Applications of Wittig Reactions in Dibenzo 18-Crown-6-Ether Substituted Phenylenevinylene Oligomer—Synthesis, Photo Luminescent, and Dielectric Properties

Subramanian Karpagam,[1] Selvam Guhanathan,[2] Pachagounder Sakthivel[1]

[1]Organic Chemistry Division, School of Advanced Science, VIT University, Vellore 14, Tamil Nadu, India
[2]Department of Chemistry, Government Arts College, Tiruvannamalai, Tamil Nadu, India

ABSTRACT: Novel phenylenevinylene oligomer substituted dibenzo 18-crown-6 ether ring (DB-OPV) was synthesized using dibenzo 18-crown-6 with terephthaldicarboxaldehyde via Wittig reaction. Formation of the oligomer was confirmed by spectral (FT-IR, ^{1}H and ^{13}C-NMR), gel-permeation chromatography and elemental analysis. The morphology of the oligomer film of one-dimensional and three-dimensional architectures was observed using atomic force microscopy. The oligomer showed excellent photoluminescence with bluish green emission maxima at shorter wavelengths of 505 nm. Stability of the oligomer was analyzed using UV spectroscopy with varying time and temperature. 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 (30–60°C). The value of dielectric constant decreased with increasing frequency, which indicates that the major contribution to the polarization 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 © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 960–967, 2011

Key words: phenylenevinylene oligomer; dibenzo18-crown-6; photoluminescence; AFM; dielectric properties

INTRODUCTION

Poly(*p*-phenylenevinylene) (PPV) is a active polymeric material of light emitting diodes,[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, poly(phenylene)s, and their derivatives have been studied extensively.[7–12] Currently, PPV and its derivatives are most popular materials in light emitting diodes. The most commonly used substituent in PPV derivatives are alkoxy,[13,14] silyl,[13,15,16] and phenyl groups.[17–21] But crown ether substituted groups are rarely found, except in the recent contributions from Babudri et al.[14] According to them, crown ether moieties into phenylenevinylene do 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. There is no work reported on the dielectric relaxtion behavior of dibenzo 18-crown-6 binded PPV oligomer. Our intention of this investigation involves the synthesis of PPV substituted dibenzo 18-crown-6 ether units in direct π-conjugation at the 2,3-position via Wittig route (DB-OPV, as shown in Scheme 1) and analyzed the photoluminescence (PL) properties. Moreover, dielectric constant and dielectric loss have also been studied with respect to change of frequency and temperature.

EXPERIMENTAL

Materials

Dibenzo18-crown-6, terephthaldicarboxaldehyde, triphenylphosphine, and paraformaldehyde, were purchased from Sigma Aldrich, Mumbai, India. *n*-
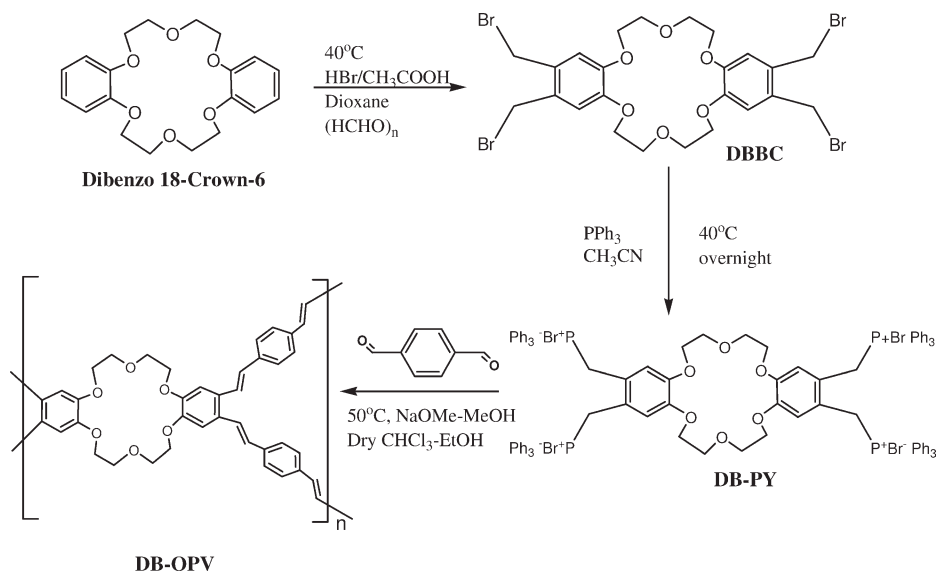
Scheme 1

Butanol, chloroform, acetonitrile, methanol, acetone, benzene, dioxane, and acetic acid were purchased from SD Fine-Chem, Chennai, India and solvents were purified by using standard procedure.

