Impedance spectroscopy of polymeric light emitting devices based on different poly(p-phenylene-vinylene) derivatives

S. Forero-Lenger [*], J. Gmeiner, W. Brütting, M. Schwoerer

Experimental Physics II, University of Bayreuth, 95440 Bayreuth, Germany

Abstract

Light emitting devices fabricated from different poly(p-phenylene-vinylene) (PPV) derivatives prepared by the precursor route (the unsubstituted homopolymer, a dimethoxy-substituted copolymer and an acetate-substituted copolymer) and devices based on a soluble dialkoxy-substituted homopolymer are compared with respect to their temperature-dependent impedance characteristics. Although similar activation energies of the conductivity in the range 0.4–0.5 eV are found for all polymers, the magnitude of the dielectric loss is significantly different in the polymers indicating a substantial difference in the amount of doping and/or impurities.

1. Introduction

During the last 10 years, conjugated polymers like poly(p-phenylene-vinylene) (PPV) have been investigated for their use in organic light emitting device (LED) structures. From the point of view of technology, there has been a rapid development enhancing luminescence and lifetime of the LEDs. Nevertheless, the physics of charge transport and luminescence mechanisms are not completely understood yet. Previous work by our group has shown that the unsubstituted homopolymer in ITO/polymer/Al devices (ITO = indium tin oxide) behaves like a doped organic semiconductor. From capacitance–voltage measurements, an acceptor dopant concentration in the order of 10^{17} cm^{-3} was determined. The occurrence of doping in PPV devices is not unexpected, since in the used precursor route to PPV the conversion process of the deposited precursor polymer film to the conjugated PPV is performed at elevated temperatures directly on the electrode used for hole injection in LEDs. The precursor leaving groups (especially HCl) can easily react with the ITO substrate forming InCl$_3$, which in turn can diffuse into the PPV layer and oxidize (dope) the polymer. The chemical reaction at the ITO substrate has been proven by energy-dispersive X-ray analysis [1] and the subsequent diffusion by secondary ion mass spectrometry (SIMS) [2]. A comparison of different substrate materials has shown that the degree of doping resulting from such chemical reactions depends on the reactivity of the subtrate material [3]. While devices based on the unsubstituted polymer on Au substrates did not show measurable doping, in devices on ITO, an acceptor dopant concentration of about 10^{17} cm^{-3} was found. Thus, we could identify the usage of ITO anodes as a major source for doping in PPV devices. As established in recent work on LEDs based on the unsubstituted homopolymer impedance spectroscopy is a powerful tool to study the occurrence of doping in LED structures especially the energy and concentration of doping states as well as their spatial distribution [4,5]. In this work, this method was applied on identically fabricated devices based on four different PPV-derivatives.

2. Experimental

The investigated devices were fabricated on ITO-coated glass (ITO-thickness 100–200 nm, sheet-resistance 40 $\Omega/\square$). On these substrates, three precursor polymers (the unsubstituted homopolymer, a dimethoxy-substituted copolymer, and an acetate-substituted copolymer) and a soluble dialkoxy-substituted homopolymer (see Fig. 1) were deposited with the doctor blade technique [6]. The Al

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[*] Corresponding author.

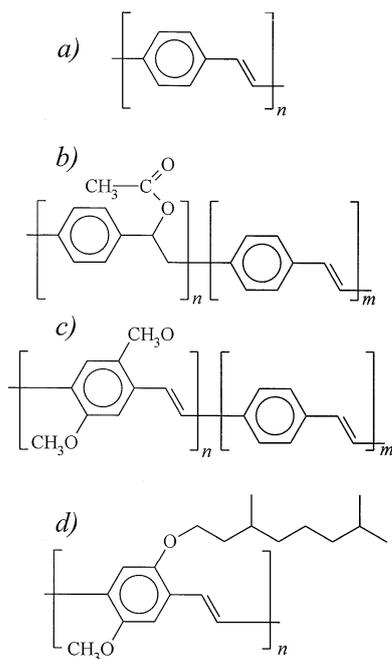*E-mail address:* stefan.forero@uni-bayreuth.de (S. Forero-Lenger).

