

Studies on monobenzo 18-crown-6-ether substituted phenylenevinylene oligomer: synthesis, photoluminescent, and dielectric properties

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Received: 2 February 2011 / Accepted: 13 August 2011 / Published online: 25 August 2011
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Abstract Partially conjugated monobenzo 18-crown-6 substituted oligo (*p*-phenylenevinylene) (MB-OPV) was synthesized via Wittig route. Formation of the oligomer was characterized by spectral (FTIR, ^1H NMR, and ^{13}C NMR), elemental and gel permeation chromatography analysis. The morphology of the oligomer film of one-dimensional (1D) and three-dimensional (3D) architectures were observed using atomic force microscopy. The oligomer showed excellent photoluminescence (PL) of bluish green emission at shorter wavelength of 542 nm. Stability of the polymer and glass transition temperature was determined by TGA/DSC. The dielectric properties such as dielectric constant and loss factor for the oligomer have also been studied with respect to change of frequency (50 Hz–5 MHz) and temperature (30–90 °C). The value of dielectric constant decreased with increasing frequency which indicates that the major contribution comes from orientation polarization. The value of dielectric constant increased with increasing temperature which is due to greater freedom of movement of the dipole molecular chains within the oligomer at high temperature.

Keywords Phenylenevinylene oligomer · Monobenzo 18-crown-6 · Photoluminescence · AFM · Dielectric properties

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Introduction

Use of poly(para-phenylenevinylene) as active polymeric materials of interest in light emitting diodes (LED) [1], plastic laser [2, 3], photovoltaic devices [4], light emitting electrochemical cells (LEC) [5, 6], and optoelectronic applications. The discovery of electroluminescence in PPV and conjugated polymers, such as poly(fluorine)s (PFs), poly(phenylene)s (PPs), and their derivatives have been studied extensively [7–12]. Currently, PPV and its derivatives are most popular materials in LEDs. The most commonly used substituent in PPV derivatives are alkoxy [13, 14], silyl [15, 16], and phenyl groups [17–21]. But, crown ether substituted groups are rarely found, except in the recent contributions from Babudri group [14]. According to them, crown ether moiety into phenylenevinylene does not reduce its basic function, but endows some new properties to the conjugated polymers.

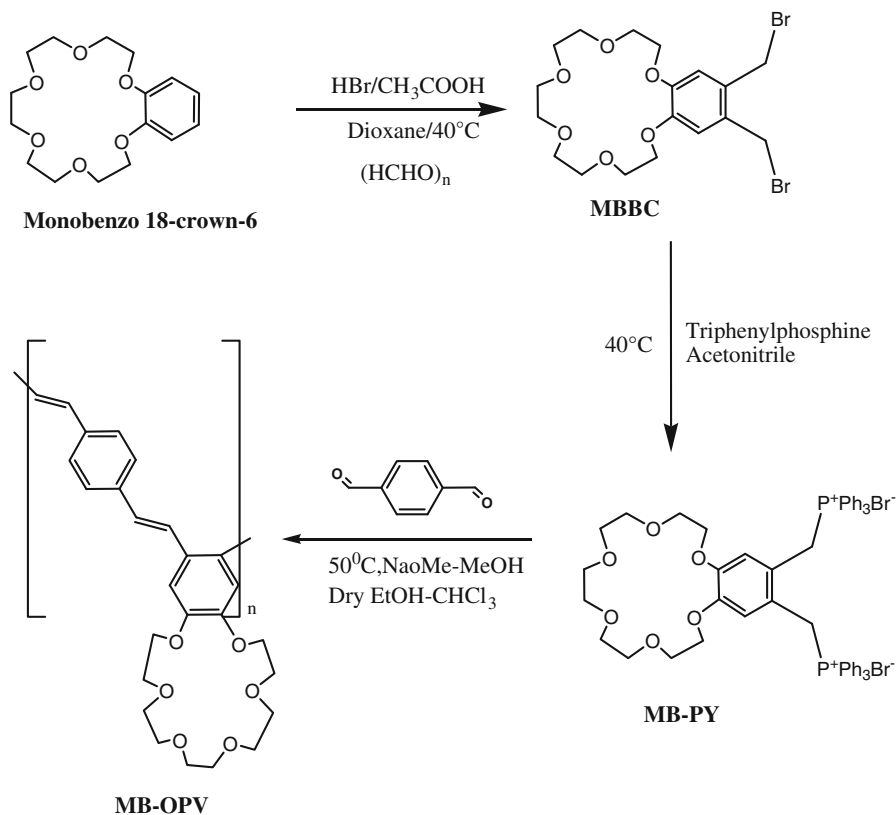
Recently, the 2,3-disubstituted derivatives of PPV, which exhibit considerably high performance, have attracted much interest owing to their ability to control the electronic properties of PPV via steric interaction of the side-substituted groups [13, 20, 21]. On the basis of all these studies, it is then postulated that PPV with crown ether units in direct π -conjugation at the 2,3-position is expected to exhibit new functional properties based on the electrical conductivity of the main chain and the cation-binding ability of the crown ether cavity.

