Impedance Spectroscopy of Siloxane-Containing Polyazomethines Blended with SiO$_2$

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ABSTRACT: Two siloxane-containing polyazomethines (PAZx) blended with SiO$_2$ were investigated. SiO$_2$ was obtained by sol-gel method. The size of obtained SiO$_2$ particles was about 408 nm as was confirmed by SEM technique. For the blended with silica polymers absorption UV-vis properties were tested and compare with unblended ones. Electrical behavior of the two kind devices indium tin oxide (ITO)/PAZx : SiO$_2$/Al and ITO/PEDOT : PSS/PAZx : SiO$_2$/Al were tested by impedance spectroscopy in dark and under illumination (halogen lamp, 100 mW/cm^2) in the frequency range of 1 Hz to 1 MHz with maximum voltage value of 20 mV. For all measured devices, Nyquist plots were presented. PEDOT : PSS interlayer improved electrical properties of made prototype polymeric solar cells. Blending PAZx with silica increased conductivity from 10^{-15} to 10^{-8} S/cm. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polyazomethines (PAZx) are mainly known as thermostable polymers exhibited photoluminescence and liquid crystalline properties.[1],[2] Conjugated PAZx in neutral (undoped) form are mainly isolators. [1–10] Doping with iodine or Ag increase the conductivity of PAZx from 10^{-12} to 10^{-6} S/cm.[3–7] In our previous paper, we investigated electrical properties of liquid crystalline PAZ by impedance spectroscopy.[11] Our results showed that in the mesophase, increase of the conductivity from 10^{-11} to 10^{-7} S/cm was observed.

Silica nanomaterials have a wide range of applications due to such unique features as little absorption in the UV-vis-NIR regions, dielectric electrons, and low toxicity.[12] Silica particles were widely introduced into polymers to improve the heat resistance, radiation resistance, mechanical and electrical properties of such polymers as polyurethanes, polypropylenes, polyesters, polyimides, poly(2-chloroaniline), or epoxidized natural rubber.[13–25] For the investigated polymers, increase in conductivity was found along with added SiO$_2$. For example, the conductivity of poly-N-[5-(8-quinolinol)ylmethyl]aniline (PANQ) : SiO$_2$ composite was reduced an order of magnitude in comparison with PANQ (2.72 $\times$ 10^{-2} S/cm and 0.122 S/cm, respectively).[24] Similar trend was observed for poly(2-chloroaniline) (P2ClAn) and P2ClAn : SiO$_2$ (4.6 $\times$ 10^{-7} and 1.3 $\times$ 10^{-5} S/cm, respectively).[25]

Increase of efficiency of charge transfer between silica and polymer chains increase conductivity. Moreover, SiO$_2$ can increase protonation effect of polymer.[23]

The aim of this work was to investigate electrical properties of two siloxane-containing PAZx blended with SiO$_2$, to best of our knowledge not yet investigated. One and double layer devices with the such architecture as indium tin oxide (ITO)/PAZx : SiO$_2$/Al and ITO/PEDOT : PSS/PAZx : SiO$_2$/Al were tested by impedance spectroscopy in dark and under illumination (halogen lamp, 100 mW/cm^2). For the blended with silica polymers absorption UV-vis properties were detected.

EXPERIMENTAL

Measurements

The constructed devices were measured with impedance spectroscopy by Solartron precision LCR meter Model SI1260 in the frequency range of 1 Hz to 1 MHz with 20 mV test signal. To determine the photogeneration of charge carriers in BHJ devices, the measurement in dark and under illumination (halogen lamp, 100 mW/cm^2) was performed.

UV-vis spectra were recorded as thin films on the glass substrate by using Jasco V670 spectrophotometer. The solutions were spread on glass using the spin-coating method. Characteristic parameters related to speed (10,000 rpm) and time (25 s) of rotation were applied to spin-coating equipment.

