Conjugated Polymers Under Confinement: Molecular Dynamics Simulations Study

Sabina Maskey
Clemson University, smaskey@g.clemson.edu

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CONJUGATED POLYMERS UNDER CONFINEMENT: MOLECULAR DYNAMICS SIMULATIONS STUDY

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Sabina Maskey
May 2016

Accepted by:
Prof. Dvora Perahia, Committee Chair
Dr. Gary S. Grest
Dr. Brian N. Dominy
Dr. Jason D. McNeill
Dr. Robert A. Latour Jr.
ABSTRACT

The conformations and dynamics of luminescent polymers, polymeric nanoparticles or polydots and polymers grafted onto inorganic nanoparticles using molecular dynamics (MD) simulation have been studied. Rigidity of the backbones of polymers effects their properties. Model polymer, dialkyl poly \textit{para} phenylene ethynylene (PPE), comprises rigid backbones substituted by flexible side chains. The degree of conjugation of these polymers depends on the conformation of their backbones, which in turn affects their electronic and luminescence characteristics. The results of single chain of PPEs followed by polydots and polymers grafted onto inorganic nanoparticles.

PPEs as a function of molecular weight and the nature of side chains in toluene and in implicit poor and good solvents were studied. Toluene is a good solvent for the polymer backbone and a poor solvent for the side chains whereas implicit poor solvent is poor for the overall polymer. Independent of solvent quality and molecular weight, PPE chains remained extended and the end-to-end distance scales with molecular weight. There was no correlation between aromatic rings of the backbones of the polymer chains.

The polymeric nanoparticles or polydots, formed by collapsing the rigid polymers into nano dimensions, retain their stability over extended period. The internal structure, stability and dynamics of polydots as a function of solvents, side chains and temperatures were studied. Static properties such as the radius of gyration, and the structure factor were calculated which showed that these polydots had a spherical shape consistent with the visual findings. These polydots remained in their confined state in a poor solvent whereas in a good solvent they unraveled. Unraveling was faster in bare polydots compared to
substituted polydots. With increasing temperature, polydots expanded and became aspherical but remained confined with no internal correlations between the aromatic rings. These studies have shown that these polydots retain their overall shape and dynamics over an extended temperature range.

The conformation of PPEs confined to five nm diameter silica nanoparticle as a function of solvent quality, coverage and molecular weights was studied. In water, which is a poor solvent for PPEs, the polymer chains aggregated to form clusters, which became more defined with increasing molecular weight and coverage whereas the chains remained extended and did not aggregate in toluene and decane, which are the good solvents. The distribution of the chains around the nanoparticle’s core was homogeneous in good solvents whereas in poor solvents the distributions were heterogeneous, independent of molecular weight and coverage. In comparison with grafted flexible hydrocarbon chains, the PPE backbones remained stretched out away from the surface of the NP.

Conjugated polymers in the confined geometry in have different conformation in polydots whereas the chains confined to NP’s surface have same conformation as the PPEs chains in solutions.
DEDICATION

I dedicate this dissertation to my late grandparents, Vijaya B. Malla and Shyama Malla who had always encouraged me to follow my dreams and to my late father Saundarya M. Maskey and my mother, Nalini Maskey for their unconditional love, support and encouragements in my endeavors. To my husband, Umesh M. Shrestha and my son, Unnabh Shrestha, my sister Neelima Shrestha, my brother Shubhashish M. Maskey and to all my large extended family for their support and encouragement throughout my graduate school without which it would have been impossible to achieve this work.
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CHAPTER ONE
INTRODUCTION

This study focuses to understand the structure and dynamics of rigid, luminescent polymers in solution, confined to a collapsed structure to form a nanoparticle and grafted onto an inorganic nanoparticle using molecular dynamics (MD) simulations. The model polymer system under consideration is poly para phenylene ethynylene, which has π-electron rich backbone and becomes conjugated upon conformational constraints. Hence, these polymers will often be referred as conjugated polymers. These polymers have wide range of application ranging from electro-optical devices to sensing; therefore, it is imperative to understand the factors that effects conformation, dynamics and association of these polymers in different conditions. This chapter contains brief review of conjugated polymers, conjugated polymer nanoparticles and polymer grafted nanoparticles.

Conjugated Polymers

Conjugated polymers are large macromolecules that are organic in nature and characterized by alternating single and double bonds in their backbone. The overlapping of p-orbitals create a system of delocalized π-electrons, which can result in interesting and useful optical and electronic properties and are inherently semiconducting. Conjugated polymers have current and potential applications in light emitting devices and displays, photovoltaic, and chemical sensors. Recently, additional potential application of the
conjugated polymers as a nano sensor for biological systems has emerged which has
opened the new direction in their applications.

In 1977, Shirakawa, Heeger and MacDiarmid found that the conductivity of the
films of polyacetylene when exposed to the vapor of iodine increase from that of semi-
conductor to that of the metals.\textsuperscript{5-7} This discovery lead to tremendous research on
investigating $\pi$-conjugated polymers to understand their optical and semiconducting
properties. Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa were awarded Nobel
Prize in 2000 in Chemistry for the discovery of conductivity in conjugated polymer by
doping. Tremendous research effort has been done in field of conjugated polymers  as they
have potential applications in electronic, optoelectronic, and optical devices.\textsuperscript{2,8} Conjugated
polymers such as poly(phenylene vinylene)\textsuperscript{4,8,9} and polythiophene\textsuperscript{10} have been focus of
much research, due to their applications in polymer light-emitting devices and in organic
semiconductors. These polymers consist of alternating double and single bonds and are
inherently conjugated. Another type of polymer in which there is alternating single and
triple bonds which increases electron density along the backbone of the polymer. These
triple bonds offer potential for higher conductivity and higher intensity of emission. The
conjugation length is dependent of the conformation of the polymer and the poly(phenylene
ethynylene)s (PPEs) belong to this group. These PPEs also possess interesting as well as
potentially useful electro-optical properties.\textsuperscript{11}

Figure 1.1 shows the chemical structure of PPE. PPE comprises of alternating triple
and single bonds in conjunction with aromatic rings in its backbone. Aromatic rings are
freely allowed to rotate along the long axis of the molecule due to the presence of single
bonds on the backbone of the polymer. When the aromatics rings are aligned in a single plane, the overlap of π orbitals resulting in delocalization of electrons along the extended segment of the backbone causing it to become fully conjugated. Presence of the triple bonds increases electron density along the backbone of the polymer. These polymers are also luminescent due to presence of π electrons. Consequently, the conformation and association of the polymers, which in turn affect their electro-optical properties, can control the degree of conjugation of PPEs. Swager et al. have shown that the conformation of a single chain of PPE can be controlled by modifying the backbone.\textsuperscript{12-14} Similar to other conjugated polymers, PPEs are semi-conducting in pristine form that can be imparted with metal-like conductivity when doped with halogens or strongly reducing agents. PPEs are fluorescent and with appropriate substitution at alkyl side chains can be conducting. Their potential use span a wide range of the applications from photovoltaic, light emitting diodes, transistors and quantum dots to bio-sensors.\textsuperscript{15-18}

![Chemical structure of poly para phenyleneethynylene (PPE)](image)

Figure 1.1: Chemical structure of poly para phenyleneethynylene (PPE) where R represents an alkyl chain.
Studies of PPEs

Based on the backbone configuration or linkage of PPEs, there are three isomers of PPEs which *meta, para* and *ortho*. Studies carried out on *meta*-PPEs$^{19}$ such as phenylene ethynylenes have shown that depending on the solvent, they form random to helical conformation due to $\pi$-$\pi$ stacking.$^{20-23}$ Another study have found that *m*-PPE have stretched out to helical conformation dependent on the side chains on the backbone of the polymer.$^{24}$ Both theoretical and experimental studies carried out on *ortho*-PPE have shown that fold to form helical structure in poor solvents.$^{25, 26}$ *Para*-PPE is shape-persistent and is considered to be rigid compared to its other isomers. *Para*-PPE tends to aggregate because of its long persistence length and the strong $\pi$-$\pi$ interaction along the backbone. Studies have shown that aggregation can be prevented by introducing bulky or bridged side chains on the backbone of PPEs.$^{27}$ This study is focused only on *para*-PPE. PPE refers to *para*-PPE in this dissertation.

The conformation of the polymer is dependent on quality of the solvent. The side chains present along the backbone of the polymer helps in solubilization as well as affects the electron density as side chains can be either electron withdrawing or electron donating. The conjugation length of these PPEs depends on the conformation of polymer along with that of backbone and side chains which in turn affects the electro-optical response. Experimental studies for the conformation and association of PPEs in dilute solution have been carried out using small angle neutron scattering (SANS).$^{28, 29}$ These studies have shown that di-alkyl PPE in toluene, which is good solvent for backbone, forms complex phase diagram with three phases depending on the concentration and temperature as shown
in Figure 1.2. In dilute solution, dialkyl PPEs in toluene form clear molecular solution in which there is no association of the macromolecules and have extended conformation. With the decrease in the temperature and increase in the concentration, they aggregate forming micellar solution. With further increase in concentration or decrease in temperature, they form fragile gel. The conformation of the PPE in these three phases depends on the degree of constraint of the molecule. These three phases are also accompanied by visual change of color from colorless to the yellow as the system goes from molecular solution to fragile gel.

![Molecular solution, Micellar solution, Fragile gel](image)

**Figure 1.2: Phase diagram of dialkyl PPEs in toluene**

The behavior of the polymers is the collective behavior of the polymers in the system. The removal of ensemble averaging is essential to understand the properties of polymers, as polymer conformation depends on the concentration, molecular weight etc. Each polymer in the polymeric system has different conformation. Understanding the conformation and physics of individual chains will provides us connection between polymer conformation and its properties. Hence, the physical properties of a single chain helps us to understand the properties of polymer. Experimentally, one of the methods to
study an individual chain is by using single molecule spectroscopy but the polymers tend to aggregate even in dilute solutions. Molecular dynamics simulation provides the tool to study a single chain of a polymer effectively. In this study, we studied a single polymer chain in dilute solutions to resolve the factors that affects the conformation of the polymers as electro-optical properties of depend on the conformations of these polymers.

**Nanoparticles**

Nanoparticles (NPs) have characteristic dimension of $1 - 100 \, nm$ and their properties differ from their bulk characteristics.$^{30,31}$ Much of the interest in NPs arises from enhancement of properties that take place due to the nano-dimensions including enhanced electromagnetic, electro-optical and mechanical properties. Some of the origin of nano enhancement is known and much is under investigation. Their electro-optical characteristics for example differ from that of bulk due to quantum confinement on the nanoscale that results in collective response of electrons. Some of the most promising applications of nanoparticles include catalysis, biosensors, and use in drug delivery. Nanoparticles are of two types based on their origin: inorganic and organic. Inorganic NPs such as gold, silver and iron provide enhanced electro-optical behavior but due to the cytotoxicity related with the metal nanoparticles, their use in bioimaging field is limited.$^{32}$ Hence, immense efforts have been made to make the nanoparticles from organic molecules that are less toxic and biocompatible. Soft nanoparticles formed from conjugated polymers garnered great attention due to their low toxicity and high fluorescence brightness.
Soft Nanoparticles or Polydots

Luminescent polymer when collapsed to nano-dimension form soft nanoparticles. Soft nanoparticles (NPs) or polydots are relatively smaller in size, bio-compatible and have low toxicity compared to the inorganic nanoparticles.\textsuperscript{33-35} In addition, they have high photostability and high brightness. Hence, these polydots are ideal candidate as biosensors and can be used as anticancer drug carriers and fluorescent probes for cell imaging as they retain their fluorescence even inside the living cells\textsuperscript{36-39} as well as for detection and imaging of tumor cells.\textsuperscript{33,40} In addition, they also have promising applications in tissue engineering, photonics, and electronics devices.\textsuperscript{41,42} Because of their biocompatibility and biodegradability, they are also used in tumor targeting, vivo imaging, and drug delivery.\textsuperscript{34,43-48} By changing by the concentration as well as by using different types of conjugated polymers, the photo physics and size of the polydots can be tuned.\textsuperscript{49} Similar to all conjugated polymers, polydots are also characterized by their delocalized electronic structures, which result in luminescence.

The most common method to prepare soft polymeric nanoparticles is to collapse linear polymer chains in dilute solutions and crosslink them by the introduction of adequate cross-linkers.\textsuperscript{50,51} A new fascinating class of nanoparticles are those that confine polymer to the nano length scales without crosslinks. McNeill and co-workers prepared the polydots by dissolving polymer in a good solvent for example tetrahydrofuran (THF) and then the polymeric solution was poured into a poor solvent for example water and mixed vigorously via sonication, to form nanometer-size droplets containing polymers distributed in the poor solvent.\textsuperscript{52,53} With the evaporation of the good solvent, the polymer collapses and remains
dispersed in the poor solvent. With the evaporations of the solvent, the polymers remain confined to nano dimensions without any additional chemical bonds. Though the stable conformation of these polymers is extended, surprisingly they are also found to be stable in their most unfavorable collapsed conformations. These collapsed configurations of PPEs remained in suspension and are optically active for months after their preparations.

Rigidity of these polymers is due to overlap of π orbitals along polymer backbone. Though the stable configuration of the most conjugated polymers is extended, surprisingly they are also found to be stable in their most unfavorable collapsed conformations. These collapsed configurations of PPEs remained in suspension and are optically active for months after their preparations. Though polydots have shown potential applications in biological fields, their conformations, and the forces that hold them together in their confined geometry remains an open question and challenging to understand. In this dissertation, we resolve to understand the factors that hold these nanoparticles in their collapsed conformation and the factors that affects their stability.

**Nanoparticle-Polymers Hybrids**

Polymer grafting onto the nanoparticles (NPs) surfaces is of interest for designing new functional organic-inorganic hybrid materials. Polymer-coated NPs are emerging as a new class of materials due to their improved properties with a wide range of potential applications ranging from electro-optical devices to biological applications. The physical properties of the NP are governed both by the shape and size of the NP core and by the type of the attached ligands. The collective behavior of the functionalized NPs
depends on the interactions between the NPs and the modifying groups as well as on the interaction between the chains themselves and with the solvent.\textsuperscript{8, 57}

Of particular interest are NPs grafted with luminescent conjugated polymers, tethering soft chromophores to a hard NP. These hybrids are potentially tunable through unique combinations of the nanoscale properties of the hard NP with the tunability offered by the conformation of the polymers. The conjugated polymers grafted onto NPs have shown to be highly fluorescent and can be used as fluorescence chemosensors for detection of nitroaromatic explosives.\textsuperscript{58} Rotello and Bunz have synthesized gold nanoparticles with conjugated polymer poly (p-phenylene ethynylene) (PPE) hybrids in which gold quenched emission of PPE disrupting NP-PPE interaction which results in improved emission intensity from PPE which is the key factor for recognition of different proteins.\textsuperscript{59} The energy transfer efficiency of the polymer - NP hybrids is dependent on the size, shape, and chemical structure of the nanoparticles as well as on both chemical and physical properties of the grafted polymers. For instance, quenching of fluorescence of the derivatives of PPEs by citrate functionalized gold nanoparticles was explained by the overlap of the emission band of the PPEs and the plasmon band of gold nanoparticles.\textsuperscript{60} Incorporation of conjugated polymer in the development of organic-inorganic hybrid material is an efficient method to fine tune electronic and optical properties which has led to the wide range of applications in organic light emitting diode (OLED), sensors and other electronic devices.\textsuperscript{61, 62} Experimental studies have found that in chemo-sensors system, NP-conjugated polymers hybrids show enhanced selectivity and sensitivity compared to conjugated polymer alone.\textsuperscript{58}
Silica nanoparticles are ideal for bio-applications because they have low toxicity, high dispersion and can be easily functionalized.\textsuperscript{63, 64} The presence of various silanol and siloxane groups present on silica NP surface determine its chemical properties. Ogawa et al. have shown that PPE with hydrophilic side chains grafted on silica microspheres are fluorescence sensors for biological targets.\textsuperscript{56} He et al. have shown that in a PPE film on a glass substrate its fluorescence properties can be tuned by changing alkyl side chains to more hydrophilic oligomers in various solvents.\textsuperscript{65} Kong and He carried out a molecular dynamics (MD) simulation of the structural conformation of PPE molecules with hexadecyloxy side chains on a flat SiO$_2$ substrate and found that the conformation of the side chains affects the fluorescence properties of PPEs.\textsuperscript{66} PPE-coated nanoparticle form an electro-optical responsive system where the PPEs tune the interactions between the NPs. Modification of silica-NP surfaces with luminescent rigid polymer dialkyl PPE may represent a new class of nanoparticle – polymer hybrids for electro-optical devices and sensors.

