

A Convenient Route to Soluble Poly(4,4'-Diphenylene-1,2-Di(*p*-Tolyl)Vinylene)

Dzulfadli Rosli¹, Rusli Daik¹, Muhamad Mat Salleh² & Mursyidah²

¹School of Chemical Sciences and Food Technology

²School of Applied Physics

Faculty of Science and Technology, Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor.

Abstract : Poly(4,4'-diphenylene-1,2-di(*p*-tolyl)vinylene) was successfully synthesised via the McMurry condensation reaction with 85% mass recovery by using an aromatic diketone 4,4'-di(*p*-toluoyl)biphenyl as the monomer. The polymerization was carried out in THF with the presence of Zinc dust and TiCl₄ as reducing agent and catalyst respectively. The monomer was synthesised via the Friedel-Crafts acylation with biphenyl and *p*-toluoylchloride as starting materials and AlCl₃ as the catalyst. The monomer was characterised by using FTIR spectroscopy, melting point measurement and GCMS. As calculated using the on-set wavelength of the UV-Vis absorption spectrum, the band gap of the polymer was 2.88 eV. The polymer was found to be soluble in common organic solvents and exhibited relatively high thermal stability with 5% weight lost at 350°C as measured by TGA. The glass transition temperature of the polymer was 234°C as shown by DSC thermogram. Number average and weight average molecular weights found were 4,400 and 9,100 g/mol respectively, with a polydispersity index of 2.07.

Abstrak : Poli(4,4'-difenilena-1,2-di(*p*-tolil)vinilena) telah berjaya disintesis melalui tindak balas gandingan McMurry daripada sebatian dwiketone aromatik 4,4'-di(*p*-toluoi)l)bifenil sebagai monomer dengan 85% penghasilan. Pempolimeran dijalankan dalam THF dengan kehadiran serbuk Zink dan TiCl₄ masing-masing sebagai agen penurunan dan mangkin. Monomer telah disintesis melalui tindak balas pengasilan Friedel-Crafts dengan bifenil dan *p*-toluoi)l)klorida sebagai bahan mula dan AlCl₃ sebagai mangkin. Monomer telah dicirikan menggunakan spektroskopi FTIR, pengukuran takat lebur dan GCMS. Berdasarkan panjang gelombang *on-set* spektrum serapan UL-Nampak, sela tenaga bagi polimer adalah 2.88 eV. Polimer didapati larut dalam pelarut organik lazim dan menunjukkan kestabilan terma yang baik dengan kehilangan berat 5% pada suhu 350°C berdasarkan analisis terma TGA. Berdasarkan DSC, suhu peralihan kaca bagi polimer adalah 234°C. Berat molekul purata nombor dan purata berat masing-masingnya adalah 4,400 dan 9,100 g/mol dengan indeks poliserakan 2.07.

Received : 02.04.03; accepted : 09.07.03

Introduction

Organic materials based light emitting diodes (LEDs) were first developed using simple organic compounds [1]. Such LEDs have serious problems including that the emissive compounds can re-crystallise during device operation leading to poor device stability and also to a decrease in emission efficiency. Conjugated polymers, particularly poly(arylene vinylene) type polymers have been the materials for the development of organic polymer based LEDs since early 1990s [2,3]. Control of the emission colour is clearly a requirement for the achievement of full-colour displays. The colour of emission is dependent on the band gap, which is the energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). This energy gap is a function of the effective conjugation length within the polymer [4]. Polymers with short conjugation lengths or relatively poor overlapping of π -electrons have larger band gaps and show a blue shift in the

emission with respect to polymers with longer conjugation lengths and good overlapping of π -electrons. The poly(arylene vinylene), PAV that was first discovered to emit light in LED showed a yellow-green emission which corresponds to a band gap of 2.5 eV [2]. To date, control of emission colour has been achieved via many different methods, including the incorporation of large aromatic units such as anthracene into the polymer chain, the attachment of either electron-donating or electron-withdrawing groups to the polymer backbone [5], increase the steric hindrance around the polymer backbone [6], the application of several layers of emissive polymers [7], incorporation of *meta*-linked phenylene along the polymer backbone [8] and so on. Such polymers have been prepared via a variety of routes [2,3,9]. The McMurry reaction, which is commonly used in the synthesis of olefins as well as pinacols, was reported to be useful in the synthesis of PAV from appropriate diketone or dialdehyde compounds [10].