Materials

Poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT : PSS) was purchased from Sigma-Aldrich and used as received. Chloroform was purchased from POCH and used as received.
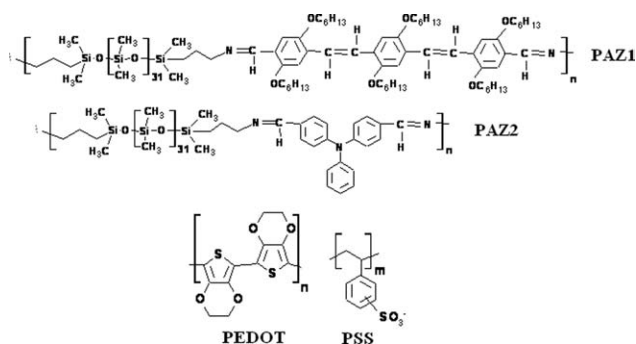
Figure 1. Chemical structure of PAZ1 and PAZ2 along with the structure of PEDOT : PSS.

ITO was purchased from Ossila company. Surface resistance of ITO was about 20 Ohm/square.

PAZx was made using a one-step polycondensation technique in solid state as was described in details in Ref. 26. The chemical structure of the polymers is presented in Figure 1.

Liquid crystalline and optical properties of both PAZx were described in Ref. 26. Both polymers formed nematic phase. The polymer PAZ1 with stilbene units showed a liquid crystal to isotropic transition at 164.6°C ($\Delta H = 2.8$ J/g), whereas the polymer PAZ2 with triphenylamine (TPA) units posses isotropization at 85.9°C ($\Delta H = 3.3$ J/g).[26] Both PAZx exhibited photoluminescence properties in chloroform solution (PAZ1 : $\lambda_{em.} = 499, 527$ nm, PAZ2 : $\lambda_{em.} = 521$ nm).[26]

Silica (SiO$_2$) was obtained by sol-gel method base-catalyzed polycondensation of tetraethoxysilane in ethanol as was described in Ref. 27. The size of obtained SiO$_2$ particles was about 408 nm as was confirmed by SEM technique (see Figure 2).

Fabrication of Organic Devices

Devices were fabricated on an ITO-coated glass substrate with the structure ITO/PEDOT : PSS/PAZx : SiO$_2$/Al and ITO/PAZx : SiO$_2$/Al in air atmosphere. The ITO-coated glass substrate was first cleaned with deionized water and ultrasonicated in isopropanol for about 20 min. PEDOT : PSS ($\sim$30 nm) was spin cast (10000 turns per minute, 25 s) from aqueous solution to form a film on the ITO substrate. A solution containing a mixture of PAZx : SiO$_2$ ($\sim$150 nm) in chloroform solution with weight ratio 1 : 1 was then spin cast on top of the PEDOT : PSS or ITO layer. For thermal annealing, the blend films were placed in oven and annealed at the temperature of 130°C for 2 h before the deposition of Al electrode. Then, an aluminum electrode ($\sim$100 nm) was deposited by thermal evaporation in a vacuum of about 5×10^{-4} Torr. The area of one photovoltaic pixel was about 4.5 mm^2. The impedance spectroscopy of PAZx with liquid crystalline properties was investigated by fabricating the polymeric devices with ITO as anode, the blend polymer with SiO$_2$ in weight ratio 1 : 1 as active layer, and Al as cathode (see Figure 3).

