Abstract

A soluble intense blue light emitting bulky ring substituted segmented PPV block copolymer, poly[1,6-hexanedioxy-(2,6-dimethoxy-1,4-phenylene)-1,2-ethylenylene-(2,5-dicyclohexylmethyloxy-1,4-phenylene)-1,2ethylenylene-(3,5-dimethoxy-1,4phenylene)] \((P3)\) was synthesized using Horner-Emmons condensation polymerization. Rigid cyclohexylmethoxy group substituted distyrylbenzene unit was the chromophoric group present in the copolymer. This rigid block was linked to flexible hexamethylene chain spacer through an ether linkage. Methoxy groups were incorporated to alter photophysical and electrochemical properties, and to improve solubility and processability of the copolymer. The obtained copolymer was soluble in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran, toluene etc. The structure of the copolymer was confirmed on the basis of FT-IR, NMR techniques and elemental analysis. GPC analysis showed that the copolymer synthesized by us has narrow polydispersity index. Thermo-gravimetric analysis shows it has excellent thermal stability with maximum degradation temperature obtained as 422°C. The HOMO and LUMO levels of copolymer were estimated from the cyclic voltammograms. XRD and DSC studies give information about the semicrystalline nature of the new copolymer. The UV-Vis absorption and fluorescent emission spectra reveals that the copolymer is a promising blue emissive material for light-emitting device application. Copolymer shows excellent fluorescent quantum yield in dichloromethane solution. Morphology of the copolymer was examined by using scanning electron microscopy (SEM). Preliminary photoluminescence studies and Schottky diode action from Voltage vs. Current data are confirmed the suitability of the copolymer for fabricating PLEDs.

4.1 Introduction and Motivation

Electroluminescence devices have been studied extensively during the past 20 years due to their commercial application as a full color flat panel displays. After the
introduction of Polymer LED in 1990, there are several light emitting polymers studied extensively such as poly(p-phenylenevinylene), poly(alkylthiophene), poly(fluorene), poly(p-phenylene) and their copolymers. Polymer LEDs have many advantages for flat panel displays because of variety of color emission, good thin film property, color tunability from blue to red emission region, low turn-on voltage, fast response time and good mechanical properties. Recently, there have been several attempts to improve the performance of PLEDs. In order to attain high purity, high photoluminescence profiles, low operating voltage and current, there has been important to develop the proper construction of the microstructures of the light emitting polymers. High thermal stability and good mechanical properties of light emitting polymers are also important to overcome device degradation and increased life time during device operation. Therefore numerous emitting polymers have been synthesized and investigated for flat panel device applications, still invention of new light emitting materials with high performance and efficiency remains a big challenge in the field of PLEDs. Mainly three principle colors such as blue, green and red emitting polymers have been demonstrated in PLEDs, but only red and green PLEDs reach the requirements for commercial uses. So efficient blue light emitting polymers are yet to be developed and optimized for commercial purposes.

It has recently been shown that shortening the effective conjugation length by attaching non-conjugated segments into the PPV backbone can alter their absorption and emission wavelengths, facilitate good film properties and induce excellent EL efficiencies. Blue emission color is not possible in fully conjugated light emitting polymers. In 1993 Karasz et al prepared highly soluble PPV copolymer containing well-defined blocks of rigid conjugated oligo(phenylenevinylene) and flexible non-conjugated aliphatic spacer units. The introduction of non-conjugated segment helps to improve the homogeneity of the film and also leads to \( \pi \)-electron confinement in conjugated segment part. Segmented block copolymers (SBC) where the conjugated backbone of the polymer is interrupted by introducing non-conjugated spacer (flexible block) exhibit enhanced solubility, provide a blue shift
in the emission spectrum and increase the energy band gap.\textsuperscript{11} The shifting of emission spectrum is related to the substituted alkyl or alkoxy side group present in the distyrylbenzene (DSB) unit.\textsuperscript{12} Non-conjugated spacer essentially reduces the conjugation length and is expected to cause hypsochromic shift of the emission, without any decrease in the high fluorescence quantum yield of the DSB unit.\textsuperscript{13} Various segmented block EL polymers have been synthesized by using Heck reaction,\textsuperscript{14} Wittig polymerization,\textsuperscript{15} Horner-Emmons reaction\textsuperscript{16} etc. Fluorescence quantum efficiency of conjugated polymers is decreased by aggregation quenching of the excited state due to interchain interactions between the polymer chains. Polymer chain interactions can be inhibited by increasing the space between the conjugated chains with bulky side chain substituents. Poly(2-methoxy-5-cyclohexylmethoxy-p-phenylenevinylene) (MCHM-PPV) exhibits enhanced photoluminescence intensity than the structurally similar poly(2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene) (MEH-PPV) due to the reduction of main chain aggregation in MCHM-PPV induced by cyclohexylmethoxy groups.\textsuperscript{17} Based on this, we reasoned that further introduction of auxochromes on the PPV backbone can provide additional advantages in terms of absorption and emission wavelengths, solubility and redox behaviour of SBCs.

