Chapter-4

Polyurethane-Oligophenylenevinylene Random Block Copolymers: Morphology and Photophysical Properties
Chapter 4  Luminescent Polyurethane Copolymers

4.1. Introduction

Polymeric assembled materials with well-defined structure on sub-micrometer and nanometer scales have fascinated researchers due to their broad potential applications in micro-and nanotechnology.\textsuperscript{1-6} Supramolecular architectures have been assembled by non-covalent secondary interactions of appropriate tectons through hydrogen bonding,\textsuperscript{5,7-9} electrostatic,\textsuperscript{10-11} aromatic π-π stacking,\textsuperscript{12-13} metal-ligand,\textsuperscript{14-15} van der Waals forces\textsuperscript{16} and charge transfer interactions,\textsuperscript{17} etc. Wurthner et al. have developed mesoscopic superstructures by complexing perylene bisimide derivatives with a ditopic melamine unit. In these structures, multiple orthogonal intermolecular interactions such as hydrogen bonding, π-π stacking and vander Waals interaction along with solvent polarity play major roles in obtaining cylindrical strands (scheme-4.1).\textsuperscript{18}

![Cylindrical Superstructure](image)

Scheme-4.1: Self-organization in complexes of perylene bisimide with melamine units (adapted from ref. 18)

Among these secondary interactions a great deal of effort has been made to self-organize molecules using π-stacking for use in molecular electronics such as field effect transistors, light emitting diodes and photovoltaic cells, etc.\textsuperscript{19} Mesoscopic ordering in π conjugated systems for their successful use in such devices depends greatly on their supramolecular organization brought about by controlling their chemical structure or by various processing methodologies.\textsuperscript{20} Recently, solvent induced self-organization of polymeric chains in the molecular level has been

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explored to produce a variety of supramolecular architectures such as honeycomb patterns, micelles and vesicles. Xie et al. have recently reported on the formation of mixed polymeric micellar clusters through the hydrogen bonding interaction between the PAA blocks in a PS-b-PAA (polystyrene-b-poly(acrylic acid)) copolymer with the PEO blocks in a PS-B-PEO (polystyrene-b-poly(ethylene oxide)) copolymer. Bang and coworkers studied the aggregation of asymmetric poly(styrene-b-isoprene) in organic solvent such as dialkyl phthalates in various combinations. They observed the formation of spheres, cylinders or vesicles depending upon the solvent combinations employed, suggesting the importance of solvent towards the formation of various self-organized structures (scheme-4.2).  

Scheme-4.2: Cryo-TEM images of poly(styrene-b-isoprene) showing varied morphologies such as spheres(a), cylinders (b) and vesicles (c) in different combinations of dialkyl phthalates as solvent (adapted from ref. 23)

Various types of polymeric architectures such as star polymers, and block copolymers of amphiphilic, rod-coil diblock and triblock and dendronized block copolymers, polyacrylates, and cellulose acetate butyrate, etc. have been reported for forming regular micron to nano-sized patterns in films. Among them polystyrene-conducting block copolymers showing high degree of ordering and strong periodicity have been studied because of their applications in various opto-electronic devices. de Boer et al. synthesized a rod-coil copolymer consisting of poly(2,5-dioctyloxy-p-phenylenevinylene) as the rod block and polystyrene as the coil. The
films of these polymers prepared from carbon disulfide were found to exhibit uniform honey-comb morphology as shown in scheme-4.3.36

Another attempt was made by Jenekhe et al. for the self-organization of rod-coil copolymer consisting of polystyrene coil block and poly(phenylquinoline) rod block in carbon disulfide. They observed discrete micellar aggregates in the form of soft hollow spheres as shown in scheme-4.4 (a and b). With the increase in concentration of the polymer solution stacks of one to eight layers of hexagonally close packed two dimensional lattices of spherical air holes in a polymeric matrix was observed (scheme-4.4c).27
Polyurethanes belong to the class of engineering thermoplastics bearing elastomeric properties due to the presence of reversible hydrogen bonds via hard-soft block self assembly. Recently, polymers containing π-conjugated oligomer: oligo-phenylenevinylene (OPV) with carbamate (urethane) linkages have been synthesized to study the performance of these polymers for opto-electronic devices, mechanochromic properties and as light emitting electrochemical cells, etc.\textsuperscript{37-40} However, there are no reports in the literature to utilize the potential of reversible hydrogen bonding in polyurethane (or polyurea) to induce various types of morphological evolution in π-conjugated polymers.

This chapter aims at synthesizing a new series of polyurethane-oligo (phenylenevinylene) random block copolymers and to utilize these copolymers to study the morphological evolution via solvent induced self-organization process in a π-conjugated backbone. The random block copolymer (scheme-4.5) has two types of secondary interaction modes namely hydrogen bonding (via hydrophilic urethane linkage) and π-stacking (via hydrophobic aromatic OPV units), and therefore, it opens up a new opportunity to trace the solvent induced self-organization by both microscopic and various spectroscopic tools.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Scheme-4.5.png}
\caption{Structure of polyurethane-oligo(phenylenevinylene) block copolymer}
\end{figure}

The random block copolymers were synthesized using a non-isocyanate and solvent free melt transurethane process as described in chapter-2. A hydroxyl terminated oligo(phenylenevinylene) (OPV) was synthesized and polycondensed with isophorone diurethane monomer (DIPD) and 1,8-tricyclodecanedimethanol (TCD-DM) under melt transurethane process to prepare the random copolymers. The amount of OPV was varied up to 50 mol % in the feed to incorporate various amounts of π-conjugated segments in the chain backbone. The selection of isophorone-ring and TCD-DM was based on the results in chapter-3 as these fully cycloaliphatic polyurethanes were novel in their structure and they demonstrated excellence in terms
of solubility, thermal stability and tendency for good morphology. The structures of the polymers were confirmed by NMR, FT-IR and the molecular weights were determined by GPC. The polyurethane-OPV block copolymers were found to produce variety of morphologies ranging from micron to nano-meter range porous membranes, hexagons, spheres (also luminescent nano-spheres) and vesicles depending upon the chemical structure of the polymer chain backbone or the nature of the solvent employed for the self-organization processes. The different types of morphologies were analyzed by techniques such as SEM, TEM and fluorescence microscopy. The role of hydrogen bonding and π-π stacking secondary interaction on the morphological evolutions were analyzed by solution FT-IR spectroscopy, absorption, emission, excitation and time resolved fluorescence decay techniques in both solution as well as solid state.