RESULTS AND DISCUSSION

In this article, electrical properties of two PAZx with different subunits were investigated by impedance spectroscopy. PAZ1
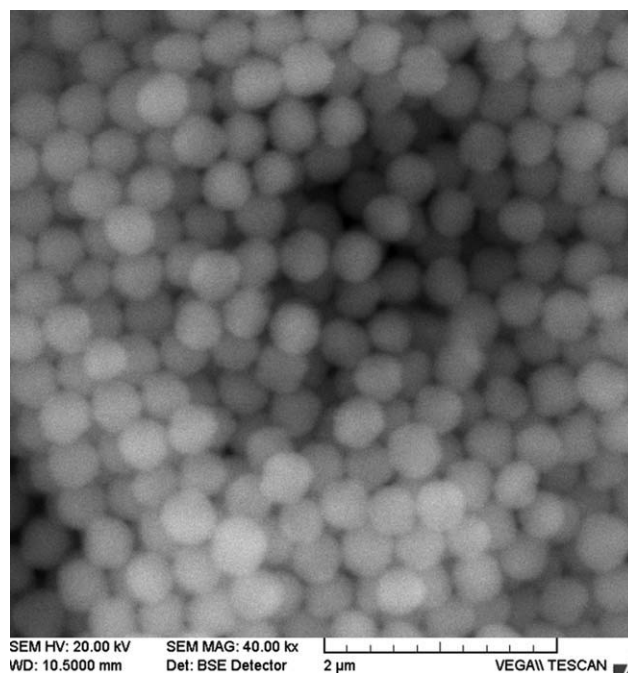

Figure 2. SEM image of SiO$_2$.

possess stilbene linkages (—C = C—), while PAZ2 TPA units as is presented in Figure 1. Differences between electrical properties of both PAZx, as is presented in the article, are caused various dialdehydes used to obtained PAZx. In the case of PAZ2, TPA unit as a hole transporting moiety was applied. Differences were observed additionally in optical properties of blended with silica polymers. The results are presented in the next part of the article.

Absorption Spectra

The optical properties of PAZx and PAZx : SiO$_2$ film were investigated in this aricle by UV-vis absorption spectroscopy. Uniform films were prepared on glass plates by spin coating from their chloroform solution. The UV-vis absorption spectra of the investigated compounds are shown in Figure 4.

The thin solid film of PAZx and PAZx : SiO$_2$ showed one main absorption band with maximum peak at 422 and 360 nm,
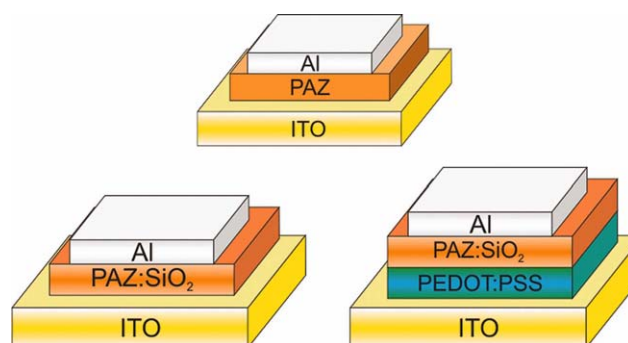

