ELSEVIER

Polymer 43 (2002) 233–237

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Short poly(phenylene vinylene) chains grafted poly(organophosphazene)

Louis M. Leung*, C.M. Liu, C.K. Wong, C.F. Kwong

Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Kowloon, Hong Kong SAR, People's Republic of China

Received 22 June 2001; received in revised form 7 July 2001; accepted 17 July 2001

Abstract

Brominated poly(bis(4-methylphenoxyphosphazene) was allowed to react with 1,4-bischloromethylbenzene or 1,4-bischloromethyl-2,5-dimethoxybenzene in solution using phase transfer catalyst or potassium *t*-butoxide. Poly(*p*-phenylene vinylene) or poly(2,5-methoxy-1,4-phenylene vinylene) grafted organophosphazene copolymers were obtained. The UV–Vis absorption, photoluminescent, and thermal properties of the copolymers were measured. The copolymers are complete soluble in common organic solvents and fluoresce in the blue color range. The copolymers were used to build a series of organic light emitting diode (OLED). Only weak to nominated intensities with emission color from blue to red were obtained. The photoluminescent and electroluminescent (EL) spectra indicated there is a distribution in the PPV conjugated length. The compositions of the copolymers before and after the graft reaction were analyzed using NMR. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(phenylene vinylene) grafted copolymers; Conductive poly(organophosphazene); Organic light emitting diodes

1. Introduction

Poly(organophosphazenes) (PPz) comprise one of the largest group of inorganic polymers and have the repeating unit structure of $[-N{=}P(R)_2-]$, in which R can be either an organic or inorganic side group [1]. The properties of the resulting polymers depend heavily on the size and nature of the substituted side groups. The physical properties of PPz have been found to vary from elastomer to glass, from insulator to conductor, from hydrophobic to totally water soluble, or from bioinert to bioactive [2]. PPz is also known for its excellent thermal and environmental stability.

Poly(phenylene vinylene) (PPV) is a widely studied conducting polymer and is best known to prepare via the water soluble sulfonium precursor route [3]. The precursor polymer could then undergo a thermal or chemical elimination process to produce the final fully conjugated polymer. Due to its excellent processability, PPV has been attempted for a range of applications including rechargeable battery, NLO devices and laser diodes, etc. [4]. In the early 90s, a Cambridge research group discovered that PPV is also an effective electroluminescent (EL) material [5,6]. A furious of works and publications have since then dedicated to the goal of developing a large-area, high resolution, and high efficiency conducting polymer based OLED display.

In order to avoid contamination from the elimination side-products of the sulfonium precursor, other methods to prepare soluble PPV have been reported. In the past, we have synthesized organic solvent soluble PPV via the phase transfer catalysis method [7]. Soluble PPV was resulted by using bulky phenyl ring substituents or by formation of *p*- and *m*-PPV copolymers. In situ polymerization of PPV on a solid substrate (Merrifield's resin) was also reported [8]. In this report, two types of short PPV chains were grafted onto a PPz inorganic polymer. The composition and physical properties of the copolymers were characterized. The grafted copolymers were found to be both photoluminescent and EL. In a previous report, we have used non-conducting polymer doped with charge transporting and emitting compounds to fabricate a series of polymer thick film organic light emitting diodes (PTF-OLED) [9]. In this study, we employed the conducting PPV grafted PPz copolymers as the matrix for the guest–host type single layer PTF-OLED. The *I*–*V*–*L* (current–voltage–intensity) properties and EL spectrum for the OLED were reported and interpretation of the results was provided as a function of the PPV chain length distribution and overall contents.

2. Experimental

All chemicals and solvent were reagent grade and used 'as received' unless specific otherwise. A scheme showing the different steps in the formation of the PPV grafted PPz

---

* Corresponding author. Tel.: +852-2339-7073; fax: +852-2339-7348.
E-mail address: s20974@hkbu.edu.hk (L.M. Leung).