4.2. Experimental Methods

4.2.1. Materials: 4-Methoxyphenol, 2-ethylhexylbromide, triethylphosphite, 4-hydroxy benzaldehyde, 2-chloroethanol, potassium-tert-butoxide, and titaniumtetrabutoxide (Ti(OBu)4) were purchased from Aldrich Chemicals and used without further purification. 1, 8-Tricyclodecanedimethanol (TCD-DM) was kindly supplied by Celanese Chemicals. HBr in glacial acetic acid, paraformaldehyde, potassium carbonate, potassium iodide, dimethyl sulfoxide, dimethyl formamide, tetrahydrofuran (THF) and all other solvents were purchased locally and purified using standard procedures.

4.2.2. Measurements: 1H, 13C-NMR and FT-IR spectra of the monomers and polymers were recorded as explained in chapter-2. The solution FT-IR spectra of the samples were recorded by dissolving appropriate amounts of the sample in THF and proceeded as given in chapter-3. The purity of the monomers was determined by JEOL JSM600 fast atom bombardment (FAB) high-resolution mass spectrometry. The compound was dissolved in CHCl3 and suspended in 3-nitrobenzylalcohol as a matrix for FAB-Mass measurements. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) using polystyrene as standards. The chromatograms were recorded using Waters 510 pump.
and Waters 410 differential RI and Waters 2487 UV-Vis detectors. The absorption
and emission studies were performed using a Perkin-Elmer Lambda 35 UV-Vis
spectrophotometer and Spex-Fluorolog DM3000F spectrofluorometer with a double
grating 0.22 m Spex 1680 monochromator and a 450 W Xe lamp as the excitation
source using the front-face mode. The fluorescence lifetime was measured using an
IBH FluoroCube Time-correlated picosecond single photon counting system
(TCSPC). Solutions were excited with a pulsed diode laser 401 nm < 100 ps pulse
duration with a repetition rate of 1 MHz. The detection system consists of a
microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps
response time coupled to a monochromator (5000M) and TCSPC electronics
(DataStation Hub including Hub-NL, NanoLED controller and preinstalled
Fluorescence Measurement and Analysis Studio (FMAS) software). The fluorescence
lifetime values were determined by deconvoluting the data with exponential decay
using DAS6 decay analysis software. The quality of the fit has been judged by the
fitting parameters such as $R^2 < 1$ as well as the visual inspection of the residuals.
Scanning electron microscopy (SEM) measurements were done on a JEOL JSM-
5600 LV scanning electron microscope. Transmission electron microscopy (TEM)
was performed on FEI, TEC NAI 30 G2 S-TWIN microscope with an accelerating
voltage of 100 kV. Fluorescence microscopy was done on a NIKON ECLIPSE TE-
2000-E using excitation filter FF01-377/50-25, emission filter FF01-447/60-25 and
dichromatic mirror FF409-DiO2 25x36. Thermal analysis of the polyurethanes was
performed as explained in chapter-2.

4.2.3. Synthesis of Monomers

4.2.3.1. Synthesis of 1-methoxy-4-(2-ethylhexyloxy)benzene (1): 4- Methoxyphenol
(10g, 0.08 mol) and powdered KOH (18.4 g, 0.33 mol) were taken in a 250 mL flask
containing 40 mL of dry DMSO and refluxed under nitrogen atmosphere for 0.5 h. 2-
Ethylhexylbromide (17.3 g, 16 mL, 0.09 mol) was added and the reaction was
continued by refluxing for 36 h under nitrogen atmosphere. It was cooled, poured into
water and extracted with dichloromethane. The organic layer was washed with 10 %
NaOH solution followed by brine solution and dried using anhydrous Na$_2$SO$_4$ and the
solvent was evaporated. The crude product was further purified by passing through a
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silica gel column using 35% CH₂Cl₂ in petroleum ether as the eluent to obtain the product as a light yellow liquid. Yield = 10.1 g (52 %). ¹H NMR (300 MHz, CDCl₃) δ: 6.85 ppm (s, 4H, Ar-H), 3.78 ppm (m, 5H, -OCH₃ and -OCH₂), 1.71-0.89 ppm (m, 15H, others). ¹³C NMR (75 MHz, CDCl₃) δ: 115.6 (Ar-C), 71.4 (Ar-OCH₂), 55.8, 39.7, 30.7, 29.3, 24.0, 23.3, 14.3, 11.3 ppm. FT-IR (cm⁻¹): ν = 3045, 2958, 2930, 2873, 1591, 1508, 1465, 1442, 1380, 1288, 1231, 1180, 1105, 1043. HRMS (FAB): calcd for C₁₅H₂₁O₂ [M⁺]: 236.36; found: 236.51

4.2.3.2. Synthesis of 1, 4-bis(bromomethyl)-2-methoxy-5-(2-ethylhexyloxy)benzene (2): Compound 1 (6 g, 0.02 mol) and paraformaldehyde (4.57 g, 0.15 mol) in 30 mL glacial acetic acid were taken in a 250 mL flask. HBr in glacial acetic acid (6 g, 22.1 mL, 132 wt %) was added dropwise to the above solution at 25 °C and stirred for 0.5 h under nitrogen atmosphere. It was gradually heated to 80 °C and stirred for an additional 5 h. The light brown coloured reaction mixture was poured into ice and washed with water until the filtrate was neutral. The solid was dissolved in 150 mL chloroform, washed with NaHCO₃ solution and saturated brine solution. The organic layer was separated and dried over anhydrous Na₂SO₄, and the solvent was evaporated to obtain a solid product which was purified by recrystallization from hot hexane. Yield = 7.02 g, (65 %) M.P. = 99 °C. ¹H NMR (300 MHz, CDCl₃) δ: 6.86 ppm (s, 2H, Ar-H), 4.53 ppm (s, 4H, ArCH₂), 3.89 ppm (d, 5H, ArOCH₃, ArOCH₂), 1.75 - 0.88 ppm (m, 15H, aliphatic). ¹³C NMR (75 MHz, CDCl₃) δ: 151.2, 127.7, 114.5 (Ar-C), 71.2 (Ar-OCH₂), 56.4, 39.8, 30.8 (Ar-CH₂Br), 29.3, 24.2, 14.3, 11.4 ppm. FT-IR (cm⁻¹): ν =2950, 2928, 2862, 1507, 1459, 1407, 1316, 1251, 1225, 1207, 1037, 772. HRMS (FAB): calcd for C₁₇H₂₆Br₂O₃ [M⁺]: 422.20; found: 422.60