Figure 3. Schematic device construction of PAZx blended with SiO$_2$ along with architecture of reference device. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
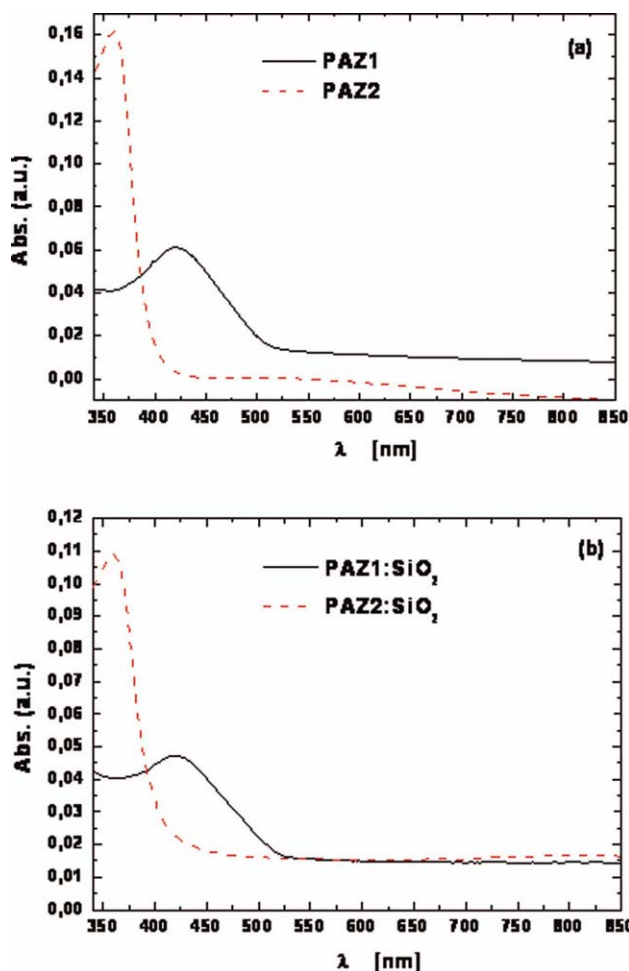
corresponding PPV derivatives, which indicates that it is less conjugated as compared to the polymers belonging to the PPV family.[28] For this reason, it is clear that presence in PAZ structure stilbene linkages decrease the value of E_g as was observed in our UV-vis experiment.

Being into consideration the chemical structure of the investigated polymers PAZ1 and PAZ2 blended with silica, some differences in optical properties were found along with change in the polymer structure. For example, the introduction of stilbene linkages as in PAZ1 in comparison with PAZ2 results in a 62 nm bathochromic shifts of $\lambda_{max.}$ band.

Siloxane linkages in poly(azomethine) PAZ1 blue-shift, the absorption bands in comparison with polymer lacking siloxane units obtained from the same dialdehyde and poly(1,4-butanediol)bis(4-aminobenzoate) ($\lambda_{max} = 440$ nm) investigated in our previous work.[11] Similar behavior was found for PAZ2. Polymer PAZ2 was 63 nm blue shifted in comparison with PAZ F-TPA obtained from the same dialdehyde and 2,7-diaminofluorene ($\lambda_{max} = 423$ nm).[10] The observed changes of the optical absorption spectra when the backbone structure is

Figure 4. Solid-state UV-vis absorption spectra of PAZx (a) and PAZx : SiO$_2$ (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively, for PAZ1 (PAZ1 : SiO$_2$) and PAZ2 (PAZ2 : SiO$_2$) (Figure 4). UV-vis spectra of the mixture PAZx : SiO$_2$ exhibited a little lower absorption intensity than UV-vis spectra of PAZx lack of SiO$_2$ (Figure 4). Optical energy band gap (E_g) was calculated from absorption spectrum. For PAZ1, value of E_g was found at about 2.31 eV, whereas for PAZ2 at $\sim$3.06 eV.

Smaller value of E_g for PAZ1 was noted and can be explaining changes in the polymer structure in comparison with PAZ2. Mer unit of polymer PAZ1 has three phenylene rings connected through two stilbene linkages, whereas PAZ2 has TPA unit.

Introduction to main chain of polymer PAZ1 phenylene rings causes probably alteration of energy levels (HOMO, LUMO) and moreover bang gap, in comparison with PAZ2. This behavior can be explained by the fact that in the case of PAZ1, two kinds of linkages are presented: HC=N— and —C=C—. It is known that the chemical structure of the simplest PAZ obtained from benzene-1,4-dicarboxaldehyde and 1,4-phenylenediamine is similar to the chemical structure of poly(p-phenylene-vinylene) (PPV).

