

Thermally stable light-emitting polymers of substituted polyacetylenes

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Abstract

We report emission from a series of aryl substituted polyacetylenes poly(phenylacetylene) (PPA), poly(*p*-ethynylphenylacetylene) (PEPA), poly(*p*-phenylethynylphenylacetylene) (PPEPA), and poly[*p*-(2-thiophenylethynyl)phenylacetylene] (PTEPA). These polymers are readily soluble, easily processable from organic solvents, and stable up to 200°C either in air or in nitrogen according to thermogravimetric analysis. Single layer light-emitting diodes using PPA, PEPA, PPEPA, and PTEPA as an emissive layer were fabricated. The effects of substituted groups on UV–vis absorption, photoluminescence and electroluminescence spectra of the polymers are discussed. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the observation of electroluminescence (EL) in semiconducting conjugated polymer poly(*p*-phenylene vinylene) (PPV) [1], polymer light-emitting diodes (LEDs) have received considerable attention for their potential application in large-area light sources and flexible color displays with low power consumption [2–6]. The polymer LEDs offer several advantages such as low cost, high-luminous efficiency, wavelength controllability, and easy processing by spin casting from organic solution. Another advantage is that the band gap and the emitting wavelength can be chemically tailored. Different research groups prepared LEDs based on a variety of polymers covering the visible spectral range. Optical, electronic, mechanical properties and π – π^* energy gap of many polymers can be altered through controlled changes in their molecular structures and the introduction of substituents [7–11]. For example, substitution on the phenyl ring of PPV with two alkoxy groups changes the luminescent colors compared with that of its parent, and affords solubility and film-forming properties of the polymer [12,13]. The PL quantum efficiency of PPV is not high enough [14]. In the preceding letter, we have found an alternating copolymer containing triphenylamine and phenylene units (TPA-PPV) has high photoluminescence quantum yield ($\phi_{\text{PL}} = 0.94$ in benzene) [15]. Therefore, to study the dependence of optical, electronic

and luminescence properties on polymer molecular structure and substituted groups are useful to enhance EL performance of LEDs made from semiconducting polymers. On the other hand, substituted polyacetylenes compose a big family of conjugated polymers. Recently, poly(phenylacetylene) (PPA) has attracted much attention due to its photoconductivity, charge carrier transporting properties and luminescence [16–18]. In this paper, we report photoluminescence and electroluminescence characteristics of the aryl-substituted polyacetylenes.

2. Experimental

Aryl substituted polyacetylenes were synthesized using $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ as the catalyst from the corresponding monomers substituted phenylacetylenes, according to the literature [19]. Their chemical structures are shown in Fig. 1. LEDs were fabricated using the polymers as an emissive material and vacuum evaporated aluminum as the cathode. Thin films of the polymers were spin-coated onto the indium tin oxide (ITO) substrates from their chloroform solutions. The active area of the EL device was 14 mm². Absorption and photoluminescence (PL) spectra were studied for thin films using quartz substrates. PL and EL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with the LED devices forward biased. Ultraviolet–visible absorption spectra were recorded on a General TU-1201 UV–vis recording spectrophotometer. The luminance was measured with an LS-1 portable luminance meter. Current–voltage characteristic was measured

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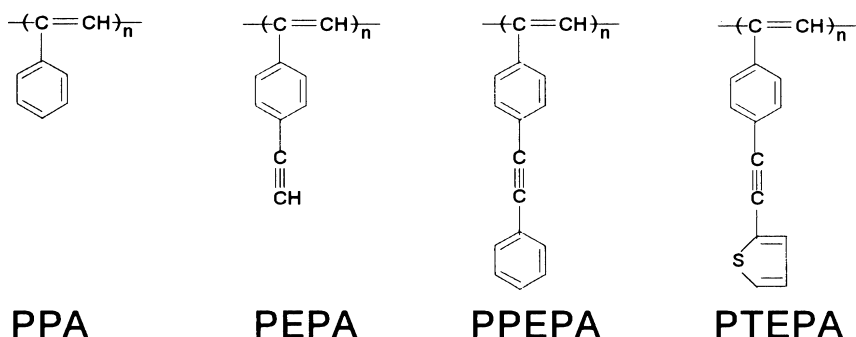


Fig. 1. The chemical structures of polymers used in this paper.

with a programmable Solartron 7081 Precision Voltmeter interfaced to a personal computer through an IEEE488 interface board. All the measurements were performed under ambient atmosphere at room temperature.