4.2.3.3. Synthesis of 4-(diethoxy-phosphoryl methyl)-2-methoxy-5-(2-ethylhexyloxy)benzyl phosphonic acid diethylester (3): Bis-bromomethylated compound 2 (6 g, 0.01 mol) and triethylphosphite (4.72 g, 4.87 mL, 0.02 mol) were taken in a 100 mL flask and was heated at 150 °C for 15 h under nitrogen atmosphere. Excess triethylphosphite was removed by vacuum distillation to obtain the ylide (3) as a brown viscous liquid. Yield = 7.36 g, (96 %) ¹H NMR (300 MHz, CDCl₃) δ: 6.87 ppm (s, 2H, Ar-H), 3.97 ppm (m, 8H, -POOCH₂), 3.74 ppm (d, 5H, ArOCH₃+
4.2.3.4. Synthesis of 4-(2-hydroxyethoxy) benzaldehyde (4): K₂CO₃ (16.9 g, 0.12 mol) and dry DMF (40 mL) were taken in a 250 mL flask and heated at 80 °C for 10 min. 4-hydroxy benzaldehyde (10 g, 0.08 mol) was added and was heated at 80 °C for 1 h. 2-chloroethanol (8.4 g, 7 mL, 0.10 mol) was added followed by adding a pinch of KI in DMF (1 mL) and heated at 85 °C for 48 h. Excess DMF was removed by vacuum distillation and the contents were cooled and poured into water to obtain a yellowish brown solution. It was extracted with chloroform, washed with 10% NaOH solution, brine and dried using anhydrous Na₂SO₄. The solvent was evaporated to obtain the product as yellow liquid. It was purified by passing through a silica gel column using dichloromethane as eluent. Yield = 6.5 g (48%). ¹H NMR (300 MHz, CDCl₃) δ: 9.76 ppm (s, 1H, -CHO), 7.73 ppm (d, 2H, aromatic), 6.93 ppm (d, 2H, Ar-H), 4.09 ppm (t, 2H, ArOCH₂-), 3.94 ppm (t, 2H, -CH₂OH), 3.30 ppm (s, 1H, -OH). FT-IR (cm⁻¹): ν = 3447, 2931, 2868, 2741, 1684, 1601, 1577, 1508, 1453, 1427, 1313, 1259, 1217, 1162, 1078, 1041, 914, 832. HRMS (FAB): calcd for C₉H₁₂O₃ [M⁺]: 166.18; found: 167.34

4.2.3.5. Synthesis of hydroxyl functionalized oligo(phenylenevinylene) (OPV): The crude ylide (3) (1.04 g, 0.002 mol) was treated with 15 mL dry THF, compound 4 (0.71 g, 0.004 mol) and potassium-tert-butoxide (12 mL, 0.002 mol) and the contents were stirred under nitrogen for 24 h at 30 °C. The contents were cooled and poured into water to obtain a yellow powder which was dissolved in chloroform, washed with water, brine and dried using anhydrous Na₂SO₄. The red sticky solid was further purified by passing through a silica gel column using ethyl acetate and hexane (1: 20 v/v) as eluent. Yield = 0.67 g (61 %). ¹H NMR (300 MHz, CDCl₃) δ: 7.48 - 6.93 ppm (3xm, 14H, Ar-H and vinylic H), 4.12-3.86 ppm (m, 10H, ArOCH₂-), 3.75 ppm (s, 3H, ArOCH₃), 1.86-0.92 ppm (3xm, 15H, aliphatic). FT-IR (cm⁻¹): ν = 3567, 3324, 3032, 2928, 2862, 1603, 1508, 1459, 1412, 1250, 1204, 1171, 1038, 965(CH=CHtrans), 913, 770. HRMS (FAB): calcd for C₃₅H₄₆O₆ [M⁺]: 560.74; found: 560.00
4.2.4. Synthesis of Polymers

4.2.4.1. Synthesis of Polyurethane-oligophenylenevinylene random block copolymers (P-X): 1, 8-Tricyclodecanedimethanol (TCD-DM) (0.50 g, 2.56 mmol), di-urethane monomer DIPD (0.77 g, 2.71 mmol) and OPV (0.08 g, 0.15 mmol) (for P-10) were taken in a test tube shaped polymerization apparatus and melted by placing in an oil bath at 100 °C with constant stirring. It was cooled and 3 drops of Ti(OBu)₄ (40 mg, 0.1 mmol) was added as catalyst and the polycondensation apparatus was made oxygen and moisture free by nitrogen purge followed by vacuum. The polymerization tube was then immersed in the oil bath at 150 °C and the polymerization was carried out along with nitrogen purge for 4 h. The resultant viscous mass was further condensed by applying high vacuum (0.01 mm of Hg) at 150 °C for 2 h. At the end of the polymerization, the polyurethane was obtained as a red solid mass. The polymer was purified by dissolving in minimum amount of glacial acetic acid and precipitating into methanol. Yield = 0.98 g (77 %). 'H NMR (300 MHz, CDCl₃) δ: 7.46-6.91 ppm (3xm, 14H, Ar-H and vinylic-H), 4.81 ppm (s, 1H, -CH₂NH), 4.58 ppm (s, 1H, cy-CHNH), 4.42 ppm (s, 4H, Ar-OCH₂), 4,18 ppm (s, 4H, ArOCH₂CH₂OCONH), 3.90-3.66 ppm (m, 11H, -COOCH₂ + cy-CH-NH + Ar-OCH₃ + Ar-OCH₂), 3.26, 2.92 ppm (s, 4H, -CH₂NH), 2.46-0.88 ppm (56H, cy-H, others). FT-IR (cm⁻¹): ν = 3325 (-NH H bond), 2976, 2860 (-CH₂), 2686, 1964, 1807, 1724 (C=O H bond), 1458, 1358, 1192, 1068, 910, 653.

4.3. Results and Discussion

4.3.1. Synthesis of Monomers

The hydroxyl functionalized OPV was synthesized through a series of steps as shown in scheme-4.6. Williamson’s synthesis was performed on 4-Methoxy phenol to convert it into 1-methoxy-4-(2-ethylhexyloxy) benzene (I) using 2-ethylhexylbromide in KOH/DMSO. I was bisbromomethylated using paraformaldehyde and HBr in glacial acetic acid to give the bisbromomethylated compound: 1, 4-bis(bromomethyl)-2-methoxy-5-(2-ethylhexyloxy)benzene (2). This compound was subsequently subjected to phosphorylation in presence of triethylphosphite to give the corresponding bis-ylide, 4-(diethoxy-phosphoryl methyl)-2-methoxy-5-(2-
ethylhexyloxy)-benzyl phosphonic acid diethylester (3). 4-Hydroxy benzaldehyde was coupled with 2-chloroethanol to give 4-(2-hydroxyethyloxy)benzaldehyde (4). 3 was reacted with 4 under the Wittig- Horner reaction conditions to give the hydroxyl functionalized oligo-phenylenevinylene (OPV). The diurethane monomer (DIPD) was synthesized by reacting isophorone diamine with dimethyl carbonate in presence of freshly prepared sodium methoxide as the base as described in chapter-2.