Dielectric properties provide information about the segmental mobility within a polymer. The study of dielectric constant and dielectric loss, as a function of frequency is one of the most convenient and sensitive methods of studying polymeric structure. Conjugated polymers exhibit conducting or semiconducting properties indeed, and the conducting and semiconducting polymers made up of conjugated polymers seem to be suitable candidates due to their optical and electrical properties such as dielectric constant, refractive index, impedance, permittivity, etc. These parameters carry valuable information for optimizations of studied materials in technological applications. Among these polymers, phenylenevinylene-based materials have emerged as one of the most promising materials due to the easiness of its synthesis, its environmental stability, and the possibility to modify with different groups [22]. In a previous report [23], we investigated the optoelectronic properties for dibenzo functionalized phenylenevinylene polymer system. There is no study reported on the dielectric relaxation behavior of monobenzo 18-crown-6 binded PPV oligomer. Our intention of this investigation involves the synthesis of PPV-substituted monobenzo 18-crown-6 ether units in direct π -conjugation at the 2,3-position via Wittig route (MB-OPV, as shown in Scheme 1) and analyzed the photoluminescence (PL) properties. Moreover, dielectric constant and dielectric loss have been studied with respect to change of frequency and temperature.

Experimental

Materials

Monobenzo 18-crown-6, terephthalaldehyde, triphenylphosphine, paraformaldehyde has been purchased from Sigma Aldrich. Chloroform, *n*-butanol, acetonitrile,



Scheme 1 Synthesis of MB-OPV

methanol, acetone, benzene, dioxane, and acetic acid were purchased from S.D. Fine-Chem and solvents were purified as per standard procedures before use.

Characterization

UV, FTIR, and NMR spectra were recorded from Shimadzu-1601, Thermo Nicolet 330 (KBr), and JEOL-GSX-400 instruments. Elemental Vario El III, Carlo Erba 1108 system were used for elemental analysis. The exact molecular weight of the phosphonium ylides (MB-PY) have been measured from JEOL GCMATE II GC-MS under with high resolution data system. Maximum resolution is 6000 Daltons and calibrated mass is 1500 Daltons. Gel permeation chromatography (GPC) was recorded on a Shimadzu instrument system against polystyrene standard using tetrahydrofuran (THF) as the eluent. PL studies were done by using fluorescence spectrometer of Horiba Jobin yvon FLUOROLOG 3-11. Oligomer sample was prepared for atomic force microscopy (AFM) study by 0.5 μM of MB-OPV in chloroform deposited into silicon glass substrates and allowed to dry for 30 min at room temperature. AFM was recorded under ambient conditions using VEECO CP2

instrument. Si cantilever tips with a resonance frequency of approximately 300 kHz and spring constant of about 40 nm^{-1} were used.

Measurement of dielectric properties

Dried and powdered MB-OPV pressed at 500 MPa into pellet of 0.83 mm thickness (d) and 13 mm in diameter were used for the study of dielectric properties such as dielectric constant and loss factor. The instrument HIOKI-3532.50 LCR Hi tester model was used and the temperature range was fixed from ambient to 600°C . The pellet was coated with an electronic grade silver paste that acts as an electrode. The dielectric constant is calculated from the recorded values of the capacitance (C_p) obtained directly from the instrument at various temperatures $30\text{--}60^\circ\text{C}$ at a frequency of $50 \text{ Hz--}5 \text{ MHz}$ using the equation,

$$\text{Dielectric constant} = C_p \times d/A \times \epsilon_0,$$

where ϵ_0 permittivity of vacuum is 8.85×10^{-12} Farad/m and A the cross-sectional area of the sample is πr^2 , r is the radius of the sample pellet.

Methods

Synthesis of 2,3-(4,5-dibromomethylmonobenzo)-1,4,7,10,13,16-hexaoxacyclooctadeca-2-ene (MBBC)

A solution of HBr in acetic acid (30 wt%, 15 ml) was slowly dropped into 1,4 dioxane (20 mL) containing monobenzo-18-crown-6 (5.92 g, 19.0 mmol) and paraformaldehyde (2.30 g, 76.6 mmol). The mixture was allowed to stir at 40°C for overnight. The resulting precipitate was thoroughly washed with 1,4-dioxane and MeOH, to give colorless crystals of MBBC (6.05 g, 70%, mp 92°C). ^1H NMR (CDCl_3 , ppm): 6.8 (2H, phenylene), 4.9 (4H, ArCH_2Cl), 4.14 (4H,), 3.89 (4H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 3.74 (6H, $\text{OCCCH}_2\text{CH}_2\text{O}$). ^{13}C NMR (CDCl_3 , ppm): 149, 129, 116, 71.3, 70.6, 69.7, 68.9, 28.3. FTIR (KBr, cm^{-1}): 1216 and 1263 (alkyl C–O–C), 1098 (aralkyl C–O–C), 1516 (phenyl nucleus), and 833 (CH_2Br). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{Br}_2\text{O}_6$: C, 43.39; H, 5.26; O, 19.27; Found; C, 42.89; H, 5.15; O, 18.89.