PII: S0032-3861(01)00584-5

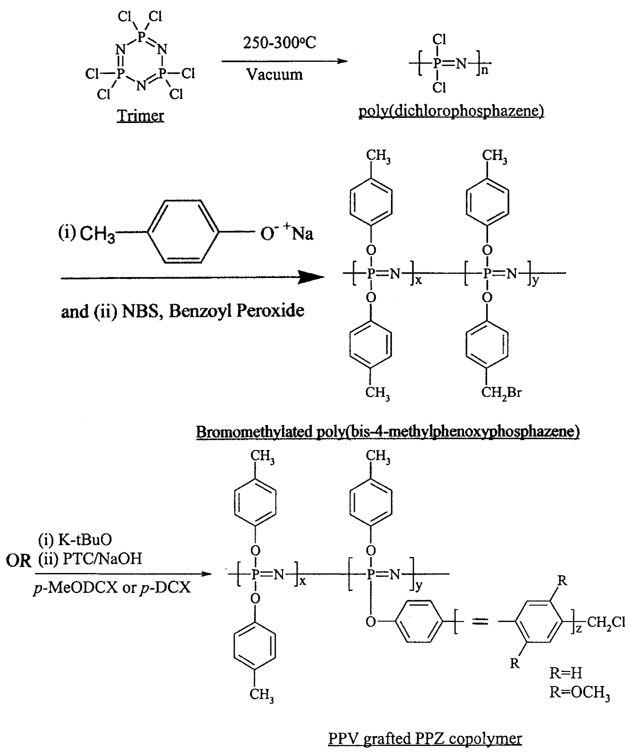


Fig. 1. Synthetic scheme for the PPV grafted poly(4-methylphenoxyphosphazene).

copolymer is shown in Fig. 1. The phosphonitrilic chloride trimer was prepared in our laboratory according to Ref. [10] and sublimed before use. Two grams of the purified trimer under vacuum was then heat sealed in a glass tube. The sealed tube was then heated in a programmable tube furnace to 250–300°C for 1–2 h until a clear viscous liquid is obtained. The viscous liquid is the hydrolytic polydichlorophosphazene precursor polymer. The precursor polymer was then dissolved in predried 1,4-dioxane, 2.2 equivalents of sodium 4-methylphenoxide was added and refluxed for days. The resulting poly(bis(4-methylphenoxyphosphazene) was purified by successive reprecipitation (hexane, ethanol and water) until a single peak in ^{31}P NMR was obtained (-17.8 ppm compared to 21.5 ppm for purified trimer as the reference). *N*-bromosuccinimide (NBS) was used for bromination. The brominated PPz copolymers were reprecipitated into petroleum ether and dried in vacuum before use. Two types of monomer were used for the synthesis of the PPV chains. They are either 1,4-bischloromethylbenzene (*p*-DCX) or 1,4-bischloromethyl-2,5-dimethoxybenzene (*p*-MeODCX). Approximately 0.2 gm of the brominated PPz copolymer was dissolved in 30 ml of toluene in a RBF. Subsequently, either (i) 10 ml of 50% NaOH and 2 mmol of tetrabutylamminium bromine (TBAB) was added to the RBF and the DCX monomers in toluene were added in dropwise under vigorous stirring at 60°C for 6 h, or (ii) the DCX monomers were added dropwise to the RBF containing a slightly excess equivalent of K*t*BuO and was stirred vigorously at room temperature for 12 h. The molar ratio of the DCX monomer to the brominated PPz repeating units was kept at either 5 or 20. The PPV grafted copolymers were then washed with plenty of water, methanol and then dried thoroughly in vacuum. The copolymers were then dissolved in predried 1,4-dioxane, filtered to remove the insoluble PPV homopolymers. The soluble fraction was then reprecipited in methanol and then soxhlet exhaustedly with methanol and hexane to remove all soluble PPV oligomers. The final product was then dried and weighted.