**Basics Polymer Physics Concepts**

A polymer is a big macromolecule comprising of monomers, which are structural repeating units, connected to each other by covalent bonds. Polymer chains are characterized by their degree of polymerization and the rigidity of their backbone. Consider a flexible polymer chain of $N + 1$ backbone atoms with bond vector $\vec{r}_i$ that go from atom $i - 1$ to $i$. The polymer is an ideal chain if there is no net interaction between the atoms
separated by the adequate number of bonds along the chain. The end-to-end vector, \( \vec{R}_N \) is the sum of all \( N \) bond vectors in the polymer chain and given by\(^{67}\)

\[
\vec{R}_N = \sum_{i=1}^{N} \vec{r}_i
\]  

End-to-end distance vector is dependent on the conformation of the polymer chain. Average end-to-end distance gives the overall size of the polymer. The mean square end-to-end distance of the polymer chain is given by\(^{67}\)

\[
\langle R^2 \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \vec{r}_i \cdot \vec{r}_j \rangle
\]  

For the polymer with the equal length of the bond vector, \( l \), and \( \theta \) is the angle between the \( \vec{r}_i \) and \( \vec{r}_j \), we represent the end-to-end vector relation as\(^{67}\)

\[
\langle R^2 \rangle = l^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \cos \theta_{ij} \rangle
\]  

The freely jointed chain is the simplest model of an ideal chain which has constant bond length, \( l \) and no correlation between directions of different bond vectors, \( \langle \cos \theta \cos \theta_{ij} \rangle = 0 \) for \( i \neq j \). The mean end-to-end distance equation is given simply by\(^{67}\)

\[
\langle R^2 \rangle = Nl^2
\]
For real polymer chain, there are correlations between neighboring bond vectors. Then the equation becomes

\[ < R^2 > = C_N N l^2 \]  \hspace{1cm} (1.5)

where coefficient \( C_N \), called the Flory characteristic ratio.

A freely rotating chain model considers all angles and bond lengths are equal as well as all torsion angles are equal and rotates freely. There is the correlation between the angles, which is transferred along the direction of the bond vectors. In this case, equation 1.2 is expressed as\(^{67}\)

\[ < R^2 > = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \sum (\cos \theta)^{|j-i|} \]  \hspace{1cm} (1.6)

With the increase in the number of bonds between the vectors \( \mathbf{r}_i \) and \( \mathbf{r}_j \), \( (\cos \theta)^{|j-i|} \) decays rapidly,

\[ (\cos \theta)^{|j-i|} = \exp \left( |j - i| \ln \cos \theta \right) = \exp \left( -\left| j - i \right| / s_p \right) \]  \hspace{1cm} (1.7)

where \( s_p \) is a persistence number and \( s_p = -1/\ln(\cos \theta) \) is number of main chain bonds in the shortest rigid segment and scales with local correlations of the bond vectors decay and leads to the final solution of the equation\(^{67}\).
\[
< R^2 > = nl^2 \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right)
\]  
(1.8)

where \( n \) = number of bonds, \( l \) = bond length and \( \theta \) is angle between the bond vectors. The persistence length is defined\(^{67}\) as

\[
l_p = s_p \cdot l = -\left( \frac{l}{\ln \cos \theta} \right)
\]  
(1.9)

The persistence length increases with a decrease in bond angle that increases the stiffness of the polymer chain. Hence, depending on the persistence length, the polymers are classified into flexible, semi-flexible and rigid polymers. The worm-like chain model describes a rigid polymer if the bond angle is very small therefore; the polymer has a large persistence length, \( l_p \). In a flexible polymer chain, \( l_p \) of the chain is smaller.

Radius of gyration is another way for measuring the size of the polymer. The square of the radius of gyration is simply defined as the average squared distance from any point in the polymer chain and the center of mass (com) of the polymer chain. \( R_g^2 \) expressed as\(^{67}\)

\[
R_g^2 = \frac{1}{N} \sum_{i=1}^{N} (\overrightarrow{r_i} - \overrightarrow{r_{com}})^2
\]  
(1.10)
where $\vec{r}_i$ is the position vector of atom $i$ and $\overrightarrow{r_{com}}$ is the position vector of the polymer’s center of mass.

The mean square radius of gyration of an ideal linear chain\textsuperscript{67}

$$< R_g^2 > = Nb^2 / 6 \quad (1.11)$$

where $b$ is Kuhn length.

**Polymer Solution Thermodynamics**

The interaction of polymers with solvents determine their conformation and in solution, two thermodynamics parameter, entropic effects and enthalpy effects determine the overall structure of the polymer. These two thermodynamics effects can be explained by Flory-Huggins lattice model\textsuperscript{68} based on mean field approximation. This model defined the systems as particles on a lattice, each lattice site is occupied either by monomer A or by a solvent molecule B. The entropy of mixing per lattice site is given by\textsuperscript{67},

$$\Delta S_{mix} = -k_B \left[ \frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln (1 - \phi) \right] \quad (1.12)$$

where $\phi$ and $(1-\phi)$ are the volume fractions of the polymer and solvent, $k_B$ is the Boltzmann constant and $N_A$ and $N_B$ are the numbers of lattice occupied by the polymer and solvent molecules respectively. Entropy of mixing always favor either mixing of polymer in the
solvents whereas the energy of the mixing can favor segregation or mixing. The energy of mixing is given by\(^{67}\)

\[
\Delta U_{\text{mix}} = k_B T \chi \phi (1-\phi)
\]

where \(T\) is temperature and \(\chi\) is the Flory-Huggins interaction parameter which describes the interaction energy between the components per site of contacts with the polymer and solvents, polymer-polymer and solvent-solvent. \(\chi\) is given by\(^{67}\):

\[
\chi_{AB} = \frac{Z [\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2]}{k_B T}
\]

where \(z\) represents the number of the nearest neighbors, \(\epsilon_{AB}\) is the interaction between A and B, \(\epsilon_{AA}\) is the interaction between A and A; and \(\epsilon_{BB}\) is interaction between BB as mentioned earlier A and B represent polymer and the solvents molecules respectively.

When \(\chi\) is positive, polymer-polymer interactions are preferred over solvent-solvent and polymer-solvent interactions. Polymer-solvent interactions are favored helping the solvation of the polymer with negative \(\chi\). Generally, with increase in temperature, \(\chi\) decreases. Hence, the type of the polymer as well as the quality of the solvent affects the polymer’s conformation. The solvents are classified into good solvent, poor solvent and theta solvent based on the interaction between the polymer and solvent.\(^{68}\)

In a good solvent, the polymer-solvent interaction is greater than the interaction between the polymers and polymer chain assumes an extended conformation. If the
interaction between the polymer-polymer and polymer-solvent is equal, the solvent is called theta solvent. In poor solvent, the interaction between the polymer-polymer is greater than interaction between the polymer-solvent and polymer chain assume collapsed conformation. The size of the polymer is dependent on the quality of the solvent. Therefore, value of $R_s$ is the largest in the good solvent and the smallest in the poor solvent for the polymer with the same molecular weight.

According to scaling theory\textsuperscript{69}, $R_g$ scales with the degree of polymerization,

$$R_g \sim N^\nu \quad (1.15)$$

Where $\nu$ is the scaling component specific to the solvent used in dilute solution and $\nu = \frac{3}{5}, \frac{1}{2}, \text{and} \frac{1}{3}$ for good solvent, theta solvent and poor solvent respectively. The polymer solutions can be categorized into three types: dilute, semi-dilute and concentrated. In dilute solutions, there is no interaction between the polymer molecules. In this study, we study rigid polymers in dilute solutions.

**Outline of dissertation:**

This dissertation is organized in the following manner. Chapter 2 introduces briefly molecular dynamics (MD) simulation technique. Chapter 3 is focused on the study of a conformation of single chain of our model polymer PPE in dilute solution as a function of molecular weights, side chains and solvent quality. Chapters 4-5 introduces polydots and their structure, stability and dynamic studies as the function of solvents quality and temperature. The study of conformation of PPE grafted silica nanoparticle as the function
of solvent quality, grafting density, and molecular weight is discussed in Chapter 6. Followed by the summarization of the studies in Chapter 7.

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CHAPTER TWO
MOLECULAR DYNAMICS SIMULATIONS

Molecular dynamics (MD) simulation is a numerical technique for modeling molecular systems, from gases and liquids to polymeric systems.\textsuperscript{1,2} MD simulations can be used to predict the evolution of a system in real time as it generates the configurations which are connected in time. Hence, in MD simulations time-dependent properties or dynamic properties, such as the diffusion coefficient, transport properties, mean square displacement, dynamics structure factors, etc. can be directly measured.

Newton’s Equation of Motion

Molecular dynamics simulation is based on a step-by-step numerical solution of Newton’s second law or equation of motions.\textsuperscript{1-3} From the information of the force on each atom, their acceleration can be calculated. Integration of the equation of the motion gives trajectories describing the positions, accelerations, and velocities of each atom as a function of time. The average values of the properties of the system are calculated using these trajectories. Moreover, the state of the system can be predicted at any time, if velocities and positions of each atom are known.\textsuperscript{1-3}

Newton’s second law of motion is given by

\[ F_i = m_i a_i \]  

\text{(2.1)}
where \( F_i \) is the force given by the particles \( i \), \( m_i \) is mass and \( a_i \) is the acceleration of particle \( i \) for a system of \( N \) particles. The force is also given by the potential energy’s gradient,

\[
F_i = -\nabla_i V
\]  

(2.2)

where \( V \) represents the potential energy of the system. The derivatives of potential energy relate the change in the position as it vary with time in Newton’s equation of motion. The motion of an object is described quantitatively by specifying the Cartesian position vector \( r_i(t) \) of the object in space at any time \( t \). This is equivalent to specifying the time dependence of the three components of \( r_i(t) \),

\[
r_i(t) = (x(t), y(t), z(t))
\]  

(2.3)

Recognizing the velocity \( v(t) \) as the first derivative of time of the position, \( v(t) = dr_i/dt \), and the acceleration \( a(t) \) is the first derivative of time of the velocity, \( a(t) = dv/dt \), the acceleration is easily seen to be the second derivative of position, \( a(t) = d^2r/dt^2 \). Therefore, Newton’s second law, \( F = ma \) is expressed as a differential equation

\[
F_i(r_1, r_2, \ldots, r_N) = m\frac{d^2r_i}{dt^2}
\]  

(2.4)
Combining these two equations (equations 2.2 and 2.4) will give,

$$-\frac{dV}{dr_i} = m_ia^2 r_i/dt^2$$  \hspace{1cm} (2.5)

It is essential to state two initial conditions, the initial position \(r(0)\) and the initial velocity \(v(0)\). Solution of equation subject to these initial conditions uniquely specifies the motion of the object all time. Hence, solving the equation of motion, the system’s total energy is conserved and the system is equivalent with an ensemble with the fixed number of particles, \(N\), constant energy and time, which represent a micro-canonical ensemble (NVE).

**Integration scheme**

Newton’s equation of motion is solved using ‘velocity-Verlet’ integration scheme, which is a modification of Verlet integration scheme.\(^4\) Intermediate half time-step at \(t + \frac{1}{2} \Delta t\) is used to update the positions and velocities of all particles in the system from time \(t\) to time \(t + \Delta t\)

\[
\begin{align*}
  r(t + \Delta t) &= r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 \\
  v \left( t + \frac{\Delta t}{2} \right) &= v(t) + \frac{1}{2}a(t)\Delta t \\
  a(t + \Delta t) &= -\left(\frac{1}{m}\right) \nabla V (r(t + \Delta t))
\end{align*}
\]  \hspace{1cm} (2.6 - 2.8)
Force $F(t + \Delta t)$ is calculated by using newer positions and velocities from Eq. (2.6) and Eq. (2.7). As Newton’s equation is being integrated, $a(t + \Delta t)$ is given by dividing the force by the mass and then the final velocity is computed as

$$v(t + \Delta t) = v(t + \frac{\Delta t}{2}) + \frac{1}{2} a(t + \Delta t) \Delta t$$  \hspace{1cm} (2.9)

This integrator is fast, simple and stable and, more importantly, it satisfies the requirements of time-reversibility and law of energy conservation.$^2$

**Force field**

The potentials governing the interactions are necessary to represent a system properly in MD simulations. MD simulations require the force between the particles to be realistic as possible. We modeled polymers and all the solvent molecules in this study using the fully atomistic Optimized Parameter for Liquid-Simulator-All Atoms (OPLS-AA) potential of Jorgensen et al.$^5, 6$ The OPLS-AA, which will be referred simply as OPLS in this study, is comprised of several potential terms,

$$U = U_{nb} + U_{bond} + U_{ang} + U_{tor}$$  \hspace{1cm} (2.10)

The non-bonded interaction $U_{nb}$ consists of a sum of standard 12-6 Lennard-Jones (LJ) and an electrostatic term, which is given by

$$U_{nb}(r_{ij}) = U_{LJ} + U_{coul} = 4\varepsilon_{i,j} \left[ \left( \frac{\sigma_{i,j}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{i,j}}{r_{ij}} \right)^{6} \right] + k_{coul} \frac{q_i q_j}{r_{ij}}$$  \hspace{1cm} (2.11)
$\varepsilon_{ij}$ represents LJ energy, $\sigma_{ij}$ is the LJ diameters of atoms $i$ and $j$, $r_{ij}$ is the distance between atoms $i$ and $j$ and partial charges on the atoms are represented by $q_i$ and $q_j$. The potential energy of induced dipole-induced dipole (dispersion forces) varies as $1/r^6$ and repulsion follows $1/r^{12}$. Non-bonded interactions for the atom pairs, which are three or more bonds apart of the same molecule as well as of the different molecules, are calculated. The interaction for the atoms, which are three bonds or more apart is reduced by a factor of $\frac{1}{2}$. The potential in the equation (2.11) has an infinite range of distance. A distance $r$ grows as $r^3$ for the number of atom pairs separated, which makes calculations more expensive for larger distances. Hence, to overcome this challenge, the potential is truncated at a distance called cutoff ($r_c$), beyond which all the interactions are discarded. The cutoff is selected at a distance where density is uniform. Generally cut off ($r_c$) of 12 Å is chosen for all LJ interactions. All the electrostatic interaction between atom pairs which are closer than 12 Å and outside this range are calculated in real space and in reciprocal (Fourier) space respectively. For calculation of reciprocal space, the particle-particle particle-mesh (PPPM) algorithm with precision of $10^{-4}$ is used. Harmonic potentials is used to model the covalent bonds between the atoms in OPLS-AA which is given as

$$U_{bond}(r_{ij}) = k_r(r_{ij} - r_0)^2$$

(2.12)
where \( r_{ij} \) is bond length of atoms \( i \) and \( j \), \( r_0 \) is the equilibrium bond length, and \( k_r \) represents the spring constant. Harmonic potential also describes angle bending of three atoms \( (i, j, k) \) covalently bonded which is given as

\[
U_{ang}(\theta_{ijk}) = k_\theta (\theta_{ijk} - \theta_0)^2
\]

(2.13)

where \( \theta_{ijk} \) is the actual angle formed by the vectors \( r_{ij} \) and \( r_{jk} \) and \( \theta_0 \) is the reference angle value. In OPLS, torsional or dihedral component is given by

\[
U_{tor}(\phi) = \sum_{n=1}^{4} \frac{k_n}{2} \left[ 1 - (-1)^n \cos(n\phi) \right]
\]

(2.14)

where dihedral angle is represented by \( \phi \) and \( k_n \) is the coefficient in Fourier series.

**Preparation of polymers and MD simulation technique**

The polymer chains and bulk solvents were built using Polymer Builder and Amorphous Cell modules of Accelrys Materials Studio package with Polymer Consistent Force Field. Minimization of the conformational energy of the molecules was also performed. The conversion of Material Studio data files into LAMMPS files and the interaction potentials from PCFF to OPLS is done using an in-house conversion code. LAMMPS classical MD code is used to perform all simulations. Numerical integration is carried out using a velocity-Verlet algorithm with a time step \( \delta t = 1 \) fs. Most of the simulations are performed at a constant volume using a Langevin thermostat with a 100 fs damping constant unless otherwise stated. Each particle in the system is weakly coupled to a heat bath formed by combining random and frictional forces. The advantages
of using Langevin thermostat are that larger time steps can be chosen compared to other thermostats and enhances stability as well as the inevitable effect of accruing mathematical error due to the long run is diminished.

To overcome the surface effects, simulation is carried out with periodic boundary conditions. In periodic boundary conditions, a periodic array is formed by replicating a cubic simulation box of particles in all directions. If the particle in the center box moves during the simulation, its periodic image in every box moves with same orientation in the same way. During the simulation, if the particle leaves the box, then it will be substituted by its image incoming from the opposite side. Advantage of periodic boundary conditions is that simulation can be carried out with a small number of particles.