This chapter describes the synthesis, characterization, structural and photophysical studies of new bulky ring substituted segmented PPV block copolymer. A. Talaie et al reported that the device performance could be enhanced in fully conjugated polymers by increasing the chain length and the size of the ring situated within the polymer chemical structures.\textsuperscript{18} The copolymer poly[1,6-hexanedioxy-(2,6-dimethoxy-1,4-phenylene)-1,2-ethylenyl-(2,5-dicyclohexylmethoxy-1,4-phenylene)-1,2-ethylenyl-(3,5-dimethoxy-1,4-phenylene)] (P3) was synthesized by using Horner-Emmons condensation polymerization under mild conditions at room temperature. The structure and properties of the copolymer have been systematically examined in this work. The structure of the copolymer was confirmed by using FT-IR, NMR techniques and elemental analysis. The results show that bulky ring (cyclohexylmethoxy)
substituted SBC have enhanced solubility, narrow molecular weight distribution (MWD) and good thermal stability. The Voltage vs Current data confirms the Schottkey diode action of the copolymer.

4.2 Results and Discussion

4.2.1 Monomer and Polymer Synthesis

The first step towards the required class of copolymer is the synthesis of appropriate monomers as depicted in Scheme 4.1. Synthesis of monomer, 2,5-din-cyclohexylmethoxy-1,4-xylene-diethylphosphonate ester (2c) has already been described in Chapter 3. Dialdehyde monomer, 1,6-Bis(4-formyl-2,6-dimethoxyphenoxy)hexane (3) was prepared by Williamson etherification type reaction on 4-hydroxy-3,5-dimethoxybenzaldehyde. Synthesis of copolymer is displayed in Scheme 4.2. Similar to general procedure of Horner-Emmons reaction, the condensation polymerization reaction was carried out between bisphosphonate ester monomer (2c) and 1,6-Bis(4-formyl-2,6-dimethoxyphenoxy)hexane (3) in anhydrous THF using potassium tert-butoxide as the base.\textsuperscript{19,20} The mixture was stirred for 24h under nitrogen atmosphere. The greenish yellow reaction mixture remained homogenous through the course of the reaction enabling high overall conversion of functional groups to completion more effectively. Work-up procedure consisted of precipitation of crude copolymer using methanol, collection of the precipitated polymer by gravity filtration, and transfer of the precipitate into an extraction thimble followed by sequential extraction with methanol, hexane and finally THF to remove the oligomers and other impurities. THF fraction was collected and again the copolymer was re-precipitated by using methanol. Copolymer obtained as pale yellow solid in 36% yield was completely soluble in common organic solvents like THF, chloroform, dichloromethane, toluene etc.
Scheme 4.1. Synthesis of bisphosphonate ester monomer (2C) and dialdehyde monomer (3)

We introduced a bulky ring substituent such as cyclohexylmethoxy groups into the 2,5 position of each distyrylbenzene (DSB) unit used for the synthesis. Resulting copolymer consists of well defined conjugation length as repeating units linked by long aliphatic flexible chain i.e. hexamethyleneglycol linkers attached through an ether bond. Methoxy groups are also attached into the backbone, in order to alter its absorption characteristics and to enhance solubility and
processability of the copolymer. The weight average molecular weight ($M_w$), number average molecular weight ($M_n$) and polydispersity index (PDI) of the copolymer was determined by GPC using tetrahydrofuran (THF) as eluent and calibrated with polystyrene as the standard. The $M_w$ of the copolymer was found to be $12644\, \text{g/mol}^{-1}$ and $M_n$ was $7966\, \text{g/mol}^{-1}$ corresponds to 11 repeating units (Figure 4.1). The polydispersity index of the copolymer was 1.6 and that is exceptional in the case of condensation polymerization reactions. The decrease of polydispersity index value of copolymer is due to the sequential extraction with different solvents such as methanol, hexane and THF. Thus, the introduction of ring substitution at the 2,5 positions of the distyrylbenzene units in segmented block copolymer resulted in better yield and improved solubility. The copolymer could be spin-cast from suitable solvents at ambient temperature to give transparent, bright greenish-yellow colored, homogeneous and pin-holes free thin films.