Characterization

UV, FT-IR, and NMR spectra were recorded from shimadzu-1601, Thermonicolet 330 (KBr), and JEOL -GSX -400 instruments. Elementar vario El III, Carlo Erba 1108 system was used for elemental analysis. Gel-permeation chromatography (GPC) was recorded on a shimadzu instrument system against polystyrene standard using tetra hydro furan as the eluent. PL studies were done by using fluorescence spectrometer of Horiba Jobin yuon FLUOROLOG 3-11. Oligomer sample was prepared for atomic force microscopy (AFM) study by 0.5 µM of DB-OPV in chloroform was deposited onto 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 $\sim$ 300 kHz and spring constant of $\sim$ 40 nm^{-1} were used.

Measurement of dielectric properties

Dried and powdered DB-OPV pressed at 500 MPa into pellet 0.83 mm thickness (d) and 13 mm in diameter was 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 (Cp) obtained directly from the instru-

ment at various temperature 30 to 60°C at a frequency of 50 Hz–5 MHz using the equation,

$$\text{Dielectric constant} = \text{Cpd}/A\varepsilon_o$$

where ε_o = Permittivity of vacuum = 8.85×10^{-12} Farad/m and A = Cross-sectional area of the sample = πr^2, r is the radius of the sample pellet

METHODS

Synthesis of 2,3,11,12-(4,4′,5,5′-tetrabromomethyl-dibenzo)-1,4,7,10,13,16-hexaoxacyclo-octadeca-2,11-diene

A solution of HBr in acetic acid (30 wt %,15 mL) was slowly dropped into 1,4 dioxane (20 mL) containing dibenzo-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 methanol to give colorless crystals of 2,3,11,12-(4,4′,5,5′-tetrabromomethyldibenzo)-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (DBBC; 6.05 g, 70.5%, M.P. 92°C).^{1}H-NMR (CDCl$_3$, ppm): 6.8(4H, Phenylene), 4.5 (8H, ArCH$_2$Br), 4.14 (8H, OCH$_2$CH$_2$O), 4.32 (8H, ArOCH$_2$CH$_2$O). ^{13}C-NMR (CDCl$_3$, ppm): 149, 129, 116, 71.3, 70.6, 69.7, 68.9, 28.3. FT-IR (KBr, cm^{-1}), 1198.83 and 1276.10 (alkyl C—O—C), 1121.02 (aralkyl C—O—C), 1509.77 (phenyl nucleus), 746.14 (CH$_2$Br).

Synthesis of 2,3,11, 12-(4,4′,5,5′-tetra (triphenyl-phosphonium methyl) dibenzo)-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-dienetetrachloride

DBBC (1.67 g, 2.5 mmol) and triphenylphosphine (2.8 g, 10.5 mmol) was dissolved together in acetonitrile

(20 mL). The solution was stirred overnight at 40°C. The resulting colorless precipitate was recrystallized from toluene-methanol mixture (2 : 1) to yield 2,3,11, 12-(4, 4′, 5, 5′-tetra (triphenylphosphonium methyl) dibenzo)-1, 4, 7, 10, 13, 16-hexaoxacyclooctadeca-2, 11-dienetetrachloride (DB-PY; 3.62 g, 85%, M.P 182°C). ^{1}H-NMR (CDCl$_3$, ppm): 7.4–7.7 (30H, Ph$_3$P$^+$CH$_2$)7.2 (2H, phenylene), 5.0 (4H, ArCH$_2$PPh$_3$), 3.6-3.8 (20H, CH$_2$O in crown ether ring), ^{13}C-NMR (CDCl$_3$, ppm): 140, 135, 130, 119.3, 118.6, 117.7, 70.9, 68.8, 30.32 FT-IR (KBr, cm^{-1}), 1176.73 (alkyl C—O—C), 1269.40 (aralkyl C—O—C),1434.45 ,1474.48, 1560.62 (phenyl nucleus), 741.62 (C—P), 692.25 (C—Br), 490.41 (P—Br)

Synthesis of oligo 4,4′,5,5′-(dibenzo-18-crown-6) bis vinylene-bis (1,4-phenylene-vinylene)