Solubility is another common problem associated with conjugated polymers. Usually, PAVs were synthesised with alkoxy or alkyl group as side chains to improve the solubility of the polymer [8]. In this paper we report our attempt to produce a soluble and 'blue shifted' PAV by introducing tolyl side group onto the polymer chain. It is expected that tolyl side group not only results in soluble polymer but also brings about steric hindrance along the polymer chain and therefore decreases the electron conjugation. In this way, soluble 'blue shifted' PAV would be produced. UV-Vis absorption spectroscopy was used to determine the band gap of the polymer.

Experimental

Synthesis of Monomer

4,4'-Di(*p*-toluoyl)biphenyl was synthesized via Friedel-Crafts acylation. Biphenyl (5.00g, 0.03mol) was added to *p*-toluoyl chloride (60.0mL, 0.76mol) under dry nitrogen in a three necked flask (250mL) fitted with a condenser. Anhydrous aluminium chloride (70.00g, 0.52mol) was added slowly and the mixture was rapidly stirred while keeping the temperature below 10°C. The mixture was then refluxed for 4 hours, cooled to room temperature and poured into acidified ice-water. The product then was filtered and washed with potassium hydroxide (1 L, 5% w/v) and water until the washing was neutral. It was then dried under vacuum. The product was then refluxed in toluene with the presence of activated charcoal. After 15 minutes, the product was filtered quickly while the mixture was still hot. The solvent was evaporated and the product was re-crystallized from toluene to give pure 4,4'-di(*p*-toluoyl)biphenyl (7.70g, 66.6%).

Synthesis of Polymer

Poly(4,4'-diphenylene-1,2-di(*p*-tolyl)vinylene) [PDPV-DT] was synthesized via

McMurry coupling reaction as depicted in Figure 1, according to the procedure outlined by Rusli Daik [11]. Dry THF (30.0mL) was added to Zinc dust (2.53g, 384mmol) in a two-necked flask (150.0mL). TiCl₄ (1.4mL, 128mmol) was added slowly to the mixture at about 0°C under nitrogen atmosphere. The mixture was stirred for 15 minutes and then refluxed for two hours. 4,4'-Di(*p*-toluoyl)biphenyl (2.50g, 64mmol) was added to the mixture at room temperature and further refluxed for 20 hours. The polymerization was quenched with dilute HCl (100.0mL, 2M) at about 0°C and the product was extracted into chloroform. The product was washed with brine and dried over magnesium sulphate. The solvent was evaporated to give concentrated polymer solution which was then re-precipitated into methanol giving poly(4,4'-diphenylene-1,2-di(*p*-tolyl)vinylene) [PDPV-DT] (2.14g, 85.6% mass recovery).

Results and Discussions

Monomer

4,4'-Di(*p*-toluoyl)biphenyl was synthesized via Friedel-Crafts acylation. In the FTIR spectrum the peak at 1645.0cm⁻¹ was referred to conjugated carbonyl ketone. The peak at 2917. cm⁻¹ was due to the stretching aromatic C-H. Two peaks at 848.9cm⁻¹ and 818.9 cm⁻¹ were referred to *para*-disubstituted phenylene ring. The mass spectrum obtained for the compound recovered shows the expected molecular ion whose *m/z* value was 390. The mass spectrum and expected pattern for molecular fragmentation were presented in Figure 2 and Figure 3 respectively. The compound obtained was of high purity as indicated by GC chromatogram. The melting point measured for this monomer was in the range of 173.2-175.5°C.