![Figure 4.1 Gel permeation chromatogram of copolymer (Waters alliance 2690 column with THF as eluent, at a flow rate of 0.5 mL/min at 25°C)](image)

Structural characterization of the copolymer was done by using $^1$H NMR, $^{13}$C NMR, FT-IR spectroscopic techniques and elemental analysis. $^1$H NMR spectra of 2,5-di-n-cyclohexylmethoxy-1,4-xylene-diethylphosphonate ester (2e) and copolymer P3 are presented for comparison in Figure 4.2. $^1$H NMR signals of dialdehyde protons in monomer (3) are observed at $\delta$ 9.79. These dialdehyde proton signals completely disappeared in the $^1$HNMR spectra of copolymer with concomitant appearance of vinylene proton signals in the $\delta$ 7.0-7.8 region along
with aromatic proton signals. Signal appearing as a singlet at $\delta$ 6.5 may be attributed to aromatic protons. It is significant to notice that no signals attributable to vinylic protons appear below $\delta$ 6.5 confirming the absence of cis-vinylene double bond. Furthermore the doublet-like pattern observed at $d$ 7.4 exhibits coupling constant 16Hz confirming trans geometry. Thus it is safely concluded that dominant trans-configuration of vinylene double bond is present in the copolymer synthesized by us. Signals at $\delta$ 3.7-3.9 correspond to the methylenedioxy protons. Other aliphatic protons are observed in $\delta$ 2.19-1.28 region. $^{13}$ C NMR signals of copolymer are also in good agreement with the proposed structure (Figure 4.3). Figure 4.4 shows the FT-IR spectrum that also is indicative of complete polymerization. Out of plane bending mode of $–CH=CH–$ group in the copolymer is observed at 960cm$^{-1}$, which is the characteristic absorption peak position of trans-vinyl group. A very strong peak at 1027cm$^{-1}$ suggests the presence of C–O–C stretching vibrations of aryl-alkyl ether linkage in this compound.
Figure. 4.2 $^1$H NMR spectra of dialdehyde monomer (3) and copolymer (P3)

Figure 4.3 $^{13}$C NMR signals of copolymer (P3)
4.2.2 Thermal Analysis

Thermal properties of the copolymer P3 under nitrogen atmosphere were evaluated by thermo gravimetric analysis (TGA, Figure 4.5) and differential scanning calorimetry (DSC, Figure 4.6). Excellent thermal stability was manifested in their TGA profile, with a maximum degradation temperature ($T_d$) at about 422°C. The onset degradation temperature was found to be 342°C. This enhanced thermal stability is due to the introduction of rigid ring substituent groups present in the distyrylbenzene blocks of the copolymer. As described in chapter 3, rigid ring substituted segmented copolymer P2 shows enhanced thermal stability than P1.
The thermal properties were further investigated by differential scanning calorimetry (DSC) with heating and cooling rate at 10°C min\(^{-1}\). Copolymer shows a glass transition temperature \((T_g)\) at 53°C. DSC profile also shows a very broad melting peak between the temperature ranges from 112°C to 128°C. Both glass transition temperature and melting temperature \((T_m)\) confirms the semicrystalline nature of the synthesized copolymer.\(^2\) No other peaks found in DSC thermogram of the copolymer.

Figure 4.6 DSC plot of copolymer (P3) with heating and cooling rate at 10°C min\(^{-1}\).

4.2.3 X-ray diffraction Analysis (XRD)

Powder X-ray diffraction (XRD) (Rigaku X-ray diffractometer, Cu-K\(\alpha\) radiation (1.542Å) was used to investigate the molecular organization of the synthesized copolymer (P3) as shown in Figure 4.7.

Figure 4.7 Powder XRD patterns of copolymer (P3)
The two major peaks are present in the powder XRD pattern. First peak $d_1=7.83\text{Å} \ (2\theta =11.2^\circ)$ is somewhat sharp whereas the second peak $d_2 = 4.31\text{Å} \ (2\theta=21.6^\circ)$ is broad. Interlayer spacing $d_1=7.83\text{Å}$ is attributed to the distance between copolymer main chains separated by bulky ring substituent groups present in the DSB units.$^{22}$ The sharp peak can be ascribed to the presence of side chain crystallinity of the copolymer. The amorphous halo peak at interlayer spacing distance at $d_2 = 4.31\text{Å}$ is typically arises from side to side distance between the rigid ring substituent groups.$^{23}$ Thus, it is clear that the new copolymer synthesized by us shows a semicrystalline nature in the solid state. Furthermore, XRD results support the DSC pattern discussed earlier.