Wittig reaction

Equimolar amounts of the bisphosphonium salt (DB-PY) (1.72 g, 1.0 mmol) and terephthaldicarboxaldehyde (0.28 g, 2.0 mmol) were dissolved in a mixture of absolute ethanol and dry chloroform (12 mL, 3 + 1 v/v) under N$_2$ atmosphere. Then, a predetermined amount of sodium methoxide (25 wt% in methanol, 1.3 mL, 5.6 mmol) was added and the resulting red solution was stirred at 50°C overnight. Precipitation in methanol gave pale yellow oligomer, which was reprecipitated from dichloromethane-methanol. Formed oligomer (DB-OPV) was purified by dissolving in acetonitrile and chloroform. (0.64 g, 71%, M.P. 79°C). ^{1}H-NMR (CDCl$_3$, ppm): 7.4–7.6 (4H, 1, 4-phenylene), 7.8 (4H, vinylene), 7.2 (2H, benzocrown), 3.5–3.8 (20H, CH$_2$O in crown ether ring), ^{13}C-NMR (CDCl$_3$, ppm): 61, 79 (CH$_2$ of crown ether), 100, 131, 137 (phenyl carbons). 132,133 (vinylnene carbons), 128 (1,4 disubstituted benzene). FT-IR (KBr, cm^{-1}), 1119.40 (Alkyl C—O—C), 1265.61 (aralkyl C—O—C), 1434.99. 1593.49 (phenyl nucleus), 961.77 (C=C), Anal.Calcd for C$_{32}$H$_{30}$O$_6$: C, 75.28%; H, 5.92; O, 18.8; Found; C, 76.17; H, 5,45; O,17.9.

RESULTS AND DISCUSSION

DB-OPV oligomer can be synthesized in different ways via Gilch or Sulfonium precursor route[22–24] and Wittig route.[25] Former finds more difficult to synthesis whereas Wittig was found to be easy perhaps with lesser yield. Tetrabromo methyl dibenzo 18-crown-6 ether (DBBC) intermediate was first prepared by bromomethylation of dibenzo 18-crown-6 and then quantitatively transformed into the phosphonium ylide (DB-PY), which was subjected to various experimental conditions to get the final oligomer (DB-OPV) by using Wittig route. The synthetic procedure was shown in Scheme 1.

Synthesis of DBBC

Tetrabromomethyl dibenzo 18-crown-6 ether (DBBC) intermediate was synthesized from dibenzo 18-crown-6 with HBr in an overall yield of 71%. Presence of bands at 746, 1560 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 1276 and 1198 cm^{-1}. This fact was further confirmed by appearance of signals at 4.14–4.32 and 4.5 ppm (for CH$_2$ protons attached to crown ether ring and bromo group) in ^{1}H-NMR spectra and singlets at 129–149 and 28.3 (for aromatic carbon and CH$_2$ -Br moiety)in ^{13}C-NMR spectra.

Synthesis of DB-PY

Dibenzo 18-crown-6 phosphonium ylide (DB-PY) has been synthesized (Scheme 1) from DBBC in the presence of triphenyl phosphine in an overall yield of 85%. The structure of the DB-PY was confirmed by appearance of strong bands at 741 and 490 cm^{-1}(for C-P and P-Br stretching) in IR spectra, multiplet formed at 7.4–7.7 ppm for aromatic hydrogens of phosphonium salt (zwitter ion) in ^{1}H-NMR spectra. Methylene signal of 4.5 ppm shifted to 5.0 ppm (^{1}H-NMR) and 28 ppm shifted to 32 ppm(^{13}C-NMR) indicates methylene group attached with phosphonium salt was confirmed.

Synthesis of DB-OPV

Through Wittig reaction, monomer DBBC was polymerized into the conjugated DB-OPV by using terephthaldicarboxaldehyde 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.[26] The final oligomer produced by the Wittig reaction was known to contain a certain amount of cis and trans PPV units.[27] The crude polymer was purified by precipitation from methanol twice and then DB-OPV was obtained as yellow solid with a yield of 71%. The purified polymer was characterized by UV-Vis, FT-IR, ^{13}C-NMR, ^{1}H-NMR, elemental analysis, GPC, and analyzed the PL properties.