The length of the PAZ mer unit is twice as long as that of PPV.[28] The optical gap of PAZ is usually higher than that of the
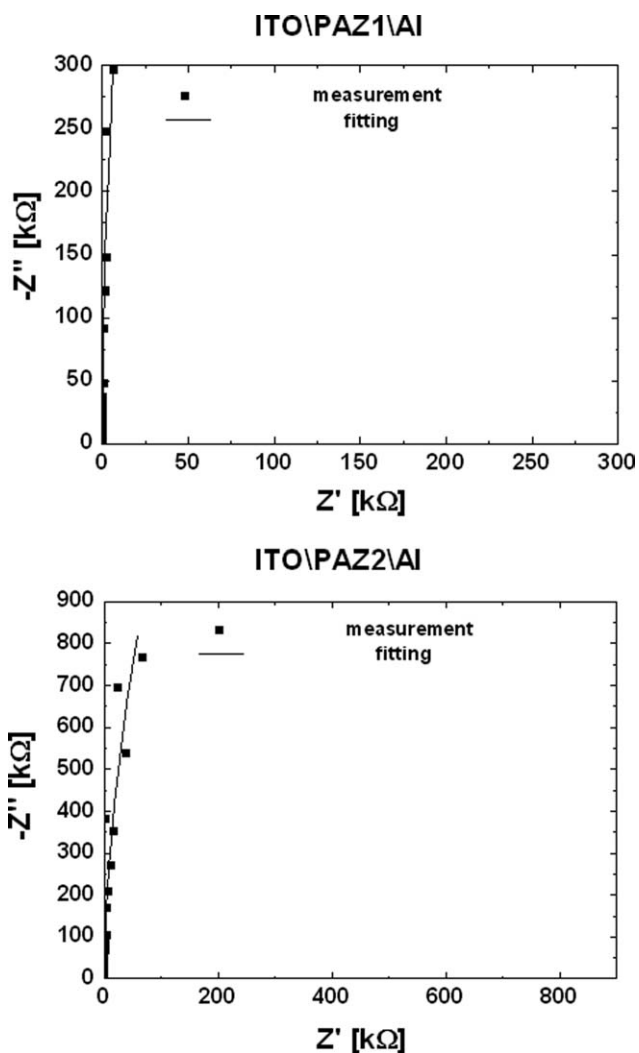

Figure 5. Nyquist plots for ITO/PAZx/Al.

Table I. Values of Equivalent Circuit Parameters for Parallel R-Q Elements for PAZ1 and PAZ2

Device	R_1 [kΩ]	Q_1-T [× 10^{-6}]	Q_1-P	R_2 [kΩ]	Q_2-T [× 10^{-9}]	Q_2-P	S (mm²)	d (nm)	σ (S/cm)	τ_1 (ms)	τ_2 (ms)
ITO\PAZ1\Al	87.1	93.8	1	177,000	209	0.98	4.5	250	3.15×10^{-15}	8169	34168
ITO\PAZ2\Al	33.8	1.09	0.9	14,700	24.7	1	4.5	250	1.64×10^{-12}	55	363

varied can be attributed to the modification of the polymer chain planarity.

This behavior clearly presents influence of polymer structure on the optical and as it will be presented in the next part of this article on the electrical properties of the investigated devices.

Impedance Spectroscopy

To determine electrical properties of two PAZx blended with SiO_2, the impedance spectroscopy measurements for ITO/PAZx : SiO_2/Al and ITO/PEDOT : PSS/PAZx : SiO_2/Al thin film structures at 30°C were performed. To determine the photogeneration of charge carriers, the measurements in dark and under

illumination were performed. As a reference, sample device with architecture ITO/PAZx/Al was tested. Values of equivalent circuit parameters along with mean relaxation times for paralel R-Q elements are presented in Table I.

The conductivity of PAZ1 was approximately 10^{-15} S/cm, whereas for PAZ2 was about 10^{-12} S/cm as determined by impedance spectroscopy (Table I). Blending PAZx with silica increase conductivity to 10^{-8} S/cm.