Synthesis of 2,3-(4,5-bis(triphenylphosphonium ethyl)monobenzo)-1,4,7,10,13,16-hexaoxacyclooctadeca-2-enedichloride (MB-PY)

MBBC (1.99 g, 4.6 mmol) and triphenylphosphine (2.8 g, 10.2 mmol) was dissolved together in acetonitrile (20 mL). The solution was stirred constantly for overnight at 40°C . The resulting colorless precipitate was recrystallized from toluene–methanol mixture to yield MB-PY (3.4 g, 76%, mp 168°C). ^1H NMR (CDCl_3 , ppm): 7.4–7.7 (30H, $\text{Ph}_3\text{P}^+\text{CH}_2$), 6.8 (2H, phenylene), 5.5 (4H, $\text{ArCH}_2\text{PPh}_3$), 3.6–4.2 (20H, CH_2O in crown ether ring). ^{13}C NMR (CDCl_3 , ppm): 140, 135, 130, 119.3, 118.6, 117.7, 70.9, 68.8, and 30.3. FTIR (KBr, cm^{-1}): 1117 (alkyl C–O–C), 1262 (aralkyl C–O–C), 1434, 1474, 1588 (phenyl nucleus), 748

(C–P), 693 (C–Br), 490 (P–Br). HRMS calculated for $C_{54}H_{56}Br_2O_6P_2$ (m/z) = 1435.2170, found 1435.6163.

Synthesis of oligo-(4,5-(monobenzo-18-crown-6) vinylene-1,4-phenylene-vinylene) (MB-OPV)

Wittig reaction Equimolar amounts of the bisphosphonium salt (MB-PY) (1.02 g, 1.0 mmol) and terephthalaldehyde (0.137 g, 1.0 mmol) were dissolved in a mixture of absolute ethanol and dry chloroform (12 mL, 3 + 1 v/v) under N_2 atmosphere. Then, a pre-determined amount of sodium methoxide (25 wt% in methanol, 0.651 mL, 2.8 mmol) was added and the resulting red solution was stirred at 50 °C overnight. Precipitation in methanol gave yellow oligomer, which was re-precipitated from dichloromethane–methanol. This was further reacted with catalytic quantity of I_2 at 70 °C. Formed isomerized oligomer (MB-OPV) was purified by precipitation in methanol (0.31 g, 71%). 1H NMR ($CDCl_3$, ppm): 7.4–7.6 (4H, 1,4-phenylene), 7.8 (4H, vinylene), 6.8 (2H, benzocrown), 3.4–4.2 (20H, CH_2O in crown ether ring), ^{13}C NMR ($CDCl_3$, ppm): 61, 70 (CH_2 of crown ether), 100, 131, 137 (phenyl carbons), 132, 133 (phenylene and vinylene), 128 (1,4 disubstituted benzene). FTIR (KBr, cm^{-1}): 1109 (alkyl C–O–C), 1265 (aralkyl C–O–C), 1494 1596 (phenyl nucleus), 961 (C=C), anal. calcd for $C_{26}H_{30}O_6$: (C, 70.56%; H, 7.74%; O, 21.69%); found; C, 70.18%; H, 7.08%; O, 22.08.

Results and discussion

Crown ether with phenylenevinylene oligomer (MB-OPV) can be synthesized in different ways via Gilch or sulfonium precursor route [24–26] and Wittig route [27]. Former finds difficulty of synthesis whereas Wittig was found to be easy perhaps with lesser yield. Dibromomethyl monobenzo 18-crown-6 (MBBC) intermediate was first prepared by bromo methylation of monobenzo 18-crown-6 and then quantitatively transformed into the phosphonium ylide which was subjected to various experimental conditions to get the final product of MB-OPV oligomer. These oligomer is highly soluble in common solvents such as THF, chloroform, methylene chloride, 1,2-dichloroethane, and DMF. The synthetic procedure is given in Scheme 1.

Synthesis of MBBC

Dibromomethyl monobenzo 18-crown-6 (MBBC) intermediate has been synthesized from monobenzo 18-crown-6 with HBr in an overall yield of 70%. The presence of bands at 833, 1516 cm^{-1} in IR spectrum clearly indicated the functional groups like C–Br and phenyl nucleus. Furthermore, IR spectra of the oligomer showed the alkyl C–O–C and aralkyl C–O–C bands at 1261 and 1098 cm^{-1} . This fact was further confirmed by appearance of signals at 3.5–4.0 and 4.9 ppm (for CH_2 protons attached to crown ether ring and bromo group) in 1H NMR spectra and singlet at 129–149 and 28.3 (for aromatic carbon and CH_2 –Br moiety) in ^{13}C NMR spectra. The results of the elemental analysis were in good agreement with the theoretical value of the brominated compound (MBBC).

