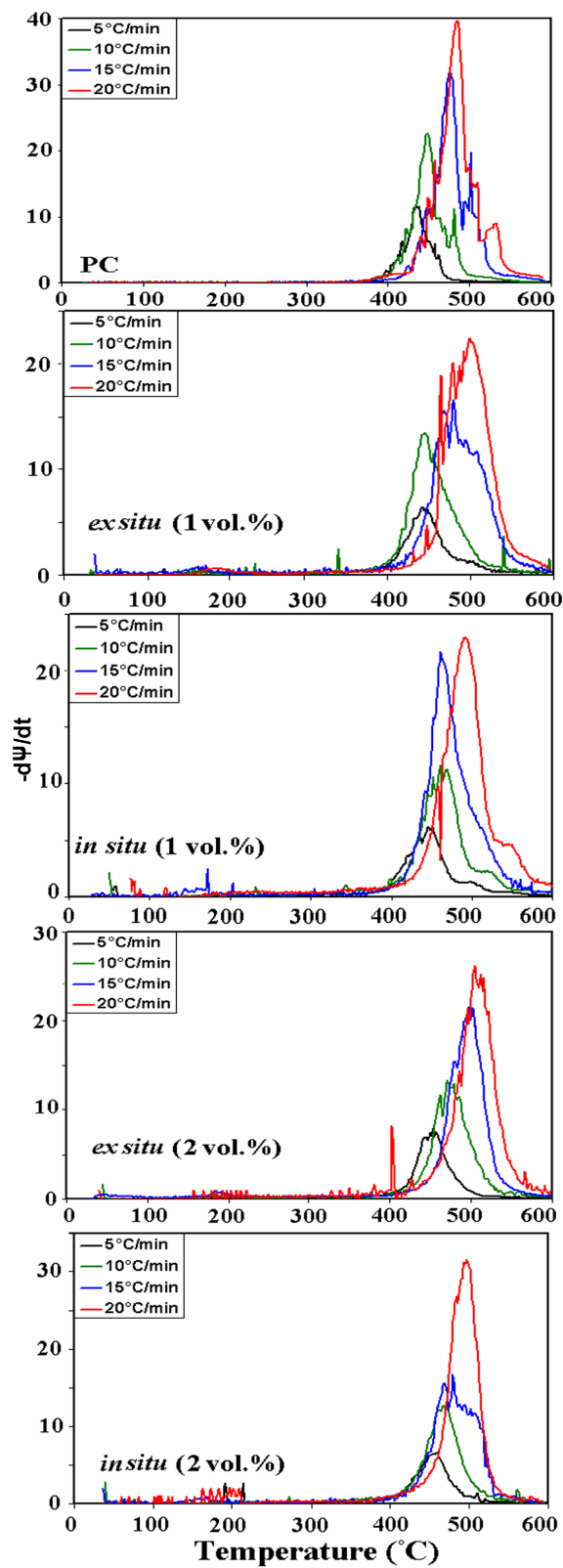


Figure 3.4: DTA for PC and Pd/PC nanocomposites with two different Pd content (1 and 2 vol.%) at different heating rates (5, 10, 15 and 20 °C/min).

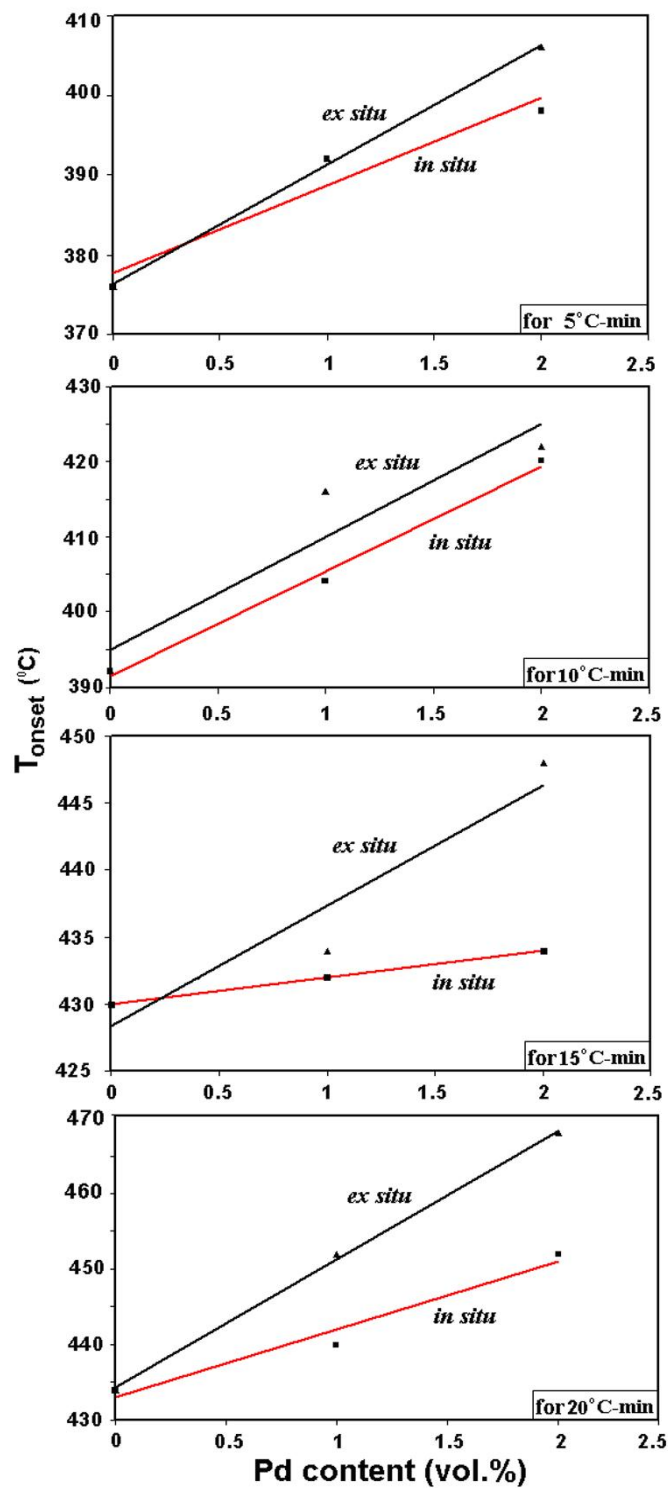


Figure 3.5: T_{onset} as the function of Pd content in both the *ex situ* and *in situ* nanocomposites at different heating rates.