Explicit solvent molecules such as toluene and decane are modeled using OPLS force field. The SPC/E model is used for water. O-H bond length, and H-O-H angle of water are constrained using SHAKE algorithm.

In addition to modeling polymer chains in an explicit solvent like toluene, decane, and water, polymer chains are simulated in the implicit solvent due to computational limitations, particularly for long chains. The behavior of the polymer in the implicit poor solvent is similar to that in the explicit poor solvent whereas implicit good solvent captures the essence of toluene and decane. Also, implicit solvents allow capturing the behavior of the polymer in the longer time run. The solvent is treated as a continuum medium. Once coupled with the thermostat, thermal energy allows polymers to move and change their conformation. If interaction energy is greater than the thermal energy, polymer will
collapse into a confined structure, which is the characteristic of the poor solvent. The poorer the solvent, the greater will be the depth of the potential well. In good solvent, monomer-monomer interaction energy is less than the thermal energy and therefore, polymer swells. To model implicit poor and good solvents, all the interactions will be truncated at 12 Å for a poor solvent whereas to model a good solvent, all the Lennard-Jones interactions will be truncated at the potential minimum \( r_c = 2^{\frac{1}{6}} \sigma_{ij} \) to produce a purely repulsive non-bonded force. In other words, to simulate the implicit good solvent, we keep only the repulsive part of potential.

A simple flow chart of an MD algorithm is shown in Figure 2.1 describes the steps during the simulations.
Figure 2.1: A flow chart for standard MD simulation algorithms. MD simulations have been performed to study the conformations, static properties and dynamics properties of a single chain polymer, confined polymers into nanoparticles and polymer grafted on to silica nanoparticles using the above stated preparation method and simulation condition with periodic boundary conditions. In each chapter, simulation methodology will be described in detail.
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CHAPTER THREE
CONFORMATIONAL STUDY OF A SINGLE MOLECULE OF POLY PARA PHENYLENE ETHYNYLENES IN DILUTE SOLUTIONS

Abstract

The conformation of single molecules of dialkyl poly para phenylene ethynyles (PPEs), electro-active polymers, is studied in solutions using molecular dynamics simulations. The conformation of conjugated polymers affects their electro-optical properties and therefore is critical to their current and potential uses, though only limited theoretical knowledge is available regarding the factors that control their configuration. The present study investigates the affects of molecular parameters including weight and side chains for PPEs in different solvents, on the conformation of the polymers. The PPEs are modeled atomistically where the solvents are modeled both implicitly and explicitly. The study finds that PPEs assume extended configuration which is affected by the length of the polymer backbone and the nature and length of substituting side chains. While the polymer remains extended, local dynamics is retained and no long range correlations are observed within the backbone. The results are compared with scattering experiments.

Introduction

Conjugated polymers are inherently organic semi-conducting materials and are electro-optically active. Hence, they have potential applications as key components of organic based electro-optical devices such as light emitting diodes, organic transistors, sensors, and solar cells.\textsuperscript{1-4} The electro-optical properties of conjugated polymers depend
on their conjugation length and inter-chain interactions; properties which are affected by the conformations of these polymers. In comparison with flexible and semi-flexible polymers, only limited knowledge is available regarding the factors affecting the conformation of highly conjugated polymers, which are more rigid in solution. When imbedded into devices, the conformation of the polymer is affected by their innate configuration coupled with confinement effects due to integration. As a first step in understanding the conformation of conjugated polymers, the current study investigates the factors that affect the structure of a single conjugated polymer in solution using 2,5-dialkyl poly para phenylene ethynlenes (PPEs) as a model system.

As shown in Figure 1, the backbone of PPEs consists of aromatic rings bridged by single and triple bonds which may rotate freely along the long axis of the molecules. Confinement of the aromatic rings into a single plane results in formation of an extended conjugated rigid segment. Structural studies carried out using small angle neutron scattering (SANS) have shown that dialkyl PPE in toluene has a complex phase diagram depending on the concentration and the temperature. At high temperatures and low concentrations, PPEs form a molecular solution with a relatively extended backbone. With decreasing temperature and increasing concentration, the molecules associate to form micelles that eventually gel. In this study, we focus on the molecular solution regime where the effects of molecular parameters such as molecular weights, side chains and interactions with solvents will be extracted.
Figure 3.1: The chemical structure of PPE where R represents an alkyl chain. In this study R includes nonyl and ethylhexyl chains and n ranges from  to 20 to 2000.

The significance of the conformation of conjugated polymers to their optical characteristics including absorption and emission has been demonstrated by numerous research efforts, in solution and in thin films\textsuperscript{6}, where the chemical structure is the primary factor to control the configuration. Kim and Swager,\textsuperscript{7} for example, were able to control the conformation of a single PPE molecule and the inter-chain interactions by substituting the backbone with the surfactant side chains of varying natures. The degree of hydrophobicity of the side chain together with their interfacial interactions at an air-water interface was used to control the degree of conjugation. These interactions exhibit a direct interrelationship of the intrinsic optical properties of a conjugated polymer, the conformation of a single chain and the inter-polymer interaction.
The present study investigates the conformation and dynamics of a single chain of dialkyl PPEs as the function of molecular parameters and solvent quality, using molecular dynamics (MD) simulations. The study explores the conformation and dynamics of single PPE chains of degree of polymerization $n$ from 20 to 2000 with different side chains, including linear and branched alky chains, in solvents of different quality ranging from a poor to very good. The conformation of flexible polymer chains in solvents of different quality is well established. In good solvent a single chain assumes a random coil configuration and in poor solvent it assumes a collapsed conformation. While the conformation of flexible and semiflexible polymers has been thoroughly studied, limited knowledge is available regarding the behavior of polymers with a large persistence length.

Here, we study dialkyl PPEs, which is a rigid macromolecule, decorated with various side chains including ethylhexyl, butyl, nonyl, and octadecyl. The affinity of the solvents is often different for the backbone and the substituting side chains. The conformational freedom along the backbone which originates from the sequence of single and triple bonds sequence is expected to affect the overall conformation. The PPEs where modeled atomistically (explicitly) and the solvents were modeled both atomistically and implicitly. PPEs with backbone of length $n = 20, 60$ and $120$, PPEs were dissolved in toluene, which is a good solvent for the backbone of the PPEs but a poor solvent for the side chains. To model longer chains, the solvent was treated implicitly due to limitations on computational resources. Combining atomistic simulation of the solvent with implicit description allows us to probe a wide range of molecular weights from $n = 20$ to 2000 and vary the solvent quality from poor to good. Figure 2 presents equilibrated states of
diethylhexyl PPE and dinonyl PPE in toluene for $n = 20$, where for clarity the toluene molecules are not shown. These snapshots show that the backbone of PPE remains extended, as was experimentally observed by small angle neutron scattering on the same system and the side chains are dispersed and separated from each other as well as away from the backbone. It differs however from light scattering studies which depicted folded polymers in mixtures of solvents.

![Equilibrated structures of a single PPE molecule with in toluene for (a) R=diethylhexyl and (b) R=dinonyl](image)

Figure 3.2: Equilibrated structures of a single PPE molecule with in toluene for (a) R=diethylhexyl and (b) R=dinonyl
This paper is organized in following manner: Sec. II describes the simulation model and methodology and in Sec. III the results for the radius of gyration, static and dynamic structure factors, and correlation of the phenyl rings in the backbone are presented, followed by a summary and conclusions in section IV.

**Simulation Method**

The PPEs and solvent molecules studied in this work are modeled using OPLS-AA (Optimized Potentials for Liquid Simulations - All Atom) framework of Jorgensen et al., which we refer here as OPLS. OPLS potential is composed of several terms,\(^9,10\)

\[
U_{OPLS} = U_{nb} + U_{bond} + U_{ang} + U_{tor} + U_{imp}
\]  

(3.1)

Nonbonded interactions \(U_{nb}\) consists of a sum of standard 12-6 Lennard-Jones (LJ) and electrostatic potentials,

\[
U_{nb}(r_{ij}) = U_{LJ} + U_{coul} = 4 \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + k_{coul} \frac{q_i q_j}{r_{ij}}
\]  

(3.2)

where \(\varepsilon_{ij}\) is the LJ energy and \(\sigma_{ij}\) is the LJ diameter for atoms \(i\) and \(j\), \(q_i\) and \(q_j\) are their partial charges. For atoms of different species, geometric mixing rules are used: \(\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}\) and \(\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}\). Nonbonded interactions are calculated between all atom pairs of different molecules in addition to all pairs on the same molecule separated by three or more bonds, though the interaction is reduced by a factor of 1/2 for atoms separated by three bonds. All LJ interactions are cut off at 12Å. All electrostatic interactions for atom pairs closer than 12Å are calculated in real space, those outside this range are calculated in reciprocal (Fourier) space by using the particle-particle particle-mesh (PPPM) algorithm.
with precision of $10^{-4}$. Direct covalent bonds between atoms are modeled in the OPLS as harmonic potentials of the form,

$$U_{bond}(r_{ij}) = k_r (r_{ij} - r_0)^2$$  (3.3)

where $r_{ij}$ is the distance between atoms $i$ and $j$ and $r_0$s are their equilibrium separations.

Harmonic forms are also used to describe the angle bending potential of directly bonding chains of three atoms $(i, j, k)$,

$$U_{ang}(\theta_{ijk}) = k_\theta (\theta_{ijk} - \theta_0)^2$$  (3.4)

$\theta_{i,j,k}$ is the angle between the vectors $r_{ji}$ and $r_{jk}$, and $\theta_0$ the equilibrium value. The torsional (dihedral) component of the OPLS potential is given by

$$U_{tor}(\phi) = \sum_{n=1}^{4} \frac{k_n}{2} [1 - (-1)^n \cos(n\phi)]$$  (3.5)

where $\phi$ is the dihedral angle and $k_n$ is energy. In the OPLS framework, the out of plane (improper) potential has the same form as that of the torsional potential.

The PPE molecules and bulk toluene samples were constructed separately using the Polymer Builder and Amorphous Cell modules in Accelrys Materials Studio©. The conformation energy of each PPE molecule was minimized in Materials Studio with the pcff force field since the OPLS potential is not available in Molecular Studio. Molecular dynamics simulations were performed using the LAMMPS classical MD code. The equations of motion were integrated using a velocity-Verlet algorithm with a time step $\delta t = 1$ fs. A Langevin thermostat with a 100 fs damping constant was used to regulate the system temperature, which was 300 K for all simulations. An in-house conversion code
was used to convert the potential parameters to OPLS and modify the Materials Studio data files into a form readable by LAMMPS.

The conformation of the PPE molecules was studied in solvents of different qualities for the backbone and side chains. Single PPE molecules with different length of the polymer backbone and nature and length of the side chains were studied in toluene which is a good solvent for the backbone and a poor solvent for the side chains. Equilibrated samples of toluene were merged with a single PPE molecule to form a solution. For $n = 20$ we used 7200 toluene molecules, while for $n = 60$ and 120, the number of toluene molecules was increased by a factor of three and six respectively. The length of the simulation box $L_x$ in the direction of the chain was set to approximately $\sim 20\%$ longer than the axis of the fully stretched PPE molecule. The width of the simulation cell $L_y = L_z$ was sufficient to prevent interaction of the PPE with its periodic image. Overlapping atoms, which resulted from merging the PPE molecule, and bulk toluene samples were removed by running for a few thousand steps with the $fix\ NVE/limit$ routine built into the LAMMPS MD package. The systems were then run at constant pressure in an $N-P-T$ ensemble with $P = 0$ for 0.5 ns before long runs were made at constant volume in an $NVE$ ensemble. All systems were run until equilibrium was reached, with at least 10 ns and up to 70 ns, depending on the specific polymer and its length.

To model longer chains, PPEs were modeled atomistically and two sets of simulations in which the solvent was treated implicitly were carried out, corresponding to a good and a poor solvent. In one, all the interactions between atoms on the PPE chain were the same as in Eq. (2) with $r_c = 12\text{Å}$. For $T = 300$ K this corresponds to a poor solvent
for both the backbone and side chains. To model a good solvent for both the backbone and side chains, all the Lennard-Jones interactions in Eq. (2) were truncated at the potential minimum \( r_c = 2^{1/6} \sigma_{ij} \), producing a purely repulsive nonbonded force. For these two implicit solvents we could simulate much longer chains, up to \( n = 2000 \), overcoming computational limitations that allowed the study of up to \( n = 120 \) in explicit toluene. These two types of implicit simulations will be referred in the rest of the paper as poor and good solvent for convenience.

**Results**

**A. Statics**

The effects of increasing the degree of polymerization \( n \) were studied in three solvents by measuring the end-to-end distance \( R \) and radius of gyration \( R_g \). The radii of gyration of given by

\[
R_g^2 = \sum_{l=1}^{N} m_l (r_l - r_{COM}) \cdot (r_l - r_{COM}) / \sum_{l=1}^{N} m_l
\]

(3.6)

where \( m_i \) is the mass of atom \( i \) and \( r_{COM} \) is the center of mass of the polymer. The instantaneous radius of gyration \( R_g \) is shown in Figure 3 as a function of time for diethylhexyl PPE for \( n = 20 \) to 120 in toluene and for \( n = 60 \) in a poor solvent. For all polymerization numbers, \( R_g \) decreases only by a few percent from its fully extended value at \( t = 0 \) over the first 1-2 ns and then remains constant up to 70 ns. Solvent quality has very limited effect as demonstrated for \( n = 60 \), where \( R_g \) is only slightly larger in toluene than in the poor solvent.
The average radius of gyration \( \langle R_g \rangle \), averaged over 5-10 ns is plotted in Figure 3.4 as a function of the degree of polymerization. \( R_g \) increases linearly with \( n \) where best fit to a straight line is shown for a poor solvent. The best fits for a good solvent and toluene overlap the same line. The correlation of \( R_g \) with the polymerization number \( \langle R_g \rangle = b' n \), with \( b' = 0.216 \pm 0.001 \) nm in all three solvents studied. Similarly for the end-to-end distance we find \( \langle R \rangle = bn \), where \( b = 0.70 \pm 0.001 \) nm. For a completely rigid chain \( b' = 0.22 \) nm and \( b = 0.79 \) nm. Thus, while there is some local flexibility as demonstrated in the snapshots shown in Figure 3.2, globally the chains remain extended at least for the degrees
of polymerization studied here. In comparison with experimental studies, the current result is consistent with SANS observations on PPEs in toluene used SANS that have shown that PPE molecules remain extended within their entire molecular weight solubility range, the average $n$ in which the studied PPEs dissolve in toluene.

Figure 3.4: Average radius of gyration (lower curve) and (upper curve) of diethylhexyl PPE as a function of the degree of polymerization in a poor solvent (circles), good solvent (squares) and in toluene (triangles). The dashed lines represent the best fit to the data. The slope of the lines are 0.70 nm for $<R>$ and 0.216 nm for $<R_g>$.
Our results differ however from light scattering studies by Cotts et al. that have observed a more folded structure in mixtures of tetrahydrofuran and chloroform. The difference between our simulation results and the scattering may be attributed to a slight variability in the regularity of the bonds in the experimental system with a small fraction of non para bonds between the phenyl groups. Some variability may also arise from the interaction potentials which were not optimized for this particular system. Further studies are currently on the way to resolve this issue.

The static structure factor $S(q)$ was calculated as the function of $q$ for $n = 20, 60$ and 120 for diethylhexyl and dinonyl PPE in toluene and for diethylhexyl PPE in an implicit solvent for chains of length $n = 60-2000$. The structure factor is determined from

$$S(q) = \sum_{i,j=1}^{N} b_i b_j \exp \left( i q \cdot (r_i - r_j) \right) / \sum_{i,j=1}^{N} b_i b_j,$$

(3.7)

where $N$ is the number of atoms in the chain and the scattering lengths are $b_H = 3.7406 \times 10^{-15} m$ for hydrogen and $b_c = 6.6511 \times 10^{-15} m$ for carbon. Results of $S(q)$ were averaged over 400 configurations and 500 different random $q$ vectors for each $q$ for $n < 2000$ and 200 $q$ vectors. $S(q)$ of PPEs displayed in Figure 5, exhibit a characteristic power law regime $q^{-\alpha}$ for intermediate values of $q$ and additional broad peaks at higher $q$ values which are signatures of the side chains. For diethylhexyl PPE in toluene $\alpha = 0.9 \pm 0.1$ for 60 and 120. For the longer diethylhexyl PPE chains in implicit solvent we $\alpha = 0.9 \pm 0.1$ for $n = 120$ and 480 and decreases to $\alpha = 0.7 \pm 0.1$ for $n = 2000$. For a fully stretched rigid rod $\alpha=1$ With extended chains, $\alpha<1$ is a result of local dynamics that originates from the rotational freedom of the single-triple bonds along the polymer
backbone. Resolving the exponent coupled with $R_g$ and the visualization of the molecules provide an insight into the structure of a fully extended molecule.