a)

b)

c)

d)

Fig. 1. Investigated PPV derivatives; polymers synthesized by the precursor route: (a) unsubstituted homopolymer, (b) acetate-substituted copolymer ($n \approx 30\%$, $m \approx 70\%$), (c) dimethoxy-substituted copolymer ($n \approx 10\%$, $m \approx 90\%$) and a soluble polymer: (d) dialkoxy-substituted homopolymer.

cathodes (about 60 nm in thickness) were fabricated by thermal evaporation at a pressure ca. 10^{-5} mbar. Two consecutive films were deposited and converted in order to separate possible chemical processes at the ITO/polymer interface from the bulk of the polymer. The layer deposited at first is expected to chemically interact with the ITO substrate. After its conversion, it is assumed to act as a buffer layer between ITO and the second layer converted on top. Both polymer films are ca. 100-nm thick each and so the devices have a total thickness of ca. 200 nm. The soluble dialkoxy-substituted homopolymer, assumed not to interact with the substrate because of no thermal process during preparation, was deposited to give 200 nm thickness, too. The thickness of the ITO and PPV layers were measured with a Dektak surface profilometer. The measurements of dielectric relaxation (or impedance) were made with a broad band impedance setup as described in Ref. [5]. The frequency-sweeps ranged from 10^7 down to 5×10^{-3} Hz with an oscillator level of 0.1–0.5 V. Additionally, the temperature was varied between room temperature and 213 K. All measurements were performed in a cryostat in inert-atmosphere (N_2) at normal pressure.

3. Results and discussion

In Fig. 2, the real parts of conductivity and dielectric function and the imaginary part of the latter are shown for all four polymers at $T = 293$ K. The unsubstituted ho-

mopolymer and the soluble dialkoxy-substituted homopolymer show a saturation in conductivity for frequencies < 100 Hz while the acetate-substituted copolymer and the dimethoxy-substituted copolymer further decrease with frequency and may saturate at much lower values (10^{-14} S/m). Apart from the differences in $Re(\sigma)$ at low frequencies, there are characteristic features seen in the frequency range 10^2–10^4 Hz. They can be better visualized in the imaginary part of ε since by the relation $Im(\varepsilon) = Re(\sigma)/(\varepsilon_0 \omega)$, the strong frequency dependence in the conductivity is eliminated. There the unsubstituted ho-

• unsubstituted homopolymer
◦ acetate substituted copolymer
▲ dimethoxy substituted copolymer
△ dialkoxy substituted homopolymer
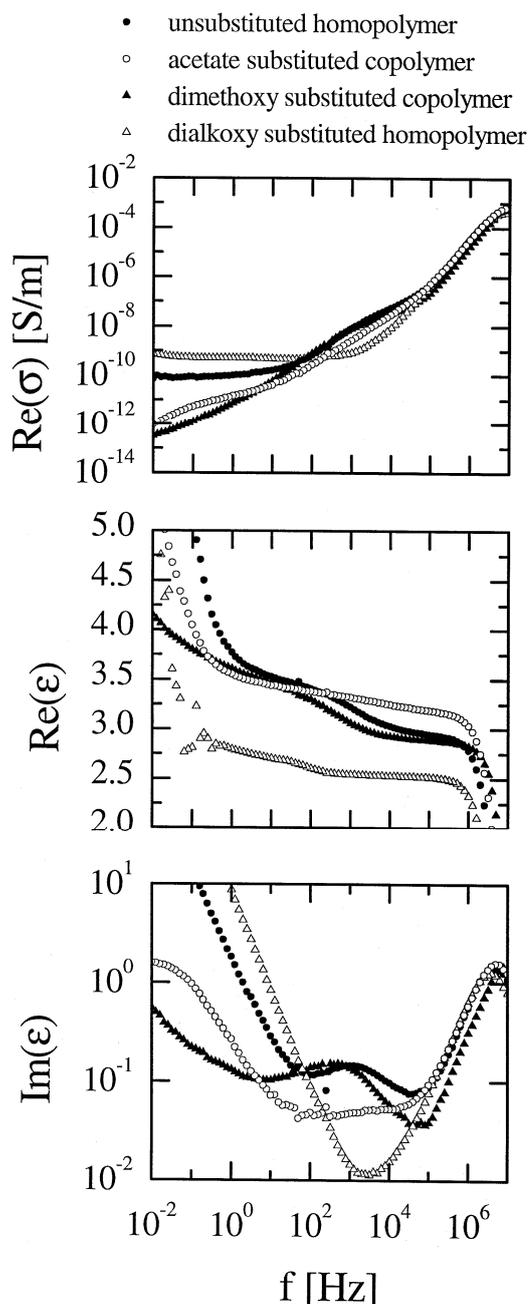