Scheme-4.6: Synthesis of monomers and polyurethane-oligo (phenylenevinylene) random block copolymers
The structure of the monomers was confirmed by $^1$H and $^{13}$C-NMR, FTIR and FAB-Mass analysis. The $^1$H-NMR spectra of the monomers used for the synthesis of OPV are shown in figure-4.1. The peaks corresponding to different types of protons in the monomers are assigned alphabetically. Figure-4.1a represents the NMR spectrum of the monomer 1. The aromatic peak for the compound appears at 6.85 ppm (a), the ArOCH$_3$ and ArOCH$_2$ appeared together as a multiplet at 3.78 ppm (b+c) and the remaining aliphatic protons appeared between 1.71 and 0.89 ppm. For the bis-bromomethylated compound 2 (figure-4.1b), the aromatic peak appeared at 6.86 ppm (a), the ArCH$_2$Br peak appeared at 4.53 ppm (b), and the ArOCH$_3$ and ArOCH$_2$ appeared together as a multiplet at 3.89 ppm (c+d) which was downfield compared to the similar protons in 2 due to the presence of the -CH$_2$Br unit along the aromatic ring.

\[ \text{Figure-4.1: } ^1\text{H-NMR spectra of monomers 1 (a), 2 (b), 3 (c) and 4 (d). The peak at the asterisk corresponds to the solvent peak.} \]
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The NMR spectrum of the crude ylide 3 is shown in figure-4.1c. The aromatic peak for the compound appeared at 6.87 ppm (a), the \(-\text{POOCH}_2\) appeared at 3.97 ppm (b), the \(\text{ArOCH}_3\) and \(\text{ArOCH}_2\) appeared together as a multiplet at 3.74 ppm (c+d) and the \(\text{ArCH}_2\) protons appeared at 3.19 ppm (e). The NMR spectrum of the monomer 4 is represented in figure-4.1d. The aldehydic proton appeared downfield at 9.76 ppm (a), the aromatic protons appeared as two peaks, one at 7.73 ppm (b), and the other at 6.93 ppm (c), the \(\text{ArOCH}_2\) proton appeared at 4.09 ppm (d), the \(-\text{CH}_2\text{OH}\) proton appeared at 3.94 ppm (e) and a small broad peak at 3.30 ppm corresponds to the \(-\text{OH}\) proton (f).

4.3.2. Synthesis of Polymers

The polyurethanes were synthesized by the solvent free and non-isocyanate melt transurethane polymerization route using \(\text{Ti(BuO)}_4\) as a catalyst. The homopolyurethane (P-0) synthesized by the melt transurethane reaction between diurethane monomer (DIPD) and diol (TCD-DM) (scheme-4.6) is described in chapter-2. The copolymers P-X (scheme-4.6) were synthesized by a similar route by keeping the mol \% of diurethane monomer (DIPD) constant and varying the molar ratio of the TCD-DM and hydroxyl functionalized OPV in the feed. The amount of OPV was varied up to 50 mol \% (in the feed) and it was noticed that at higher incorporation of OPV content (>50 mol \%), the polymer became insoluble in common solvents for further characterization. The structure of the polyurethanes was confirmed by \(^1\text{H}-\text{NMR}\) and FT-IR spectroscopies. \(^1\text{H}-\text{NMR}\) spectra of the OPV, homopolyurethane (P-0), and copolymer (P-41) are shown in figure-4.2. The structures of the molecules are given and the different types of protons are assigned by alphabet. The \(^1\text{H}-\text{NMR}\) spectrum of the OPV is represented in figure-4.2a. The aromatic protons and the vinylic protons appeared between 7.48 to 6.93 ppm (aromatic, vinylic), \(\text{ArOCH}_3\) protons appeared as a multiplet at 4.12-3.86 ppm (a-c), the \(\text{ArOCH}_2\) proton appeared at 3.75 ppm (d) and the remaining aliphatic protons appeared between 1.86 to 0.92 ppm. The \(^1\text{H}-\text{NMR}\) spectrum of the homopolyurethane P-0 is shown in figure-4.2b. Two broad peaks at 4.85 ppm and 4.60 ppm corresponds to the \(-\text{NH}\) protons (e and e', respectively), the \(-\text{COOCH}_2\) and cy-CH-NH appeared together at 3.79 ppm (f and g), the \(-\text{CH}_2\text{NH}\) proton appeared as two separate peaks at 3.24 and 2.89 ppm (h), the bridge headed proton on the tricyclic ring appeared at 2.46 ppm (i). The protons from the OPV block as well as the homopolyurethane block were observed in the copolymer as shown in

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In order to determine the mol % incorporation of the OPV unit into the copolymer backbone, \(^1\)H-NMR peak corresponding to the OPV unit ('b' proton, see figure-4.2a) was compared with that of the TCD-DM unit ('i' proton, see figure-4.2b). From \(^1\)H-NMR spectra the mol % of OPV incorporated in the polyurethane copolymers were determined as 10, 26 and 41 mole % for their incorporation of 5, 20 and 45 mole % in the feed, respectively.

Figure-4.2: \(^1\)H-NMR spectra of OPV (a), homopolymer, P-0 (b) and copolymer, P-41 (c). The peak at asterisk corresponds to the solvent peak.
The polymers were named as P-X, where X-represents (X= 0, 10, 26 and 41), the amount of OPV content in the copolymers (table-4.1). All the polyurethanes were devoid of any gels (or insoluble mass) and they were soluble in common organic solvents such as chloroform and tetrahydrofuran for further characterization and morphological studies. The molecular weights of all the polyurethanes were determined by GPC in THF and the GPC molecular weights are given in table-4.1.

Table 4.1: Mole % of OPV in the copolymer, molecular weights and thermal data of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>mol % of OPV</th>
<th>$M_w$</th>
<th>PDI</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_D$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>(in mole %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-0</td>
<td>0</td>
<td>7,800</td>
<td>2.4</td>
<td>118</td>
<td>270</td>
</tr>
<tr>
<td>P-10</td>
<td>5</td>
<td>10,000</td>
<td>1.5</td>
<td>120</td>
<td>286</td>
</tr>
<tr>
<td>P-26</td>
<td>20</td>
<td>12,000</td>
<td>2.0</td>
<td>108</td>
<td>270</td>
</tr>
<tr>
<td>P-41</td>
<td>45</td>
<td>15,400</td>
<td>3.6</td>
<td>103</td>
<td>278</td>
</tr>
</tbody>
</table>

a. Determined from $^1$H-NMR spectra.
b. Molecular weights as determined by gel permeation chromatography in THF at 30 °C using polystyrene standards for calibration.
c. Values indicate polydispersities as determined by gel permeation chromatography.
d. Measured for the quenched sample in the second heating cycle at 10 °C/min.
e. Temperature represents 10 % weight loss in TGA measurements under nitrogen.