3. Results and discussion

Polymers PPA, PEPA, PPEPA, and PTEPA are soluble in common organic solvents and especially in chloroform they can dissolve readily to give clear solutions. PPA, PPEPA, and PTEPA are stable up to 200°C either in air or in nitrogen according to thermogravimetric analysis (TGA) (Fig. 2). However, PPEPA and PTEPA show a slower weight-loss below 200°C with respect to the PPA. Therefore, the introduction of phenylethynyl and 2-thiophenylethynyl groups do not give a clear improve for thermal stability. PEPA demonstrates an excellent thermal stability with a decomposition temperature in excess of 400°C, and shows a somewhat weight increasing between 200–400°C. DSC examined the thermal properties of the polymers. The glass transition temperature (T_g), melting temperature (T_m), enthalpies of melting (ΔH), and changes in heat capacity at T_g (ΔC_p) are summarized in Table 1. PTEPA and PPEPA exhibit a clear endothermic peak on second heating at 144.6 and 136.62°C, however, on third heating at 189.87 and 164.98°C, respec-

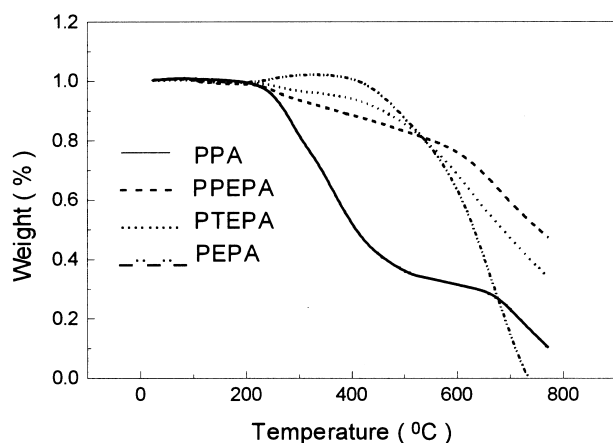


Fig. 2. The thermogravimetric analysis (TGA) curves of polymers.

tively. The PPA shows a glass transition temperature at 72.1°C. The highest glass transition temperature of 130.07°C is observed for the PEPA.

Fig. 3 shows absorption spectra of PPA derivatives in chloroform. The absorption spectrum of PPA shows a maximum at 253 nm with a shoulder at 338 nm. The absorption from 300 to 400 nm is due to π - π^* interband transition of the polymer main chain and that from 200 to 300 nm is attributed to the π - π^* transition of phenyl group. As the conjugated degree of aryl side group becomes greater, the absorption maxima shift to longer wavelength. This means that aryl group at the side chain exerts a significant effect on the absorption spectra of the poly(phenylacetylene) derivatives. The absorption maxima of PPEPA, PTEPA and PEPA appear at longer wavelength than that of PPA. However, the absorption peaks of PTEPA is at the same wavelength as that of the PPA, and the peak at 350 nm becomes the main one. The band gap of PPA was evaluated to be about 3.4 eV from the $(\alpha h\nu)^2$ - $h\nu$ plot of the absorption edge of the interband absorption peak, where α , h , and ν are the absorption coefficient, Plank's constant, and the frequency of the light, respectively. The band gap energy of PTEPA is nearly the same as that of PPA. It should be noted that the band gap energy of PPEPA is approximately 3.0 eV, which is identical with that of PEPA.