Synthesis of MB-PY

Monobenzo 18-crown-6 phosphonium ylide (DB-PY) has been synthesized (Scheme 1) from MBBC in the presence of triphenyl phosphine in an overall yield of 76%. The structure of the DB-PY was confirmed by appearance of strong bands at 748 and 490 cm^{-1} (for C–P and P–Br str) in IR spectra, multiplet formed at 7.4–7.7 ppm for aromatic hydrogens of phosphonium salt (zwitter ion) in ^1H NMR spectra. Methylene signal of 4.9 ppm shifted to 2.5 ppm (^1H NMR) and 28 ppm shifted to 32 ppm (^{13}C NMR) indicates methylene group attached with phosphonium salt was confirmed.

The molecular weight of the phosphonium salt from the HRMS spectrum was found to have 1435.6163. This value was in good agreement with the theoretical value 1435.2170.

Synthesis of MB-OPV

Through Wittig reaction, monomer MBBC was polymerized into the conjugated MB-OPV by using terephthalaldehyde in the presence of NaOMe (Scheme 1). The polymerization was performed in a mixture of dry chloroform and absolute ethanol (1 + 3 v/v) to enhance the solubility of the ylid (zwitterion) and the resulting material [28]. The crude polymer was purified by precipitation from methanol twice and then MB-OPV was obtained as yellow solid with a yield of 71%. The purified polymer was characterized by UV–Vis, FTIR, ^{13}C NMR, ^1H NMR, elemental analysis, GPC and analyzed the PL properties.

The final oligomer produced by the Wittig reaction was known to have a 65% *cis* double bonds, which can be converted into the 91% *trans* linkages by adding catalytic amount of iodine [29]. This was confirmed in the FTIR spectrum showed the peaks at 961 cm^{-1} corresponding to an out-of-plane mode of the *trans*-vinylene and a very weak absorption at around 852 cm^{-1} (*cis*-vinylene), suggesting that the polymers in the configuration of *trans*-vinylene is predominant. This proves that the vinylene double bond formation and consequently the polymerization reaction have been successful. ^{13}C NMR signals formed at 132 and 133 ppm corresponds to vinyl carbons and phenyl carbons. In addition, existence of benzyl carbons and CH_2 of crown ether formed at 100–137 and 70 ppm, appearance of 128 ppm confirmed the vinylene group attached directly at para position of phenylene ring (1,4 position). The oligomer showed that ^1H NMR signals of vinyl protons and aromatic protons were formed at 7.8 and 7.4–7.6 ppm. In addition, existence of crown ether ring and benzyl hydrogens peak formed at 3.4–4.2 and 6.8 ppm. It can be noted the assigned solution ^1H and ^{13}C NMR spectra given in Fig. 1a, b. The experimental elemental analysis data (C, 70.18%; H, 7.08%; O, 22.08%) were agreed well with that calculated (C, 70.56%; H, 7.74%; O, 21.69%) for $\text{C}_{26}\text{H}_{30}\text{O}_6$. Although, the weight average molecular weight (M_w) was analyzed for MB-OPV from GPC measurement was 3455 g mol^{-1} and M_w/M_n is 1.60, which correspond to about 4.9 monomer units on average, which is much lower than the crown ether containing PPV at 2,3 position ($M_w = 86,900$) prepared by Liu et al. [26]. The reason behind that is the Wittig product formed usually have low molecular weight and polydispersity index,