Differences in conductivity (σ) and relaxation times (τ_1 and τ_2) confirm influence of polymer structure on electrical and optical properties of both PAZx. For polymer PAZ1, which mer unit is
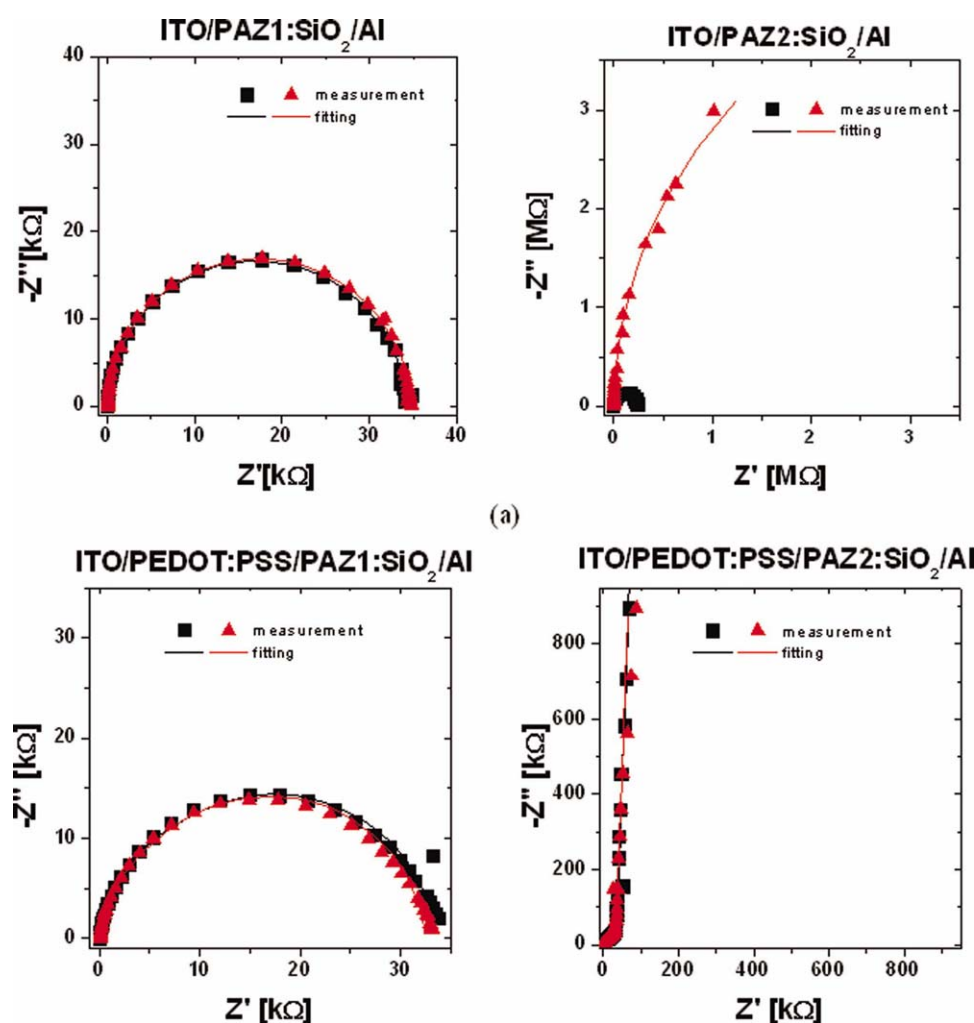

Figure 6. Nyquist plots for one layer (a) and double layer (b) structures based on polymers doped with SiO_2 (red color corresponds to illuminated samples). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
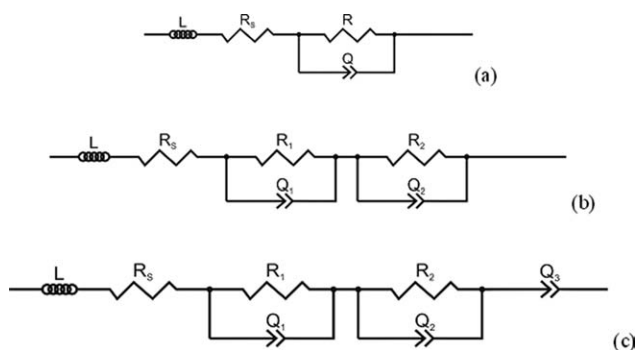
Figure 7. Equivalent circuit for modeling the measurement results for monolayer devices (a), along with equivalent circuit used for modeling of device with PEDOT : PSS/PAZ1 : SiO_2 (b), and ITO/PEDOT : PSS/PAZ2 : SiO_2/Al layers (c).