### 4.2.4 Scanning electron microscopy (SEM)

Figure 4.8 shows the SEM image of copolymer in powder form. SEM pattern suggests that the copolymer shows a featureless morphology due to lack of structural coplanarity in their solid state.

![Figure 4.8 SEM micrograph of copolymer (P3)](image)

### 4.2.5. Photophysical studies

The UV-Vis absorption and PL spectra of the copolymer in dichloromethane solution and in thin film are shown in Figure 4.9 and spectral details are displayed in Table 4.1. Copolymer is a pale yellow solid with absorption maxima in the UV range of the spectrum (398nm). The optical band
gap obtained from the onset of the absorption spectrum in solution was determined as 2.72eV. In the solid state as a thin film, the copolymer is having absorption at 401nm. Negligible 3nm red-shift in the solid state is indicative of insignificant aggregation between the polymer chains in its film state i.e. copolymer shows weak interchain π-π stacking in their ground state. The photoluminescence (PL) spectra in dichloromethane solution consist of a strong peak present at 451nm and a shoulder peak at 480nm. PL spectrum in the film state shows a strong peak at 481nm and shoulder peak at 460nm. Red shifted PL suggests the formation of intermolecular excited state dimers called excimers. PL spectrum of the copolymer in film state is 30nm red shifted compared with its solution state because of the dense packing of copolymer in its solid state than solution state that promotes excimer formation. Figure 4.10 shows emission spectrum of copolymer (\( \lambda_{ex} = 365 \)nm). The fluorescence quantum yield (\( \Phi_F \)) of the copolymer was determined by using comparative fluorescence quantum yield method of Williams et al. The detailed description of the measurement of fluorescence quantum yield has already been presented in Chapter 3. The solution measurements conducted versus coumarin-481 dye in ethanol as the standard gave a fluorescence quantum yield (\( \Phi_F \)) of 0.08. The fluorescence quantum yield (\( \Phi_F \)) of copolymer (P3) in dichloromethane solution was obtained as 0.93. Therefore the synthesized copolymer shows enhanced fluorescence quantum yield in dichloromethane compared to coumarin-481 dye.

![Figure 4.9 UV-Vis spectra and photoluminescence spectra of copolymer (P3) in solution and film state](image-url)
Figure 4.10 Light emission under UV irradiation with light at 365nm

<table>
<thead>
<tr>
<th>UV-Vis (nm)</th>
<th>PL (nm)</th>
<th>$E_g^{OP}$ (eV)</th>
<th>Fluorescence quantum yield ($\Phi_F$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>Film</td>
<td>Solution</td>
<td>Film</td>
</tr>
<tr>
<td>398</td>
<td>401</td>
<td>451, 480</td>
<td>460, 481</td>
</tr>
</tbody>
</table>

Table 4.1 Photophysical data of copolymer (P3)

4.2.6. Electrochemical studies

The redox potentials of copolymer were estimated by cyclic voltammetric measurement at room temperature in dichloromethane containing 0.1M tetra-$n$-butyl mmonium hexafluorophosphate as supporting electrolyte. A platinum disc electrode was used as working electrode and a platinum wire was used as counter electrode and the potentials referred to Ag/AgCl (calibrated against the FC/FC$^+$ redox system) was 4.8eV below vacuum levels. A detailed description of the procedure is available in Chapter 3. Figure 4.11 shows the current-voltage curve for copolymer from the cyclic voltammetry measurements.
From the onset oxidation potential and onset reduction potential of the copolymer, HOMO and LUMO energy levels as well as the electrochemical band gap were calculated according to the following equations:\textsuperscript{26}

\[ E_{\text{HOMO}} = (\text{IP}) \text{ eV} = -e (E_{\text{ox, on}} - E_{\text{foc}}) - 4.8 \]
\[ E_{\text{LUMO}} = (\text{EA}) \text{ eV} = -e (E_{\text{re, on}} - E_{\text{foc}}) - 4.8. \]

\[ E_g = e (E_{\text{ox, on}} - E_{\text{re, on}}) \]