Figure 3.5 $S(q)$ of (a) diethylhexyl PPE and of (b) dinonyl PPE as the function of $q$ for different degrees of polymerization, and (top to bottom) in toluene. Results for in a poor and, and in a good solvent are shown for diethylhexyl PPE.
At high $q$ values, a broad peak centered on 0.45 Å$^{-1}$ corresponding to fully stretched side chains is observed. A weak signature of an inter chain distance is observed for $q \sim 1.09$ Å$^{-1}$ corresponding to a distance of approximate 5Å. Similar trends were observed for dinonyl PPE in toluene, with differences in the slopes which are measured to be $\alpha=0.7\pm0.1$ and $0.8\pm0.1$ for 60 and 120 respectively. In addition, comparing the $S(q)$ for these two side chains at high $q$ values, the dimensions of side chains affect the correlations.

To further resolve the effects of the side chains on the conformation of the macromolecules the length of the side chains were systematically varied. Fig. 6 shows snapshots of the center sections of 20 repeat units of an equilibrated $n = 60$ with 4 and 18 carbons alkyl side chains in different solvents. The center segment is shown to visualize the conformation of the side chains where the rest of the polymer follows a similar behavior. The overall conformation is similar to that observed in Fig.2 for ethylhexyl and nonyl substituted PPEs. For all alkyl chains studied, the backbone is extended. For shorter alkyl side chain (Figs.6(a) and 6(b)) hardly any changes are observed between PPEs in toluene and in a poor solvent. However, the longer side chains (Fig.6(c)) collapse towards the backbone in poor solvent. Even though the side chains assume different configuration depending on the quality of the solvent, backbone remains extended which is shown by the previous results for the end-to-end distance $<R>$. 
Figure 3.6: Snapshots of center section of 20 repeat units for an equilibrated chain of length \( n = 60 \) of dibutyl PPE (a) in toluene (b) in a poor solvent and dioctadecyl PPE (c) in toluene and (d) in a poor solvent.

\( S(q) \) as a function of \( q \) is shown in Fig.3.7 for PPEs substituted by different alkyl side chains for 4, 9 and 18 carbons. All three patterns decay with \( q^\alpha \) in the intermediate \( q \) range and exhibit a broad peak in the high \( q \) region, corresponding to real space values commensurate with the length of the side chains. Those peaks in \( S(q) \) are centered around \( q \sim 0.61, \sim 0.36 \) and \( \sim 0.22 \text{ Å}^{-1} \) for C4, C9 and C18 respectively. These values correspond
to distance of approximately 10Å, 18Å and 29 Å which are the lengths of the fully stretched side chains. With increasing side chain length the intensity of these lines increase. For dioctadecyl which has the longest side chains of length 18 carbons, the peak is most prominent while for dibutyl which is the shortest PPE side chain studied, merely 4 carbons, the peak is less pronounced. Similar to surfactant chains, higher correlations are observed with increasing chain length. For all three side chains, weak signatures of interchain distance is observed at approximately at $q \sim 0.93-0.96 \, \text{Å}^{-1}$ which corresponds to a distance of 6.5 Å. The slope of $S(q)$ in the intermediate $q$ range is approximately 0.9 for C4, 0.86 for C9 and 0.72 for C18. With increasing length of the side-chains the local rigidity of the PPE backbone is reduced.
The correlation between the aromatic rings is one of the most significant conformational parameters to the overall electro-optical properties of PPEs as it determines the conjugation length of the backbone. The correlation of the aromatic rings within the PPE backbone was obtained using a first order orientation order parameter, given by:

\[ P_\theta = \frac{1}{2} \left< 3\cos^2\theta - 1 \right> \]  \hspace{1cm} (3.6)
where $P_{\theta}$ corresponds to the average alignment of aromatic rings with a particular spatial direction, and $\theta$ is the measure of deviation perpendicular to the interface for two aromatic rings which are separated along the backbone by a degree of polymerization $\Delta n$. $P_{\theta}$ has a range of $[-1/2,1]$. A positive value for $P_{\theta}$ corresponds to a parallel alignment of the aromatic rings whereas a negative value indicates a perpendicular alignment. For fully parallel aromatic rings within the backbone $P_{\theta} = 1$ and for completely random orientation of no correlation, $P_{\theta} = 0$.

Figure 3.8: Order parameter $P_{\theta}$ as the function of $\Delta n$, where $\Delta n$ is the separation of phenyl rings in the aromatic plane for dibutyl PPE (solid) and dioctadecyl PPE (dashed) for $n = 60$ in toluene.
Figure 3.8 shows an example of $P_\theta$ versus $\Delta n$ for dibutyl and dioctadecyl PPEs. For a single molecule, no correlations are observed between the orientation of the aromatic rings beyond the error in the estimate of $P_\theta$ except possibly for near neighbor rings in any of the solvents studied.

**B. Dynamics**

The degree of association of the solvent with the backbone of a conjugated polymer would affect different optical characteristics such as the life time of fluorescence. To understand correlation between the solvent and the PPE molecules, we determined the residence time of toluene near a phenyl rings for diethylhexyl PPE at cut off distances away from the backbone of 8, 12 and 16 Å. For comparison we also determined the residence time of two toluene molecules in neat toluene for the same 3 cut-off distances. Figure 9 introduces three snapshots of the toluene molecules within a distance of 8 Å. from the backbone of an ethylhexyl PPE at different times. While most of the toluene molecules have migrated away from the backbone, others remain within the proximity of the PPEs for an extended time.
Figure 3.9: Snapshots of toluene which are within a distance of 8 Å from the phenyl rings of backbone of an ethylhexyl PPE at $t = 0$ for $t = 0, 0.5$, and 1.0 ns.

The residence time of the toluene molecules was calculated by first identifying which of the toluene molecules are within the specified distance of any backbone phenyl
ring and then determining when each of those molecules moved away from the backbone a distance larger than the specified cutoff. The data are normalized by the average number of toluene molecules that reside within the cut-off distance of the backbone over the length of the run. For toluene molecule in a neat liquid we followed a similar procedure except that we determined the time that two toluene molecules remain closer than the specified cutoff distance. Results for the residence time of toluene near the backbone phenyl rings for ethylhexyl PPEs for three cutoff distances is shown in Fig. 10a for n=20. Results for toluene in a neat liquid are shown in Fig.10b for comparison. While the average residence time for a toluene molecule near a phenyl backbone ring or another toluene molecule is comparable, some toluene molecules remain locally trapped near the PPE chain for very long times. These long lived toluene/phenyl ring pairs can affect the dynamics of the PPE chains. These results, together with previous experimental nuclear magnetic resonance studies concluding that the relaxation time of the toluene is strongly affected by the dynamics of the PPE molecules, show that the toluene is associated with the PPE chains.
Figure 3.10: Residence time of a toluene molecule near (a) phenyl ring of diethylhexyl PPE and (b) near a toluene in neat toluene for cut off distances of 8, 12 and 16 Å.

The dynamic processes of the polymer chains was studied by calculating the dynamic structure factor $S(q,t)/S(q,0)$, shown in Fig.11 for ethylhexyl and dinonyl substituted PPEs for $n = 60$ in toluene. The dynamic structure factor reflects the diffusion of the entire polymer molecule and internal motions, depending on the q range. Qualitatively, in q range that corresponds to overall size of extended polymer molecules, $S(q,t)/S(q,0)$ does not decay within the time frame of the measurements, which means that within the times we probe in this study we do not detect the diffusion of the entire polymer backbone. This result is consistent with the diffusion constant of the center of mass of the polymer which we calculated to be $D \sim 6.2 \times 10^{-12} \pm 0.5$ m$^2$/s, which corresponds to an average mean square displacement of $\sim 1$ nm over the time scale of 40 ns shown in Fig.~11.
These results show a more rigid system than observed experimentally. These differences may be attributed to enhanced rigidity observed in the simulations. At higher $q$ ranges which correspond to internal dimensions, $S(q,t)/S(q,0)$ decays in an exponential way.

Figure 3.11: $S(q,t)/S(q,0)$ as a function of time for (a) ethylhexyl PPE and (b) dinonyl PPE in toluene. $q$ is in units of Å$^{-1}$.
The results of $S(q,t)/S(q,0)$ have been analyzed to extract effective diffusion coefficients. Using a single exponential for low $q$ and double exponential for high $q$, $S(q,t)/S(q,0)$ was expressed as:

$$S(q, t)/S(q, 0) = A_1 e^{\Gamma_1 t} + A_2 e^{\Gamma_2 t}$$

and the values for the effective diffusion $\Gamma_1$ and $\Gamma_2$ were calculated. The values of $\Gamma_1$ and $\Gamma_2$ as the function of $q$ are presented in Fig.12. By definition $\Gamma_1 < \Gamma_2$. The overall trends observed is consistent with the experimental data obtained from neutron spin echo studies by Jiang et al. for dinonyl PPE, however all the dynamic constants are ~4 time slower. We attribute the difference to enhanced rigidity of the PPE molecule in the simulations.

![Figure 12](image)

Figure 3.12: $\Gamma_1$ and $\Gamma_2$ as the function of $q$ for dinonyl PPE. The values of $\Gamma_1$ are multiplied by 10.
Conclusions

The conformation of a single chain of dialkyl substituted PPEs has been studied in toluene, and in poor and good solvents. The chains were found to be fully extended, independent of solvent quality or the nature of the side chains. The average radius of gyration $<R_g>$ was only slightly larger in toluene and in the good solvent compared with poor solvents. In the intermediate q range, $S(q)$ scales with $q^{-\alpha}$ where $\alpha$ ranges from 0.7-0.9, which is consistent with extended chains, though not fully rigid.

No correlation was found between the aromatic rings within the PPE backbone, in either poor or good solvents. The conformation of the substituting side chains and their inter-chain correlations are affected by their dimensions and by solvent quality. The side chains are more dispersed in toluene and in the good solvent than in a poor solvent.

At high q characteristic peaks of side chains depends on the length of the side chains where longer chains are slightly more correlated. However with increasing length of the substituting side chain, the backbone becomes locally more dynamic as revealed by the decrease of $\alpha$ with chain length in the intermediate q range. $S(q,t)$ revealed that on the time scale of the simulation the extended PPE hardly diffuses, where internal dynamics persists.

This study elucidates for the first time the conformation and dynamics of a single PPE molecule in solvents. It has shown that even though the molecules are extended, local dynamics is retained, where the length of the side chains affects the dynamics. Future studies are on the way to explore the realm of aggregates of PPEs.
Acknowledgments

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CHAPTER FOUR
INTERNAL CORRELATIONS AND STABILITY OF POLYDOTS, SOFT CONJUGATED POLYMERIC NANOPARTICLES

Abstract

Conjugated polymers collapsed into long-lived highly luminescent nanoparticles, or polydots, have opened a new paradigm of tunable organic particles with an immense potential enhancing intracellular imaging and drug delivery. Albeit the chains are not in their equilibrium conformation, they remain stable over astounding long times. Using atomistic molecular dynamics simulations with an innovative method to controllably collapse an inherently rigid polymer, we determined for the first time internal structure and stability of poly-dots made of dialkyl para phenylene ethynylene, immersed in water, a relevant biological medium. In contrast to natural aggregates, the aromatic rings within the poly-dot in water are uncorrelated within the nanoparticle, with little to no water in its interior. The lack of correlation explains the difference of luminescence characteristics between the spontaneously aggregated conjugated polymers and poly-dots. Resolving the conformation and stability of these particles will enable in transforming an idea to a new effective tool.

Introduction

Conjugated polymers collapsed into long-lived, nanometer-size, globular conformations form a new class of light-emitting and absorbing soft particles. Their luminescence characteristics differ significantly from those of spontaneously aggregated
conjugated polymers, pointing to the new conformation of the rigid polymers in confined geometry.\textsuperscript{1} The chemistry and the softness of these nanoparticles (NP) present a new tunable manifold that will augment the use of organic NPs at interfaces with biological membranes, as sensors, as imaging markers, and as targeted-drug delivery tools.\textsuperscript{1-5} These particles consist of a multitude of chromophores confined into small dimensions, often on the same order of magnitude as the size of biological membranes. They are luminescent, and their surface can be modified to either tether them to an interface or graft functionalities that allow their insertion into living organisms. Packing a large number of chromophores into a small particle while retaining the ability of the molecule to absorb and emit light results in a unique hybrid that combines the advantages of organic dyes and the high brilliance characteristics of inorganic NPs and quantum dots. Therefore, the polydots open a new paradigm, where a single molecule-particle can be detected. Here we probe the internal conformation and stability of one model polydot which is a critical first step to design soft organics NPs with defined properties, using newly designed computational tools. Beyond the insight into the structure and stability of polydots, the study provides the new insight into the behavior of confined polymers.

The majority of conjugated polymers are relatively rigid, and their collapsed state is a far from equilibrium conformation.\textsuperscript{6, 7} These macromolecules are often forced into the nano dimension by imposing constraints on the polymer backbone, either cross-linking or physically trapping the chains into a confined space. The most common approach to achieve long-lasting nanoconfiguration is to cross-link the polymer, where the resulting dimensions depend on the molecular weight of the polymer, its smallest rigid segment, and
the number of crosslinks. A new fascinating pathway to form highly luminescent NPs is to confine the polymer to a nanoparticle without crosslinking. These particles are of particular interest since rearrangements of the chromophores can take place. The conformational freedom of the polymer chains leads to a new class of tunable particles. Their unique photo physics is often determined by the conformation of the polymer backbone.

Here we probe the interactions that underlie the formation and internal structure of these long-lived soft NPs formed by physical confinement of the macromolecules using atomistic molecular dynamics (MD) simulations. Computational studies are among the very few methodologies that can directly probe the conformation of the polymer chains and derive the internal correlations within a soft NP. The highly congruent experimental and computational structure factors of the shape of the polydot serves as a bridge between macroscopically measured properties and internal structure and correlations within the polydot obtained from computational studies.

Experimentally, these soft NPs are formed by dissolving an aliquot of polymer in a good solvent, below the critical micellar concentration. The solutions are then dripped into a poor solvent such as water, while vigorously mixed via sonication, forming polymer-containing nanometer size droplets disperses in the poor solvent. As the good solvent evaporates, the polymer collapses into NPs that remains suspended in the poor solvent.

The process results in long-lived, luminescent NPs that consist of polymers collapsed into dimensions that are smaller than their inherent rigid segment. These polymeric NPs, often referred to as polydots, not only remain fluorescent, but can be inserted into living
organisms. The fluorescence characteristics of polydots indicate that the structure of the confined polymer molecules differs from that in melts or in spontaneously formed aggregates. The soft nature of the polydots and their inherently organic exterior enhance the ability to tailor specific chemistries at the polymer interface needed for different functions. Resolving the internal structure and dynamics of these confined polymers is fundamental to the design of poly-dots with well-defined photophysics.

The current study uses MD simulation to probe directly for the first time the internal structure of long-lived NPs formed by dialkyl para phenylene ethynylene (PPE). PPEs are hardly soluble in water and assume extended conformation even in the good solvents such as toluene and tetrahydrofuran.

Experimentally, these PPEs polydots remain in aqueous solutions without cross-linking for extended periods of time. PPEs are uniquely tunable polymers since the degree of co-planarization of the backbone aromatic rings determines the degree of conjugation and therefore the absorption and emission characteristics. The backbone becomes fully conjugated when all aromatic rings lie in the same plane. The side chains grafted on the backbone impact the solubility and assembly of the PPEs and, indirectly, electronic structure of the polymer. Overall, the light emitting and absorption characteristics of PPEs strongly depend on the chemical structure of the backbone and the side chains that together determine the conformation of the polymer and its packing.
Model and Methodology Details

The PPE chains studied in this work were modeled using the fully atomistic optimized parameter for liquid simulator–all atoms (OPLS–AA) potential of Jorgensen et al.\textsuperscript{17,18}. The OPLS–AA was comprised of both bonded and non-bonded interactions. The non-bonded interactions were a sum of the standard 12-6 Lennard-Jones (LJ) and electrostatic potentials. For atoms of different species, geometric mixing rules were used: $\varepsilon_{ij} = (\varepsilon_i \times \varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i \times \sigma_j)^{1/2}$, where $\varepsilon_{ij}$ and $\sigma_{ij}$ are the LJ units of energy and distance between atoms $i$ and $j$, respectively. Non-bonded interactions were calculated between all atomic pairs on different molecules, in addition to all pairs on the same molecule separated by three or more bonds. The interaction was reduced by a factor of $1/2$ for atoms separated by three bonds. All LJ interactions were cut off at $r_c=12\text{Å}$. All electrostatic interactions for atom pairs closer than 12 Å were calculated in real space; those outside this range were calculated in reciprocal (Fourier) space by the particle–particle, particle–mesh (PPPM) algorithm\textsuperscript{19} with a precision of $10^{-4}$. Bonded interactions included a harmonic interaction between bonded atoms, a harmonic three-body angle term, and a four-body dihedral interaction. The form of the interaction and all relevant interaction parameters are described in detail in ref\textsuperscript{17,18}.

All simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) molecular dynamics code\textsuperscript{20}. The equation of motion was integrated using the velocity–Verlet algorithm with a time step of $\delta t = 1\text{fs}$. To regulate the temperature at $T = 300\text{K}$, we coupled the system weakly to a heat bath using a Langevin thermostat\textsuperscript{21} with 100 fs damping time. PPE chains of length 240 repeat units...
were built using the Polymer Builder in Material Studio from Accelrys Inc using polymer consistent force field (pcff), as OPLS–AA potential is not implemented in Material Studio, and converted to OPLS–AA. Water was modeled using SPC/E. The SHAKE algorithm was used to constrain the O-H bond length and H-O-H angle.

Using a process close to the experimental preparation method, we were successful computationally forming poly-dots that consist of PPEs. The NPs were formed by compressing an isolated chain in an implicit poor solvent. The molecules were enclosed in a large spherical cavity, the radius of which was slowly reduced over 1 ns. The cavity wall interacted with the PPE chain via a harmonic potential. The encapsulation within a spherical cavity provide a parallel to the experimental process in which polymers are trapped in droplets of good solvents that are immersed in the poor solvent. As a good solvent evaporates experimentally the polymer cage becomes smaller, mimicked here by decreasing the size of the confining cavity. PPE with the polymerization number of 240 with disubstituted by ethyl hexyl side chains, as prepared and in its early stages of compression is shown in Figure 1a and 1b. The polymer molecules were initially compressed to dimensions that result in internal density comparable to that of the polymer melt. This criterion resulted in a final diameter of 5.0 nm for a diethyl-hexyl PPE and 2.0 nm for a PPE without side chains. Once the melt density reached bulk value, the spherical cavity was removed and the poly dots were placed in solvents.

A snapshot of the diethyl-hexyl PPE polydot as prepared is shown in Figure 4.1c. Following the release of the cavity, the polydot assumed a fully spherical shape with a smooth interface dominated by the side chains. Following the short equilibration in an
implicit poor solvents, the collapsed polydots were relaxed in solvents of varying quality, including water and toluene, as well as in good and poor implicit solvents.

Figure 4.1. Snapshots of diethylhexyl PPE for (a) t =0 ns, (b) t= 0.5 ns and (c) t = 1 ns in an implicit poor solvent. The final diameter of the indenter is 5.0 nm. (d) poly-dot in water after 25 ns and (e) a sliced through the center of the poly dot presented in (d). For clarity, dark blue correspond to Carbon atoms on side chains, Hydrogen atoms on side chains are white and the backbone is represented by magenta.

Water and toluene samples of 648,000 atoms were first equilibrated. To immerse the polydots, solvent molecules needed to be displaced. A void was created in the center of each of the liquids by inserting a soft, repulsive, spherical pseudoparticle indenter into each of the solvents. This process was similar to that by which the poly-dots were made, but in
reverse, whereby a cavity was grown slowly from radius zero to a size capable of accommodating one polydot. The overall system dimensions were allowed to expand at constant pressure through the void growth. When the desired size was reached, the pseudoparticle was removed, leaving a void space into which one poly-dot was placed. The system was then equilibrated at constant pressure for 1 ns, after which it was run at constant volume for up to 100 ns.

**Results and discussion**

The stability of the polydot strongly depends on the solvent quality, as one would expect for a collapsed polymer that is not cross-linked. When placed in water, the polydots slightly changed their conformation, as shown in Figure 4.1d, but remained in their nanoconfiguration for up to 25 ns in water and 100 ns in explicit poor solvent. Water is a poor solvent for PPEs; however, the small number of molecules do not dissolve and remain extended or aggregated rather than collapsed. This stability over extended periods was consistent with experimental observations where the polydots remain stable over months in their collapsed state, dispersed in water. In comparison with neutron spin echo results, these computational intervals are sufficient for most local dynamics to take place. A first insight into the structure of the polydot was obtained by slicing it through its center, as shown in Figure 1e. The center of the polydot is dense, and no obvious spatial correlations were observed and no water molecules.

In contrast to the conformation of the polydot in water, in toluene, the chain rapidly unfolded. Snapshots of di ethylhexyl PPE polydots in toluene at times ranging from 5 to 100 ns after the indenter was removed are presented in Figure 4.2. To probe longer time
We found that the results for poor solvents are similar to those obtained for water. The results for polydots in good solvents were similar to those obtained for toluene, while reflecting the fact that the backbone and the side chains interacted equally with the solvent, whereas toluene was a better solvent for the backbone than for the side chains of the PPE. These two types of implicit simulations will be referred in the rest of the paper as poor and good.

Figure 4.2 Time sequence for poly-dots that consist of diethyl ethyl PPE in toluene. Carbon atoms on side chain are marked in dark blue, hydrogen on side chain in white and backbone is represented by magenta.

The dimensions of the polymers in toluene were smaller than the dimensions of those in a good implicit solvent for the same unraveling time. These differences present a remarkable demonstration of the significance of specific interactions of different segments of polymers with solvents. In an implicit good solvent, the interactions of the backbone and the side chains with the solvent were equally good, whereas the interactions of toluene with the backbone and side chains were different. In contrast, the dimensions of the poly-dots in
both water, which is a poor solvent for both the backbone and the side chains, and in a poor implicit solvent, are similar. After a very small expansion of the poly-dot in the first few picoseconds after the indenter was removed, the poly-dots remained collapsed for the length of the simulation in both water and the poor implicit solvent.

The radius of gyration of the polymer was measured as a function of time after the polydots were immersed in the four solvents. Figure 3 presents $R_g$ as a function of time for PPE polydots with and without side chains. After a very small expansion of the polydot in the first few picoseconds after the indenter was removed, the polydots remained collapsed for the length of simulation in both water and poor solvent.

![Figure 4.3](image)

Figure 4.3. Radius of gyration $R_g$ of PPE molecule as a function of time in water, toluene, poor and good solvents for of substituted PPE (solid symbols) and without side chains (open symbols). The inset presents the ratios for the moment of inertia for an implicit poor solvent for first 0.12ns.
Surprisingly, the presence of alkyl side chains did not enhance the stability of the polydot in poor solvents. This observation suggests that the stability is achieved through arrest of the backbone motion at temperatures below the glass transition of the polymer rather than the interdigitation of the side chains. In the two good solvents, however, R_g of the polydot continued to increase over the course of the simulation as the chain unraveled. After an initial faster increase in R_g in the good solvent compared to toluene, the rate of increase in R_g was comparable for the two model solvents for late times. From these results, it was clear that the conformational stability of the polydot depends strongly on the solvent–polymer interactions.

In contrast to having little or no effect on the stability of the NPs in poor solvents, the lack of side chains enhanced the rate of unraveling of the polymer in good solvent, as shown in Figure 3. Though the polydots were locked into place by the backbone in the poor solvents, their packing was impacted by the side chains. As the backbone becomes dynamic, the side chains affected the conformational dynamics of the polymer.

The evolution of the shape of the polydots was probed by calculating the three eigenvalues of the moment of inertia tensor \( \lambda_1, \lambda_2, \) and \( \lambda_3 \). The ratios of the two largest eigenvalues to the smallest one, immediately following the release of the constraints for implicit poor solvent, are shown in the inset of Figure 3. The ratio of the eigenvalues which is one at the onset as expected for a fully spherical particle\(^{25}\) increases with the time for the first 20 ns and then fluctuates around tensor \( \lambda_3/\lambda_1=1.2 \) and \( \lambda_2/\lambda_1=1.1 \). For PPEs with no side chains, \( \lambda_3/\lambda_1=1.6 \) and \( \lambda_2/\lambda_1=1.2 \). These eigenvalues show that the PPEs with the side chains are significantly more spherical than those made of bare PPEs. This is the first observation that
the side chains impact the packing of the backbone. The ability of the polymer to rearrange following the removal of the constraints shows that the preparation method does not lock the polymer conformation.

The radial density of the polydots from their center of mass is shown in Figure 4 in water and in a poor solvent. The density of the polydot with side chains was uniform, within the noise of the measurement, while the density for the polydot without side chains was lower near the center. Little or no water molecules were found inside the polydot in both cases; however at the boundary between the outer surfaces of the polydots a higher density of water is observed over a range of approximately 1 nm. The access is in part due to the fact that the polydots were not perfectly spherical, and their external interface is rough, particularly those without side chains
Figure 4.4. Radial mass density of the polymer and water within polydots. Zero corresponds to the center of the particle. The solid symbols correspond to substituted PPEs and open symbols to PPEs without side chains. The PPE in water is represented by diamonds and in poor solvent by circles. The densities profiles of water are marked by triangles.

Comparing the density of the side chains and the backbone separately, the side chains dominates the surface of the polydots. Undulations observed may correspond to the dimensions of a tube that encapsulate the backbone and the side chains.

An important aspect of the functionality of polydots for light absorption and emission is the correlation between the aromatic rings. One measure of the correlation of the aromatic rings within the PPE backbone was obtained using a first-order orientation order parameter, given by $P_\theta = \frac{1}{2} <3 \cos^2 \theta - 1>$, where $P_\theta$ corresponds to the average alignment
of aromatic rings with a particular spatial direction, and $\theta$ is the measure of deviation perpendicular to the interface for two aromatic rings which are separated along the backbone by a degree of polymerization $\Delta n$. $P_\theta$ has a range of $[-1/2, 1]$. Results for $P_\theta$ for polydots with and without side chains in water are shown in Figure 5.

In agreement with our previous results for extended PPE chains, no correlations were observed between the orientations of the aromatic rings beyond the error in the estimate of $P_\theta$, except for the nearest neighbor ring, which had a tendency to align perpendicularly. This lack of correlation between the aromatic rings accounted for their light emission and absorption characteristics.

![Figure 4.5](image)

**Figure 4.5.** Order parameter $P_\theta$ as a function of the separation of phenyl rings $\Delta n$ in the aromatic plane for poly-dots substituted (solid black line) and without (dashed red line) side chains in water. Insert shows the snapshot of the poly-dot with side chains in which
only the backbone carbon atoms are shown and side chains and hydrogen atoms are removed for clarity. Data are averaged over 200 configurations.

The calculation of the correlations within the polydots have provided the first insight into their luminescence behavior. In order to bridge between the structural experimental studies and computational ones we calculated by structure factor \( S(q) \), where \( q \) is the momentum transfer vector. \( S(q) \) is the most accurate experimental measure of structure of polydots. The analysis of the scattering data is often model-dependent and requires further support. The correlation between results from simulations and scattering provide a powerful strategy to determine the structure of polydots in solution. The scattering factor of the polydots was calculated using:

\[
S(q) = \left| \sum_i b_i e^{iq_i r_i} \right|^2
\]

where \( b_i, q_i, \) and \( r_i \) are the scattering length, momentum transfer vector, and position vector of atom \( i \), respectively.\(^{27}\) The results for the calculated \( S(q) \) of the polydots in water are shown in Figure 6. These simulation results capture the shape of the NPs in the low \( q \) region together with internal structural features at high \( q \).

The calculated \( S(q) \) was modeled with a typical sphere scattering convoluted with a Gaussian to describe a gradual drop-off in the scattering length density.\(^{28}\) The results are shown in Figure 6. This fitting resulted in a radius of gyration of 25.1 Å for the PPE with side chains and 17.6 Å without side chains. These compare to the values of \( \langle R_g^2 \rangle^{1/2} = 26.8 \) Å for PPE with side chains and 18.2 Å without side chains determined directly.
Figure 4.6. $S(q)$ as the function of $q$ for poly-dots substituted (solid triangles) and without (open triangles) side chains in water. Best fit to a fuzzy spherical form factor is shown by solid lines.

The results obtained by the simulations are similar to those obtained separately by neutron scattering. This multiple length scale insight into the structure of the polydot is unique to computational studies and cannot be done experimentally.

**Conclusions**

This study introduces the first insight into the structure of a new type of luminescent particles that consist of conjugated polymers collapsed into the nano dimension, as obtained from MD simulations. The simulations conceptually mimic the experimental
caging of the polymer within boundaries of a droplet to force a collapsed geometry. A spherical smooth NP with the alkyl chain dominating the surface of their interface was formed. The NPs were placed in four different solvents, and their structure was followed as a function of time. In water and poor solvent, the poly-dots remained predominantly spherical and compact, while their interface became significantly rough. In toluene as well as in a good solvent, the polymer unraveled as a function of time. The alkyl side chains affected the symmetry of the NP in water, where the alkyl-substituted polymer forms a more spherical NP, but no effect was observed for the stability of the poly-dot. This suggests that the frozen conformation of the polymer below the glass transition temperature is the prime factor that retains the stability of the poly-dots in poor solvents. No internal correlations were observed between the aromatic rings on the polymer within the poly-dot, consistent with the experimental luminescence of PPEs. This study has opened the way to explore internal structures of soft nano-particles that in turn will impact the design of new NPs with well defined luminescent characteristics.

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CHAPTER FIVE
DYNAMICS OF POLYDOTS, SOFT LUMINESCENT NANOPARTICLES

Abstract

The conformation and dynamics of luminescent polymers collapsed into nanoparticles or polydots were studied using fully atomistic molecular dynamics (MD) simulations, providing a first insight into their internal dynamics. Controlling the conformation and dynamics of confined polymers is essential for realization of the full potential of polydots in nano medicine and biotechnology. Specifically the shape and internal dynamics of polydots that consist of highly rigid dialkyl para phenylene ethynylene (PPE) are probed as a function of temperature. At room temperature, the polydots are spherical without any correlations between the aromatic rings of the PPEs. With increasing temperature, they expand and become slightly aspherical; however, the polymers remain confined. The coherent dynamic structure factor reveals that the internal motion of the polymer backbone is arrested and the side chains dominate the internal dynamics of the polydots. These new soft nanoparticles retain their overall shape and dynamics over an extended temperature range and their conformation is tunable via their degree of expansion.

Introduction

Soft nanoparticles (NPs) or polydots formed by collapsed luminescent polymers are emerging as promising candidates for various bio-applications due to their photostability, high brightness, and low toxicity. Their biocompatibility and biodegradability enable their use in vivo as biosensors, drug carriers, and fluorescent probes for detection and
imaging.\textsuperscript{8-14} The photophysics of polydots depends on the chromophore’s chemical structure, chain conformation, the size of the NP, and the degree of correlations between the aromatic rings.\textsuperscript{8-10} While polydots find increasing applications, there is limited understanding of the effects of confinement of conjugated polymers into NPs. In contrast to confinement into aggregates in solution, in polydots the molecules are trapped in the nano dimensions with no correlation between the chromophores. Building on our previous study where we demonstrated the ability to prepare polydots computationally,\textsuperscript{11} the structure and stability of polydots as a function of temperature are probed and their internal dynamics is revealed.

Long-lasting, soft polymeric nanoparticles are commonly made by collapsing macromolecules in dilute solutions followed by crosslinking of the confined state.\textsuperscript{12, 13} Polydots or luminescent polymeric NPs form a new, fascinating class of NPs that consist of polymers confined to nano length scales without chemical crosslinking, enabling formation of a dynamic luminescent nano cage. These are formed by initially confining the polymers into droplets in a good solvent that is then dispersed into water, which is a poor solvent for the polymers. With the evaporation of the good solvent, the polymers remain confined to nano dimensions without any additional chemical bonds. The confinement without chemical crosslinking offers a potential for tunability.\textsuperscript{14-17} The factors that determine the internal structure, stability, and dynamics of these long-lived, soft polymeric nanoparticles, however, have not been resolved. Here using the computational methodology previous derived\textsuperscript{11} for assembly of these confined nanoparticles and response to solvents, we probe the temperature stability and dynamics of polydots that consist of
confined polymer, dialkyl \textit{para} phenylene ethynylene (PPE), whose chemical structure is shown in Figure 1. The backbone of PPEs consists of numerous chromophores whose conjugation is strongly affected by the respective orientation of the aromatic rings. Only segments where consecutive aromatic rings are confined into a single plane are fully conjugated. The alkyl substituents that often serve as solvation moieties affect the electronic structure through conformational dynamics and impact assembly. One unique feature of PPEs is their extended conformation in dilute solutions shown both experimentally\textsuperscript{3, 17} and computationally\textsuperscript{18}. While the most stable conformation in dilute solution is extended,\textsuperscript{24} polydots in water remain confined over long periods of time.\textsuperscript{11} These two entirely different conformations raise intriguing questions regarding the stability of the confined state, and the dynamic processes that ultimately control the polydots and their photophysics. Here, we probe the dynamics of the confined state as the temperature is varied. Surprisingly, we find that though the polydots expand somewhat with increasing temperature, they remain confined. Also, the backbone remains rigid while the side chains are dynamic.