The FT-IR spectrum showed the peaks at 961 cm^{-1} corresponding to an out-of-plane bending 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 was predominant. ^{13}C-NMR signals formed at 132 and 128 ppm corresponds to vinyl carbons and phenyl carbons. In addition, existence of benzyl carbons and CH$_2$ of crown ether formed at 100–137 ppm and 70 ppm, appearance of 128 ppm confirmed
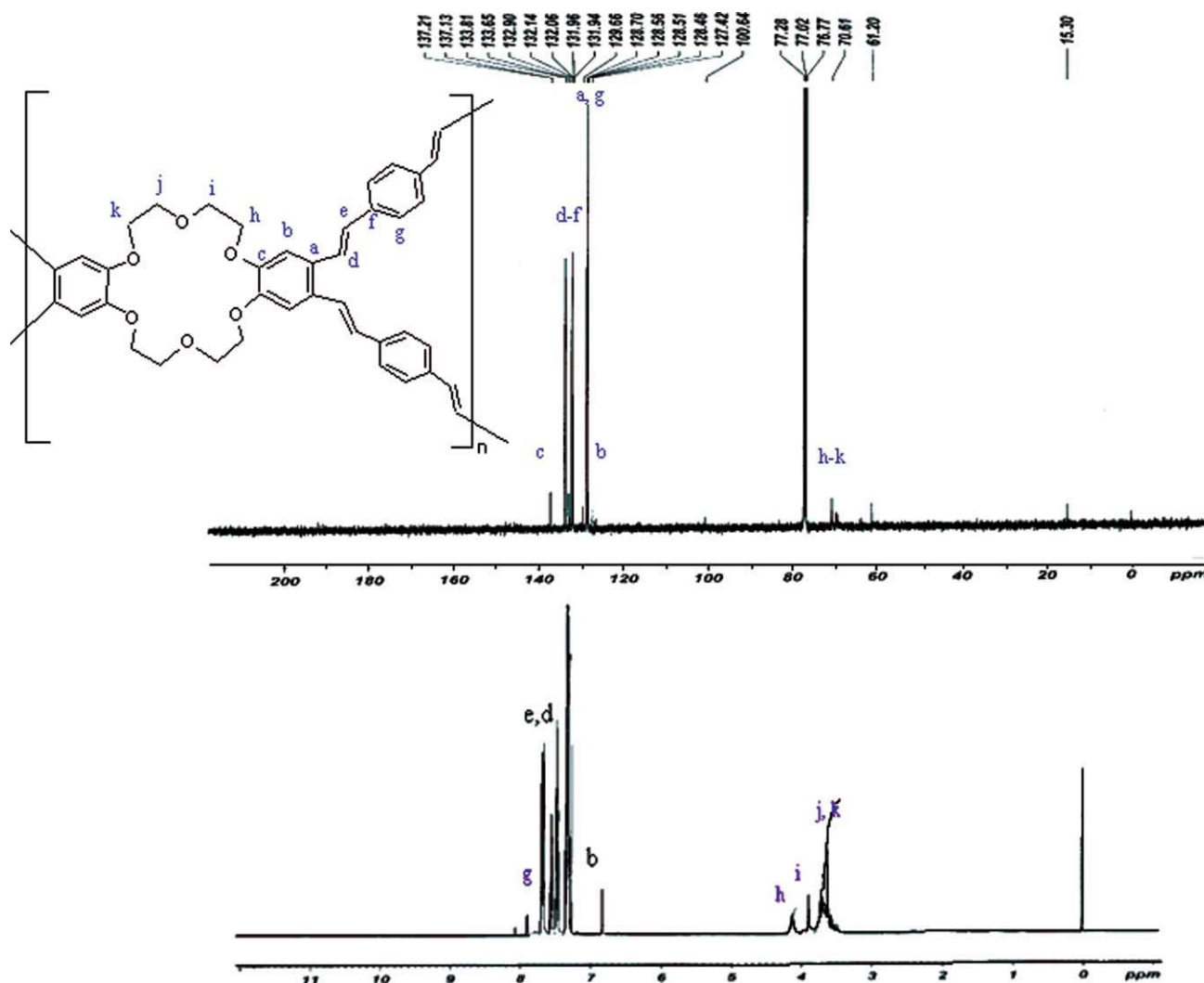
Figure 1 (a) ^{13}C-NMR (b) ^{1}H-NMR spectra of DB-OPV in CDCl$_3$.

the vinylene group attached directly at para position of phenylene ring (1, 4 position). The oligomer showed that H^{1} NMR signals of vinyl protons and aromatic protons were formed at 7.8 ppm, and 7.4–7.6 ppm. In addition, existences of crown ether ring and benzyl hydrogens peak were formed at 3.5–3.8 and 7.2 ppm. It can be noted that the assigned solution ^{13}C and ^{1}H-NMR spectra given in Figure 1(a,b). The experimental elemental analysis data (C, 76.17%; H, 5, 45%; O, 17.9%) are in agreement with that calculated (C, 75.28%; H, 5.92%; O, 18.8%) for C$_{32}$H$_{30}$O$_6$. Although, the weight average molecular weight was analyzed for DB-OPV from GPC measurement was 4100 g mol^{-1} and M_w/M_n was 1.7, which corresponds to ~ 4.7 monomer units on average.