The GPC chromatograms of the polyurethanes are shown in figure-4.3 and the chromatograms represents a mono-modal distribution of the molecular weights.

Figure 4.3: GPC chromatograms of Polymers
The values for the weight average molecular weight; \( M_w \) ranges from 7800-15,400 with polydispersities in the range of 2.0-3.6. On comparing the value of the molecular weights of the polyurethanes, it was found that the homopolymer, \( P-0 \) had the lowest molecular weight and with the incorporation of the OPV units into the polymer backbone the molecular weights were found to increase. The TGA analysis (figure-4.4) confirmed that all the polymers were thermally stable from 270-286 °C (table-4.1) and so they could be used for various high temperature applications.

![TGA plots of Polyurethanes](image)

*Figure-4.4: TGA plots of Polyurethanes*

The thermal analysis by DSC (figure-4.5) proved that all the polyurethanes were sluggish to crystallise and they showed only \( T_g \) (table-4.1).

![DSC thermograms of quenched samples of Polyurethanes at 10°C/min](image)

*Figure-4.5: DSC thermograms of quenched samples of Polyurethanes at 10°C/min*
The DSC plot indicates a single \( T_g \) for all the copolymers and a comparison of the \( T_g \) values of the copolymers with that of the homopolymer showed a decreasing trend with the increase in the OPV content in the polymer backbone. The lowering of \( T_g \) points to the fact that with the increase in the amount of OPV in the copolymer, the polymer backbone becomes less rigid.

### 4.3.3. Scanning Electron Microscopy (SEM) Analysis

Solvent induced self-organization of random block copolymers were studied by dissolving the polymer (5 wt % solution) in dry THF or THF: water - 90:10 (v/v), filtered and drop cast on a glass substrate. All the polymer films were subjected to slow evaporation for 24 h under ambient conditions in air. SEM pictures of polymer films of homopolymer P-0 and the copolymers P-10 to P-41 in THF and THF + water are shown in figure-4.6. It is very clear from the SEM pictures that all the polymers produce a typical micro-porous membrane type morphology for the films prepared from THF (image a, c and e in figure-4.6). The average pore size and the distance between each pore were calculated from the SEM-images and reported for the polymers in table-4.2. In all the cases the size of the pores were found to be uniform and they were straight through pores and no traces of 3D-honey-comb pattern could be noticed along the entire polymer films (figure-4.7).

#### Table-4.2: Morphology data of Polyurethanes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>SEM Data of Films</th>
<th>TEM Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>THF alone</td>
<td>THF+H(_2)O</td>
</tr>
<tr>
<td>P-0</td>
<td>500 nm ± 40 nm(^a)</td>
<td>1.48 (\mu \text{m} \pm 80 \text{ nm})(^c)</td>
</tr>
<tr>
<td></td>
<td>1.28 (\mu \text{m} \pm 100 \text{ nm})(^b)</td>
<td></td>
</tr>
<tr>
<td>P-10</td>
<td>0.92 (\mu \text{m} \pm 10 \text{ nm})</td>
<td>400 nm ± 50 nm</td>
</tr>
<tr>
<td></td>
<td>360 nm ± 50 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-26</td>
<td>680 nm ± 60 nm</td>
<td>1.97 (\mu \text{m} \pm 30 \text{ nm})</td>
</tr>
<tr>
<td></td>
<td>1.14 (\mu \text{m} \pm 160 \text{ nm})</td>
<td></td>
</tr>
<tr>
<td>P-41</td>
<td>790 nm ± 60 nm</td>
<td>2.07 (\mu \text{m} \pm 440 \text{ nm})</td>
</tr>
<tr>
<td></td>
<td>1.88 (\mu \text{m} \pm 170 \text{ nm})</td>
<td></td>
</tr>
</tbody>
</table>

a. Values indicate the size of the pores calculated from figure-4.6.
b. Values indicate the pore distance calculated from figure-4.6.
c. Values indicate the size of spheres calculated from figure-4.6.
d. Value indicates the size of vesicle calculated from figure-4.10.
e. Value indicates the wall thickness of vesicle calculated from figure-4.10.
f. Values indicate the size of spheres calculated from figure-4.10.

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**Figure-4.6: SEM images of polyurethanes in THF alone and THF: water-90:10**

P-0 has pore sizes in the range of 500 nm ± 40 nm and they were separated by 1.28 μm ± 100 nm. P-10 has much bigger pores (0.92 μm ± 10 nm) but the pores are more closely packed (360 nm ± 50 nm) compared to P-0. In the case of P-26 the pore size was bigger than P-0 but smaller than P-10 (680 nm ± 60 nm) with a much bigger pore distance of 1.14 μm ± 160 nm.
Figure-4.7: Expanded SEM images of P-0 (a) and P-10 (b) in THF alone

The porous morphology is not confined to small domains or edges and it appeared throughout the sample for more than 100 micron square meters as shown in the lower magnification SEM images in figure-4.7. It is often noticed in the literature that the amount of water in the solvent combinations plays a crucial role in the self-assembly and morphological changes in the block copolymers. With the increase in the amount of water in the THF + water combinations, the pores (in THF alone) disappeared and the formation of micron to nano-meter sized spheres were noticed (THF: water-90:10, images b, d, f and g in figure-4.6). The size of the spheres (diameter) in the random copolymers were found to vary in the order P-10 (400 nm) < P-26 (1.97 μm) < P-41 (2.07 μm). This suggests that, with the increase in the amount of OPV content in the polymer backbone, the size of the spheres is found to increase (except for P-0, without OPV units) from nano-meter to micron size. The SEM pictures gave clear evidence for the appearance of spheres in a vertical direction in P-26 (bottom to top, see figure-4.6f) and laterally arranged in a single layer in P-41 (figure-4.6g). To investigate the effect of large amount of water on the morphology of polymers, P-10 was subjected to solvent induced self-organization with up to 50:50 of water/THF (figure-4.8). On increasing the amount of water (THF: water-70:30) the spheres are distributed in random along the substrate and the number of spheres have decreased to a very great extent as seen in figure-4.8c. For THF: water-50:50, the aggregation becomes uncontrollable resulting in the vanishing of the polymeric spheres and the successive formation of polymeric flakes as evident in figure-4.8d.
It is also important to mention that the polymer solutions were clear up to 30% of water in THF, however, large amounts of water (50% and more) rendered the polymer solutions hazy. Therefore, the amount of water in THF + water is very crucial in obtaining a good morphology of polymers via solvent induced evaporation process. The variation of water content in P-26 interestingly showed the appearance of polymer hexagons (figure-4.9) for THF: water-95:5.