![Figure 5.1: The chemical structure of PPE where $R$ represents an alkyl chain. In this study, $R$ includes ethylhexyl and H and $n =240.$](image-url)
The paper is organized as follows: we first present the simulation model and methodology followed by the results of the analysis of the static structure of the polydots. The dynamic studies are then presented, followed by conclusions.

**Model and Methodology**

The PPE chains are modeled using the fully atomistic optimized parameter for the liquid simulator—all atoms (OPLS–AA) potential of Jorgensen et al. They are comprised of both bonded and non-bonded interactions. The non-bonded interactions are a sum of the standard 12-6 Lennard-Jones (LJ) potential and a Coulomb electrostatic term. For atoms of different species, geometric mixing rules are used: \( \varepsilon_{ij} = (\varepsilon_i \cdot \varepsilon_j)^{1/2} \) and \( \sigma_{ij} = (\sigma_i \cdot \sigma_j)^{1/2} \), where \( \varepsilon_{ij} \) and \( \sigma_{ij} \) are the LJ units of energy and distance between atoms \( i \) and \( j \), respectively. Non-bonded interactions are calculated between all atomic pairs on different molecules, in addition to all pairs on the same molecule separated by three or more bonds. The interaction is reduced by a factor of \( 1/2 \) for atoms separated by three bonds. All LJ interactions were cut off at \( r_c = 12\text{Å} \). The electrostatic interactions for atom pairs closer than 12 Å are calculated in real space; those outside this range are calculated in reciprocal (Fourier) space by the particle–particle, particle–mesh (PPPM) algorithm with a precision of \( 10^{-4} \). Bonded interactions include a harmonic interaction between bonded atoms, a harmonic three-body angle term, and a four-body dihedral interaction. The form of the interaction and all relevant interaction parameters are described in detail in ref. 29, 30.

All simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) molecular dynamics code. The equations of motion were integrated using the velocity–Verlet algorithm with a time step of \( \delta t = 1\text{fs} \). To regulate the
temperature $T$, we coupled the system weakly to a heat bath using a Langevin thermostat\textsuperscript{33,34} with 100 fs damping time. PPE chains of length 240 repeat units were built using the Polymer Builder in Material Studio from Accelrys Inc. using the polymer consistent force field (pcff), as OPLS–AA potential is not implemented in Material Studio and converted to OPLS–AA.\textsuperscript{27}

For modeling polydots in water, we first equilibrated a system of 648,000 water atoms. Water model used was SPC/E.\textsuperscript{35} The SHAKE algorithm was used to constrain the O-H bond length and H-O-H angle.\textsuperscript{36,37} To immerse the polydots in water, a void in the center of the liquid was created by inserting a soft, repulsive, spherical pseudoparticle into the solvent. This process was similar to that by which the polydots were made, but in reverse, whereby a cavity was grown slowly from radius zero to a size capable of accommodating one polydot. The overall system dimensions were allowed to expand at a constant pressure through the void growth. When the desired size was reached, the pseudoparticle was removed, leaving a void space into which one polydot was placed. The system was then equilibrated at constant pressure $P = 1$ atm for 1 ns, after which it was run at constant volume and run for at least 300 ns at 300 K. This range probes significantly longer times in comparison with our previous simulations of polydots in water, enabling the study of dynamics.\textsuperscript{11}

In addition, following the similarities between the behavior of polydots in water and in implicit solvents, simulations were run in implicit poor solvents offering a means to study the behavior of the polydots for longer times, capturing further dynamic information. The quality of implicit solvents was controlled by varying the strength of the attractive
interactions between non-bonded atoms.\textsuperscript{28} To model a solvent that was poor for both the backbone and side chains, all the LJ non-bonded interactions were truncated at $r_c = 1.2$ nm. The simulations in an implicit poor solvent were run at temperatures $T = 300, 400, \text{ and } 600$ K for at least 300 ns each. Polydots equilibrated in an implicit poor solvent at 300 K for 25 ns were also heated to 400 and 600 K. After equilibrating polydots at 400 and 600 K for 150 ns, they were then cooled down to 300 K.

**Preparation of Polydots**

Using a process close to the experimental preparation method, the polydots were formed by compressing an isolated chain to a collapsed state and then letting it relax in a poor solvent.\textsuperscript{28} A schematic representation of the preparation is shown in Figure 2. The molecules were enclosed in a large spherical cavity, the radius of which was slowly reduced over 1 ns. The cavity wall interacted with the PPE chain via a harmonic potential. PPE as prepared and in its early stages of compression is shown in Figure 2a to 2d. The polymer molecules were initially compressed to dimensions that result in internal density comparable to that of the polymer melt. This criterion resulted in a final diameter of 5.0 nm for a diethylhexyl substituted PPE and 2.0 nm for a bare PPE chain. Once the density of the polydot reached its bulk value, the spherical cavity was removed and then allowed to relax in water or an implicit poor solvent. A sample image of the diethylhexyl PPE polydot as prepared is shown in Figure 5.2e. The polydot equilibrated at 300K retained its spherical shape with a smooth interface dominated by the side chains as shown in Figures 2f,g after 300 ns for implicit poor and water respectively. Limited parts of the backbone reside at the particle interface.
Figure 5.2: Sample images of diethylhexyl PPE for (a) $t=0$ ns, (b) $t=0.5$ ns, (c) $t=0.75$ ns, (d) $t=0.9$ ns, (e) $t=1$ ns, (f) polydot in implicit poor solvent and, (g) polydot in water at 300 ns. The distances marked correspond to the dimension of the full object. For clarity, dark blue corresponds to Carbon atoms on side chains, Hydrogen atoms on side chains are white and all atoms on the backbone are represented by magenta.

Our previous results have shown that\textsuperscript{28} in both an implicit poor solvent and water, polydots remain compact over 100 ns at 300 K consistent with the experimental findings.\textsuperscript{15,16} The polydot immersed in water and in implicit poor solvent assumes the same radius of gyration, density profiles, and static structure factor $S(q)$. These similarities persist for both substituted and bare PPES. Here we probe in greater detail the dynamics of the polydots in water and implicit solvent at 300 K and study the effect of increasing the temperature in an implicit solvent.
Results and Discussion

A. Static Structure

Snapshots of diethylhexyl PPE polydots and polydots of the bare PPE in an implicit poor solvent are shown in Figure 5.3 at three temperatures. These polydots are depicted 300 ns after the removal of the constraint at 300 K and 300 ns after heating to higher temperatures. Two different conformations of the polydots, shown in Figures 2e and 2f, were then heated to 400 K and 600 K. Starting from both conformations resulted in the similar final state. However, the polydots heated from the equilibrated state at 300 K reached their final state faster than the polydot which started from the as made spherical configuration. Comparing the images in Figure 5.3a and Figure 5.3b, clearly shows that the conformation of the backbone of the polydots of substituted PPE differs from that of the backbone conformation of the polydots formed by bare PPE. The alkyl chains appear to prevent the close packing of PPEs without side chains. While some of the coiling observed may be a result of the preparation method, the tight packing in absence of the side chains is an inherent characteristic for conjugated polymers that are assembled without side chains. The comparison between the two conformations presented in Figure 5.3a and 5.3b provides a clear evidence that the side chains tune the internal conformation and, therefore, could serve as a potential design tool for polydots with specific photophysics.
Figure 5.3: Sample images of (a) alkyl substituted PPE and its backbone and (b) bare PPE in an implicit poor solvent after 300 ns. (c) Time evolution of substituted PPE polydots as function of time at 600 K. Carbon atoms on side chain of substituted PPE polydot are marked in dark blue and hydrogen atoms in white and backbone in both polydots are represented by magenta.
The radii of gyration $R_g$ of substituted PPE polydots in implicit poor solvents as a function of time for $T = 300$, 400, and 600 K are shown in Figure 4. At 300 K, after an initial small expansion in the first ns, $R_g$ remains constant over the entire length of the simulation. Increasing the temperature to 400 K of substituted PPE polydot results in a slow increase in the instantaneous $R_g$ over $\sim 150$ ns, after which the size of the polydots remains stable. The root mean square radius of gyration $<R_g^2>^{1/2}$ increases from $\sim 26$ Å at 300K to $\sim 28$Å for the substituted PPE polydot. For the bare PPE polydots, the increase is much larger, from $\sim 18$Å to $\sim 24.7$ Å and the chains rearrange to form a 2 nm diameter cavity. Both types of polydots become more aspherical at 400 K compared to 300 K. At 600 K, the increase in $R_g$ is more dramatic and the chains rearrange, as shown in Figure 3c for the substituted PPE polydots. For polydots of bare PPE, the size of the cavity increases to $\sim 4$nm in diameter. We attribute the formation of the hollow center to stress release as the temperature is raised.

Figure 5.4: Radius of gyration $R_g$ versus time of the substituted PPE polydot as a function of time at indicated temperature
The symmetry of the polydots was quantified through calculating the three eigenvalues of the moment of inertia tensor, \(\lambda_1, \lambda_2, \lambda_3\) for both types of polydots. For a fully spherical object, these three eigenvalues are equal.\(^{30}\) The calculated ratios of the eigenvalues for substituted PPE polydots, \(\lambda_3/\lambda_1 = 1.2\) and \(\lambda_2/\lambda_1 = 1.1\) and for bare PPE polydots, \(\lambda_3/\lambda_1 = 1.6\) and \(\lambda_2/\lambda_1 = 1.2\) in both implicit poor solvent and in water at 300 K. These values are larger than 1; i.e. the polydots shape diverges from a sphere. Increasing the temperature from 300 to 400 K, \(\lambda_3/\lambda_1\) increased from 1.2 to 1.4 for the substituted polydots and 1.6 to 2.0 for the bare polydots. These values are consistent with the visual observations in Figure 3 that the polydots become significantly more aspherical at higher temperature. The increase in asphericity with increasing temperature is consistent with the PPE chains assuming a more extended conformation within the confined state.

The radial density profiles of the polydots were calculated and the results at 300 K are shown in Figure 5 in water and in an implicit poor solvent. The density of the polydots with substituted PPEs is uniform, within the noise of the measurement. Due to the large stiffness of the backbone, the centers of the polydots with substituted PPE consist almost entirely of the flexible side chains, whereas the centers of the polydots of bare PPE are hollow. For the substituted PPE polydots, the solvent exposed outer surface is mostly comprised of the flexible side chains. As shown in Figure 5, it is notable that hardly any water molecules reside inside either of the polydot; however, at the boundary of the polydots with the solvent, a higher density of water is observed over a range of approximately 1 nm. The appearance of a broad water/polydot interface is in part due to the fact that the polydots are
not perfectly spherical, and their external interface is broad, particularly without side chains.

Figure 5.5: Radial mass density as a function of from the center of the polydot in water (diamonds) and in an implicit poor solvent (triangles) at T=300K for (a) substituted PPE and (b) bare PPE. The density of water is shown by squares. For polydot with side chains in (a) orange represents the side chains and magenta represents the backbone.

The temperature dependence of the radial densities of the polydots from their center of mass in an implicit poor solvent is shown in Figures 6a and b for the substituted and bare PPEs respectively. At 300 K the density of the substituted PPE polydots shown in Figure 6a forms a well-defined boundary with the solvent with undulations of the order of the radius of the substituted chain. Increasing the temperature to 400 K results in slight broadening of the interface with the solvent and broadening of the undulations. At 600 K, the density profile is smooth and broad, consistent with the expanded structure shown in
Figure 3. With increasing temperature, the bare PPE polydot reorganizes, as previously shown in Figure 3b, with a hollow center. This results in a density profile with its maximum offset from the center of mass, as seen in Figure 6b.

![Figure 3](image)

Figure 5.6: Density as the function of distance from the center of polydots for (a) substituted PPE and (b) bare PPE chains at indicated T. Black line represents entire polydot, red represents the side chains and green represents the backbone for substituted PPE, polydot in (a).

The relaxed polydots after 300 ns at 400 K and 600 K were cooled back to 300 K. After an initial slight decrease in the size, they remained in the configuration of the elevated temperature for 300 ns. This shows that once the polydots reach their higher temperature state, they remain in that state and do not return to the low-temperature, initial quasi-spherical shape.

While the overall structure of the polydots in solution is obtained computationally by visualizing the atomic coordinates, their overall shape and their internal structure are often determined experimentally through scattering techniques in which the overall structure
factor of the polydots, $S(q)$ is measured, where $q$ is the momentum transfer vector. Experimentally, the analysis of the scattering data is model dependent and requires further support. The correlation between results from simulations and scattering provides a powerful strategy to determine the structure of polydots in solution. The scattering factor of the polydots was calculated using

$$S(q) = \frac{1}{N} \sum_{i,j=1}^{N} b_i b_j \exp[iq \cdot (r_i - r_j)]$$

where $b_i$, $q_i$, and $r_i$ are the scattering length for neutrons, momentum transfer vector, and the position vector of atom $i$, respectively. Results for $S(q)$ were averaged over 500 configurations and 500 different $q$ vectors. $S(q)$ as a function of $q$ for polydots in an implicit poor solvent at different temperatures is shown in Figure 7. $S(q)$ shows a $q^\alpha$ dependence with $\alpha \sim 4$ in the intermediate $q$ regime, characteristic for a spherical object. These simulation results capture the shape of the polydots in the low $q$ region together with internal structural features at high $q$.

Figure 5.7: $S(q)$ as the function of $q$ for polydots with (a) substituted PPE and (b) bare PPE chains in an implicit poor solvent at the indicated temperatures. The solid line represents a fit to fuzzy sphere model.

With increasing temperature, $S(q)$ in the low $q$ regime for the polydot that consist of substituted PPEs, is shifted to lower $q$ values as expected for an object that expands, as
shown in Figure 5.6a. At 600 K, however, the slope $\alpha$ at the intermediate $q$ range changes from 4 to 2.3, consistent with the visual transition from a sphere to fused rings. Further, the peaks that correspond to the side chains and other internal dimensions broaden as expected from a more dynamic chain, which will be further discussed in the dynamics section. To compare with experimental studies and the visualization of the particle shown in Figure 5.3, a form factor of a fuzzy sphere$^{32}$ was used to fit $S(q)$. The form factor for a fuzzy sphere incorporates the typical sphere scattering convoluted with a Gaussian to account for the gradual drop-off in the density of the object. While the polydots at 300 K and 400 K could be well described by a fuzzy sphere form factor, the polydot at 600 K assumed a different shape. The value of the radius of gyration for polydots at 300 K and 400 K obtained from the fits fit are 25.1 Å and 30.7 Å, respectively, which are consistent with the calculated radii of gyration. Experimental studies of polydots in water have shown the evolution of their shape from spherical to oblate as the function of temperature$^{33}$ but did not access this high-temperature regime.

For polydots comprising of bare PPEs, with increasing temperature, $S(q)$ changes as the polydot loses its shape, as shown in Figure 5.7b. With increasing temperature, the slope decreases from $\alpha = 4$ to $\sim 2.2$, which validates the visual observation shown in Figure 5.3 that at higher temperatures the polydot becomes aspherical. In this case, $S(q)$ was fitted using the fuzzy sphere form factor at 300 K. The polydot at higher temperatures were fitted to a donut-like shape of the polydot.
B. Dynamic Studies

To examine the relaxation of the polydots on different length scales, we calculated the coherent dynamic structure factor $S(q, t)$, where $q$ is the momentum transfer vector and $t$, reflecting dynamics as measured by neutron spin echo spectroscopy. $^{34}$

$$S(q, t) = \frac{1}{N} \sum_{i,j=1}^{N} b_i b_j \langle \exp [i \mathbf{q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(0))] \rangle.$$

$S(q, t)$ was calculated using 2,000 configurations, each separated by 0.1 ns, and averaged over 500 q vectors. $S(q, t)/S(q, 0)$ for the polydot with substituted PPE chains as a function of time in water and in implicit poor solvent at 300 K are shown in Figure 5.8. The values of $q$ chosen correspond to a dimension of 1–10 nm, which probes the relaxation of the polydot together with their internal motions. In order to resolve the internal dynamics $S(q, t)$ was compared to that measured for the polydots whose translational motion was removed in the analysis. $S(q, t)$ is nearly independent of whether the center of mass motion is arrested in water, as demonstrated in Figure 5.8a, indicating that the translational diffusion of the polydot is slow and the relaxation observed is due largely to internal relaxation or rigid body rotation. This finding is consistent with the measured diffusion constant $D \sim 8.0 \times 10^{-5}$ nm$^2$/ns of the polydots or an average mean square displacement of 0.14 nm over the 40 ns time scale shown in Figure 5.8a. On the length scale of the polydots, hardly any relaxation occurs. At higher $q$ values, however, $S(q, t)$ decays, indicative of dynamic
processes within the length scales and Fourier times probed. Similar results were found for the polydot in an implicit poor solvent, as shown in Figure 5.8b. The overall trends in $S(q,t)$ obtained in the implicit poor solvent are similar to those obtained in the water. Comparing the diffusion constant of the polydot in water with that in the implicit poor solvent, $D \sim 3.4 \times 10^{-6} \text{ nm}^2/\text{ns}$, we find that the effective damping constant of water at 300K is $\sim 24$ fs.