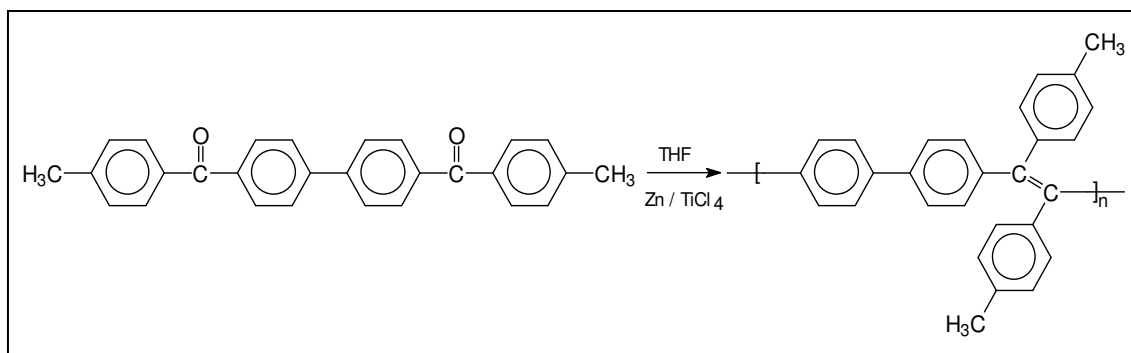


Figure 1: Synthesis of PDPV-DT via the McMurry reaction

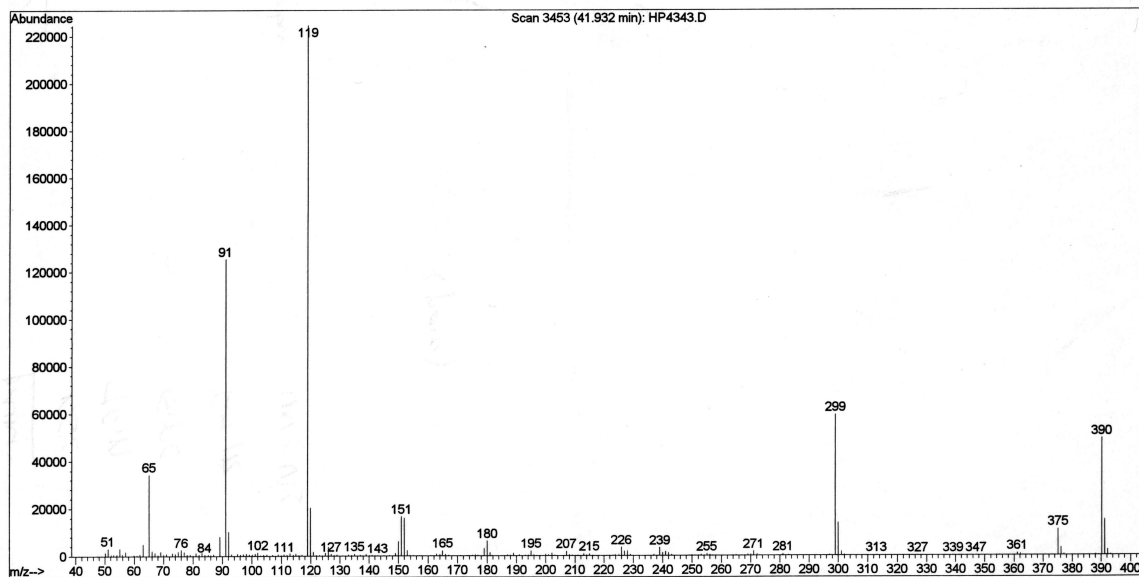


Figure 2: MS spectrum of the monomer

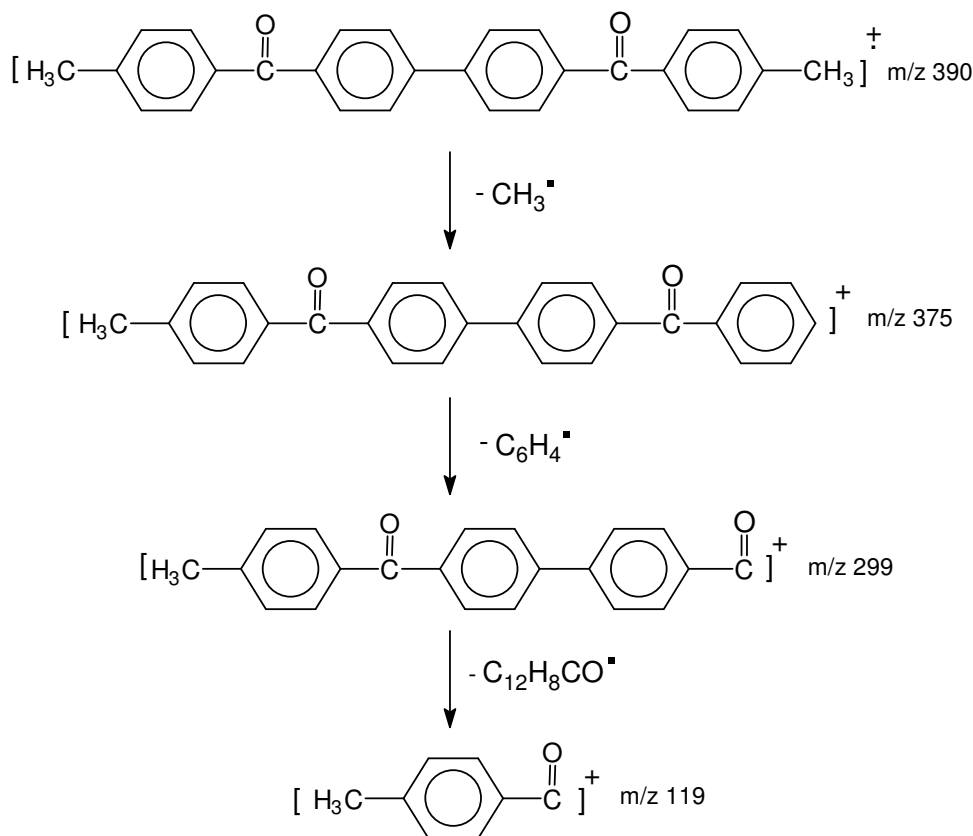


Figure 3 : Fragmentation pattern of the monomer

Polymer

Poly(4,4'-diphenylene-1,2-di(*p*-tolyl)vinylene) [PDPV-DT] was prepared from diketone monomer namely 4,4'-di(*p*-toluoyl)biphenyl via McMurry condensation with 85.6% mass recovery. The polymer gave bright yellowish-green fluorescence

when exposed to U.V. light. In the FTIR spectrum, the peak at 1604.9 and 1509.0 cm^{-1} can be attributed to the stretching of aromatic ring. As shown by GPC chromatogram (Figure 4), the number average molecular weight (M_n) and the weight average molecular weight (M_w) for PDPV-DT were 4,400

and 9,100 g/mol respectively, with a polydispersity index of 2.07. The presence of small peaks in the chromatogram was due to the telomeric units. PDPV-DT showed good solubility in common organic solvents such as chloroform, toluene and THF. Glass transition temperature, T_g for the polymer was 234.0°C as measured by DSC. The polymer was relatively stable thermally as it shows only 5% degradation at 350 °C. Thin films of PDPV-DT were successfully prepared by spin-coating technique and were then used for the characterization with UV-Vis absorption spectroscopy. In the UV-Vis absorption spectrum (Figure 5), there were two broad peaks appeared at 274 nm and 344 nm respectively. Absorption band at shorter wavelength (274 nm) was possibly due to π - π^* electron transition associated with tolyl

pendant group. Absorption peak at longer wavelength (344 nm) can be attributed to π - π^* electron delocalised along the conjugated polymer backbone. As calculated using the on-set wavelength of this peak, the band gap of the polymer was 2.88 eV, a slight increase as compared to that of a similar polymer that we reported previously, namely poly(4,4'-diphenylene diphenylvinylene) with a band gap of 2.86 eV [12]. The result clearly shows that the incorporation of tolyl group as the polymer side group in PDPV-DT has increased the band gap and yet retains the solubility of the polymer. Due to good solubility and high fluorescence brightness, the polymer is now being studied for application in LED.