A closer look at the polymeric hexagon indicates that the hexagonal edges are perfect and the hexagonal faces are slowly transforming into curved surfaces which gives a
clear indication for the formation of spheres from these hexagons. This observation was in accordance with the results in chapter-3 that the homo polyurethane, P-0 (P-2 of chapter-3 and also another polyurethane having 1,4-cyclohexanedimethanol instead of TCD-DM in the backbone, P-1 of chapter-3) showed the appearance of perfect edged polymer hexagons in the film obtained in the presence of trace amount of water (THF: water- 95:5). The observation of hexagons in the present investigation strongly supports the possibilities for the existence of polymeric hexagons in the morphological development of solvent evaporated self-organization process. However, attempts to obtain hexagons in the other two polymers P-10 and P-41 was not successful. Since, the hexagons were not observed in all polymer samples, it can be assumed that the formation of hexagons is an intermediate stage between pores to spheres and they are not the stable final products of the solvent evaporation process.

4.3.4. Transmission Electron Microscopy (TEM) Analysis

The polymer samples were also subjected to transmission electron microscopic (TEM) analysis. The TEM images of 1 wt % polymer solution were recorded for P-10 and P-41 in films obtained from THF alone or THF: water-90:10 (see figure-4.10).

![TEM images of P-10 in THF alone (a), P-10 in THF: water-90:10 (b) and P-41 in THF: water-90:10 (c)](image)

Figure-4.10: TEM images of P-10 in THF alone (a), P-10 in THF: water-90:10 (b) and P-41 in THF: water-90:10 (c)

The polymer films were prepared by drop casting the above solution on the top of Formvar coated copper grid at ambient conditions. The TEM image of P-10 (films obtained from THF, figure-4.10a) showed the existence of vesicles as there is an obvious contrast between the contour and the centre of the aggregates. These
vesicles varied in sizes ranging from 1.2-1.7 μm with a wall thickness of around 100 nm (table-4.2). The comparison of TEM and SEM images of P-10 films prepared from THF alone showed the appearance of two different types of morphology: for instance pores in SEM and vesicles in TEM. The difference in this trend is correlated to the variation in the concentration of polymer solutions in sample preparations (for TEM 1 wt % and SEM 5 wt %). Deepak et al. and Tung et al. have recently reported that polymers like polyacrylics and poly(vinyl phenol)-block-polystyrene diblock copolymers also showed similar dissimilarities in the TEM and SEM images. For example, the PVP-b-PS diblock copolymers showed 3D- honey-comb morphology in SEM whereas vesicles were observed in TEM images. It was postulated that with the increase in the concentration of solutions, the vesicles transform into honey-comb morphology. In the present investigation also, a similar concentration range was employed for the analysis, and therefore, the formation of vesicle in TEM images may be due to the concentration effect. In the presence of water, (for THF: water-90: 10 solvent combinations, figure-4.10b and 4.10c), the morphology of P-10 and P-41 were observed as solid spheres, which are in accordance with that of SEM images. For P-10 the size of the spheres ranges from 50 nm to 200 nm (figure-4.10b) whereas in the case of P-41 the size of the spheres ranges from 250 nm to 500 nm (figure-4.10c).

4.3.5. Fluorescence Microscopic Analysis

The random block copolymers contain fluorescent OPV units in the polymer backbone, and therefore, shining of light on the nano-spheres is expected to transform these solid spheres into luminescent balls (under fluorescence microscope). The polymer solutions (5 wt % in THF alone or THF: water-90:10) were drop cast on a glass slide and the dry film was observed under the fluorescence microscope with an excitation at 377 nm (the absorbance maxima of OPV = 370 nm). Figure-4.11a represents the fluorescence microscopic images of P-10 (films obtained from THF) and the image shows the presence of very faint blue fluorescent spheres. The films obtained from THF + water mixture showed large number of highly luminescent fluorescent solid spheres (figure-4.11b), which is in accordance with SEM and TEM images. In the case of P-41 (in THF: water-90:10, figure-4.11c) the number and size
of the spheres are found to increase and in some areas these spheres are seen to coexist with each other.

Figure-4.11: Fluorescence microscopy images of P-10 in THF alone (a), P-10 in THF: water-90: 10 (b) and P-41 in THF: water-90:10 (c)

The luminescent behaviour of the spheres is uniform in all parts, which suggest that the OPV segments in the copolymer are homogeneously distributed throughout the entire polymer chain during the sphere formation. Though there is a variation in each microscopic technique such as SEM, TEM and fluorescence microscopy, in the present investigation micron or nano-sized materials were created in good reproducibility via solvent induced self-organization process. It is evident from the above morphological analysis that the polymer films showed porous morphology when cast from THF (or vesicles at low concentration inferred from TEM) and increasing the amount of water in the polymer solution induce the formation of spheres. Further, depending upon the amount of OPV present in the copolymers, they either appeared as isolated (also small) or aggregated (bigger in size) spheres. It is very important to add here that this is for the first time that such a variety of morphologies- porous membranes, spheres (luminescent), vesicles and hexagons were observed for any type of \( \pi \)-conjugated polymers or \( \pi \)-conjugated-block copolymers in the literature. Therefore, both the solvent combination as well as the chemical composition of copolymer backbone (i.e. the amount of OPV units) play major role in determining the morphology of the solvent evaporated films.

4.3.6. Solution FT-IR Spectroscopy

In the present case, the self-organization during solvent evaporation may arise via two non-covalent interactions: (i) hydrogen bonding through urethane linkage and (ii) \( \pi \)-\( \pi \) stacking of OPV aromatic core. In order to study the effect of hydrogen
bonding in the polyurethane segments, the polymers were subjected to solution FTIR studies in THF. The expanded region of the N-H stretching vibration of FT-IR spectra of P-0 to P-41 for $2 \times 10^{-2} \text{ M}^{-1}$ in THF are shown in figure-4.12.

![FT-IR spectra of Polyurethanes in THF alone](image)

Figure-4.12: FT-IR spectra of Polyurethanes in THF alone

The two peaks at higher wave numbers (3572 and 3500 cm$^{-1}$) are corresponding to the free anti-symmetric and symmetric stretching vibrations of the N-H group in the urethane linkage, respectively. The peak at lower wavenumber (3329 cm$^{-1}$) is corresponding to the hydrogen-bonded N-H stretching vibration. The hydrogen bonded peaks are more intense in P-0, P-10 and P-26 and they are almost absent in P-41. It suggests that with the increase in the amount of OPV in the polyurethane backbone, the extent of hydrogen bonding is disrupted. This observation was well supported by the T$_g$ values of the polymers (table-4.1). The more hydrogen bonded polymer possesses higher rigidity and so the glass transition temperature is expected to be higher than that of weakly hydrogen bonded polymers. Hence the driving force for aggregation for copolymers with lower OPV content is mainly due to hydrogen bonding whereas this may be a weak force for higher OPV content polymer.