Fig. 2. Real part of the conductivity and real and imaginary parts of the dielectric function at 293 K for the investigated PPV derivatives.

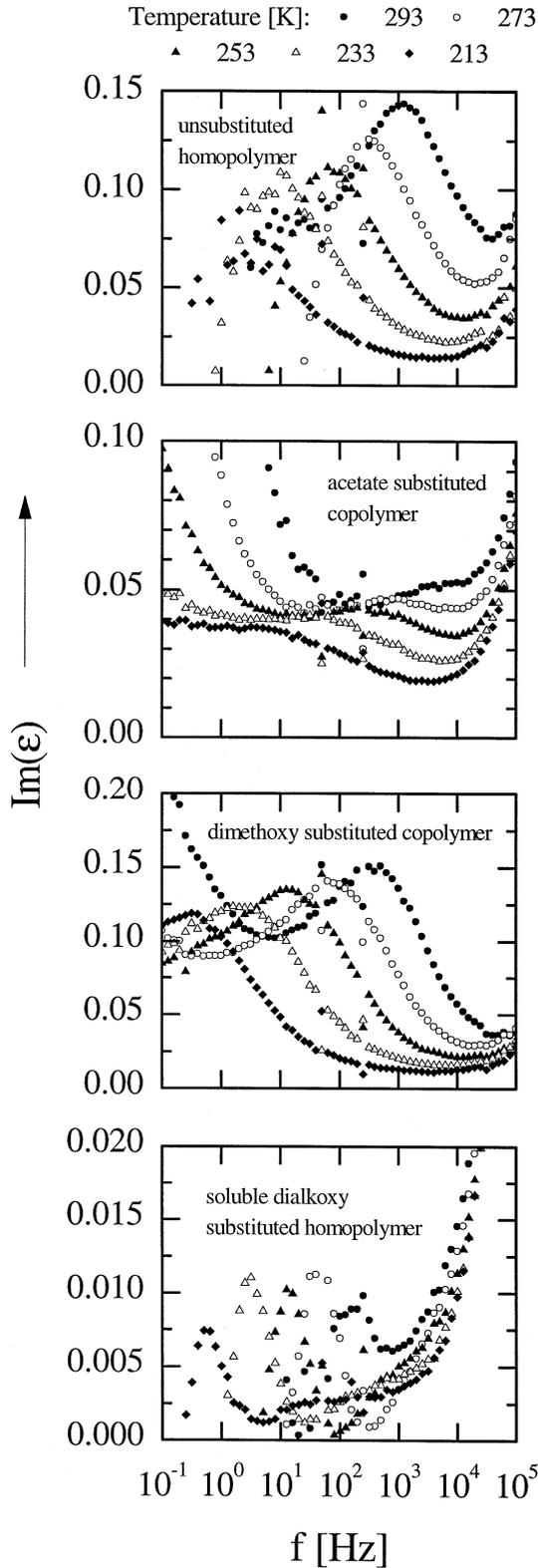Temperature [K]:   •   293   ∘   273
         ▲   253   △   233   ◆   213