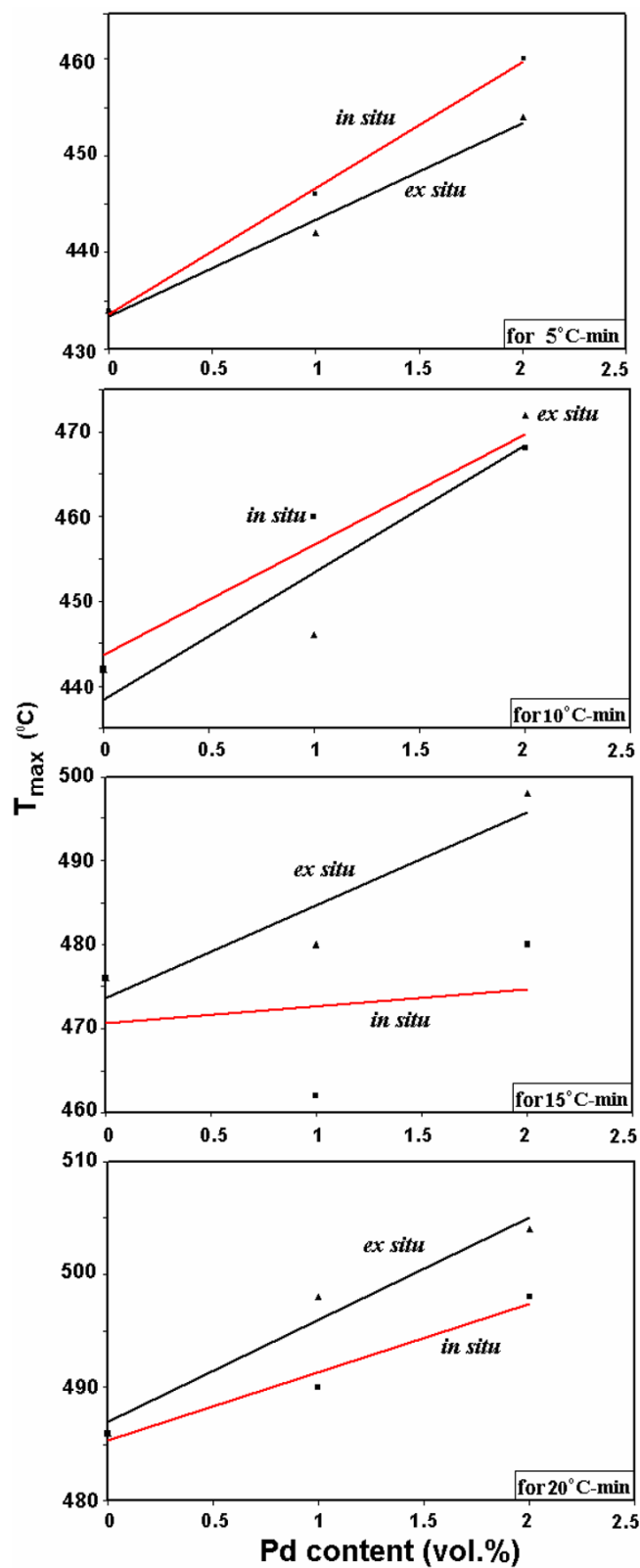


Figure 3.6: $T_{\max}$ as the function of Pd content in both the *ex situ* and *in situ* nanocomposites at different heating rates.

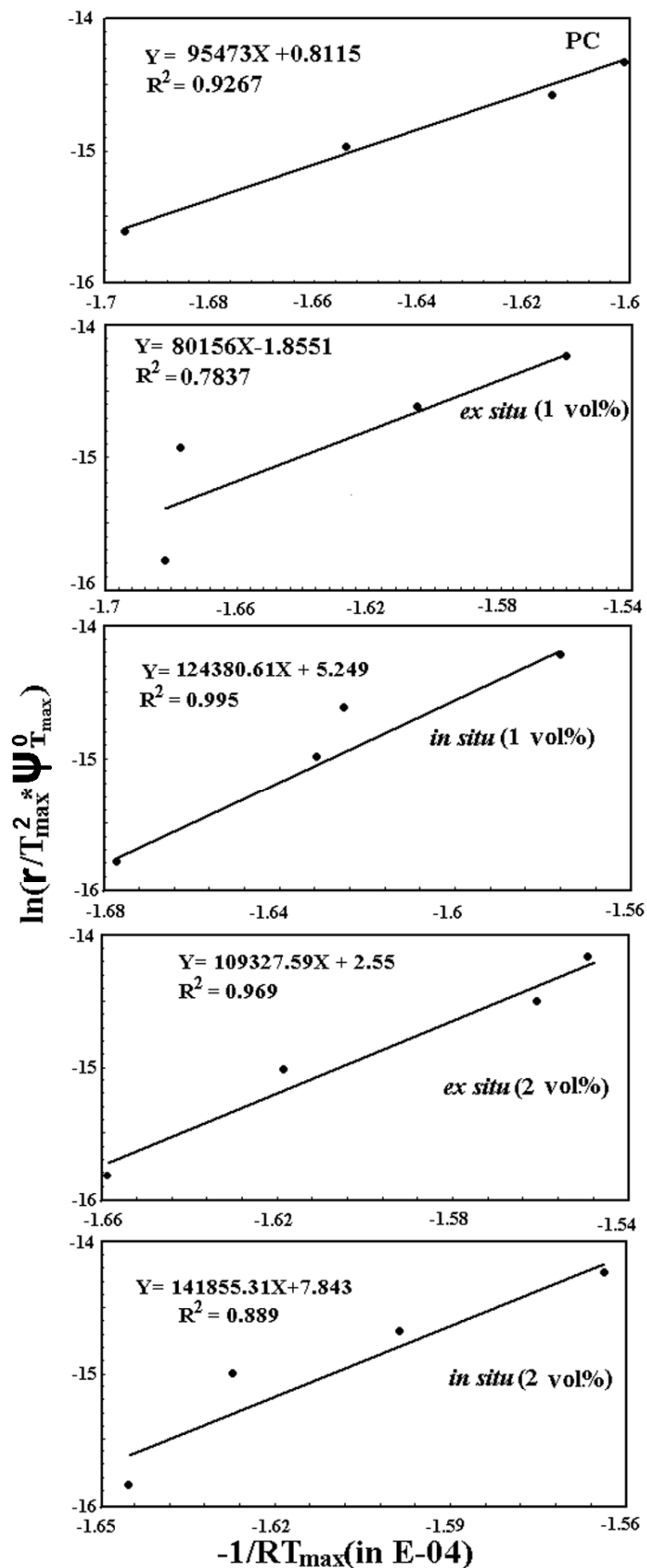


Figure 3.7: Determination of activation energies by the Kissinger Method.