Figure 2 shows the UV analysis of heat resistance test for DB-OPV oligomer in film state. The oligomer sample are coated separately on glass plate of 6 cm × 1 cm × 0.2 cm size and were kept for heating at 25°C and 75°C at 5 h and 10 h duration of time. All spectra are comparable in shapes. There was no

additional band or any deformation of the existing bands due to the thermal treatment. In fact, it is possible to observe a little increase in the intensity with
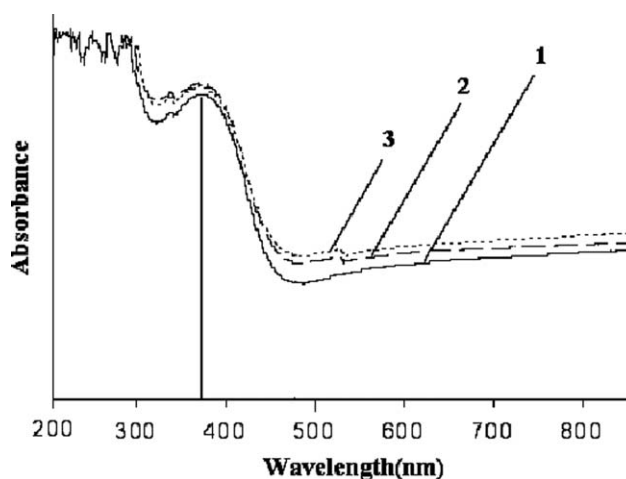

Figure 2 UV analysis of oligomer in film state after annealed at (1) 25°C (2) 75°C for 5 h (3)75°C for 10 h.
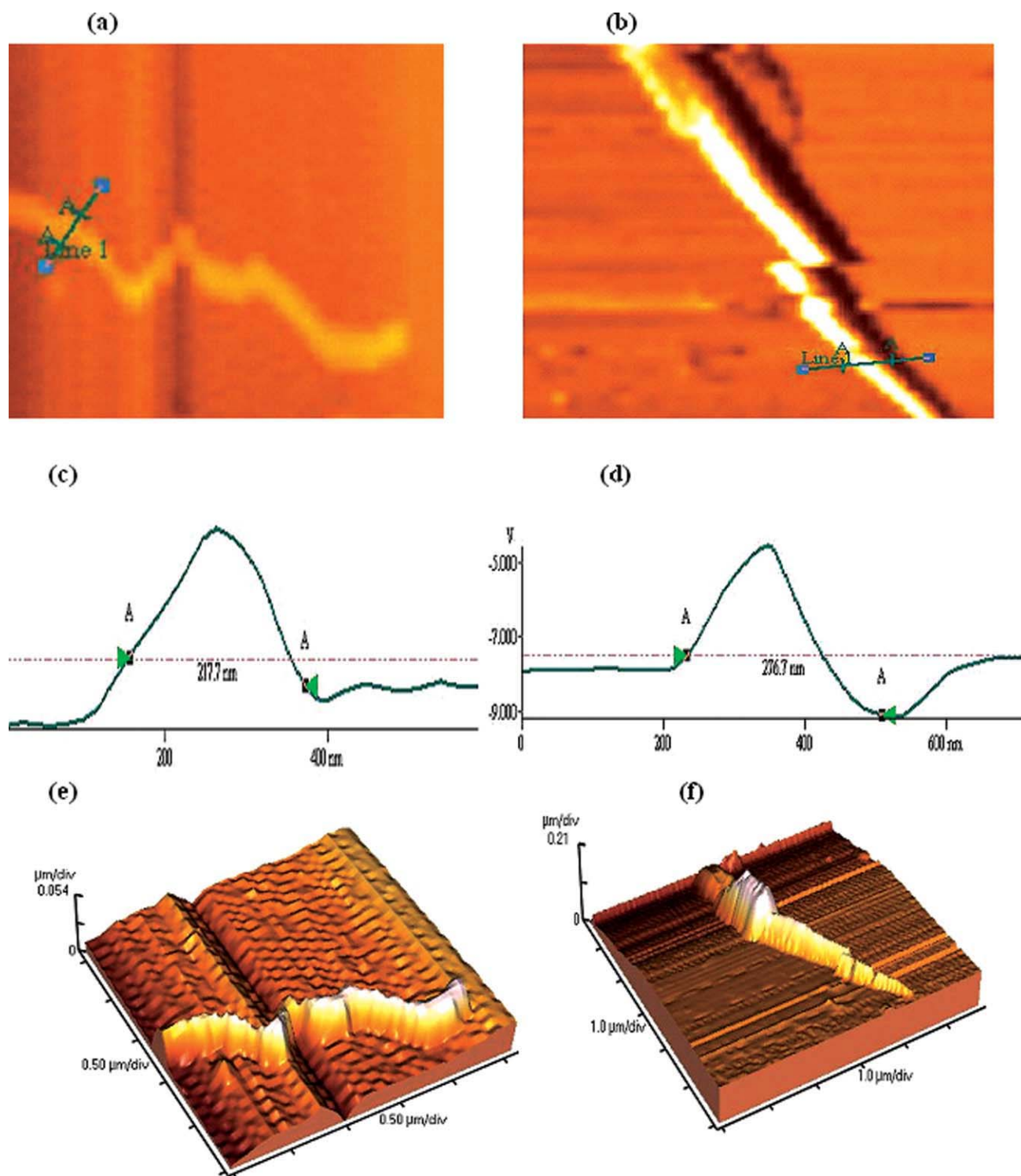
Figure 3 AFM image of (a) ribbon type structure (b) rod like structures (c, d) AFM Cross section profiles (e, f) 3-D image surface profile for DB-OPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the increase of temperature and time interval. Similar the solution spectrum, only one absorption band was observed at 380 nm for film state. These observations reveal that synthesized new material was thermally stable and maintain at 75°C at longer time intervals.