Where \( E_{\text{ox, on}} \) and \( E_{\text{re, on}} \) are the measured onset potentials relative to Ag/Ag\textsuperscript{+}. The \textit{p-doping} and \textit{n-doping} processes occur under the anodic and cathodic scans. Electrochemical data were displayed in Table 2. On the basis of measured oxidation and reduction potentials, corresponding HOMO and LUMO values are determined as \( -5.23 \text{eV} \) and \( -2.52 \text{eV} \). The electrochemical band gap of the copolymer \( P_3 \) was evaluated as \( 2.71 \text{eV} \). Band gap obtained from cyclic voltammetry was very close to the optical band gap derived from UV-Vis spectra (\( E_{\text{g OP}} = 2.72 \text{eV} \) as indicated in Table 4.1).

<table>
<thead>
<tr>
<th>( E_{\text{ox, on}} ) (V)</th>
<th>( E_{\text{re, on}} ) (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>( E_g^{\text{EC}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.88V</td>
<td>-1.79V</td>
<td>-5.23 eV</td>
<td>-2.52 eV</td>
<td>2.71 eV</td>
</tr>
</tbody>
</table>

Table 4.2 Electrochemical data of copolymer (P3)
4.2.7. Measurement of I-V characteristics

The homogenous, transparent greenish-yellow coloured thin film of copolymer was made by spin casting (SPS Spin wafer 150, 2000 rpm, 30s) of solution of copolymer in dichloromethane on top of Indium Tin Oxide coated glass plates which act as anode. Aluminium contacts (top-electrode as cathode) were made on top of the spin coated copolymer layers by thermal evaporation to form a Schottky (metal- semiconductor) junction. The current-voltage characteristics were analysed using Keithley 2400 source meter (2-point probe method) for the two diode configurations to confirm the formation of metal-semiconductor junction. Forward bias current was obtained, when the ITO electrode was positively biased and the Al electrode was negatively biased. Therefore the current increased with increasing the forward bias voltage, which is mandatory for the fabrication of polymer light emitting diodes. The diode behaviour of the device suggests that electrons and holes are injected from the ITO and Al electrodes. Figure 4.12 shows the Current vs. Voltage graph of copolymer in the forward and reverse bias respectively. From the graph, copolymer shows an onset voltage is 2.8V. Figure 4.13 shows a three dimensional atomic force microscopy (AFM) image of the spin coated film of copolymer from dichloromethane solution. The thickness of the film thus obtained was measured using Dektak 6M stylus profilometer and film with thickness 50nm (±5nm). AFM analysis show that copolymer have very smooth surface with the root mean square (RMS) value of 1.53nm.

Figure 4.14 shows the energy diagram of ITO/Copolymer(P3)/Al device configuration of the copolymer. The barrier heights of the copolymer was found to be 0.53eV at the interface of ITO (4.7eV)/HOMO state for holes and 1.68eV at the interface of Al (4.2eV)/LUMO for electrons. The HOMO level of polymer is very close to the work function of ITO which enables the effective supply of holes through ITO. An intermediate layer between the emissive polymer and ITO can also be avoided as a result of this. From the energy band diagram, one can assume

* The device fabrication and related characterizations are carried out in collaboration with Department of Physics, CUSAT
that copolymer easily injected holes from the ITO electrode. Therefore, the diode behavior and good film forming property of this copolymer demonstrate its suitability of fabricating LEDs.

![Figure 4.12 I-V characteristics: ITO/copolymer (P3)/Al device](image)

![Figure 4.13 Three dimensional atomic Force Microscopy image of the spin coated film of copolymer P3 from dichloromethane solution.](image)

![Figure 4.14 The hypothesized energy diagram of ITO/Copolymer (P3)/Al device](image)

**4.3 Conclusions**

A new type of rigid cyclohexylmethoxy ring substituted segmented PPV block copolymer was synthesized using Horner-Emmons condensation
polymerization. The chemical structure of the SBC was assigned on the basis of \(^1\)H NMR, \(^{13}\)C NMR, FT-IR and elemental analysis data. Crude copolymer was purified by sequential extraction method. Purified copolymer exhibited high solubility in several polar and non-polar organic solvents. Gel permeation chromatography indicated narrow polydispersity index for the purified polymer sample used in this investigation. TGA studies show that the copolymer has good thermal stability. DSC thermogram shows both glass transition temperature (\(T_g\)) and broad melting temperature (\(T_m\)). Semicrystalline characteristic of the copolymer was confirmed by XRD and DSC analysis. AFM studies confirm the very low surface roughness of the spin coated film. In addition, the effect of structure on the optical properties was also investigated. Photoluminescence studies show that the copolymer gives intense blue light emission. Schottky diode characteristics from Voltage vs. Current data confirmed the suitability of the copolymer for fabricating PLEDs.