Figure 5.8: $S(q,t)/S(q,0)$ as the function of time at 300 K for polydots with substituted PPE chain (a) in water and (b) in poor solvent. The dotted lines represent data without the center of mass subtracted and the dashed lines represent the data with the center of mass motion arrested. The solid line is the fit to the data with the center of mass motion removed. All the data have been fitted with single exponentials for $q < 0.1 \text{Å}^{-1}$ and double exponentials for $q > 0.1 \text{Å}^{-1}$.
S(q,t) for the polydot in water and in poor solvent at 300K with the center of mass removed was analyzed to extract the effective diffusion coefficients $\Gamma_i$. A single exponential fit the data for $q < 0.1\text{Å}^{-1}$, while for $q > 0.1\text{Å}^{-1}$ a sum of two exponentials, $S(q,t)/S(q,0) = A_1e^{-\Gamma_1 t} + (1-A_1)e^{-\Gamma_2 t}$, is required to fit the data. The values for the effective diffusion $\Gamma_1$ and $\Gamma_2$ as a function of $q$ are presented in Figure 5.9 (by definition $\Gamma_1 < \Gamma_2$). The overall trend shows that the effective diffusion constant increases with increasing $q$, $\Gamma_1 \sim q^x$ with $x \sim 2.6$ for water and 2.2 in implicit solvent at 300K. The relaxation is slightly slower (larger $\Gamma_i$) for the polydot in water than in implicit poor solvent, presumably due to the effect of the interfacial water compared to an implicit solvent.

![Figure 5.9: $\Gamma_1$ (black circles) and $\Gamma_2$ (red squares) as the function of $q$ for polydot of substituted PPE in water (open) and implicit poor solvent (closed) at 300K.](image-url)
The dynamic structure factor in an implicit poor solvent at 300 and 400 K is shown in Figure 5.10. At high q values, which measure the internal motions including the side chain dynamics and backbone fluctuations, $S(q,t)$ fully decays within the time range measured at both 300 and 400 K. However as the temperature increases, $S(q,t)$ decays faster over the time scale measured. The values for the effective diffusion $\Gamma_1$ and $\Gamma_2$ as a function of q are presented in Figure 5.11 ($\Gamma_1 < \Gamma_2$). For the slowest relaxation $\Gamma_1$ the scaling exponent $x$ decreases from 2.2 to 2.0 as the temperature is increased from 300 to 400 K. The overall internal effective diffusion increases with increasing temperature.

Figure 5.10: $S(q,t)/S(q,0)$ as the function of time for polydots of substituted PPE in a poor solvent at a different temperature.
Figure 5.11: $\Gamma_1$ (open symbol) and $\Gamma_2$ (closed symbol) as the function of $q$ for polydot of substituted PPE chain in an implicit poor solvent at the indicated temperature.

To separate the internal relaxation from the rigid body rotation, we also simulated the polydot in a poor solvent with the constraint that the linear and angular momenta of the entire object are both zero. $S(q,t)$ for this case is shown in Figure 5.12a. $S(q,t)$ decays very slowly, as the overall motion of the polydot has been removed. These data show that when the backbone and side chains were probed separately as shown in Figures 5.12b, the side chains remain dynamic, while the backbone of the confined PPE chain is glassy. For short time scales of a few picoseconds, the relaxation is due predominantly to the motion of the side chains. To further validate that the side chain motion is predominant, we measured the mean square displacement for the end C atom of the side chains; the results show that they move, on average, 1.6 nm in 1 ns, which accounts for the observed decay in $S(q,t)$. 
Figure 5.12: (a) $S(q,t)/S(q,0)$ as the function of time for polydots of substituted PPE chain in poor solvent at 300 K with the both angular and linear momentum set to zero. (b) Represents $S(q,t)/S(q,0)$ of side chains (dashed lines) and backbone (solid line) of polydots for $q = 0.06 \text{ Å}^{-1}$ (black), $q = 0.10 \text{ Å}^{-1}$ (red), $q = 0.23 \text{ Å}^{-1}$ (green), $q = 0.37 \text{ Å}^{-1}$ (blue) and $q = 0.63 \text{ Å}^{-1}$ (orange).

The $S(q,t)$ decay pattern of the backbone shows that in the confined geometry the backbone is glassy. The autocorrelation function $\langle N(t) \cdot N(0) \rangle$, where $N(t)$ is the normal to the plane of the aromatic ring, was then measured. While it takes only about 3 ns for the aromatic ring to rotate and become uncorrelated for an extended PPE chain, under confinement the motion is significantly restricted, as shown in Figure 5.13.
Figure 5.13: Autocorrelation function for aromatic rings in substituted PPE backbone of polydot in a poor solvent with linear and angular momentum arrested (red). Blue line represents the best fit to stretched exponential. The lower inset shows the backbone of polydot where red colored aromatic rings have rotated more than 180° after 200 ns and the upper inset shows 10 aromatic rings of the backbone at indicated time.

The inset shows the backbone of the polydot, in which aromatic rings that have undergone rotation of > 180° after 300 ns are represented in red. The snapshot clearly shows that the rings are free to rotate and are distributed throughout the polydot, not just confined to the interface. The relaxation does not fit a simple exponential but can be fit using the Kohlrausch-Williams-Watt (KWW) function $\langle N(t)\rangle = A \exp(-t/\tau)_\beta$, where
β is the stretched exponential and τ is the characteristic relaxation time for motion. The fitted values of τ = 3.5 μs and β = 0.8.

**Conclusions**

This study has provided for the first time an insight into the structure, stability, and dynamics of soft nanoparticles or polydots. The conformation and dynamics of the polymers within their confined geometry were probed as a function of temperature for alkyl-substituted PPE and bare PPE chains. We find that the substituting side chains strongly impact the overall conformation of the PPE polydots and affect their structure and stability. The presence of side chains results in a random pattern of the PPE backbones within the polydots in contrast to more periodic structures without the side chains. With increasing temperature, the polydots evolve from spherical to aspherical objects and, surprisingly, develop cavities in their centers. The decrease in density in the center of the polydots is more pronounced for bare PPE polydots. We attribute these conformational changes to a stress release path of the PPE, whose lowest energy conformation is extended.

The dynamic studies have shown that the backbone of the PPE within the polydot is glassy and hardly moves, while the side chains remain dynamic. The autocorrelation of the aromatic rings results in a time constant in the microsecond range, while the side chains remain dynamic in the nanosecond time range. With increasing temperature, the polydots slightly expand, and the chains become more dynamic. However, the backbone motion is hardly increased.

This study has shown that polydots are glassy soft nanoparticles whose internal conformation and dynamics are tunable by the nature of the substituents of the conjugated...
backbone. This understanding provides an insight into designing tools for soft polymeric nanoparticles with tunable photophysics.

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 CHAPTER SIX
STRUCTURE OF RIGID POLYMERS CONFINED TO NANOPARTICLES:
MOLECULAR DYNAMICS SIMULATIONS INSIGHT

Abstract

Nanoparticles (NPs) grafted with organic layers form hybrids able to retain their unique properties through integration into the mesoscopic scale. The organic layer structure and response often determine the functionality of the hybrids on the mesoscopic length scale. Using molecular dynamics (MD) simulations we probe the conformation of luminescent rigid polymers, dialkyl poly para phenylene ethynylenes (PPE), grafted onto silica nanoparticles in different solvents as the molecular weights and polymer coverages are varied. We find that in contrast to NP-grafted flexible polymers, the chains are fully extended independent of the solvent. In toluene and decane, which are good solvents, the confined PPEs assume a similar conformation to that observed in dilute solutions. In water which is a poor solvent for the PPEs, the polymer chains form one large cluster but remain extended. The radial distribution of the chains around the core of the nanoparticle is homogeneous in good solvents whereas in poor solvents clusters are formed independent of molecular weights and coverages. The clustering is distinctively different from the response of grafted flexible and semi-flexible polymers.
Introduction

Polymers grafted onto nanoparticles (NPs) are inherent to designing new functional organic-inorganic hybrid materials with a wide range of potential applications from lightweight materials and electro-optical devices to biological applications. Their size and shape largely govern the properties of the NPs. The collective behavior of organically grafted NPs depends on the interactions between the particles themselves and that of the tethered chains and their environment. The technological significance of these hybrids has driven numerous studies to probe the properties of the organic layer with the majority focusing on brush-like flexible polymers. Of particular interest are NPs grafted with luminescent polymers, where soft chromophores are tethered to an inorganic core. The photophysics of these hybrids is potentially tunable through the unique combination of the nanoscale properties of the NPs with the control of optical characteristics offered by the conformation of macromolecules. Luminescent polymers are often stiff and their light emitting characteristics strongly depends on their degree of tethering. However, while confined flexible polymers have been thoroughly studied, there is limited understanding of confinement effects on the conformation of rigid polymers. Here we probe the conformation of rigid polymers grafted to NPs. In contrast to flexible polymers, we find that inter polymer clustering dominates the response of these macromolecules crowding and reduced solvent quality.

In-depth studies of flexible polymers tethered to NPs have shown that in good solvents the chains form brush-like or swollen corona structures while accounting for curvature of the NPs similar to polymers confined to flat surfaces. However in poor
solvents, the geometry of the grafting surface often drive inhomogeneity of the tethered chains. Unlike flat interfaces, the NPs curvature offers the chains additional free volume to explore even for high grafting density.\textsuperscript{15-18}

With a rich field of nanoparticles and rigid luminescent polymers this study centers on one hybrid that consists of silica NPs grafted by dialkyl \textit{para} phenylene ethynylene (PPE). Silica NPs are ubiquitous and offer a coverage that can be readily controlled via the number of hydroxyl groups at the interfaces. Silica NPs are effective for bioapplications because their low toxicity, high dispersion and are easily functionalized.\textsuperscript{19, 20} Further, silica PPE hybrids bear a potential as tunable biomarkers\textsuperscript{3} whose fluorescence can be altered by modifications of the substituents on the polymer backbone and solvents.\textsuperscript{21}

PPEs are rigid polymers whose structure in solution and at interfaces has been well studied.\textsuperscript{23, 24} Further, the conformation of the individual PPE chains coupled with their aggregation state determine their electronic and photophysical properties.\textsuperscript{13,25} The backbone of PPE consists of alternate single and triple bonds in conjunction with aromatic rings, as shown in Figure 6.1. The single bonds along the backbone allow the aromatic rings to freely rotate around the long axis of the molecule. For aromatic rings along the PPE backbone, confined into one plane, the overlap of $\pi$ orbitals results in delocalization of electrons forming extended conjugated segments. The photophysics of PPEs is therefore highly dependent on the backbone conformation.
Neutron scattering studies have shown that in solution PPEs exhibit three distinctive phases: dilute solutions in which the molecules are isolated and assume an extended configuration, micellar phase in which the PPEs form flat aggregates, and a fragile gel phase formed by aggregates jamming into each other.\textsuperscript{26} Our molecular dynamics (MD) simulations have further confirmed that in contrast to many conjugated polymers\textsuperscript{27}, dialkyl PPEs assumes extended conformation in dilute solutions up to $n = 2000$ monomers. The end-to-end distance scales linearly with the number of monomers independent of solvent quality.\textsuperscript{28}

Here, we use MD simulations to study chain conformation and structure of diethylhexyl PPE chains tethered to silica NPs as a function of molecular weight and coverage as well as the interaction of the PPEs with different solvents. Specifically the hybrids are studied in toluene, decane and water. Toluene is a good solvent for the
backbone of the PPE, decane is a good solvent for the side chains, and water is a poor solvent for both the PPE side chains and backbone. We find that similar to solution structure, independent of the solvents, the confined PPE chains remain extended. In contrast to flexible polymers with the decreasing quality of solvent, PPE chains cluster.

This paper is organized as follows: Section II presents the simulation model and methodology, Section III discusses the conformation and orientation of polymer chains around the NP core including radial mass density as a function of solvent quality, coverage and chain length and section IV presents a brief summary and conclusions.

**Simulation Methodology**

All of the simulations used OPLS-AA (Optimized Potentials for Liquid Simulations-All Atoms) force fields of Jorgensen and co-workers. Nonbonded interactions consist of a sum of standard 12-6 Lennard-Jones (LJ) and electrostatic potentials, with the nearest and next-nearest neighbor pair excluded and interaction reduced by a factor of 2 for all 1-4 neighbor pairs. All LJ interactions were cut off at $r_c = 1.2$ nm. The OPLS-AA potentials also include harmonic bond and angle terms and torsional interactions. The long-range Coulomb interactions were calculated with the particle-particle particle-mesh (PPPM) algorithm with precision of $10^{-4}$. Coulombic interactions for two atoms closer than 1.2 nm are calculated directly, while those outside this range are calculated in reciprocal Fourier space.

Fifty diethylhexyl PPE chains of $n=6$, 20 and 40 monomers were grafted to a 5 nm diameter silica NP with resulting coverage of 0.64 chains/nm$^2$. 5 nm is the smallest size that can conveniently be made monodispersed experimentally. For the shortest chain length
of 6 repeat units, higher coverages of 0.90 (70 chains) and 1.14 chains/nm$^2$ (90 chains) were also studied. This is comparable to the maximum coverage of ~1.16 chains/nm$^2$ for PPE chains with a flexible spacer at the attached end of the chain on a glass substrate.$^{21}$ PPE chains as well as toluene, decane and water samples were made using Polymer Builder and Amorphous Cell modules of Material Studio from Accelrys Inc©. The as-built samples were initially run with polymer consistent force field (pcff) in Material Studio and then converted to OPLS. All of the MD simulations were carried out using the LAMMPS classical MD code.$^{32}$ Numerical integration was performed using velocity-Verlet algorithm with a time step $\delta t = 1$ fs. Most of the simulations were carried out at a constant volume using a Langevin thermostat with a 100 fs damping constant.$^{33,34}$

The nanoparticle was cut from a bulk amorphous silica which was generated from a melt-quenched process as described by Lorenz et al.$^{35}$ and then annealed to produce a surface with OH concentration consistent with experimental values.$^{36,37}$ The NP was treated as a rigid body. The PPE chains were attached to the NP by randomly removing hydrogen atoms from the silicon surface OH groups and a hydrogen atom from one of the terminal carbons on the PPE chain. A new bond was then formed between the carbon of PPE chain and the surface oxygen. A minimum separation of 0.7 nm between grafting sites was maintained to avoid overlap of the chains. To maintain charge neutrality, the charges on the oxygen atom on the surface, the two hydrogen atoms and the carbon atom at the point of attachment were modified based on the OPLS charges for an ester group. For these connecting atoms, the charge of H was changed from 0.06 to 0.03, O from -0.683
to -0.465 and C from -0.12 to 0.14. All charges of all the other C and H atoms along the PPE chains are same as that of a free PPE chain.