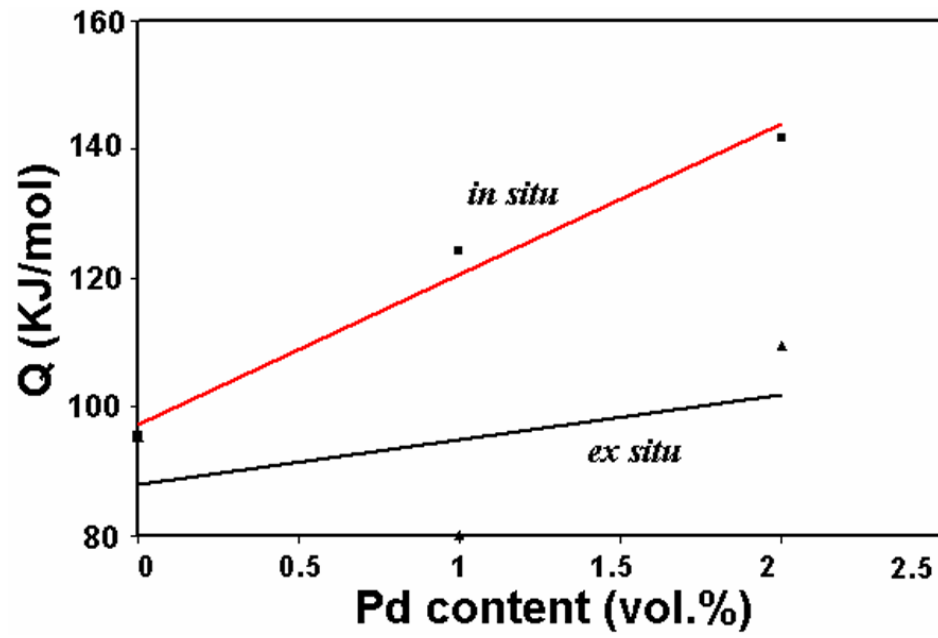


Figure 3.8: Activation energies as the function of Pd content in both the *ex situ* and *in situ* nanocomposites.

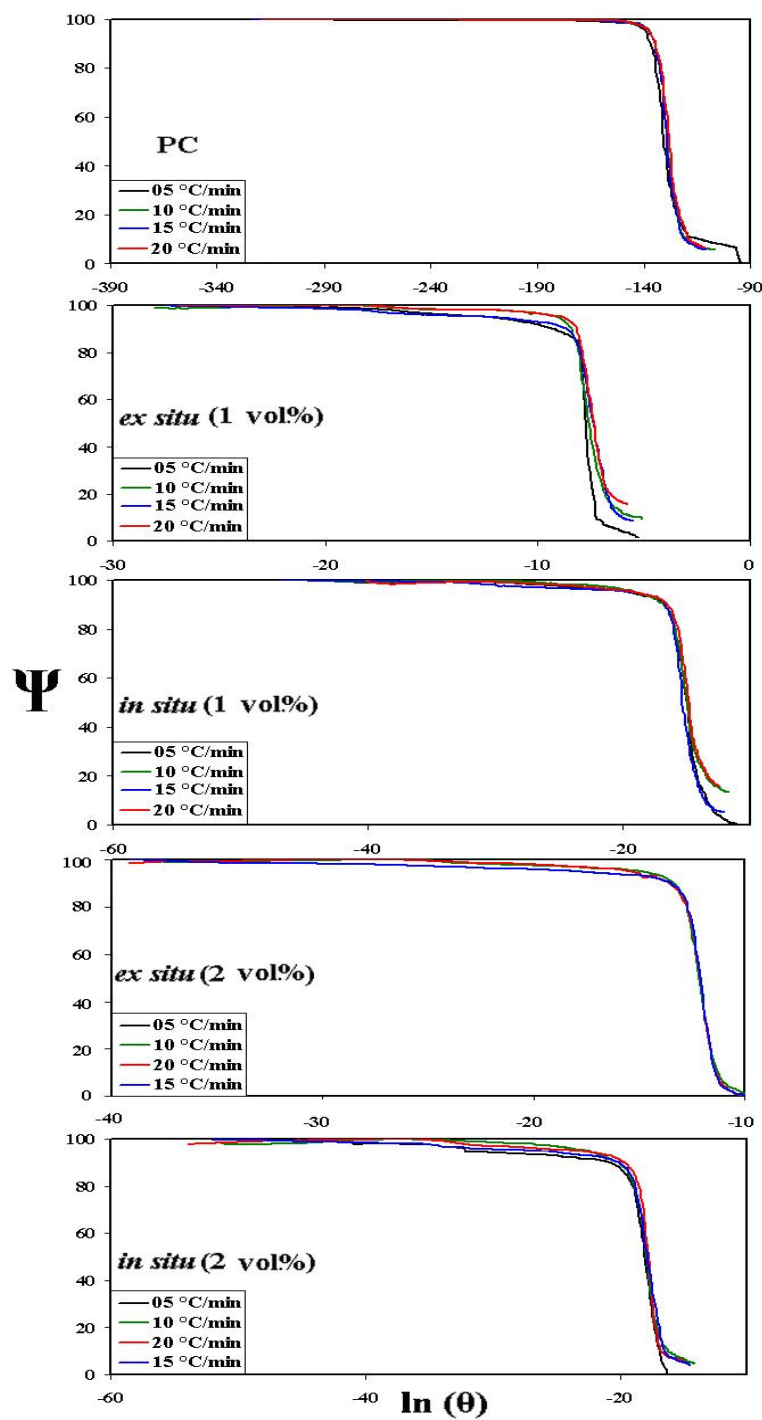


Figure 3.9: Master Decomposition Curve for PC and Pd/PC nanocomposites.