longer than in the case of PAZ2, a mobility and concentration of charges must be lower than in PAZ2. Polymer PAZ1 has greater value of relaxation time than in the case of PAZ2 (see Table I). Calculated value of relaxation time suggests that PAZ1 possess lower value of conductivity than PAZ2 (see Table I and Figure 5) and it was confirmed experimentally.

Blending polymers with silica caused that whole process of charge conduction is connected with doping polymers via SiO_2. The conductivity of devices ITO\PAZ1(PAZ2) : SiO_2\Al was increased to 10^{-8} S/cm independent on the polymer structure applied.

In the Figure 6(a), the results of measurement are presented by symbols and fitting by curves, whereas the black and red colors represent results for measurements in dark and under illumination, respectively.

The semicircles in the Nyquist plots were visible for all cases, however, for device with PAZ2, only the portion of large semi-

circle was visible. Results of measurements were fitted with equivalent circuit presented in Figure 7(a). Inductive element L and resistance R_S represents the lead induction and resistance, respectively, whereas R and Q are resistor and constant phase element of investigated layer, respectively.

Values of equivalent circuit parameters along with mean relaxation times for paralel R-Q elements are presented in Table II.

The equivalent circuits for each sample were composed of parallel connection of resistance with constant phase element Q, with frequency dependence of impedance in the form:

$$Z_Q = \frac{1}{T(j\omega)^p}$$

where $0 \leq p \leq 1$. Such element describes the nonideal frequency dependence of capacitance. It is applicable in such situations as processes with distribution of relaxation times or imperfections at interfaces. The mean relaxation time, τ, is equal to $(RT)^{1/p}$.

Coefficient χ^2 was very small, which indicates good fitting of proposed equivalent circuit to experimental data. Mean relaxation times τ span of two orders of magnitude for different samples. Smaller values of τ were found for PAZ1, which originates from the small values of resistance for this material and indicates better charge transfer.

The response on illumination was negligible in the case of PAZ1, whereas for PAZ2, increased of resistance under illumination occurred. The nature of this phenomenon is unclear at this stage and requires further investigations.

Indeed, there is stated that for both, PAZ1 and PAZ2 materials, the conductivity rises, due to the addition of SiO_2. The increase in resistivity is observed for PAZ2 under illumination when compared with measurement in dark.

Table II. Values of Equivalent Circuit Parameters along with Mean Relaxation Times for Parallel R-Q Elements

Measurement conditions	χ^2	L [μH]	R_S [Ω]	R [Ω]	Q-T [$\times 10^{-9}$]	Q-P	τ [μs]
ITO/PAZ1 : SiO_2/Al							
In dark	0.002041	2.27	95.03	34,052	15.6	0.99	490
Under illumination	0.002431	2.32	94.73	34,544	15.9	0.99	500
ITO/PAZ2 : SiO_2/Al							
In dark	0.001748	2.27	94.3	2.51×10^5	7.46	0.99	1756
Under illumination	0.015162	2.26	94.41	9.62×10^6	7.28	0.99	68,525

Table III. Parameters of Equivalent Circuit for ITO/PEDOT : PSS/PAZ1 : SiO_2/Al Structure