The PPz homopolymers were characterized by a 270 MHz Joel JNM-EX270 FT-NMR using the ^{31}P probe. The degree of bromination was determined by ratios of $-CH_2Br$ and $-CH_3$ signals using ^{1}H NMR. The number averaged number of repeating units for the grafted PPV segments was calculated from the ratios of integrated proton signals for the methyl groups ($-CH_3$) to the protons in all aromatic rings at a given degree of bromination from ^{1}H NMR. The glass transition temperature of the copolymers was measured using a Shimadzu DSC50 with a LTC-50 cooling units at a heating rate of 20°C/min under nitrogen purge. The absorption and fluorescent spectrum was recorded from a Cary UV-100 double beam UV–Vis spectrophotometer using 100 ppm chloroform solutions. The OLED was fabricated by spin coating the copolymer on a thoroughly cleaned ITO glass and then dried under vacuum and nitrogen purge. A silver cathode was applied onto the organic layer using an Edwards evaporator (Auto 306). The film thickness was measured using a profilometer. Additional hole transporter *N*,*N*′-diphenyl-*N*,*N*′-(3-methyl phenyl)-1,1′-biphenyl-4,4′-diamine (3-MeTPD) and electron transporter aluminum trishydroxquinoline (Alq_3) were also added to improve the efficiency of the OLED. The two types of OLED have the general cell structures: (Type 1) ITO (80 Ω/sq)/copolymer layer (100 nm)/Ag (100 nm); (Type 2) ITO (80 Ω/sq)/mixture of copolymer, 3-MeTPD,Alq_3(100 nm)/Ag(100 nm). The *I*–*V*–*L*, absolute intensity, and EL spectrum of each device was measured and reported.

3. Results and discussion

The PPV grafted PPz is soluble in common organic solvents such as chloroform, dioxane, THF and toluene completely. Although molecular weight of the copolymers was not measured, free standing films can be solvent cast from the copolymers. A single ^{31}P NMR peak at -17.8 ppm for the poly(bis(4-methylphenoxyphosphazene) homopolymer also indicated a high molecular weight polymer has been resulted [10]. The grafted copolymers have colors ranging from yellow to orange red (see Table 1). It is known that PPV homopolymer prepared from *p*-DCX is bright yellow and PPV prepared from *p*-MeODCX is bright

Table 1
Chemical composition of the PPV grafted PPz copolymers

PPV grafted PPz copolymers	Degree of bromination (from NMR) (mol%)	PPV monomer type	PPV synthesis method	Ratio of DCX monomer to $-\mathrm{CH_2B_r}$	Degree of polymerization of PPV (z) (from NMR)	Yield (wt%)	Color
PPz1	21.5	*p*-MeODCX	PTC	20:1	1.21	17.6	Reddish yellow
PPz2	16.9	*p*-DCX	K-*t*BuO	5:1	1.34	19.2	Yellow
PPz3	21.5	*p*-DCX	K-*t*BuO	20:1	1.96	21.6	Brownish yellow
PPz4	16.9	*p*-MeODCX	K-*t*BuO	5:1	1.75	19.8	Orange
PPz5	21.5	*p*-MeODCX	K-*t*BuO	20:1	2.10	20.7	Orange red

Table 2
Physical properties of the PPV grafted PPz copolymers (ND: not determined)

PPV grafted PPz copolymers	UV–Vis absorption max (nm)	Photoluminescent[a]		EL max (nm)[b]		Turn-on voltage (V) type 2	Maximum intensity (Cd/m^2) type 2	T_g (mid-point) (°C)
		Max (nm)	FWHM (nm)	Type 1	Type 2			
PPz1	362	469	103	ND	522	22	95	3.0
PPz2	329,452 (broad)	441	105	442,579 (weak)	558	30	4	0.4
PPz3	326	402 (broad)	150	ND	522	25	90	−22 (broad)
PPz4	362	468	113	427,542 ND (weak)	ND	ND	ND	0.3
PPz5	362	469	104	ND	ND	ND	ND	2.2

[a] UV–Vis absorption and PL was measured in a 100 ppm chloroform solution using same slit size.

[b] Type 1 OLED contains PPz copolymer only; Type 2 OLED contains PPz copolymer, 3Me-TPD and $\mathrm{Alq_3}$ in a 1:5.5:3.5 weight ratio.

red in color [7]. The appearance of the copolymers indicated the respective PPV chains have been successfully synthesized.