4.4 Experimental Section

4.4.1 Materials and Instruments

General description of spectroscopic and other characterization techniques used in this study is available in Chapter 3 of this thesis. All reactions were carried out in oven-dried glassware using reagents and chemicals as commercially supplied from Aldrich and Merck unless otherwise noted. Tetrahydrofuran (THF) was distilled from calcium hydride and then from sodium/benzophenoneketyl. Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were distilled prior to use. Hydroquinone, bromomethylcyclohexane, triethylphosphite, 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde), 1,6-dibromohexane and potassium tert-butoxide were purchased from Aldrich Chemicals. HBr in glacial acetic acid, paraformaldehyde and all other reagents/solvents were purchased locally and purified by following the standard procedures.
4.4.2 Synthesis of Monomers

Synthesis of compounds 1, 2 and 2c has already been described in Chapter 3

4.4.2.1 1,6-Bis(4-formyl-2,6-dimethoxyphenoxy)hexane (3)

A mixture of 4-hydroxy-3,5-dimethoxybenzaldehyde (4g, 0.02mol) and 1,6-dibromohexane (2.5g, 0.01mol) in 50mL distilled DMF was stirred and heated to reflux. A total of 3g (0.02mol) of potassium carbonate was added in portions and the mixture was stirred and refluxed for 24h. The resulting mixture was poured into 1L of distilled water and the precipitate was collected after standing for 4h, dried in air at ambient temperature and recrystallized from methanol to separate pure dialdehyde (yield=75%, mp 84°C).

\[
^1H \text{ NMR (400 MHz, CDCl}_3) \delta \text{ (ppm): 9.79 (s, 2H), 7.04 (s, 4H), 3.99-4.02 (t, 4H), 3.83 (s, 12H), 1.44-1.77 (m, 8H).}
\]

4.4.3 Synthesis of Polymer

4.4.3.1 Synthesis of Poly[1,6-hexanedioxy-(2,6-dimethoxy-1,4-phenylene)-1,2-etheneylene-(2,5-dicyclohexylmethoxy-1,4-phenylene)-1,2-etheneylene–(3,5-dimethoxy-1,4-phenylene)] (P3)

A suspension of potassium \textit{tert}-butoxide (0.25g) in anhydrous freshly distilled tetrahydrofuran (THF) was added to a stirred solution of the 2,5-di-\textit{n}-cyclohexylmethoxy-1,4-xylene diethylphosphonate ester monomer (2c), (1.5g, 2.4mmol)) and of dialdehyde monomer (3) (0.8g, 1.7mmol) in 10mL of distilled THF at room temperature. The mixture was stirred 24h under nitrogen atmosphere. A viscous greenish-yellow precipitate was formed. The reaction mixture was poured into methanol, stirred vigorously for 1h, and the precipitated crude polymer was separated by gravity filtration. After drying, the crude polymer mixture was subjected to sequential extraction with methanol, hexane and THF. The polymer was recovered
from the THF fraction by rotary evaporation. The resultant pale yellow solid was
dried under vacuum over night. The yield was 38% (0.628g).

\[ \text{**1H NMR** (400 MHz, CDCl}_3\text{)} \delta \text{ (ppm): 7.34-}
7.30 \text{ (d, 2H), 6.98-7.04 (t, 4H), 6.68 (s, 4H),}
3.95-3.82 \text{ (m, 16H), 3.79-3.77 (m, 5H),}
2.19-1.28 \text{ (m, 26H).}

\[ \text{**13C-NMR** (100MHz, CDCl}_3\text{)} \delta \text{ (ppm):}
153.6, 151.2, 137.2, 133.5, 128.5, 126.8,
125.5, 122.8, 110.7, 103.6, 75.1, 73.6, 56,
38.2, 30.3, 30.1, 26.6, 25.9, 25.7.

\[ \text{**IR** (KBr)} \nu \text{2916, 2848, 1579, 1498, 1471,}
1418, 1378, 1315, 1252, 1198, 1131, 1023,
952, 844, 804, 669, 633 \text{ cm}^{-1}.

Anal.Calcd. For C\text{46H60O}_4: \text{ C} 81.65, \text{ H}
8.87; Found: C 81.38, H 8.29.

### 4.5 References


\textit{37}, 402.