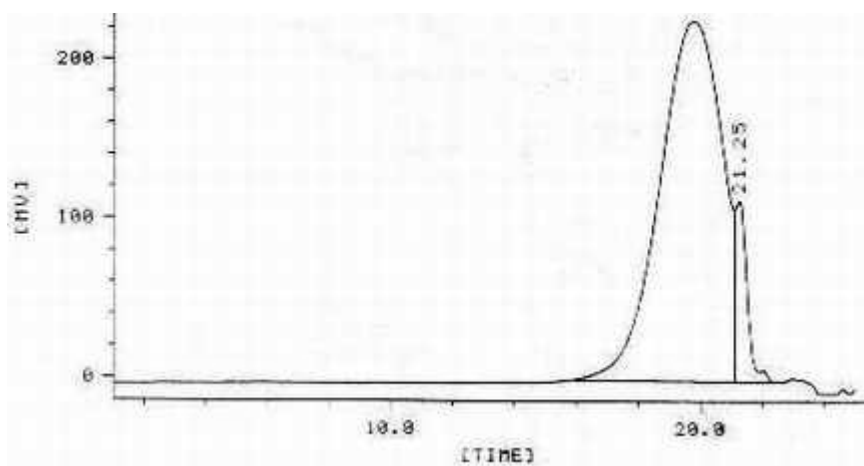


Figure 4: GPC chromatogram of PDPV-DT

PDPV-DT

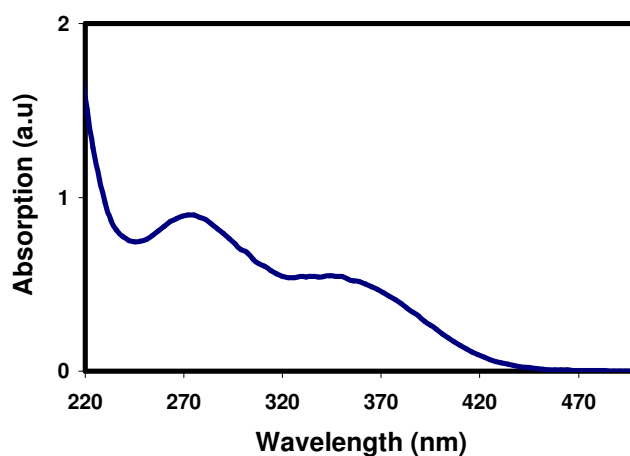


Figure 5: UV-Visible absorption spectrum of PDPV-DT solution

Conclusions

Poly(4,4'-diphenylene-1,2-di(*p*-tolyl)vinylene) [PDPV-DT] was successfully synthesized via McMurry coupling reaction with good mass recovery and relatively high molecular weight. The polymer was found to be soluble in common organic solvents. The UV-Vis absorption data showed that the band gap for PDPV-DT was slightly bigger as compared to that of poly(4,4'-diphenyl diphenylvinylene). This implied that the incorporation of tolyl group as the side group has increased the band gap of the polymer.

Acknowledgements

Authors would like to acknowledge the financial support provided by Ministry of Science, Technology and Environment, Malaysia through IRPA grant and also by FELDA Foundation.

References

- Mori, T., Obata, K., and Mizutani, T. (1997) EL mechanism of organic LED alternately deposited with diamine derivative and Alq₃, *Synthetic Metals*, **91**, 199 - 201.
- Burroughes, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., Mackay, K., Friend, R.H., Burns P.L., and Holmes, A.B. (1990.) Light Emitting Diode Based on Conjugated Polymers, *Nature*, **347**, 539 - 541.
- Botta, C., Geng, Z., Bolognesi, A., Flores, C., and Denti, L. (1995) Modified poly(3-alkylthiophene) for LED preparation, *Synthetic Metals*, **71**, 2191 - 2192.
- Campbell, D., and White, J.R. (1989) "Polymer Characterisation - Physical Techniques", Chapman and Hall, London, **43**.
- Horhold, H.H., and Tillmann, H. (2000) Synthesis, optical and redox properties of novel segmented cyano-PPV derivatives, *Synthetic Metals*, **101**, 138 - 139.
- Brouwer, H.J., Hilberer, A., Werts, M., Krasnikov, V.V., Wildeman, J., and Hadziioannou, G. (1997) LEDs based on conjugated PPV block copolymers, *Synthetic Metals*, **84**, 881 - 882.
- Brown, A.R., Greenham, N.C., Burroughes, J.H., Bradley, D.D.C., Friend, R.H., Burn, P.L., Kraft, A., and Holmes, A.B. (1992) Electroluminescence from multilayer conjugated polymer devices: Spatial control of exciton formation and emission, *Chemical Physics Letters*, **200**, 46 - 54.
- Song, S.Y., Ahn, T., Shim, H.K., Song, I.S., and Kim, W.H. (2001) Synthesis and electroluminescence properties of ortho-, meta- and para-linked polymers containing oxadiazole unit, *Polymer*, **42**, 4803 - 4811.
- Blake, A.J., Cooke, P.A., Doyle, K.V., Gair, S., and Simpkins, N.S. (1998) Poly-orthophenylenes: Synthesis By Suzuki Coupling and Solid State Helical Structures, *Tetrahedron Letters*, **39**, 9093 - 9096.
- Johansson, D.M., Theander, M., Ingones, I.O., and Anderson, M.R. (2000) A Convenient Synthetic Route to Poly(*p*-phenylene diphenylvinylene), *Synthetic Metals*, **113**, 293 - 297.
- Rusli Daik (1997) "Synthesis and Characterisation of Poly(arylene vinylene)s", Ph.D Thesis, Durham University.
- Daik, R., Rosli, D., and Mehamod, F.S. (2002) Band Gaps of A Few Poly(arylene vinylene)s, *Journal of The Institute of Materials Malaysia*, **3**, 53 - 64.