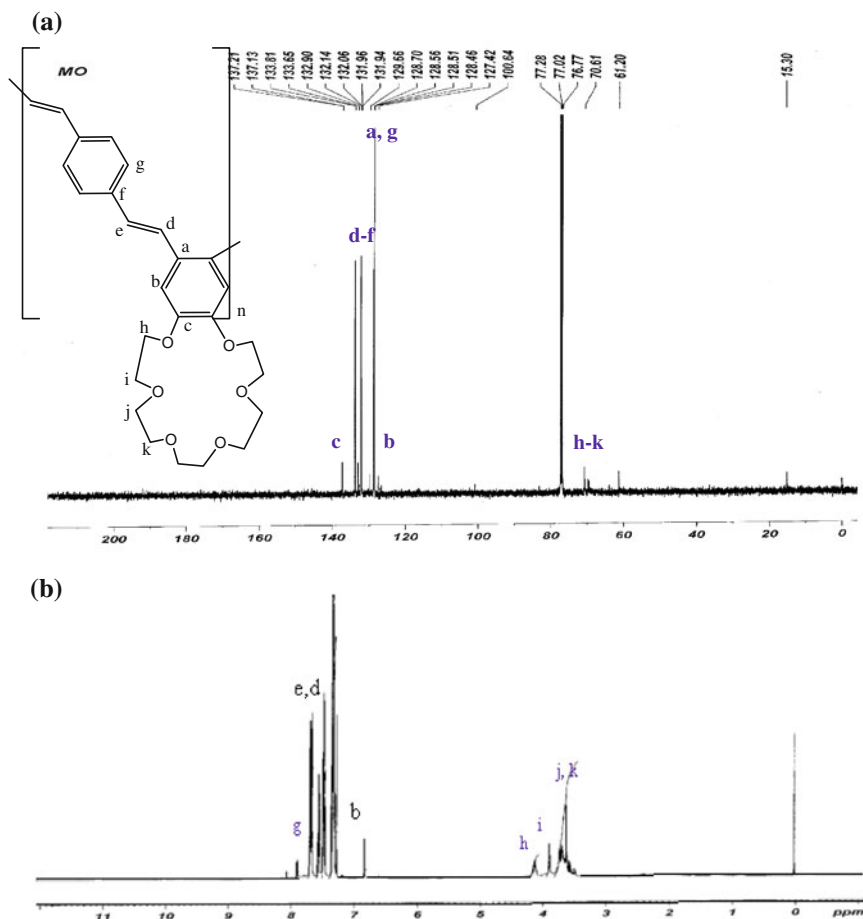


Fig. 1 **a** ^{13}C -NMR, **b** ^1H -NMR spectra of MB-OPV in CDCl_3

which was supported by Winkler et al. [24] ($M_w = 3900$) and Babudri et al. [14] ($M_w = 1880$).

Thermal analysis

While the polymer LED devices operate at high voltages, the temperature of the device will increase and also possible to loss of mechanical strength. Higher thermal stability and glass transition temperature (T_g) of the polymer must be needed to satisfy these requirements in LED devices. Thermal analysis (TGA, DSC) is the most favored techniques for ranking the thermal stability and T_g of the synthesized polymer. TGA spectra are presented in Fig. 2. The initial thermal decomposition temperature (T_{onset}) begins at 352 °C. These polymers have better thermal stability than that of phenylenevinylene copolymers reported elsewhere [30] because of the

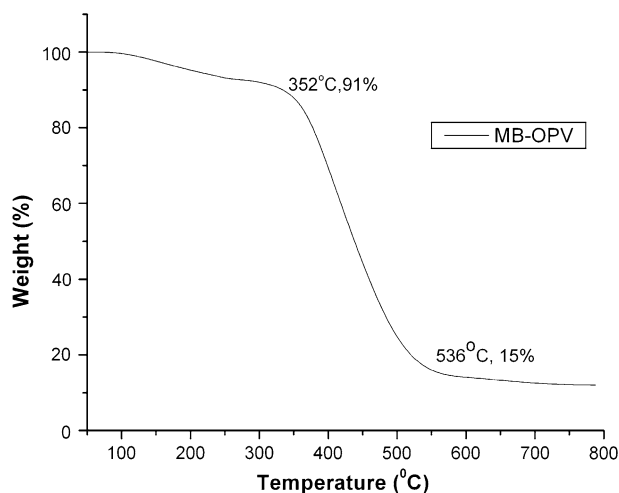


Fig. 2 TGA thermogram of MB-OPV

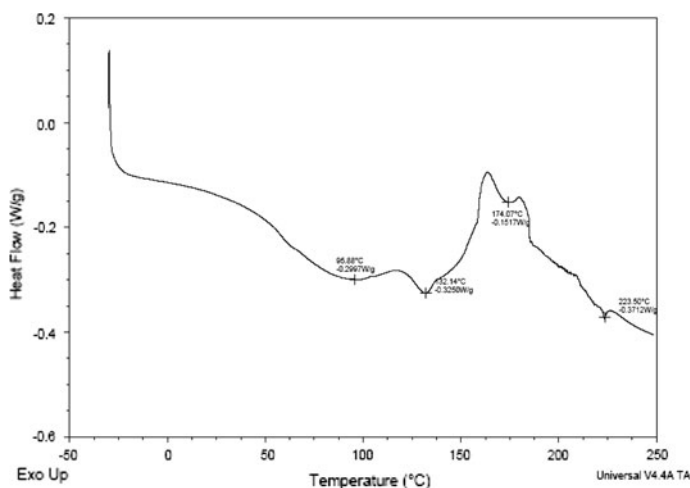


Fig. 3 DSC thermogram of MB-OPV

high C–O bond strength (1076 kJ/mol) of the crown ether side chains attached into PPV system. The drastic decrease in weight was observed from 352 °C and reaches to final thermal decomposition temperature (T_{\max}) at 536 °C. This may be due to the degradation of the crown ether chain present in the polymers.

DSC thermogram for the oligomer is shown in Fig. 3. Glass transition temperature of MB-OPV was exhibited (T_g) at 95.8 °C. This temperature was higher than linear copolymers reported elsewhere [31] which usually have 60–80 °C. Thus, high glass transition temperature of light emitting polymers is favorable for longevity of device operation.

Morphology analysis

The AFM technique provides the information about microscopic morphology of the polymeric material. Figure 4 shows AFM images of the MB-OPV. It can be seen that the spherical shape of the particles was found from the MB-OPV surface. From the cross-section profiles of the oligomer, the shape and diameter of the domains were approximately round and uniform diameter; it ranges from 153 to 200 nm.