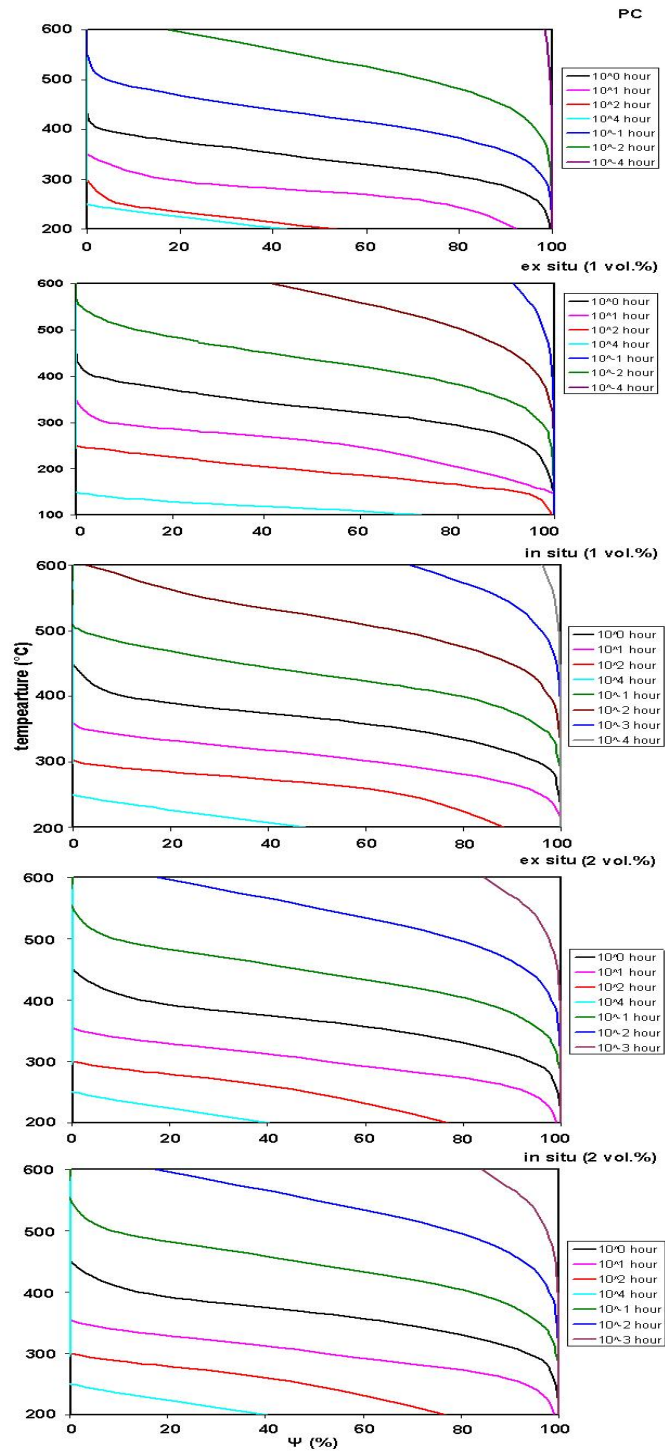


Figure 3.10: Weight (α) - temperature (T) – time (t) plots for Pd/PC nanocomposites.

Tables

Table 1: Characteristic Temperatures of Pd/PC nanocomposites

Sample	Heating Rate (H) (°C/min)	T _{onset} (°C)	T _{end} (°C)	ΔT (°C)	ΔT/H (min)	T _{max} (°C)
PC	5	376	482	106	21.2	434
	10	392	508	116	11.6	442
	15	430	538	108	7.2	476
	20	434	554	120	6	486
1 vol.% <i>ex situ</i>	5	392	502	110	22	442
	10	416	518	102	10.2	446
	15	434	556	122	8.13	480
	20	452	570	118	5.9	498
1 vol.% <i>in situ</i>	5	392	522	130	26	446
	10	404	544	140	14.0	460
	15	432	558	126	8.4	462
	20	440	580	140	7	490
2 vol.% <i>ex situ</i>	5	406	514	108	21.6	454
	10	422	540	116	11.6	472
	15	448	556	108	7.2	498
	20	468	576	108	5.4	504
2 vol.% <i>in situ</i>	5	398	516	118	23.6	460
	10	420	524	104	10.4	468
	15	434	556	122	8.13	480
	20	452	556	104	5.2	498

Table 3.2: Activation energy (Q) and rate constant (k_0) for the Pd/PC nanocomposites

Sample	Q (J/mol)	k_0 (s ⁻¹)
PC	95743	25926
1 vol.% <i>ex situ</i>	80156	1508
1 vol.% <i>in situ</i>	124381	2850944
2 vol.% <i>ex situ</i>	109328	168411
2 vol.% <i>in situ</i>	141855	43510901

Chapter 4

Conclusions

The synthesis and characterization of the Pd/PC nanocomposites were discussed in the prior sections of this thesis. The following are some of the important conclusions obtained from this work.

- ✓ Pd/PC nanocomposites were synthesized by two different techniques, *ex situ* and *in situ* methods. With different methods, the Pd/PC nanocomposites exhibited completely different morphology. Well-dispersed nanoclusters of 15 nm size were seen in the *ex situ* method while agglomerated nanoclusters in the *in situ* method.
- ✓ Changes in the FTIR peak positions for the *in situ* nanocomposites suggest possible conformational changes in the PC chains.
- ✓ The nanocomposites exhibited a strong dependence of optical, thermal and electrical properties on their morphology.
- ✓ The light transmittance of PC matrix was drastically decreased with the Pd nanocluster incorporations. The *in situ* nanocomposites filter light up to 564 nm than the *ex situ* ones which filtered light only up to 501 nm.
- ✓ The T_g of both the nanocomposites were lower than PC by 15°C.
- ✓ Both the nanocomposites were found thermally more stable than PC. The T_{onset} of the *ex situ* and *in situ* nanocomposites are higher than PC by 40°C and 20°C, respectively.
- ✓ The semi-conducting nature of the *in situ* nanocomposites suggests that they could be best-suited for electrical applications.
- ✓ Factors like heating rate and Pd content were found to have positive impact on the thermal stability of the *ex situ* and *in situ* nanocomposites.

- ∇ At any given heating rate and Pd content, the *ex situ* nanocomposites were found thermally more stable than the *in situ* ones.
- ∇ Activation energies for the nanocomposites were determined using the Kissinger method. The activation energies of both the nanocomposites increased with increase in the Pd content.
- ∇ Master decomposition curves (MDC) for the Pd/PC nanocomposites were constructed based on the calculated activation energies.
- ∇ Weight-time-temperature plots determining the feasible working conditions for the Pd/PC nanocomposites were constructed.

4.1 Future Research:

The current work involved synthesizing dodecanethiol protected Pd nanoclusters of 15nm size. Studies can be performed on the effect of Pd nanoclusters with different size on the structure and properties of Pd/PC nanocomposites. This can be done by synthesizing triphenylphosphine protected Pd nanoclusters of 2 nm size using Schmidt's method [1]. Ligand exchange of this triphenylphosphine protected Pd nanoclusters with dodecanethiol might result in better distribution and stability of the nanoclusters.

Nanocluster size can be varied by changing the reaction conditions like reaction temperature. For example, Brust et al [2] synthesized gold (Au) nanoclusters of 2-5 nm size at ice-cold conditions. Current synthesis procedures involve only room temperatures. Thus, morphology of the nanoclusters can be studied by synthesizing them in an ice-cold condition.

The Brust method [2] generally involves a surfactant (tetraoctyl ammonium bromide) for synthesizing Au nanoclusters. These surfactants ease the transfer of nanoclusters from the aqueous phase to the organic phase. Faster the transfer is, more smaller will be the nanoclusters. However, no surfactants were involved in the current synthesis procedures. Hence, studying the effect of the surfactant on the structure and properties of the Pd/PC nanocomposites is another possible research area.