Although there is no limitation to the degree of bromination for the poly(bis(4-methylphenoxyphosphazene) homopolymer. We found that at high degree of bromination, the brominated PPz is not very stable even in storage at room temperature. The brominated PPz is found to cross-link readily into insoluble product for degree of bromination above 20 mol%. Even those we used the brominated products immediately after bromination, the insoluble fraction increased dramatically in the PPV chain formation step. To achieve a balance in yield and solubility, we therefore kept the degree of bromination at approximately 20 mol%. According to Table 1, the number of PPV repeating units (z) calculated from ^{1}H NMR is not very high, in the range

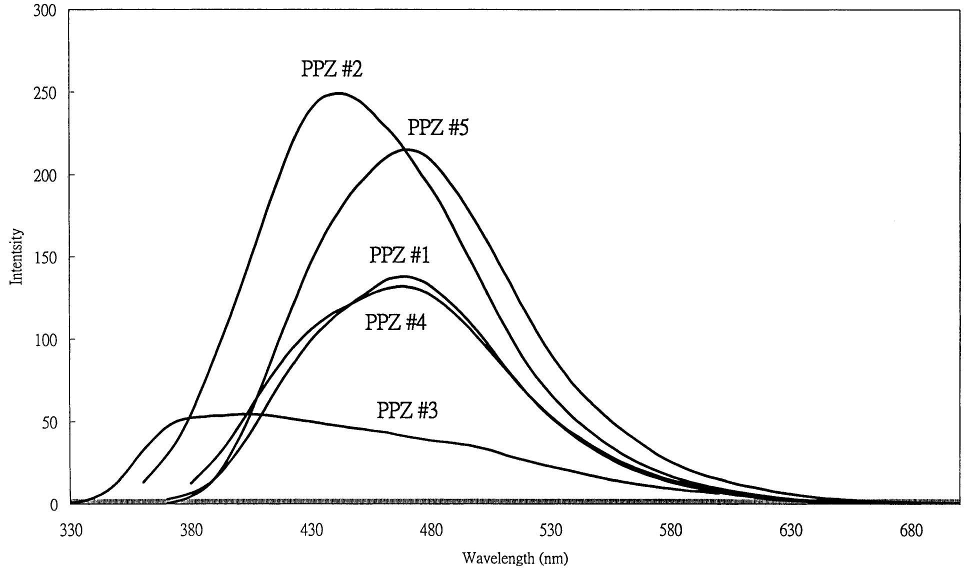
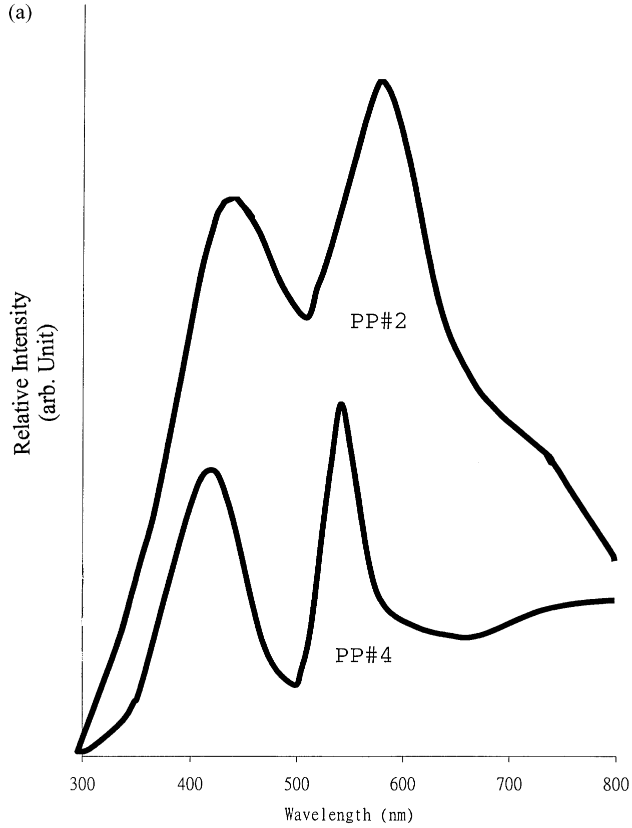


Fig. 2. Photoluminescent spectra for 100 ppm chloroform solutions of PPV grafted PPz. The absorption maximum was used as the excitation wavelength. The intensities shown were not adjusted and were under the same operating conditions.

of 2. Indicated only very short PPV chains were produced on the grafted copolymers. The lowest *z* value is obtained for the PTC method while the highest *z* is achieved for the K-*t*BuO method having higher monomer to $-CH_2Br$ ratio. Irrespect of the PPV synthesis method and monomer ratio, the yield remains at approximately 20 wt%.