AFM topography was also used to find out the average surface roughness (R_a), root mean square roughness (R_q) for the oligomer. It is clear from the Fig. 4 that MB-OPV had good surface roughness. The RMS roughness were found to have 40 nm, which is higher than the unsubstituted PPV (0.9 nm) reported elsewhere [32]. Increased surface roughness may be due to the presence of monobenzo crown

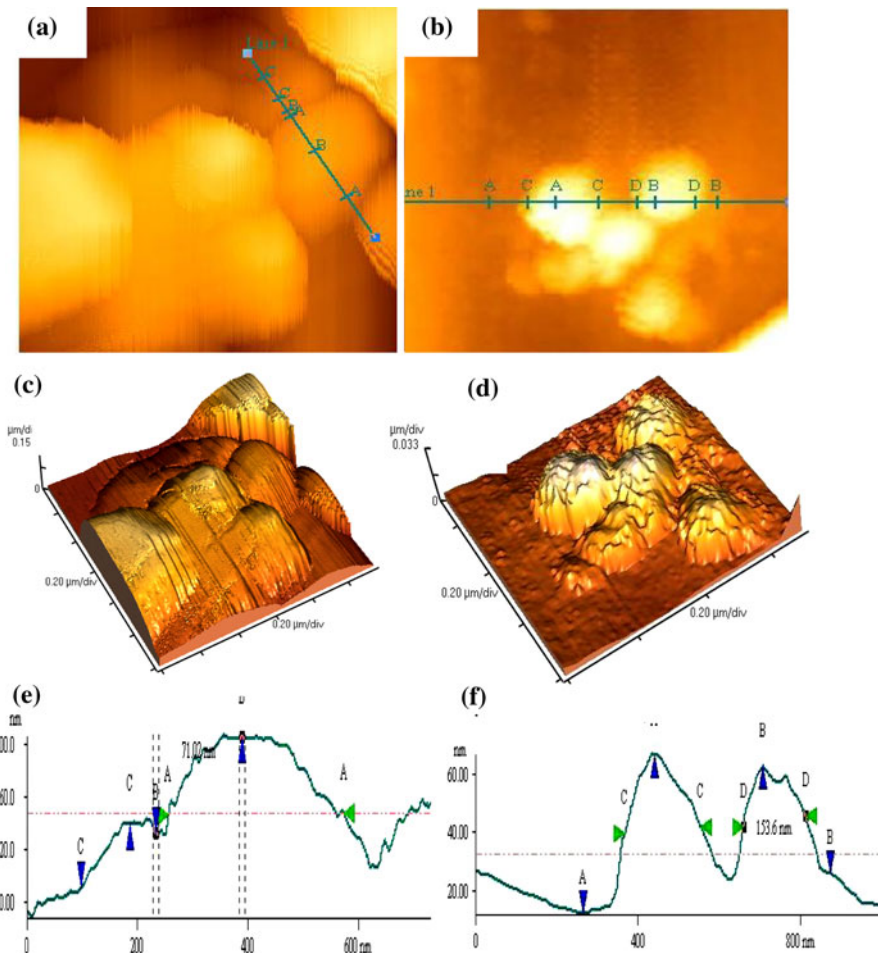


Fig. 4 AFM images of **a, b** spherical shaped structures, **c, d** 3D image surface profile, and **e, f** AFM cross-section profiles for MB-OPV

ether groups and also the lack of strong interaction between crown ether moieties [33]. Feng et al. [33] also reported the positive correlation between the surface morphology and glass transition temperature for the crown ether system. The similar correlation was also observed in this investigation, which showed that the higher T_g of the MB-OPV (95.8 °C) had more average surface roughness (148 nm).

Optical and photoluminescent properties

Figure 5a, b displays the absorption and PL spectra of the MB-OPV in the CHCl_3 solution. The synthesized MB-OPV showed the maximum absorption wavelength (λ_{max}) appeared at 380 nm, which is due to the π – π^* electronic transition associated with the π -conjugated polymer backbone. The well-known reported polymer poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) showed the λ_{max} at 510 nm [34], which has red shifted compared to the present MB-OPV system. This is because of interrupting the π -electron delocalization of the polymer main chain, resulting in the reduction of the π -conjugation length. In this case, crown ether connected with ortho linkages of (*p*-phenylenevinylene), which is more bent structure than that of the 4,5 dialkoxy substituted para linkages of (*p*-phenylenevinylene) [35]. Consequently, the π -electron delocalization of the polymer main chain was also interrupted by ortho linkages, yielding decrease of conjugation length. The energy gap calculated from the edge of the absorption spectrum (480 nm) was estimated to be 2.58 eV.