Prior studies by Chatterjee et al [3] showed that the capping rate of polymers increases with decrease in the molecular weight. The current *in situ* method involves PC with molecular weight 160,000. Hence, further studies on the effect of different low molecular weight PC on the morphology and properties of the *in situ* nanocomposites are possible.

Varying the Pd content in the nanocomposites can also control the structure and properties of the nanocomposites. Current studies involved only 2 vol.% Pd. Thus, another research goal will be the synthesis and characterization of Pd/PC nanocomposites with varying Pd content. Conducting FTIR studies for these nanocomposites will help us in understanding the possible chemical interactions between Pd nanoclusters and the PC matrix at different Pd levels.

Aymonier et al [4] found that Pd/PMMA nanocomposites show more thermal stability in nitrogen atmosphere than in air. The current TGA studies in Pd/PC nanocomposites were conducted in nitrogen atmosphere. The thermal stability of the Pd/PC nanocomposites in normal atmosphere should be

determined by conducting TGA in air. This will help determine the suitability of the nanocomposites in normal atmosphere at elevated temperatures.

With respect to synthesis of metal/polymer nanocomposites, emphasis should also be given in choosing the type of polymer. PC is a homopolymer and shows same capping action and properties throughout its matrix. Replacing PC, with block copolymers as capping agents may result in the nanocomposites with controlled spatial arrangements and enhanced properties.

As mentioned in Chapter 1, the affinity of Pd towards H_2 and its catalytic properties may be utilized for developing fluid sensors. Prior studies [5, 6] involved the application of Pd based polymer nanocomposites in H_2 and methanol sensors. There are on-going efforts in our research group to develop *in situ* Pd/PC nanocomposites for gas sensors. For example, ammonia (NH_3) sensors are based on the affinity of the Pd toward H_2 and affinity of lone pair of electrons in NH_3 towards H_2 . Current NH_3 sensors are based on ammonium salt aerosols where sulphuric acid and nitric acid react with the NH_3 to form ammonium sulphate and ammonium nitrate [7]. Recently, Bekyarova et al [8] developed sulfonic acid functionalized single wall carbon nanotubes to detect ammonia in parts per billion level. We are also currently investigating a coating of 2 vol% *in situ* Pd/PC nanocomposites with carbon nanoparticles (1 wt%) on a gold electrode for sensing NH_3 . The purpose of carbon nanoparticles is to amplify and increase the surface area. However, the carbon nanoparticle content is kept to a minimum so as to avoid any decrease in the sensitivity. Parts of the

NH₃ sensor that is currently under construction and testing are given in Figure 4.1. The development of such sensors will also be a focus of future work.

References

1. Weare W.W., Reed S.M., Warner M.G., and Hutchison J.E., *Journal of American Chemical Society*, (2000), 122, 12890.
2. Walker B.M., Bethell M., Schiffrin D., and Whyman D.J., *Journal of Chemical Society and Chemical Communication*, (1994), 20, 801.
3. Jewrajka S.K., and Chatterjee U., *Journal of Polymer Science Part A: Polymer Chemistry*, (2006), 44, 1841.
4. Aymonier C., Bortzmeyer D., Thomann R. and Mulhaupt R., *Chemical Materials*, (2003), 15, 4874.
5. Raviprakash J., McDaniel A.H., Horn M., Pilione L., Sunal P., R. Messier R., McGrath R.T. and Schweighardt F.K., *Sensors and Actuators B*, (2007), 120, 439.
6. Athawale A.A., Bhagwat S.V., and Katre P.P., *Sensors and Actuators B*, (2006), 114, 263.
7. Timmer B., Olthuis W. and Vandenberg A., *Sensors and Actuators B*, (2005), 107, 666.
8. Bekyarova E., Davis M., Burch T., Etkis M.E., Zhao B., Sunshine S. and Haddon R.C., *Journal of Physical Chemistry B*, (2004), 108, 19717.

Figures

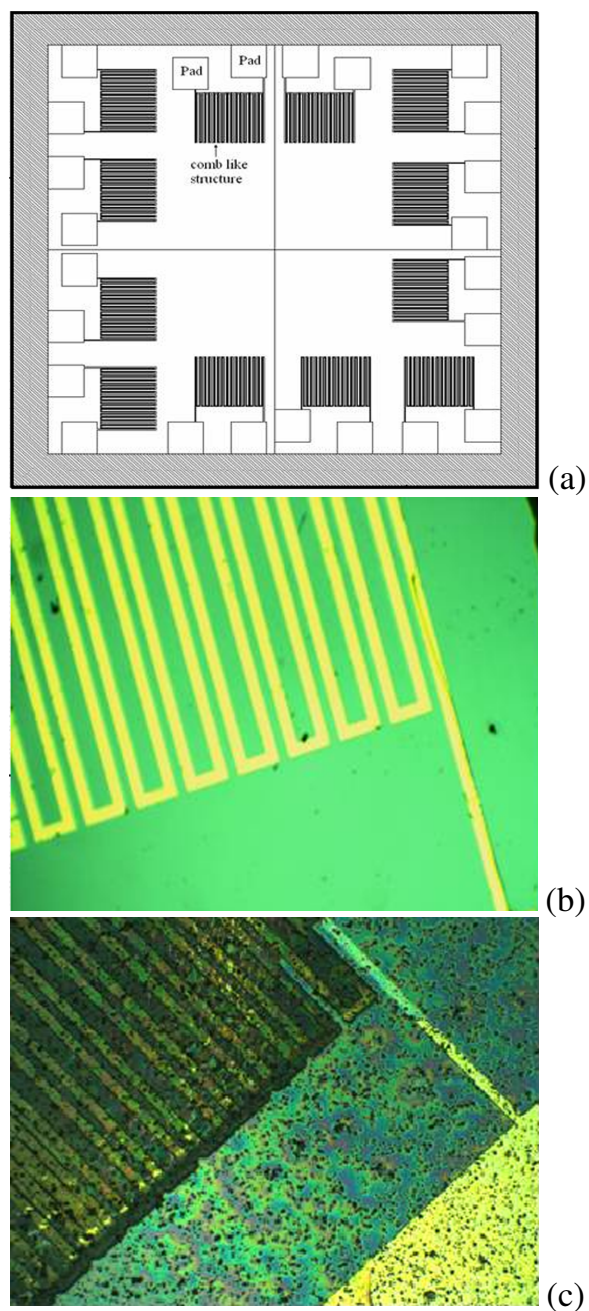


Figure 1: Schematic representation of NH_3 sensors (a); gold electrode (b); gold electrode coated with mixture of 2 vol.% *in situ* nanocomposites and 1 wt% carbon nanoparticles (c).