Measurement conditions	χ^2	L [μH]	R_S [Ω]	R_1 [kΩ]	Q_1-T [$\times 10^{-9}$]	Q_1-P	τ_1 [μs]	R_2 [kΩ]	Q_2-T [$\times 10^{-9}$]	Q_2-P	τ_2 [μs]
ITO/PEDOT : PSS/AI4 : SiO_2/Al											
In dark	0.005505	2.81	111.8	29.48	23.2	0.94	434	4.06	28.5	1	116
Under illumination	0.001742	2.67	114.8	29.05	21.7	0.95	417	3.54	28.3	1	100

Table IV. Parameters of Equivalent Circuit for ITO/PEDOT : PSS/PAZ2 : SiO$_2$/Al Structure

Measurement conditions	$\chi 2$	L [μH]	RS [Ω]	R_1 [kΩ]	Q_1-T [$\times 10^{-9}$]	Q_1-P	τ_1 [μs]	R_2 [kΩ]	Q_2-T [$\times 10^{-9}$]	Q_2-P	τ_2 [μs]	Q_3-T [$\times 10^{-9}$]	Q_3-P
In dark	0.001811	2.90	94.94	24.48	12.3	0.93	166	9.21	5.62	0.93	24.8	20.0	0.98
Under illumination	0.002296	2.90	95.17	22.47	11.1	0.95	155	9.24	5.64	0.92	24.2	20.8	0.97

Contrary to single layer samples, the Nyquist plots for double layer samples were characterized with clearly deformed semicircles, which indicate two different layers in investigated devices [Figure 6(b)]. For PEDOT : PSS/PAZ1 : SiO$_2$ layer, semicircles were situated very close to each other.

For the two layer device with PEDOT : PSS/PAZ2 : SiO$_2$ layers, the capacitive character dominates in lower frequency range. Sample with PEDOT : PSS/PAZ1 : SiO$_2$ layers was modeled with equivalent circuit presented in Figure 7(b), which is composed of two parallel R-Q connections and correspond to two distinct layers. For device with PEDOT : PSS/PAZ2 : SiO$_2$ layers, additional constant phase element connected in series is presented in Figure 7(c).

Table III represents results of fitting of equivalent circuit presented in Figure 7(b) to experimental data. Contrary to results presented above, the mean relaxation times were smaller, which originates from the smaller resistance values. It is important to note, that the values of resistance for ITO/PEDOT : PSS/PAZ1 : SiO$_2$/Al device were the same order of magnitude as for the single layer structure (lack of PEDOT : PSS layer).

Table IV presents the parameters of equivalent circuit from Figure 7(c). Despite the smaller values of resistances as compared to the single layer structure, additional constant phase element Q_3 indicates possible reaction between adjacent polymer layers, which results in formation of insulating layer at their interface.

Our preliminary photovoltaic study showed that PAZx : SiO$_2$ compositions exhibited no photovoltaic response which is probably caused by dielectric character of silica and break of the conjugation in polymer chain via long aliphatic chain.

PAZ1 and PAZ2 presented in this article exhibited photoluminescence properties as was described in our previous paper[26] and in our point of view can be potentially applied as a blends with silica in organic light emitting devices.[23] This part of our work is in progress.

CONCLUSIONS

Here, we have described the electrical properties of two siloxane-containing PAZx blended with SiO$_2$. Our study showed that the chemical structure of polymer used strongly influence on the electrical properties of the constructed devices. For one ITO/PAZx : SiO$_2$/Al and double ITO/PEDOT : PSS/PAZx : SiO$_2$/Al layer devices, Nyquist plots were presented as was deter-

mined by impedance spectroscopy. PEDOT : PSS interlayer improves electrical properties of made prototype polymeric solar cells. Blending PAZx with silica increase conductivity from 10^{-15} to 10^{-8} S/cm.PAZ1 blended with silica covered the absorption spectrum to about 550 nm, whereas PAZ2 : SiO$_2$ to about 420 nm. For the practical application more prosperous appear polymer PAZ1 with stilbene linkages.

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