The solvents were prepared at T = 300 K and pressure P = 1 atm using the Nosè-Hoover temperature thermostat/barostat. Resulting densities of 0.867, 0.723 and 0.989 g/cc for toluene, decane and water respectively are within 0.5% or less of experimental values. The samples consist of 43,200 toluene molecules, 49,890 decane molecules and 512,000 water molecules, which were sufficient to completely solvate the silica nanoparticle grafted with short PPE chains (6 repeat units) which contained 23,365 atoms for 0.64 chains/nm² (4965 atoms in the silica nanoparticle and 18,450 atoms for 50 PPE chains each containing 369 atoms) in a periodic box. A void was created in each solvent sample to accommodate the nanoparticle by inserting a soft-repulsive spherical pseudo-particle into the solvent. The radius of the pseudo-particle was increased from an initial radius of zero to a size capable of accommodating the NP-PPE hybrid. When the desired size was reached, the pseudo-particle was removed leaving a void in the center of the sample. The systems were further equilibrated for 1 ns before the hybrid and the solvents were merged. The combined system was equilibrated for 2 ns at a constant pressure of P=1 atm after which the system was run at constant volume. The length of the final simulation cell was 4.0 nm larger than the diameter of silica nanoparticle decorated with the PPE, which was sufficient to prevent the interaction of PPE with itself through the periodic boundaries. Water was modeled using the SPC/E water model with the SHAKE algorithm used to constrain the O-H bond length and H-O-H angle.
The hybrids were also studied in implicit solvents whose quality was controlled by varying the strength of the attractive interactions between non-bonded atoms. For poor solvent, all the Lennard-Jones non-bonded interactions were truncated at a cutoff radius $r_c = 1.2$ nm. For good solvent, all the Lennard-Jones interactions were truncated at the potential minimum ($r_c = 2^{1/6} \sigma_{ij}$). The silica nanoparticles grafted with short chains were studied in toluene, decane and water at coverage of 0.64 chains/nm$^2$ whereas all other systems, with higher molecular weights and higher coverage, were studied only in an implicit solvent due to the high computational resources required for explicit solvent simulations.

All simulations were run for ~30 ns at 300 K and then heated to 600 K for ~30 ns to allow the systems to equilibrate. The systems were considered to be equilibrated if the end-to-end distance of the chains and total radius of gyration of the entire system remained constant during the simulation time. We found that after 10-30 ns, these quantities did not change. The systems were cooled back to 300 K at rates of 150 K/ns and 15 K/ns and then run for an additional 10 ns which was sufficient to equilibrate the system. As the conformations and density profiles for the two cooling rates are indistinguishable, all the results presented will be for systems cooled from 600 to 300 K at 150 K/ns rate and then run for 10 ns.

**Results and Discussion**

*a-Hybrid Formation* The hybrids in an implicit solvent at different temperatures are shown in Figure 2a. Starting from the homogeneous, extended state at 300 K, the chains form a number of clusters that are kinetically trapped. After thermally annealing the system at 600
K, the clusters merge and reach a state closer to equilibrium. For this reason all the results below are presented after heating to 600 K and then cooling back to 300 K.

The degree of clustering is described through mapping the position of the chains around the NP creating a *radial space map*. The position of each chain is defined by measuring the solid angles of the long axis of the chains with respect to y-axis as described in Figure 6.2b. The long axis of the chains is defined by a vector $r$ that propagates from of the terminal carbon atom of each chain to the center of mass of the NP. The azimuthal angle $\theta$ which varies from 0 to $\pi$ and the polar angle $\phi$ that ranges from 0 to $2\pi$ are determined for each of the chains. An area-preserving mapping, plotting $\phi \sin \theta$ as a function of $\theta$ was used to convert these 3D spherical angular coordinates into two dimensions where the relative orientation of the chains is represented by the points in the plot.\(^{43}\) The initial homogenous density distribution of these points on the mapping corresponds to homogeneous distribution of chains around the NP; heterogeneous distribution reflects clustering of chains.
Figure 6.2: (a) Images of silica NP with 50 chains of diethyl hexyl PPE chains of n=6 at different temperatures in poor solvent. b) The schematic representation of solid angle for distribution of PPE chains around silica nanoparticle in (i). Distribution of PPE chains around silica NP with 50 PPE chains in implicit poor solvents at 300 K and 600 K at t = 0 (black circle), t = 10 (red square), 20 (green diamond) and 30 ns (blue triangle).

Figures 6.2b presents the relative position of PPE chains at four different times in the kinetically trapped state at 300 K and after heating to 600 K in implicit poor solvent. In this presentation, each symbol corresponds to one polymer chain. For 600 K, t = 0 corresponds to the time when the temperature was raised from 300 to 600 K. Each symbol corresponds to one polymer chain. At 300 K the chains quickly aggregate to form a number...
of small clusters which are largely immobile. At 600 K, the clusters merge and form a very inhomogeneous structure. To avoid the kinetically trapped state at 300 K, all the results in the following sections are at 300 K after thermal annealing at 600 K.

b- Solvent Effects

The hybrid was studied in solvents of different quality. Figure 6.3 shows equilibrated hybrids with short PPE chains in several solvents including an implicit good solvent, toluene, decane, an implicit poor and water. In toluene and decane, solvents which are preferential to the backbone and side chain respectively, the PPE chains remain extended and separated from each other. This elongation remains even in implicit good solvent where the solvent is as good for all PPE components. In water, the PPE chains remain extended but they form a large cluster with all chains collapsing in average to one side of the NP. Similar behavior is observed in the implicit poor solvent, with a slight difference in the overall number of clusters. While the curvature of the grafting surfaces impact the interfacial profiles of polymers we find that for these rigid PPEs, the polymers confined to a highly curved surfaces assume a similar configuration to that of PPEs confined to a flat silica substrate.\textsuperscript{22}
In all the solvents, the polymer chains remain extended as shown by the average end-to-end distance calculation of ~ 45 Å. The extended configuration of the confined PPE chains in all solvents, independent of their radial distribution is rather surprising. However it is consistent with our previous MD simulations of dialkyl PPEs in the dilute limit for both explicit and implicit solvents$^{28}$ in which PPE molecules assume a rigid rod-like
conformation in all solvents. Confinement to a highly curved surface drives association as was observed experimentally in dilute toluene solutions.\textsuperscript{26}

Figure 6.4: Radial mass density from the center of nanoparticle core for the PPE chains at T=300 K in indicated solvents.

The radial mass density profile of the PPE chains as a function of the distance from the center of mass of the NP in different solvents is shown in Figure 6.4. Two groups of profiles one for the good and one poor solvents are observed. In toluene, decane and implicit good solvents the profiles consist of distinctive undulations that decay with distance from the center, whereas in water and implicit poor solvent a single signature is observed. In toluene, decane and implicit good solvent, the highest of the densities corresponding to the amplitude of the adulations is $\sim 0.4 \text{ g/cm}^3$, with a second height of
~0.3 g/cm³. We will show that for higher grafting density hybrids, these features are at separations which correspond to the locations of aromatic rings along the chains.

In water, a single feature with a density of ~ 0.85 g/cm³ dominates the profile which is consistent with the snapshots shown in Figure 3, where chains are clumped on one side of the NP. In implicit poor solvent, a single prominent signature at ~1.1 g/cm³ is observed and consistent with the aggregation.

Figure 6.5: Distribution of PPE chains with n=6 around of silica NP with grafting density of 0.64 chain/nm² in (a) toluene, (b) decane, (c) implicit good, (d) water and (e) implicit poor solvents at 300K. t = 0 (black circle), t = 5 ns (red square) and t = 10 ns (green triangle).
The clustering as decided by the spatial correlations of the chains are shown in Figures 6.5a-d where \( t = 0 \) is the starting state after annealing from 600 K to 300 K, followed by measurements at \( t = 5 \) and 10 ns. Each symbol corresponds to a polymer chain. At \( t = 0 \), in all three good solvents, toluene, decane and implicit good, the points are dispersed. Following the relative position of the chains as a function of time shows that hardly any of the chains coincide with their starting positions and the homogeneous distribution is maintained. These results confirm that there is no clustering between the PPE chains in the good solvents and the chains are dynamic.

In water and implicit poor solvents at \( t = 0 \) the PPE chains are strongly correlated with each other as the black circles are clustered and shows heterogeneous distribution of PPE chains. Further, most of PPE chains are oriented to one side of the NP as shown in Figures 6.5d and e. Following the position of the chains with time shows that though the PPE chains form several clusters, the PPE chain position changes as a function of time as reflected in the fact that there is a time evolution of points in space. This could be attributed either to some freedom of the PPE chains or rotation of the entire hybrid.

The morphology of the clusters in poor solvents is asymmetric and is a result of minimization of contact area of the PPEs with the solvent while retaining the PPEs extended conformation. These types of asymmetric clusters have been observed in previously by Lane and Grest\(^4^4\) for alkanethiol coated Au nanoparticles in water at high grafting density when the length of the attached polymer is larger than the size of the NP. As is the case here, the chains associate to one side of the NP to reduce contact with the solvent. For NPs comparable to and larger than the length of the chain, in poor solvents the
chains form multiple clusters since the constraint on the chain ends being tethered to the surface limits their association.

Internal correlations within the PPE chains were probed through extracting the first-order orientation order parameter \( P_\theta = \frac{1}{2} (3 <\cos^2 \theta> - 1) \). \( P_\theta \) corresponds to the average alignment of aromatic rings with a particular spatial direction and \( \theta \) is the measure of deviation perpendicular to the interface for two aromatic rings, which are separated along the backbone by a degree of polymerization \( \Delta n \).\(^{45}\) In all solvents studied, no correlations were observed. These results, which are not shown since \( P_\theta \) is zero for all \( \Delta n \) for the confined state, are similar to those previously observed for PPE chains in dilute solutions.\(^{28}\)

**c-Coverage effects** Short PPE chains of 6 monomers grafted to silica NP’s surface have been studied as the coverage was increased from 0.64 to 0.90 and 1.14 chain/nm\(^2\) in both implicit poor and good solvents. The hybrids with different coverages are shown in Figure 6.6 together with the corresponding radial space map. In implicit good solvents, the polymer chains are extended and remain unassociated. The measured end-to-end distance does not change with the increasing coverage for these rigid polymer chains. In implicit poor solvent for all three coverages, the PPE chains form clusters which become more defined with an increasing coverage, as expressed in the bunching of location reflected in the radial space map. Small changes observed as a function of time correspond to the rotation of the entire hybrid. This is in contrast with flexible polymer chains grafted onto flat\(^{18}\) and curved\(^{37,39,46}\) surfaces in which the polymer chains become increasingly extended with increasing grafting density.
Figure 6.6: Images of silica NP grafted with coverage of (a) 0.64 (b) 0.90 and (c) 1.14 chain/nm$^2$ in implicit poor solvent at 300K and distribution of PPE chains.

The radial mass density as a function of distance with increasing coverage in implicit poor and good solvent are shown in Figures 6.7a and b. In implicit poor solvent, a single feature, which peaks at a density of $\sim1.1$ g/cm$^3$ for the lowest coverage and shifts to density of $\sim0.9$ g/cm$^3$, is observed. Further oscillations are observed, for higher coverages, which are not directly correlated to an obvious molecular dimension. The density profiles of the PPEs in implicit good solvent consist of six oscillations that become more distinct with increasing coverage. These correspond to the position of the center of six aromatic rings evenly distributed away from the center of the hybrids. The height of these peaks
decreases as the distance from the surface increases. While there position is well defined, increasing coverage does not lead to any correlations between the orientations of the aromatic rings.

Figure 6.7: Radial mass density from the center of nanoparticle core for the PPE chains as a function of distance in (a) poor solvent and (b) good solvents at 300 K for 0.64 (black circles), 0.90 (red squares) and 1.14 chains/nm$^2$ (green triangles). Inset in (b) is the snapshot of silica nanoparticle with 90 chains (1.14 chains/nm$^2$) in implicit good solvent.

d- Molecular weight effects. The molecular weight of PPE chains was increased from n = 6 to 20 and 40 keeping coverage at 0.64 chains/nm$^2$. Snapshots of equilibrated hybrids at 300 K, following heating to 600 K and then cooling back again to 300 K are shown in Figure 6. 8a for n=40. For these longer PPE chains a unique aggregation pattern is observed centered around the silica NP. The polymer chains form a supramolecular branched morphology. Heating to 600K enables a rearrangement process that decreases the
degree of branching. The structure formed at 600K is retained as the temperature is decreased.

Figure 6.8: a) Images of silica nanoparticles grafted with longer PPE chains for \( n = 40 \) and 0.64 chains/nm\(^2\) in a poor solvent at indicated temperatures. b) Backbone of chains in one of the clusters from image on the right.

Similar to lower \( n \) hybrids no correlation of the aromatic rings or any \( \pi-\pi \) stacking takes place as demonstrated in zooming into one branch in Figure 6.8b. This dependence on molecular weights is distinctively different from that of grafted flexible polymers that form a dense collapsed layer at the interface with poor solvents.\(^{16}\) The nature of these
aggregates in confinement is similar to that observed experimentally in solutions, where PPEs aggregate with the molecules randomly stacked.\textsuperscript{26}

In implicit good solvent for all molecular weights, the PPE chains remain extended. In implicit poor solvent however, the mean square end-to-end distance of the PPEs $<R^2>^{1/2}$ /n is ~ 7.4 Å, 6.7 Å and 6.3 Å for n = 6, 20 and 40 respectively. While the chains become slightly less extended with increasing molecular but they do not coil or collapse on the NP’s surface. This is significantly different from polymer brushes that assume a Gaussian profile which becomes thicker with increasing molecular weight.

**Conclusions**

This study has shown that by changing the solvent quality, coverage and molecular weight, we can tune the conformation of attached PPE chains. We find that in contrast to NP-grafted flexible and semi-flexible polymers, the PPE chains retain an extended conformation independent of the solvents quality. The PPE chains become less extended with the increase in molecular weight whereas the coverage has no effect. In poor solvents the chains tend to form clusters and are whereas in good solvents they tend to remain homogeneous for all molecular weights and coverage. These clusters become more defined with the increase in coverage. Further analysis of the clusters formed by the polymer chains in the poor solvents shows that there is no π-π stacking between the aromatic rings of different polymer chains. As in our previous results for extended PPE chains in dilute solution,\textsuperscript{28} solvent quality, coverage and molecular weight have no effect on the correlation between the orientations of the aromatic rings of polymer chains grafted on silica NP.
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References


CHAPTER SEVEN

SUMMARY

The goal of this research was to study the conformation and dynamics of poly
\textit{para} phenylene ethynylenes (PPEs), PPEs confined into polydots and polymer grafted on
to the silica nanoparticles using molecular dynamics (MD) simulations. The forces
between the nanoparticles were also studies. The research findings of the studies are
summarized below.

1. Conformation of a single chain of polymers in dilute solutions: The
conformation of a single chain of dialkyl substituted PPEs in toluene, implicit poor and
implicit good solvents has been studied. The chains were fully extended, independent of
solvent quality or the nature of the side chains. No correlation between the aromatic rings
within the PPE backbone, in either poor or good solvents. The side chains were more
dispersed in toluene and in the good solvent than in the poor solvent. It showed that even
though the molecules were extended, local dynamics was retained.

2. Structure and stability of polydots in different solvents: The structure and
stability of the bare and substituted polydots were studied in four different solvents and
followed as a function of time. In water and in a poor solvent, the polydots remained
predominantly spherical and compact whereas in toluene as well as in a good solvent, the
polydots unraveled as a function of time. The alkyl side chains affected the symmetry of
the polydot in the water, where substituted polydot formed a more spherical NP. No
internal correlations were observed between the aromatic rings on the polymer within the
polydot.
3. Conformational dynamics of polydots: The conformation and dynamics of confined polymers, polydots were studied as a function of temperature for alkyl substituted PPE and bare PPE chains, and we found that the substituting side chains strongly impacted the overall conformation of the PPE as well as their structure and stability. The presence of side chains resulted in a random pattern of the PPE backbone within the polydots in contrast to a more periodic structure without the side chains. With increasing temperature, the polydots evolved from spherical to aspherical objects and, surprisingly, developed a cavity in their center. The decrease in density in the center of the polydots was more pronounced for bare PPE polydots.

The dynamic studies have shown that the backbone of the PPE within the polydot is glassy and hardly moves while the side chains remain dynamic. The autocorrelation of the aromatic rings results in a time constant in the microsecond range while the side chains remain dynamic on the nanosecond time range. With increasing temperature, the polydots slightly expand and the chains become more dynamic. However, the backbone motion hardly increases.

4. Morphology of the PPE chains grafted onto inorganic nanoparticles: The polymer chains grafted on to silica nanoparticles have an extended conformation independent of the solvent’s quality. With the increase in molecular weight (repeat units), the chains become less extended whereas the coverage has no effect. In poor solvents, the chains formed clusters whereas in good solvents they remained homogeneous for all molecular weights and coverage as shown by the orientation of the chains around NP’s core calculations. These clusters become more defined with the increase in the coverage.
Further analysis of the clusters formed by the polymer chains in the poor solvents shows that there is no \( \pi-\pi \) stacking between the aromatic rings of different polymer chains. As in our previous results for extended single PPE chains, the solvent quality, the coverage and the molecular weight have no effect on the correlation between the orientations of the aromatic rings of polymer chains grafted on silica NP.
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APPENDIX

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