Fig. 4 shows PL spectra of PPA derivatives in chloroform. All the PL spectra were measured at the same excitation wavelength of 300 nm. All polymers emit strong fluorescence under ultraviolet irradiation. The emission peak of PTEPA is at 404.6 nm with a shoulder at 427 nm. The PEPA shows emission maxima at 399.8 and 439.4 nm, which is in the blue region. The PL peaks shift from 400.4 and 427 nm (PPA) to 367.6 and 379.8 nm (PPEPA) due to the introduction of *p*-phenylethynylphenyl group, and the color of emitting light changes from blue to purple-blue. The full width at half-maximum (FWHM) of the PL spectrum of PPA is 0.82 eV, which is broader than that of PTEPA (0.45 eV) and PEPA (0.75 eV). The polymer consists of a mixture of different conjugation chain lengths and different π - π^* transition energies. Emission always occurs from states with the lowest energy, since energy is transferred from the states with higher π - π^* transition

Table 1

Thermal properties of the polymers. This table also shows the band gap energy of these polymers. Optical band gap derived from the absorption spectra of the polymers in chloroform

Polymer	T_g (°C) ^a	ΔC_p (J/g °C)	T_m (°C) ^b	ΔH_m (J/g)	T_{onset} (°C)	Band gap (eV)
PPA	72.1	0.653	—	—	50.35	3.4
PEPA	130.07	0.265	—	—	125.47	3.0
PTEPA	—	—	144.6	49.41	—	3.4
PPEPA	—	—	136.62	95.34	—	3.0

^a Glass transition temperature (T_g).

^b Melting temperature.

energy (polymer segments with shorter conjugation length) to the states with the lower energy (polymer segments with longer conjugation length), before radiative deactivation takes place. Each excited state with the lowest energy return to the different ground states of the different conjugation lengths. Therefore, the FWHM depends on the molecular weight distribution of the polymer.

Optical properties of the polymer thin films were also investigated. Under ultraviolet irradiation, PL of PPA, PPEPA and PTEPA thin films are negligible, but strong PL was observed in the PEPA thin film. Fig. 5 shows PL

and EL spectra of the PEPA thin film. The PL peak of the PEPA thin film is at 521 nm and the FWHM of the PL spectrum is 0.43 eV. The PL spectrum of the PEPA thin film has a red shift with respect to that of the solution. The red shift can be attributed either to the difference in the energy transfer processes between the film and the solution, due to the presence of rotational conformers in the solution reducing the conjugation of the chromophore, or to the effect of packing and local geometry of the polymers [20].

Single layer LEDs were fabricated using PEPA as an emissive layer. When the LEDs were forward biased with the ITO electrode at positive polarity, yellow–green light emission was observed. The emission intensity starts to increase above 8.8 V. Under a driven voltage below 15 V, the EL is uniform and stable in air, and the brightness increases with the forward voltage. The EL threshold voltage of PEPA is relatively higher (8.8 V) attributed to its higher band gap (3.0 eV), by which a higher driven voltage is required for a sufficient carrier injection from the electrodes to the polymer layer. EL spectrum of PEPA is shown in Fig. 5. The EL peak is at around 521.2 nm, which is comparable with that of PL of the PEPA film, indicating a similar recombination mechanism of charge carriers for the PL and EL of PEPA. We conclude that the recombination of electron and hole eventually leads to the formation of PEPA single excited states, and then undergoes radiative deactivation. Fig. 6 shows the current–voltage

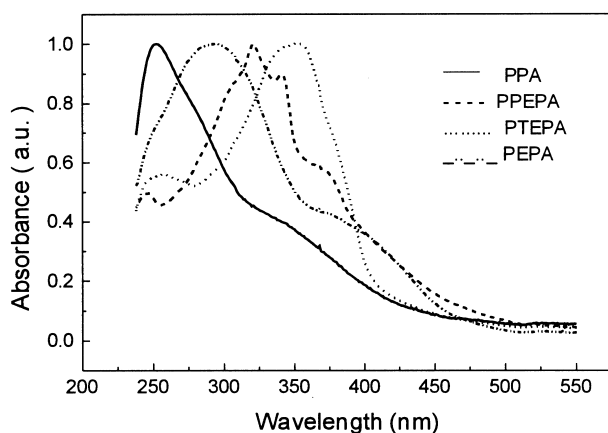


Fig. 3. Absorption spectra of the polymers in chloroform.