The physical properties of the grafted copolymers are listed in Table 2. The UV–Vis absorption and PL of the copolymers were measured with a 100 ppm chloroform solution. The absorption maximum for the *p*-DCX copolymers was detected at approximately 326 nm while for *p*-MeODCX copolymers was found at 362 nm. The PL spectra for the different copolymers in solution under the same operating conditions were shown in Fig. 2. With the exception of PPz3, the photoemission spectra have a maximum at around 460 nm which is blue indicating very short PPV conjugation length. The PL spectra also extended into the yellow to red region (from 540 to 600 nm), which is the normal emission color for a highly conjugated PPV polymer. Compared to PL and EL spectra for PPV derived from the sulfonium precursor method, which is yellowish [5], the results indicated the grafted PPV chains are rather short on the average, which is in agreement with the NMR calculations. Only a small population of the grafted PPV chains has attained the conjugation length required to emit in the normal yellowish range. The overall strong fluorescence intensity could be induced by the electron withdrawing (–OR) and electron donating ($-CH_2Cl$) at the ends of the PPV chains. PPz3 has a very broad PL spectrum (almost white light), which maybe related to a rather broad distribution in the grafted PPV chain length. The result could be related to the specific synthesis conditions.

Two types of OLED were built. For type 1, only the pure PPV grafted PPz copolymers were used. In order for the OLED to work properly, the PPV copolymers should perform the dual function of charge transport and as an emitter. The optimum device configuration from our previous experiences with polymer thick film OLED was adopted [9]. Mostly of the devices, however, failed to work properly with the exception of a few. The failure may be due to either poor charge transport properties or poor charge injection at the metal/polymer interface. The PPz2 and PPz4 both give only very weak and unstable signal. We suggested it was due to the overall PPV fraction in the copolymers is low and the conductive segments are not well dispersed. As a result, a much higher voltage is required to pump the charges across the electrodes and in turn degraded the organic layer. The emission spectra for the type 1 OLED are presented in Fig. 3(a). The EL spectra have



Electroluminescent Spectra

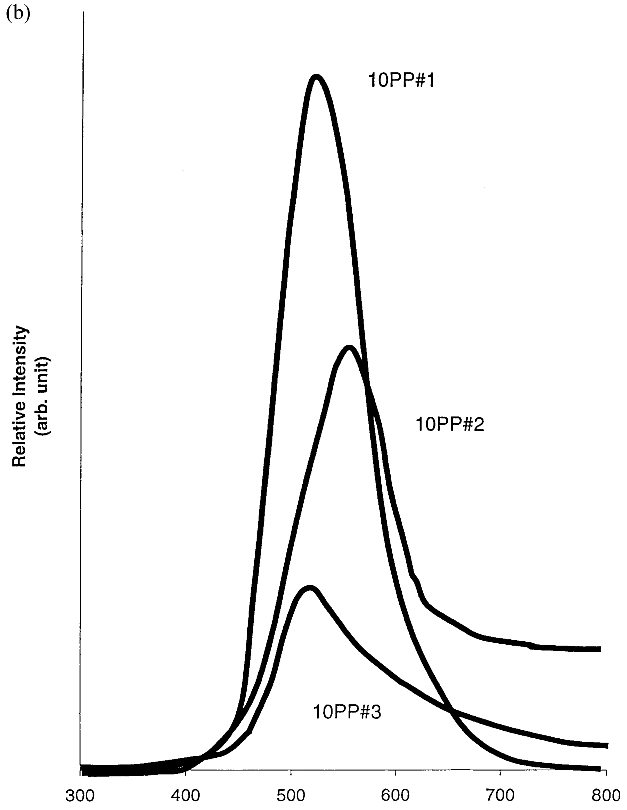


Fig. 3. EL spectra for the PPV grated PPz copolymers: (a) Type 1 OLED has the structure ITO (80 Ω/sq)/copolymer layer (100 nm)/Ag (100 nm); (b) type 2 OLED has the structure ITO (80 Ω/sq)/copolymer + 3-MeTPD + Alq_3 (Ratio 1:5.5:3.5, 100 nm)/Ag (100 nm).

two components in which one is blue (corresponding to the shorter PPV chains) and the other is yellow (corresponding to the longer PPV chains). The performance of the OLED did not related directly to the *z* value.