The AFM technique provides the information about microscopic morphology of the oligomer material. Figure 3a,b shows AFM height image of the nanoribbons and nanorods of the DB-OPV oligomer sample. Nanoribbons and rods, with an average width of 217 nm and 276 nm can be clearly observed.
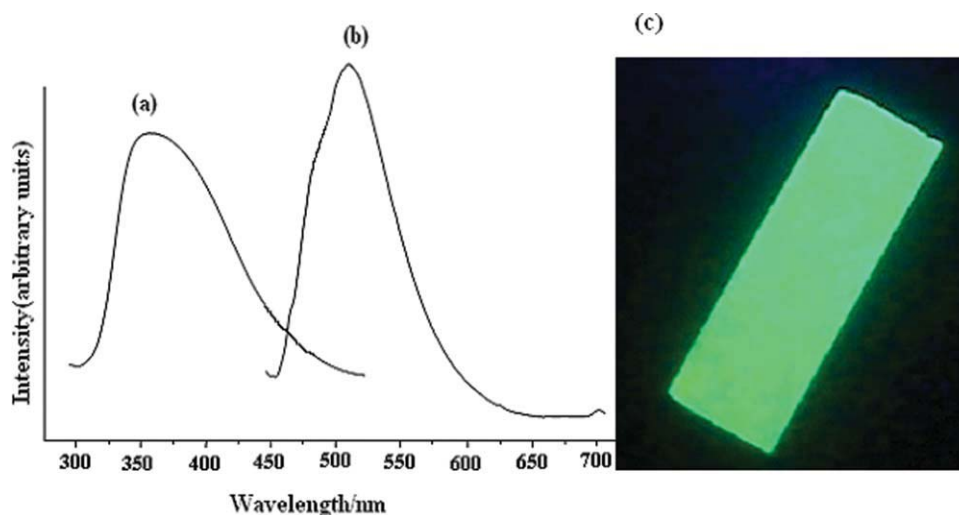
Figure 4 (a) UV-VIS (b) PL spectra of DB-OPV in chloroform solution (c) PL was observed under UV-light illumination at 505 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3c and 3 days shows the cross section profile of Figure 3a,b. It was found that the average thickness of the nanoribbons was less than the nanorods. From the 3D image of DB-OPV was shown in Figure 3e,f, average length for nanoribbons was found to be 2.5 μm and for nanorods was 5 μm.

Photoluminescent properties

Figure 4a,b displays the UV-Vis absorption and PL spectra of the DB-OPV in the CHCl$_3$ solution. The UV-Vis absorption spectra of the solution exhibited the maximum peak at 350 nm. It illuminates that the molecular structure of DB-OPV has great rigidity despite large spacers in its molecule. The absorption spectra of the film state shown at 380 nm may be due to the π–π* electronic transition associated with the π-conjugated polymer backbone. The energy gap between HOMO and LUMO taken from the edge of the absorption spectrum (450 nm) was estimated to be 2.75 eV. When an excitation at 350 nm was applied, the oligomer exhibits a strong bluish green emission ∼ 505 nm with a full width at half maximum of ∼ 143 nm. The feature of this spectrum was similar to mono benzo 18-crown-6 ether system.[24,25] Bluish green PL was observed for DB-OPV oligomer thin film at 505 nm displayed in Figure 4c.