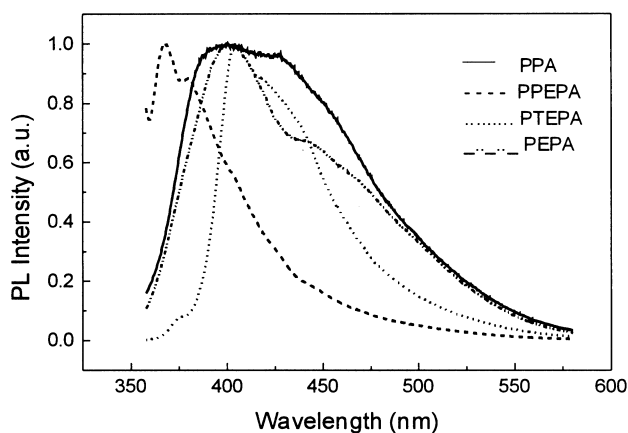


Fig. 4. PL spectra of the polymers in chloroform.

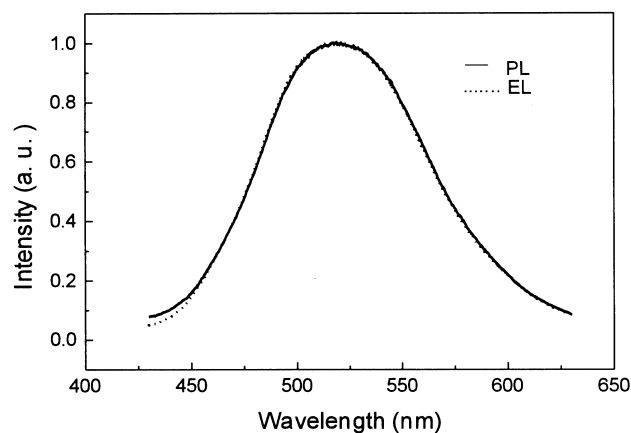


Fig. 5. PL and EL spectra of the PEPA thin film.

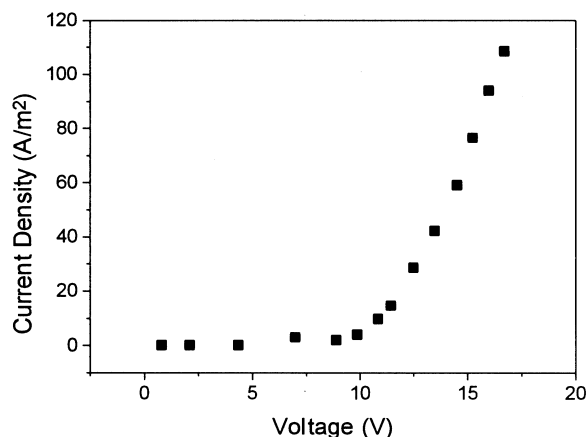


Fig. 6. Current–voltage characteristic of the EL device ITO/PEPA/Al.

characteristic of the device ITO/PEPA/Al. The turn voltage for this device was approximately 10.2 V. Single layer LEDs using PPA, PPEPA and PTEPA instead of PEPA exhibited blue emission. The EL threshold voltages of PPA, PPEPA and PTEPA are 12, 10 and 9.8 V, respectively.

4. Conclusion

Four substituted poly(phenylacetylene)s poly(phenylacetylene) (PPA), poly(*p*-ethynylphenylacetylene) (PEPA), poly(*p*-phenylethynylphenylacetylene) (PPEPA), poly[*p*-(2-thiophenylethynyl)phenylacetylene] (PTEPA) were synthesized. The polymers show strong photoluminescence under ultraviolet-lamp illumination and can be used as luminescent materials for light-emitting devices. The substituents have great effect on thermal behavior, optical, photoluminescence and electroluminescence properties of PPA derivatives.

Acknowledgements

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