Appendix

Chapter 1

References

64. Feldheim D.L. and Keating C.D., *Chemical Society Review*, (1998), 21, 1.
65. Carolyn M., Sih B.C., Scott T.L. and Wolf M.O., *Journal of Materials Chemistry*, (2005), 15, 2433.
66. Huang H. and Yang X., *Colloids and Surfaces B: Biointerfaces*, (2004), 39, 31.
67. Carotenuto G., Nicolias L. and La peruta G., *Sensors and Actuators B*, (2006), 114, 1092.
68. Xia X., Cai S. and Xie C., *Materials Chemistry and Physics*, (2006), 95, 122.
69. Wang L. and Chen D., *Colloid Polymer Science*, (2006), 284, 449.
70. Liu F.K., Hsieh S.Y., Ko F.H. and Chu T.C., *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, (2002), 231, 31.
71. Aymonier C., Bortzmeyer D., Thomann R. and Mulhaupt R., *Chemical Materials*, (2003), 15, 4874.
72. Zhang Z., Wang F. Chen F. and Shi C., *Materials Letters*, (2006), 60, 1039.
73. Hsu S.H., Chou C.W. and Tseng S.M., *Macromolecular Materials and Engineering*, (2004), 289, 1096.
74. Peng Z., Kong L.X., Li S.D. and Spiridonov P., *Journal of Nanoscience and Nanotechnology*, (2006), 6, 3934.
75. Gole A. and Murphy C.J., *Chemistry of Materials*, (2005), 17, 1325.
76. Akamatsu K., Takei S., Mizuhata M., Kajinami A., Deki S., Takeoka S., Fuji M., Hayashi S. and Yamamoto K., *Thin Film Solids*, (2000), 359, 55.
77. Sarma T.K., Chowdhury D., Paul A. and Chattopadhyay A., *Chemical Communications*, (2002), 10, 1048.
78. Briemer M.A., Yevgeny G., Sy S. and Sadik O.A., *Nano Letters*, (2001), 1, 305.
79. Hayat M.A., *Colloidal Gold: Principles, Methods and Applications*, Academic Press, New York, (1989).

80. Kamat P.V. and Shanghavi B., *The Journal of Physical Chemistry B*, (1997), 101, 7675.
81. Walker B.M., Bethell M., Schiffrin D., and Whyman D.J., *Journal of Chemical Society and Chemical Communication*, (1994), 20, 801.
82. Weare W.W., Reed S.M., Warner M.G., and Hutchison J.E., *Journal of American Chemical Society*, (2000), 122, 12890.
83. Selvakannan P.R., Senthilkumar P., More A.S., Shingt R.D., Wadgoankar P.P., and Sastry M., *Langmuir*, (2004), 20, 295.
84. Sarathy K.V., Gargi R., Yadav R.T., Kulkarni G.U., and Rao C.N.R., *Journal of Physical Chemistry B*, (1997), 101, 9876.
85. Sih B.C., and Wolf M.O., *Chemical Communications*, (2005), 3375.
86. Rao C.N.R. and Cheetham A.K., *Journal of Materials Chemistry*, (2001), 11, 2887.
87. Edwards P.P., Johnston R.L., and Rao C.N.R., *Metal clusters in Chemistry*, Wiley-VCH, Weinham, (1999).
88. Schmid G., *Clusters and Colloids: From Theory to Application*, Wiley-VCH, Weinham, (1994).
89. Kirkland A.I., Jefferson D.E., Duff D.G., Edwards P.P., Gameson I., Johnson B.F.U., and Smith D.J., *Process Royal Society London A*, (1993), 440, 589.
90. Wang H., Qiao X., Chen J., and Ding S., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, (2005), 256, 111.
91. Brown L.O., and Hutchison J.E., *Journal of American Chemical Society*, (1998), 121, 882.
92. Jia W., Mc Lachlan J., Xu J., Tadayyon S.M., Norton P.R., and Eichhorn S.H., *Canadian Journal of Chemistry*, (2006), 84, 998.
93. Zhu H., Tao C., Zheng S., Wu S., Li J., *Colloids and Surface A: Physiochemical and Engineering Aspects*, (2005), 256, 17.
94. Jewrajka S.K., and Chatterjee U., *Journal of Polymer Science Part A: Polymer Chemistry*, (2006), 44, 1841.

95. Tamilselvan S., Hayakawa T., Nogami M., Kobayashi Y, Marzan L., Hamanaka Y. and Nakamura A., *Journal of physical chemistry*, (2002), 106, 10157.
96. Corbierre M.K, Cameron N.S, Sutton M, Laaziri K. and Lennox R.B, *Langmuir*, (2005), 21, 6063.
97. Laibinis P.E., Whitesides G.M., Allara D.L., Tao Y.T., Parikh A.N. and Nuzzo R.G., *Journal of the American Chemical Society*, (1991), 113, 7152.
98. King J.A. and Codella P.J., *Macromolecules*, (1990), 23, 345.
99. Kamat P.V., *Journal of Physical Chemistry B*, (2002), 106, 7729.
100. Balamurugan B. and Maruyama T., *Applied Physics Letters*, (2005), 87, 143105.
101. Gao J., Bender C.M. and Murphy C.J., *Langmuir*, (2003), 19, 9065.
102. Gole A. and Murphy C.J., *Chemistry of Materials*, (2005), 17, 1325.
103. Akamatsu K., Takei S., Mizuhata M., Kajinami A., Deki S., Takeoka S., Fujii M., Hayashi S. and Yamamoto K., *Thin Film Solids*, (2000), 359, 55.
104. Nemamcha A., Rehsrpringer J.L. and Khatmi D., *Journal of Physical Chemistry B*, (2006), 110, 383.
105. Merkel T. C., He Z. and Pinnau I., *Macromolecules*, (2003), 36, 6844.
106. Ash B.J., Schadler L.S. and Siegel R.W., *Journal of Polymer Science Part B: Polymer Physics*, (2004), 42, 4371.
107. Ash B.J., Schadler L.S. and Siegel R.W., *Materials Letters*, (2002), 55, 83.
108. Kissinger H.E., *Analytical Chemistry* (1957), 29, 1702.
109. Flynn J. H., Wall L. A., *Polymer Letters*, (1966), 4, 323.
110. Ozawa T., *Journal of Thermal Analysis*, (1970), 2, 301.
111. DiAntonio C.B., Ewsuk K.G. and Bencoe D., *Journal of American Ceramic Society*, (2005), 88, 10, 2722.
112. Aggarwal, G., Park, S. J., Smid, I., and German R. M., *TMS Annual Meeting, MPMD 7th Global Innovation Process: Trends in Materials R and D for Sensor Manufacturing Technologies*, (2006), 29.