4.3.7. Photophysical Studies of Polyurethane Copolymers

To trace the $\pi-\pi$ stacking of OPV aromatic core and photophysical properties of conjugated segments, the copolymers were subjected to absorption and emission studies in both solution and solid state (table-4.3).
Chapter 4  
Luminescent Polyurethane Copolymers

Table 4.3: Photophysical properties of the polyurethane-oligo
phenylenevinylene random block copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent THF:H₂O</th>
<th>In solution</th>
<th>In film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ_max (abs) (nm)</td>
<td>λ_max (em)² (nm)</td>
<td>Φₚₑ⁰</td>
</tr>
<tr>
<td>P-10</td>
<td>100:0</td>
<td>396</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>90:10</td>
<td>396</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>396</td>
<td>490</td>
</tr>
<tr>
<td></td>
<td>10:90</td>
<td>396</td>
<td>517</td>
</tr>
<tr>
<td>P-26</td>
<td>100:0</td>
<td>396</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>90:10</td>
<td>396</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>398</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>10:90</td>
<td>407</td>
<td>522</td>
</tr>
<tr>
<td>P-41</td>
<td>100:0</td>
<td>396</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>90:10</td>
<td>396</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>399</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>10:90</td>
<td>405</td>
<td>528</td>
</tr>
</tbody>
</table>

a. Excitation wavelength used is 396 nm
b. Calculated using Quinine sulphate as standard and excited at 396 nm; the absorbance of solutions was maintained as 0.1 at 396 nm.
c. Excitation wavelength is the absorbance maximum.
d. The emission intensity of the polymers at the emission maxima.

The absorbance and emission spectra of the copolymers P-10 and P-41 were recorded in THF: water (from 0-100 %, v/v) solvent combinations and shown in figure-4.13. The absorbance peaks over 390-520 nm can be attributed to the π-π* electron transition for OPV in polymer backbones. In both P-10 and P-41 (in THF), there is a strong absorption at 396 nm and a shoulder at 467 nm, which increased in intensity with the addition of water (figure-4.13a and 4.13c). This red shift in the peak maxima may be caused by the inter-chain interactions resulting from aggregation upon adding a non-solvent such as water into the polymer solution in THF. The ratio of the absorbance intensities (I₄₆₇/I₃₉₆) were plotted against the volume % of water in the polymer solution for P-10 and P-41 and shown in figure-4.13e. The plot shows a sigmoidal nature with the existence of two types of species with a break point at around 40-60 volume % of water where there is a sudden jump in the intensity at 467 nm. The plot also indicates that the increase in intensity of peak at 467 nm is more in the case of P-41 when compared to P-10. It suggests that the polymer with more

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number of OPV units (P-41) experience strong π-π stacking compared to that of polymer with few OPV units (P-10).

Figure 4.13: UV-visible absorption and Fluorescence emission spectra of P-10 (a, b) and P-41 (c, d) in THF and THF/water solvent combinations and the plot of absorbance intensity versus volume % of water for P-10 and P-41 (e) and quantum yield versus volume % of water for P-10 and P-41 (f). Emission spectra were obtained at 396 nm.
The emission spectra of the above solutions (0.1 O. D.) were obtained by exciting at the absorption maximum (figure-4.13b and 4.13d). The solution emission spectra are fine structured with a peak maximum at 441 nm corresponding to blue light emission upon excitation and another peak at 468 nm. With the increase in the amount of water the peak changes from a structured shape to one with less vibronic structure and a peak emerges at 517 nm, which corresponds to the emission from the aggregated species. The excitation spectra of the three polymers in various solvent combinations were also compared (figure-4.14).

![Figure-4.14: Normalised excitation spectra of the polymers in THF alone and THF: water-10:90 in the solution state (excited at 515 nm)](image)

The nature of the spectra remained the same in all the three cases but the peak at 465 nm was found to intensify with the increase in the amount of the OPV content from P-10 to P-41 in THF alone and THF: water-10:90 solvent combinations. The quantum yields for the emission spectra were calculated using quinine sulphate as standard following the equation 

$$\phi = \phi_r (F_r/A_r/n_r)(n/s)^2$$

where $\phi$ is the fluorescent quantum yield, $F$ is the area of the emission, $n$ is the refractive index of the solvent and $A$ is the absorbance of the solution at the exciting wavelength. The subscripts $r$ and $s$ denote the reference and sample, respectively. A plot of quantum yield versus the volume % of water in the polymer solution for P-10 and P-41 are shown in figure-4.13f. The plot shows a decrease in the $\phi$ with the increase in the amount of water and as seen in figure-4.13e, the plot is sigmoidal with a breakpoint at 40-60 volume % of water. The
decrease in the fluorescence quantum yield denotes a quenching of fluorescence through a non-radiative decay arising from the strong π-stacking interaction.\textsuperscript{55} It should also be noted that the quenching of fluorescence is more in the case of \textbf{P-41} when compared to \textbf{P-10}, as this could be due to greater aggregation in \textbf{P-41} via aromatic π-stacking.

\textbf{4.3.8. Time-resolved Photoluminescence Decay Studies}

The time-resolved photoluminescence decay dynamics were carried out for the copolymers at an excitation wavelength of 401 nm to understand the nature of their excited state. The PL decay dynamics in THF alone and in THF/water solvent combinations were best fitted using a single exponential and bi-exponential function, respectively (table-4.4).

\textit{Table-4.4: Time correlated fluorescence lifetime data of Polyurethane block copolymers}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent\textsuperscript{a} THF:H\textsubscript{2}O</th>
<th>(\lambda\text{_{\text{monitor}}}) (nm)\textsuperscript{b}</th>
<th>(\tau\text{\textsubscript{1}}) (ns)\textsuperscript{c}</th>
<th>(\tau\text{\textsubscript{2}}) (ns)\textsuperscript{c}</th>
<th>(R^2\textsuperscript{d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{P-10}</td>
<td>100:0</td>
<td>467</td>
<td>1.52</td>
<td>-</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>518</td>
<td>1.85</td>
<td>1.34</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>10:90</td>
<td>518</td>
<td>1.15</td>
<td>0.95</td>
<td>0.999</td>
</tr>
<tr>
<td>\textbf{P-26}</td>
<td>100:0</td>
<td>467</td>
<td>1.51</td>
<td>-</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>518</td>
<td>1.50</td>
<td>0.71</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>10:90</td>
<td>518</td>
<td>0.73</td>
<td>0.55</td>
<td>0.986</td>
</tr>
<tr>
<td>\textbf{P-41}</td>
<td>100:0</td>
<td>467</td>
<td>1.48</td>
<td>-</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>518</td>
<td>1.25</td>
<td>0.63</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>10:90</td>
<td>518</td>
<td>0.66</td>
<td>0.66</td>
<td>0.998</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The optical density of the solutions was maintained at \textsim 0.1 for the life time measurements.