A second type (type 2) OLED were also attempted, in which 3Me-TPD, an excellent hole transporter, and Alq_3, a good electron transporter and also a dye, were loaded into the copolymer in a 1:5.5:3.5 weight ratio [9]. In this case, the PPV copolymers performed as a binder for the small molecule organic compounds. The doped OLEDs improved in performance, although its efficiency is still lower than other polymer OLEDs we fabricated previously. The type 2 OLED has EL maximum in the 522 nm range (greenish) which is also the characteristic emission of Alq_3 (see Fig. 3(b)). A reddish shoulder in the EL spectra was also observed which could be related to the population of longer conjugation length PPV chains in the copolymers. It is surprisingly that type 2 OLED from PPz4 and PPz5 with the higher *z* value did not perform well either. We observed that the copolymer solutions did not wet the surface of the ITO glass very well and as a consequence failure may occur at the interface of the organic-metal layers.

The T_g midpoint measured for the copolymer is in the range of 0–3°C, which is comparable to the T_g of the poly(4-methylphenoxyphosphazene) homopolymer at 1.6°C (see Table 2). With the exception of PPz3 which has a broad T_g and suggested to be the effect of a broad distribution in the PPV chain length as seen from the PL spectrum. The low T_g of the copolymers allowed the fabrication of flexible OLED although the stability of the OLED might also be affected due to effects such as thermal mismatch with the metallic electrodes.

4. Conclusion

In this report, we described the synthesis of a series of highly soluble PPV chains grafted PPz copolymers. The PPV chains on the average are rather short and have a distribution in the conjugation length. Surprisingly, the grafted copolymers have strong emission in the blue color range which is known to be difficult to achieve for main-chain conjugated polymers [11]. The copolymers were used to build a series of OLEDs. Both the PL and EL spectra were measured and compared. For improvement, it was shown that either a higher volume fraction for the conductive segments or a well dispersed conductive fraction in the copolymer layer is required.

Acknowledgements

We acknowledged the support by research grants from the Hong Kong SAR government, grant number RGC/97-98/33 and HKBU-2057/98E and a faculty grant from the Hong Kong Baptist University FRG99-00/II-68.

References

[1] Mark JE, Allcock HR, West R. Inorganic polymers. Englewood Cliffs: Prentice-Hall, 1992.
[2] Zeldin M, Wynne KJ, Allcock HR. Inorganic and organometallic polymers, ACS Symposium Series, vol. 360. Washington DC: ACS, 1988.
[3] Wessling RA, Zimmerman RG. US Patent 3,401,152, 1968 and 3,706,677, 1972.
[4] Leung LM. Polyphenylene vinylene. In: Olabisi O, editor. Handbook of thermoplastics. New York: Marcel Dekker, 1997. p. 817.
[5] Brown AR, Bradley DDC, Borroughes JH, Friend RH, Greenham NC, Burn PL, Holmes AB, Kraft A. Appl Phys Lett 1992;61(23):2793.
[6] Greenham NC, Moratti SC, Bradley DDC, Friend RH, Holmes AB. Nature 1993;365:628.
[7] Leung LM, Chik GL. Polymer 1993;34(24):5174.
[8] Leung LM, Yam CM. Polym Bull 1993;30:629.
[9] Leung LM, Kwong CF, Kwok CC, So SK. Displays 2000;21:199.
[10] Allcock HR. Phosphorous–nitrogen compounds. New York: Academic Press, 1972.
[11] Kraft A, Grimsdale AC, Holmes AB. Angew Chem Int Ed 1998; 37:402.