113. Athawale A.A., Bhagwat S.V., and Katre P.P., *Sensors and Actuators B*, (2006), 114, 263.
114. Simon U., *Advanced Materials*, (1998), 10, 1487.
115. Brousseau L. C., Zhao Q., Shultz D. A. and Feldheim D. L., *Journal of American Chemical Society*, (1998), 120, 7645.
116. Houbertz R., Feigenspan T., Mielke F., Memmert U., Hartmann U., U. Simon U., Schoen G. and Schmid G., *European physics Letters*, (1994), 28, 641.
117. Zhai L and McCullough R. D., *J. Mater. Chem.*, (2004), 14, 141.
118. Tang H.L., Pan M., Jiang S. P. and Yuan R. Z., *Materials Letters*, (2005), 59, 3766.
119. Ahn H., Chandekar A., Kang B., Sung C. and Whitten J.E., *Chemistry of Materials*, (2004), 16, 3274.
120. Park J.E., Kim S., Mihashi S., Hatozaki O. and Oyama N., *Macromolecules Symposia*, (2002), 186, 35.
121. Park J. E., Park S. G., Koukitu A., Hatozaki O. and Oyama N., *Synthesis of Materials.*, (2004), 140, 121.
122. Houdayer A., Schneider R., Billaud D., Ghanbaja J. and Lambert J., *Applied Organometallic Chemistry*, (2005), 19, 1239.
123. Ciebien J.F., Cohen R.E. and Duran A., *Supramolecular Science*, (1998), 5, 31.
124. Li X., Hristov H.A. and Yee A.F., *Polymer*, (1995), 36, 4, 759.
125. Choi Y.K., Sugimoto K.I., Song S.M. and Endo M., *Materials Letters*, (2005), 59, 3514.
126. Checchetto R., Miotello A. and Chayahara A., *Journal of Physics: Condensation Matter* (2000), 12, 9215.

Chapter 2

References

53. Ziolo, R. F. Giannelis, E. P.; Weinstein, B. A.; O'Horo, M. P.; Ganguly, B. N.; Mehrotra, V.; Russell, M. W. and Huffman, D. R. *Science* (1992), 257, 219.
54. Wuelfing, W. P., Gross, S. M.; Miles, D. T. and Murray, R. W. *Journal of American Chemical Society* (1998), 120, 12696.
55. Aslam M; Mulla I.S., and Vijayamohanan K., *Langmuir* (2001), 17, 7487.
56. Aslam M; Mulla I.S. and Vijayamohanan K, *Applied Physics Letter* (2001), 79, 689.
57. Aslam M; Gopakumar G., Shoba T.L., Mulla I.S.; Vijayamohanan K, Kulkarni S.K., Urban J., and Vogel W., *Journal of Colloid and Interface Science* (2002), 255, 79.
58. Liu F.K., Hsieh S.Y., Ko F.H., and Chu T.C., *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (2002), 231, 31.
59. Whetten R.L., Khoury J.T., Alvarez N.M., Murthy S., Vezmar I., Wang Z.L., Stephens P.W., Cleaveland C.L., and Landman U., *Advanced Materials* (1996), 8, 248.
60. Gonsalves K.E., Carlson G., Chen X., Gayen S.K., Perez R., and Yacaman M.J., *NanoStructured Materials* (1996), 7, 293.
61. Huang H., and Yang X., *Colloids and Surfaces B: Biointerfaces* (2004), 39, 31.
62. Chattopadhyay S, and Datta A., *Synthetic Metals*, (2005), 155, 365.
63. Aymonier C., Bortzmeyer D., Thomann R. and Mulhaupt R., *Chemical Materials* (2003), 15, 4874.
64. Houdayer A., Schneider R., Billaud D., Ghanbaja J. and Lambert J., *Applied Organometallic Chemistry* (2005), 19, 1239.
65. Liu F.K., Hsieh S.Y., Ko F.H. and Chu T.C., *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (2002), 231, 31.
66. Sondi I., Goia D.V. and Matijevc E., *Journal of Colloid and Interface Science* (2003), 260, 75.

67. Zamborini F.P., Gross S.M. and Murray R.W., *Langmuir* (2001), 17, 481.
68. Henglein A. and Giersig M., *Journal of physical Chemistry:B* (1999), 103, 9533.
69. Ramirez E, Jansat S, Philippot K, Lecante P, Gomez M, Bulto A.M.M. and Chaudret B., *Journal of organometallic chemistry* (2004), 689, 4601.
70. Wang H., Qiao X., Chen J. and Ding S., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2005), 256, 111.
71. Chen M., Falkner J., Guo W.H., Zhang J.Y., Sayes C. and Colvin V.L., *Journal of Colloid and Interface Science* (2005), 287, 146–151.
72. Sun Y, Frenkel A.I., Isseroff R, Shonbrun C., Forman M., Shin K, Koga T, White H, Zhang L., Zhu Y., Rafailovich M.H. and Sokolov J.C., *Langmuir* (2006), 22, 807.
73. Jewrajka S.K. and Chatterjee U., *Journal of Polymer Science Part A: Polymer Chemistry* (2006), 44, 1841.
74. Corbierre M.K, Cameron N.S, Sutton M, Laaziri K. and Lennox R.B, *Langmuir* (2005), 21, 6063.
75. Ronga M, Zhanga M., Liua H. and Zenga H., *Polymer* (1999), 40, 6169.
76. Walker B.M., Bethell M., Schiffrin D. and Whyman D.J., *Journal of Chemical Society and Chemical Communication* (1994), 20, 801.
77. Koga K., Ikeshoji T. and Sugawara K., *Physical review letters* (2004), 92, 11507-1.
78. Tamilselvan S., Hayakawa T., Nogami M., Kobayashi Y., Marzan L., Hamanaka Y. and Nakamura A., *Journal of physical chemistry* (2002), 106, 10157.
79. Khanna P.K., Singh N., Charan S., Subbarao V.V.V.S, Gokhale R. and Mulik U.P., *Materials Chemistry and Physics* (2005), 93, 117.
80. Yukihide S. and Naoki T., *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (2000), 169, 59.
81. Wang J., Montville D. and Gonsalves K.E., *Journal of Applied Polymer Science*, (1999), 72, 1851.