Fig. 3. Imaginary part of the dielectric function (dielectric loss) for different temperatures.

loss processes. Values for the acetate-substituted copolymer are about a factor of two lower and the soluble dialkoxy-substituted homopolymer even shows a minimum of the dielectric loss between 10^3 and 10^4 Hz with the lowest value of all four polymers. A dielectric loss peak in this frequency range was also observed in a previous work on the unsubstituted homopolymer [5]. There, the high frequency loss peak is interpreted as coming from the bulk conductivity and characterizing the p-doping of the polymer-film with $InCl_3$. A second low frequency loss peak was observed for high thicknesses (400–1000 nm) and was assigned to the depletion region at the cathode side. In the specimens investigated here, the second polymer layer may be doped to a much lower degree so that the dielectric process connected with the cathode/polymer interface cannot be resolved in the measured frequency window. In order to get further information about the behaviour of the dielectric loss peak due to doping of the polymer bulk material, we have analyzed the temperature dependence of this feature.

Fig. 3 shows the imaginary part of the dielectric function corrected by the contribution of the DC conductivity $Im(\varepsilon) = [Re(\sigma) - \sigma_{DC}]/(\varepsilon_0 \omega)$ in the case of the unsubstituted homopolymer and the soluble dialkoxy-substituted homopolymer. Even the soluble dialkoxy-substituted homopolymer, which is not expected to react with the ITO substrate, shows a dielectric loss peak. Although the magnitude and the visibility of the loss peak is largely different for all four polymers, it is seen that the maximum shifts to lower frequencies with decreasing temperature for all materials. From previous work, it is expected that the temperature dependence of the peak maximum frequencies f_0 follows a thermally activated behaviour: $f_0 \propto \exp(-E_a/kT)$.
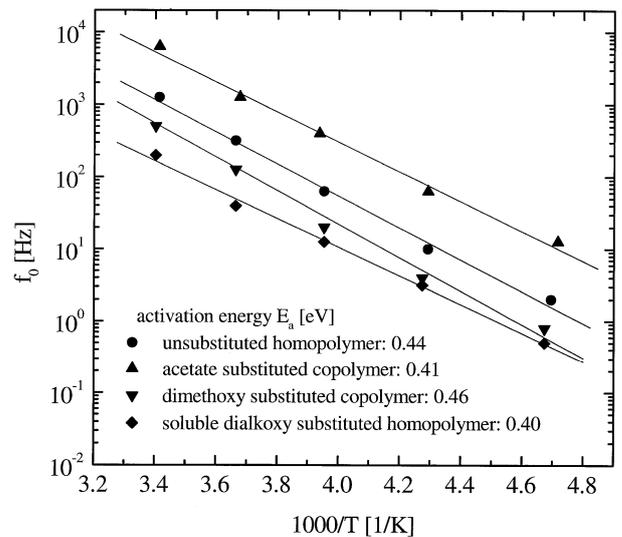

Fig. 4. Arrhenius plot of the temperature-dependent loss peak frequency observed in Fig. 3.

mopolymer and the dimethoxy-substituted copolymer show clearly resolved maxima, which can be related to dielectric

Fig. 4 shows the temperature dependence of f_0 in an Arrhenius representation. It can be seen that all four polymers show such a thermally activated behaviour with very similar activation energies between 0.4 and 0.46 eV. These values are in good agreement with previous impedance spectroscopy measurements on unsubstituted homopolymer ($E_a = 0.4$ eV) [5] and also with temperature-dependent mobility measurements on soluble dialkoxy-substituted homopolymer ($E_a = 0.48$ eV) [7].

4. Conclusion

The comparison of temperature-dependent impedance spectra of LEDs based on four different PPV derivatives has shown that in spite of significantly different values of the dielectric loss, the activation energies are very similar in all materials. This result is somewhat unexpected since the soluble PPV is not expected to show a reaction with the ITO substrate. Other possible origins could be a doping by oxygen from the ITO or ambient air or In [8]. Further investigations have to clarify the nature of the observed loss peaks.

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