The PL spectra were recorded with an excitation wavelength corresponding to the λ_{max} of the polymer. Bluish green PL is observed in the Fig. 5c. The emission of MB-OPV was 542 nm. This was blue shifted about 38 nm when compared to MEH-PPV system (580 nm) [34], which might be due to the crown ether attached in the alternating PPV system. As a result, increase the band gap thus by decreasing the

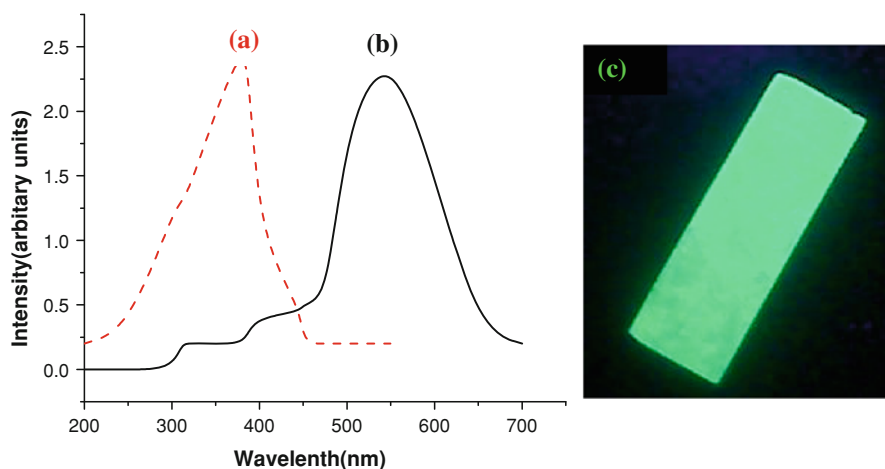


Fig. 5 a UV–VIS and b PL spectra of MB-OPV in chloroform solution. c PL was observed under UV-light illumination at 542 nm

electron density of the conjugated main chain. The feature of this spectrum was similar to alkoxy-substituted PPV system [36].

The ortho linkage of PPV also played important role in PL spectra. The measured value of crown ether substituted ortho linked PPV were higher than para linked PPV and lower than para linked PPV [35]. This is due to the hindrance in the packing of the polymer chains. These results revealed that ortho linkage in the alternating copolymer system interrupt the conjugation and interfere with the packing of the polymer chains, which results in the formation of amorphous polymers for an increased luminescence [37].

Electrical properties

Dielectric constant of a material is the ratio of its permittivity to the permittivity of vacuum (ϵ_0). Figure 6 shows the variation of dielectric constant with frequency at different temperatures (30–90 °C) for MB-OPV oligomer. It is evident that the decrease in dielectric constant is very prominent at both low frequencies and at high temperature. The decrease of dielectric constant with increasing frequency is the expected behavior in most dielectric materials. This is due to dielectric relaxation which is the cause of anomalous dispersion. The initial high value of dielectric constant at relatively lower frequencies may be due to the contributions from space charge polarization in the bulk material, structural defects, and electrode effects [38]. At higher frequencies, the rotational motion of the polar molecules of dielectric was not sufficiently rapid for the attainment of equilibrium with the field. Hence, dielectric constant seems to be decreasing with increasing frequency [39].

Figure 7 shows the variation of dielectric constant with temperature at different frequencies. The value of dielectric constant increases with temperature at fixed frequency. At lower frequencies this effect is more prominent. The increase in

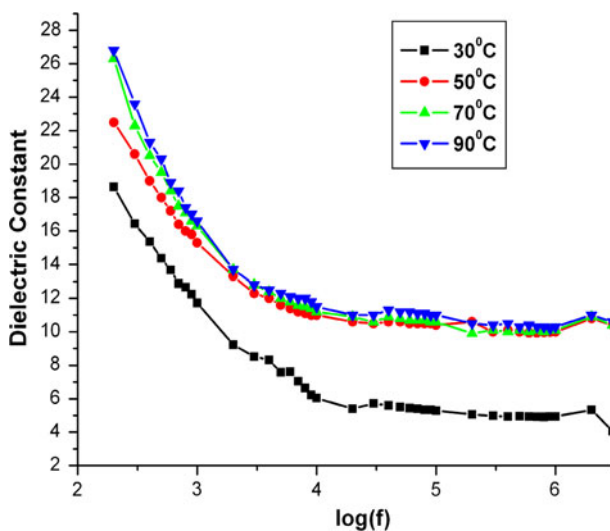


Fig. 6 Variation of dielectric constant with frequency of MB-OPV

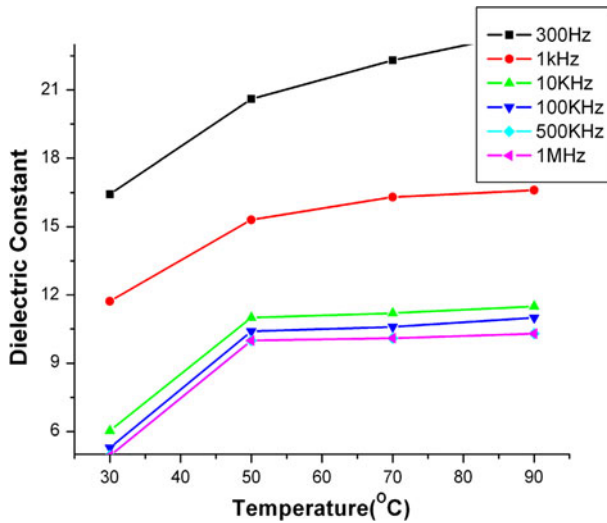


Fig. 7 Temperature dependence of dielectric constant at different frequencies for MB-OPV