82. Laibinis P.E., Whitesides G.M., Allara D.L., Tao Y. T, Parikh A. N. and Nuzzo R.G., *Journal of the American Chemical Society* (1991), 113, 7152.
83. Heymans N. and Rossum S.V., *Journal of Material Scienc*, (2002), 37, 4273.
84. Hopfe I., Pompe G. and Eichhorn K.J., *Polymer* (1997), 38, 10, 2321.
85. Ning P. and Ko T.M., *Polymer Engineering and Science* (1997), 37, 7, 1226.
86. Liu C. K., Hu C.T. and Lee S., *Polymer Engineering and Science* (2005), 45, 5, 687.
87. Dehaye F., Balanzat E., Ferain E. and Legras R., *Nuclear Instruments and Methods in Physics Research B* (2003), 209, 103.
88. Wang Y., Jin Y., Zhu Z., Liu C., Sun Y., Wang Z., Hou M., Chen X., Zhang C., Liu J. and Li B., *Nuclear Instruments and Methods in Physics Research B* (2000), 164-165, 420.
89. Checchetto R., Miotello A. and Chayahara A., *Journal of Physics: Condensation Matter* (2000), 12, 9215.
90. Akamatsu K., Takei S., Mizuhata M., Kajinami A., Deki S., Takeoka S., Fujii M., Hayashi S. and Yamamoto K., *Thin Film Solids* (2000), 359, 55.
91. Nemamcha A., Rehsrpringer J. L. and Khatmi D., *Journal of Physical Chemistry B* (2006), 110, 383.
92. Chang S.S., Shih C.W., Chen C.D., Lai W.C. and Wang C.R.C., *Langmuir* (1999), 15, 701.
93. Balamurugan B. and Maruyama T., *Applied Physics Letters* (2005), 87, 143105.
94. Xiang X.C., Brioude A. and Pileni M.P., *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (2006), 277, 201.
95. Gao J., Bender C.M. and Murphy C.J., *Langmiur* (2003), 19, 9065.
96. Gole A. and Murphy C.J., *Chemistry of Materials* (2005), 17, 1325.
97. Hsu S.H., Chou C.W. and Tseng S.M., *Macromolecular Materials and Engineering* (2004), 289, 1096.
98. Merkel T. C., He Z. and Pinnau I., *Macromolecules* (2003), 36, 6844.

99. Ash B.J., Schadler L.S. and Siegel R.W., *Journal of Polymer Science Part B: Polymer Physics*, (2004), 42, 4371.
100. Ash B.J., Schadler L.S. and Siegel R.W., *Materials Letters* (2002), 55, 83.
101. Tirrell M., Tannenbaum R., King S., Lecy J. and Potts L., *Langmuir* (2004), 20, 4507.
102. Huang H.M., Chang C.Y., Liu I.C., Tsai H.C., Lai M.K. and Tsiang C.C.R., *Journal of Polymer Science: Part A: Polymer Chemistry* (2005), 43, 4710.
103. Athawale A.A., Bhagwat S.V. and Katre P.P., *Sensors and Actuators B* (2006), 114, 263.
104. Rao C.R.K. and Trivedi D.C., *Catalysis Communications* (2006), 7, 662.

Chapter 3

References

23. Carolyn M., Sih B.C., Scott T.L. and Wolf M.O., *Journal of Materials Chemistry*, (2005), 15, 25, 2433.
24. Xia X., Cai S. and Xie C., *Materials Chemistry and Physics*, (2006), 95, 1, 122.
25. Chattopadhyay S. and Datta A., *Synthetic Metals*, (2005), 155, 2, 365.
26. Aymonier C., Bortzmeyer D., Thomann R. and Mulhaupt R., *Chemical Materials* (2003), 15, 4874.
27. Liu F.K., Hsieh S.Y., Ko F.H. and Chu T.C., *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (2002), 231, 31.
28. Hsu S.H., Chou C.W. and Tseng S.M., *Macromolecular Materials and Engineering*, (2004), 289, 12, 1096.
29. Peng Z., Kong X., Li S.D. and Spiridonov P., *Journal of Nanoscience and Nanotechnology*, (2006), 6, 12, 3934.
30. Gole A. and Murphy C.J., *Chemistry of Materials* (2005), 17, 1325.
31. Akamatsu K., Takei S., Mizuhata M., Kajinami A., Deki S., Takeoka S., Fujii M., Hayashi S. and Yamamoto K., *Thin Film Solids* (2000), 359, 55.

32. Sarma T.K., Chowdhury D., Paul A. and Chattopadhyay A., *Chemical Communications*, (2002), 10, 1048.
33. Briemer M.A., Yevgeny G., Sy S. and Sadik O.A., "Incorporation of *Nano Letters*, (2001), 1, 6, 305.
34. Walker B.M., Bethell M., Schiffrin D. and Whyman D.J., *Journal of Chemical Society and Chemical Communication* (1994), 20, 801.
35. Chen M., Falkner J., Guo W.H., Zhang J.Y., Sayes C. and Colvin V.L., *Journal of Colloid and Interface Science* (2005), 287, 146.
36. Jewrajka S.K. and Chatterjee U., *Journal of Polymer Science Part A: Polymer Chemistry*, (2006), 44, 6, 1841.
37. Wang H., Qiao X., Chen J. and Ding S., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, (2005), 256, 2-3, 111.
38. Yukihide S. and Naoki T., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2000), 169, 59.
39. Huang H.M., Chang C.Y., Liu I.C., Tsai H.C., Lai M.K. and Tsiang C.C.R., *Journal of Polymer Science: Part A: Polymer Chemistry*, (2005), 43, 20, 4710.
40. Sui X., Chu Y., Xing S. and Liu C., *Materials Letters*, 2004, 58, 7-8, 1255.
41. Kissinger H.E., *Analytical Chemistry*, (1957), 29, 1702.
42. Liu C., Yu J., Sun X., Zhang J. and He J., *Polymer Degradation and Stability*, (2003), 81, 197.
43. DiAntonio C.B., Ewsuk K.G. and Bencoe D., *Journal of American Ceramic Society*, (2005), 88, 10, 2722.
44. Aggarwal, G., Park, S. J., Smid, I. and German R. M., *TMS Annual Meeting, MPMD 7th Global Innovation Process: Trends in Materials R and D for Sensor Manufacturing Technologies*, (2006), 29.

Chapter 4

References

9. Weare W.W., Reed S.M., Warner M.G., and Hutchison J.E., *Journal of American Chemical Society*, (2000), 122, 12890.
10. Walker B.M., Bethell M., Schiffrin D., and Whyman D.J., *Journal of Chemical Society and Chemical Communication*, (1994), 20, 801.
11. Jewrajka S.K., and Chatterjee U., *Journal of Polymer Science Part A: Polymer Chemistry*, (2006), 44, 1841.
12. Aymonier C., Bortzmeyer D., Thomann R. and Mulhaupt R., *Chemical Materials*, (2003), 15, 4874.
13. Raviprakash J., McDaniel A.H., Horn M., Pilione L., Sunal P., R. Messier R., McGrath R.T. and Schweighardt F.K., *Sensors and Actuators B*, (2007), 120, 439.
14. Athawale A.A., Bhagwat S.V., and Katre P.P., *Sensors and Actuators B*, (2006), 114, 263.
15. Timmer B., Olthuis W. and Vandenberg A., *Sensors and Actuators B*, (2005), 107, 666.
16. Bekyarova E., Davis M., Burch T., Etkis M.E., Zhao B., Sunshine S. and Haddon R.C., *Journal of Physical Chemistry B*, (2004), 108, 19717.