Electrical properties

Dielectric constant of a material is the ratio of its permittivity to the permittivity of vacuum (ε_o). Figure 5 shows the variation of dielectric constant with frequency at different temperatures (30–60°C) for DB-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. 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.[28] 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.[29]

Figure 6 shows the variation of dielectric constant with temperature at different frequencies. The value of dielectric constant increases with temperature is due to the greater freedom of movement of dipole molecular chain of oligomer. At lower frequencies this effect is more prominent. At lower temperature, as the dipoles are rigidly fixed in the dielectric, the
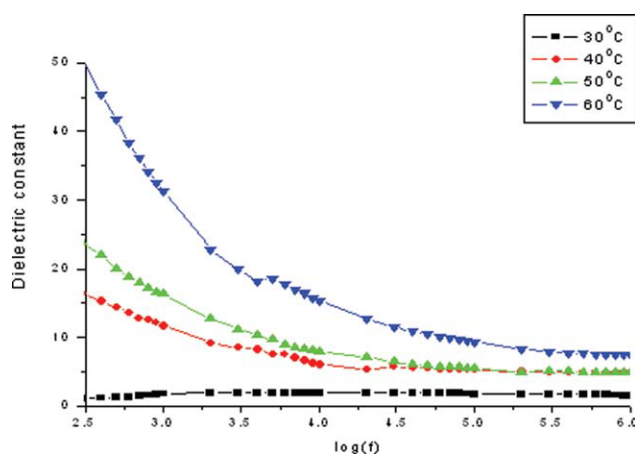

Figure 5 Variation of dielectric constant with frequency of DB-OPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
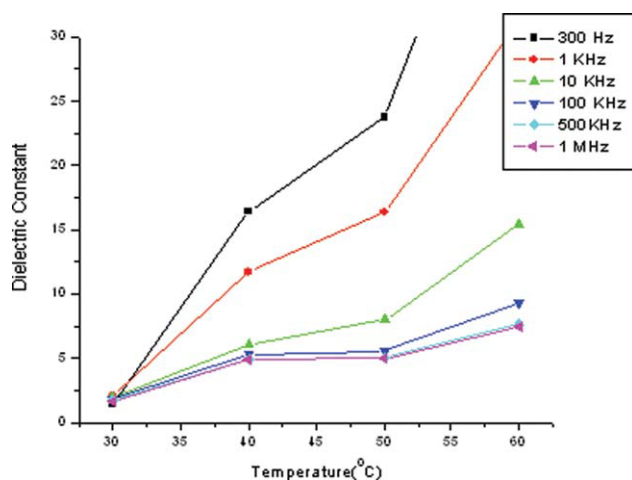
Figure 6 Temperature dependence of dielectric constant at different frequencies for DB-OPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 Temperature dependence of dielectric loss at different frequencies for DB-OPV 150 × 121mm (96 ×96DPI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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.[30]

Figure 7 shows the variation of dielectric loss factor with frequency at different temperatures for DB-OPV oligomer. The value of dielectric loss decreases with the 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 8 shows the variation of dielectric loss factor with temperature at different frequencies. The dielectric loss factor increases with temperature is due to chain motion of oligomer is more effective. At high frequencies, however, the dielectric loss factor is low
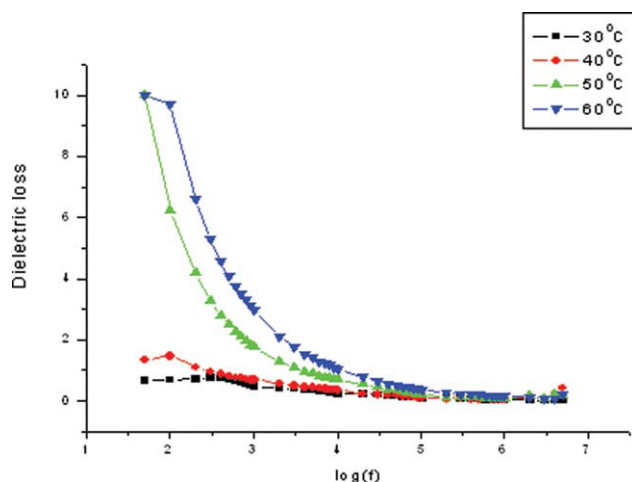
and remains more or less constant with increasing temperature because the orientation polarization due to chain motion of polymer cannot keep phase with the rapidly oscillating electric field.[31]

CONCLUSIONS

1. Dibenzo18-Crown-6 based PPV oligomer has been successfully synthesized using Wittig reaction.
2. Formation of the oligomer was confirmed with FT-IR, ^{1}H-NMR, ^{13}C-NMR spectral studies, GPC, and elemental analysis. Photoluminescent property of the newly synthesized DB-OPV oligomer was investigated using UV-Vis and flourescence spectrometers.
3. Stability of the oligomer was analyzed by using UV absorption spectroscopy.
4. AFM provides the surface morphology of the nanoribbons and nanorods of the DB-OPV oligomer.
5. The spectroscopic results indicate that DB-OPV, a class of highly photoluminescent material of unusual optoelectronic properties for electroluminescent applications.
6. Frequency and temperature dependence of dielectric constant and dielectric loss of DB-OPV oligomer has been studied in the frequency range of 50 Hz-5 MHz and the temperature range 30–60°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 temperature is due to greater freedom of movement of dipole molecular chain of oligomer.