\textsuperscript{b} Emission wavelengths for which the decay was monitored (\(\lambda\text{_{exc}} = 401\) nm).

\textsuperscript{c} Lifetimes obtained from the exponential decay fitting.

\textsuperscript{d} Values indicate the fitting parameter obtained from the exponential decay fitting.

The PL decay curves for \textbf{P-10}, \textbf{P-26} and \textbf{P-41} in THF alone and in THF: water-50:50 and THF: water-10:90 solvent combinations are shown in figure-4.15. For all the three copolymers the decay is very rapid with increasing amount of water indicating the enhancement of aggregated luminescent quenching. A single exponential fit in THF alone suggested the existence of a single luminescent species.
Two decay components in THF/water solvent combinations confirm the existence of two types of luminescent species corresponding to the aggregated and isolate chains.

Figure 4.15: Time resolved Fluorescence lifetime spectra of P-10, P-26 and P-41 in THF, THF:water-50:50 and THF:water-10:90. The excitation wavelength is 401 nm.

In THF alone, $\tau_1$ is in the range of 1.52 ns for P-10 but the incorporation of more OPV units decrease its lifetime: for example 1.51 ns for P-26 and 1.48 ns for P-41. With the addition of water the first and the second decay life times were found to decrease. For instance in THF:water-50:50, the decay life time of P-10 are 1.85 ns where as for P-26 it is 1.5 ns which further decreases to 1.25 ns for P-41. In the case
of THF: water-10:90 solvent combinations the values were found to decrease from 1.15 ns for P-10, 0.73 ns for P-26 and 0.66 ns for P-41. The time resolved FL measurements confirmed the presence of strong aggregates in THF + water solution via π-stacking and also the enhancement of aggregation with increase in OPV content in the random block copolymers.

4.3.9. Solid State Photoluminescence Studies

The solid state photophysical properties of the copolymers were studied and the representative plots for P-10 and P-41 are shown in figure-4.16.

Figure-4.16: Normalised Absorbance (a), normalised PL spectra (b) and normalised excitation spectra of P-10 (black) and P-41 (red) in THF (—) and THF: water-90:10 (—) of the films. Emission spectra were obtained at peak maxima.
The polymer solution in THF or THF: water solvent combinations were drop cast on a glass slide and allowed to evaporate under ambient conditions to obtain polymer films (same conditions applied for SEM analysis). The solid state absorbance spectra of the polymers are shown in figure-4.16a. The absorption spectra of the polymers in solid state (from THF solution) were much broader compared to their solution spectra with a peak maximum at around 401 nm and a shoulder at 465 nm. For the films prepared in THF: water-90:10, there is a red shift in the peak maximum from 401 nm to 432 nm and a considerable broad tailing of the spectra which suggests greater tendency for aggregation through \( \pi-\pi \) stacking.\(^{57-59}\) The normalized emission spectra of these films excited at the peak maximum are shown in figure-4.16b. On comparing figure-4.16b with figure-4.13b (or 4.13d), it is clear that for the same solvent combination, the emission maxima in the film is more red shifted when compared to solution (table-4.3). This suggests that under the conditions employed for the morphological study in the present investigation, there is considerable aggregation in the copolymers, and this is found to be greater in the case of P-41. In order to understand the nature of the emissive species, the excitation spectra of the solid polymer films were monitored at 518 nm (figure-4.16c). The excitation spectra were identical for all the polymers except for an increase in intensity of the peak at 465 nm which suggests that the emissive species are identical in all the cases.\(^{42}\) The figure also shows that the peak at 465 nm corresponding to the aggregate formation intensifies both with the increase in the amount of OPV content in the polymer backbone and also with the increase in the volume % of water in the solvent combinations. (This observation was comparable with the solution state excitation spectra).

![Scheme-4.7: Aggregation in polyurethane-oligophenylene vinylene block copolymers](image)

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All these studies revealed that solvent induced self-organization takes place in copolymers but the extent to which it undergoes is determined by the solvent combination as well as on the mol % of OPV in the copolymer backbone. The aggregation can be driven by two forces, viz. hydrogen bonding or π-π stacking (scheme 4.7). For P-10 having less amount of OPV in the copolymer backbone, the addition of water into polymer solution in THF results in controlled aggregation which could be mostly favoured through hydrogen bonding interaction. In the case of P-41 with higher OPV content the major driving force for aggregation could be π-π stacking resulting in uncontrolled aggregation with the addition of water.
4.4. Conclusion

The above studies provide a clear insight into the solvent-induced self-organization in polyurethane-OPV random copolymer for various morphologies and sizes ranging from micron to nano-meter sized pores, hexagons, vesicles and solid luminescent spheres. The polyurethane-OPV random block copolymers were synthesized by the melt transurethane route and the polymers possess high thermal stability and solubility in common solvents to study the self-organization process. The approaches demonstrated here as well as the resultant nano-materials have many advantages: (i) polyurethane-OPV random block copolymers were synthesized with various amounts of π-conjugated segments to trace the solvent-induced self-organization process, (ii) various polymeric architectures such as micropores, vesicles, hexagons and micron to nano-sized spheres luminescent under shining light were produced for the first time in the literature, (iii) SEM, TEM and fluorescent microscopic techniques were employed to confirm the formation of various types of morphologies, (iv) $T_g$ values and solution FTIR studies revealed that the increase in the OPV content in the copolymer resulted in a decrease in the extent of hydrogen bonding (v) the absorption and emission studies of the polymers uncovered that π-stacking is strongly favoured in polymers with higher OPV content, and (vi) the time resolved fluorescent techniques confirmed the formation of molecular chain aggregates. The present investigation showed that polyurethane copolymers containing OPV units are very interesting classes of polymers, which are soluble, thermally stable and also have tendency to form self-organized structures through solvent evaporation process. The mechanistic aspects of the self-organization process were studied by many experimental techniques in solid as well as solution state to trace the factors which control the morphology of the polyurethane-OPV systems. The approach demonstrated here may be adopted to produce variety of thermoplastic-conducting polymeric micron to nano structures, which may be very promising candidates in opto-electronics and sensor applications.
4.5. References

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