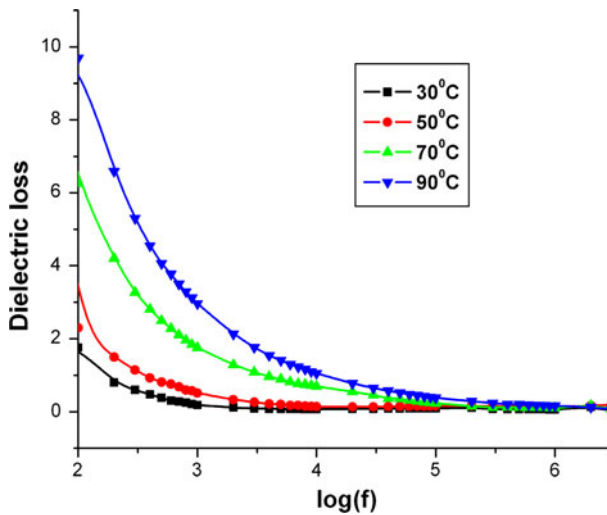


Fig. 8 Variation of loss factor with frequency of MB-OPV

dielectric constant with temperature is due to the greater freedom of movement of dipole molecular chain of oligomer. At lower temperature, as the dipoles are rigidly fixed in the dielectric, the field cannot change the condition of dipoles. As the temperature increases, the dipoles comparatively become free and they respond to the applied electric field. Thus, polarization increased and hence dielectric constant is also increased with the increase of temperature [40, 41].

Figure 8 shows the variation of dielectric loss factor with frequency at different temperatures for MB-OPV oligomer. The value of dielectric loss decreases with the

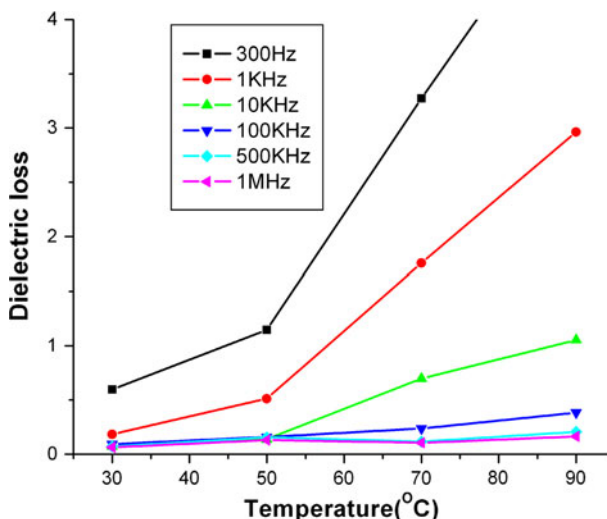


Fig. 9 Temperature dependence of dielectric loss at different frequencies for MB-OPV

increase of frequency at fixed temperature. The higher value of dielectric loss at low frequency is due to the free charge motion within the materials. Figure 9 shows the variation of dielectric loss factor with temperatures at different frequencies. The dielectric loss factor increase with temperature, particularly at lower frequencies at which dielectric loss due to chain motion of oligomer is more effective. At high frequencies, however, the dielectric loss factor is low and remains more or less constant with increasing temperature because the orientation polarization due to chain motion of polymer cannot keep phase with the rapidly oscillating electric field [42].

Conclusions

Monobenzo 18-crown-6-based poly(phenylenevinylene) oligomer (MB-OPV) has been successfully synthesized using Wittig reaction. Formation of the oligomer was confirmed with FTIR, ^1H NMR, ^{13}C NMR spectral studies, GPC, and elemental analysis. This oligomer showed good thermal stability and spherical shaped of the particles, which was observed from AFM topography. Photoluminescent property of the synthesized oligomer was investigated using UV–Vis and fluorescence spectrometers. The results indicated that MB-OPV is considerably high photo luminescent material which has unusual optoelectronic properties for electroluminescent applications. Frequency and temperature dependence of dielectric constant and dielectric loss of MB-OPV oligomer have been studied in the frequency range of 50 Hz–5 MHz and the temperature range 30–90 °C. The experimental results indicate that dielectric constant and dielectric loss decreased with increase of frequency is due to the orientation polarization and increase in dielectric constant with increase of temperature is due to greater freedom of movement of dipole molecular chain of oligomer.

Acknowledgment We thank VIT University for providing laboratory facilities, VIT-TBI and SAIF-IIT for recording spectral data.

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