Figure 7 Variation of loss factor with frequency of DB-OPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
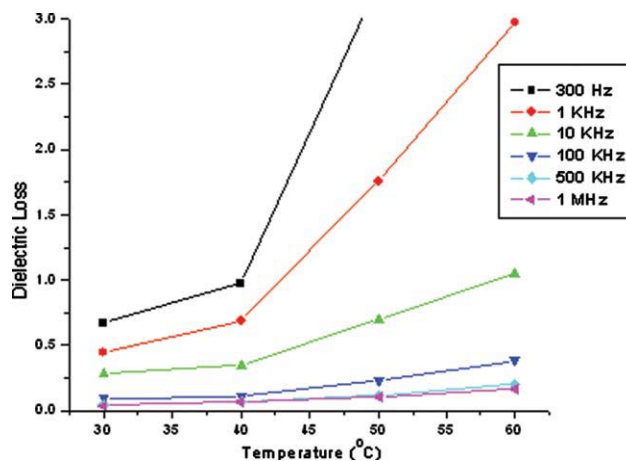
References

1. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H. Nature 1990, 347, 539.
2. Tessler, N.; Denton, G. J.; Friend, R. H. Nature 1996, 382, 695.
3. Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. Science 1996, 273, 1833.
4. Granstroem, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. Nature 1998, 395, 257.
5. Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. Science 1995, 269, 1086.
6. Pei, Q.; Yang, Y.; Yu, G.; Zhang, C.; Heeger, A. J. J Am Chem Soc 1996, 118, 3922.
7. Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. S. Adv Mater 2000, 12, 1737.
8. Mcgehee, M. D.; Heeger, A. J. Adv Mater 2000, 12, 1655.
9. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C. D.; Bradley, D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlundh, M.; Salaneck, W.R. Nature 1999, 397, 121.
10. Segura, J. L. Acta Polym 1998, 49, 319.
11. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew Chem Int Ed 1998, 37, 402.
12. Cacialli, F. Curr Opin Colloid Interface Sci 1999, 4, 159.
13. Martin, R. E.; Geneste, F.; Riehn, R.; Chuah, B. S.; Cacialli, F.; Friend, R. H.; Holmas, A. B. Chem Commun 2000, 291.
14. Babudri, F.; Cicco, S. R.; Chiavarone, L.; Farinola, G. M.; Lopez, L. C.; Naso, F.; Scamaricio, G. J Mater Chem 2000, 10, 1573.
15. Johansson, D. M.; Srdanov, G.; Yu, V.; Theander, M.; Inganas, O.; Andersson, M. R. Macromolecules 2000, 33, 2525.
16. Lee, S.; Jang, B.; Tsutsui, T. Chem Lett 2000, 1184.
17. Chen, Z.; Huang, W.; Wang, L.; Kang, E.; Chen, B. J.; Lee, C. S.; Lee, S. Macromolecules 2000, 33, 9015.
18. Ahn, T.; Song, S.; Shim, H. Macromolecules 2000, 33, 6764.
19. Pei, J.; Yu, W.; Huang, W.; Heeger. A. J. Chem Lett 1999, 1123.
20. Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. J Am Chem Soc 1998, 120, 231.
21. Wan, W. C.; Antoniadis, H.; Choong, V. E.; Razafitrimo, H.; Gao, Y.; Feld, W. A. Hsieh, B. R. Macromolecules 1997, 30, 6567.
22. Winkler, B.; Dai, L.; Mau, A. W. H. Chem Mater 1999, 11, 704.
23. Yamazaki, N.; Imai, Y. Polym J 1983, 15, 905.
24. Liu, H.; Wang, S.; Luo, Y.; Tang, W.; Yu, G.; Lin, Li; Chen, C.; Liu, Y.; Fu, Xi, J. Mater Chem 2001, 11, 3063.
25. Winkler, B.; Mau, A. W. H.; Dai, L. Phys Chem Chem Phys 2000, 2, 291.
26. Yang, Z.; Sokolik, I.; Karasz, F. E. Macromolecules 1993, 26, 1188.
27. Sonoda, Y.; Suzuki, Y.; Van Kerun, V.; Matsuda, H. Macromolecules 1996, 29, 288.
28. Chaudhry, M. A.; Jonscher, A. K. J Mater Sci 1988, 23, 208.
29. Smyth, C. P. Dielectric Behavior and Structure; McGraw Hill: New York, 1955, p 53.
30. Frohlick, H. Theory of Dielectrics; Oxford University Press; Oxford, 1956, p 13.
31. Akram, M.; Javed, A.; Rizvi, T. Z. Turk J Phys 2005, 29, 355.