



Synthesis and electrooptical characterization of polysiloxanes containing indolyl groups acting as photoconductive substrates for photorefractive materials

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Abstract: Synthesis and electrooptical analysis of polysiloxane and poly-*N*-vinyl derivatives containing indolyl groups are reported. The indole group and some of its methyl derivatives have been taken into account in order to evaluate their behaviour, with respect to that of the widely employed carbazole group, when used as photoconductive centres attached to a polymer chain. The obtained data show that photoconductivity and traps formation mechanism can be inferred as functions of the physico-chemical parameters (electric dipole moment and ionization potential) of the different groups and polymers involved. To this end such parameters have been carefully computed for a series of pyrrole, indole and carbazole derivatives. The 2,3-dimethylindole derivative appears to be particularly promising due to its electrooptical behaviour in the red absorption region where measurements have been accomplished and are shown to be consistent with the theoretical predictions.

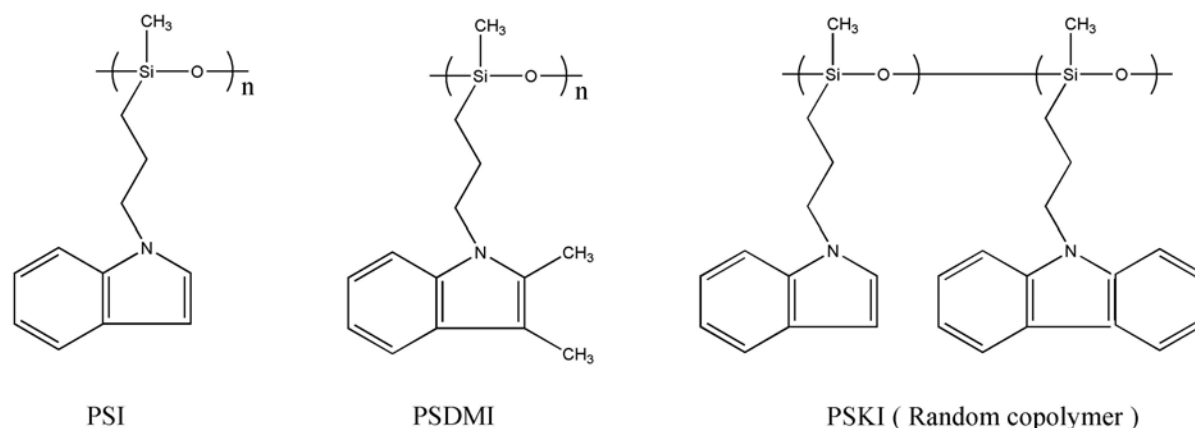
Introduction

Due to the increasing interest towards the potentialities of photorefractive materials as fundamental components of cells suitable for many different electrooptical devices, much work has been recently devoted to the synthesis and study of new substrates for optical applications [1,2]. After the good results obtained with inorganic crystals [3], it has been demonstrated that even more attractive performances can be attained when organic, especially polymeric materials, are employed. These last are particularly suitable as they can be modified along the backbone or on the side-chains with active centres giving to the polymer the essential characteristics for photorefractivity, namely the photoconductivity and the non-linear optical (NLO) behaviour. The most frequently studied materials are of intermediate nature, i.e., the active centres are present in the blend partly bound to the polymer chain and partly dissolved in it as free molecules [2]. The carbazole group and some of its derivatives have been extensively studied owing to the good resulting photoconductivity and photorefractivity [4,5]. Poly-*N*-vinylcarbazole (PVK) [6] and the most studied carba-

zole derivative of polysiloxane, viz. poly[methyl-3-(9-carbazolyl)propylsiloxane] (PSK) [7-9] are here used as reference because of their well-established electrooptical characteristics. In the new polymers studied here the carbazole group was replaced with the indole group and some of its methyl derivatives [10-12]. The reasons why we have considered the indolyl groups are based on the intent to rationalize and compare the effect of those groups on the different factors influencing the photoconductivity and the formation of electrostatic 'traps' that are so important in determining the extent of the photorefractive effect. It will be also important to evaluate if topologies and charge distributions of the different indole derivatives can be proven to be useful to ameliorate the compatibility between the different molecular moieties present in the blend. For instance, it is well known that the NLO species of a photorefractive PVK-based material tend to segregate rapidly with an unavoidable opacization of the electrooptical cell. Our efforts are aimed to find experimental supports to theoretical treatments [13,14] that ascribe the electrooptical behaviour to some of the most relevant features of the active centres, like electric dipole moment (edm), ionization potential (ip) and the average distance among the centres [15-17]. To this aim, we have taken advantage of the fact that, contrary to what happens for carbazole, several methyl derivatives of indole are commercially available with the corresponding variability of their edm and ip values. The photoconductivity and its efficiency of polysiloxane derivatives containing some of these groups, viz. poly[methyl-3-(*N*-indolyl)propylsiloxane] (PSI), poly[methyl-3-(*N*-(2,3-dimethylindolyl))-propylsiloxane] (PSDMI) and a mixed polysiloxane containing both indole and carbazole groups (PSIK), Scheme 1, were measured.

The already reported [12] photoconductivities of poly-*N*-vinylindole (PVI) and poly-*N*-vinyl-2,3-dimethylindole (PVDMI) were considered for comparison purposes. The photosensitizer giving the charge-transfer complex with the indolyl and carbazolyl centres was 2,4,7-trinitrofluorenylidene malonitrile (TNFM).

Scheme 1.



Results and discussion

edm and ip values

The availability of a series of polymeric methylated indole derivatives gives the opportunity to analyze comparatively the results of the electrooptical measurements and provide a predictive scheme for the general behaviour of indole-based materials. Besides the topological differences existing among the active groups inside the

material (distance R and relative geometry), the most important factors influencing the photoconductivity are the values of the electric dipole moment (edm) and of the ionization potential (ip) of the groups themselves. Also the formation of the 'traps' is an important event, chiefly for photorefractivity, as it will be discussed later. Very few edm and ip values can be found in the literature [21,22] and of those that are available the experimental ones are even scarcer and strongly dependent on the employed experimental method [17,21,22]. For this reason, we computed the edm and ip values by using a semi-empirical MOPAC-7 program that gave figures sufficiently well consistent with the reported experimental values. Tab. 1 reports the computed values for indole, carbazole and pyrrole derivatives that can be considered for future electrooptical materials, including those related to the polymeric materials considered here. Tab. 1 reports also the code by which the acronyms of the considered compounds can be easily read.

Tab. 1. Computed electric dipole moments (edm) and ionization potentials (ip). (I = indole, K = carbazole, Py = pyrrole, M = methyl, E = ethyl, P = propyl, N = substituted heterocyclic nitrogen)

Compound	edm in Debye	ip in eV	Compound	edm in Debye	ip in eV
I	2.09	7.85	NP4MI	2.36	8.14
NMI	2.24	7.81	NP5MI	2.37	8.14
NM2MI	2.37	8.21	NP6MI	2.44	8.17
NM3MI	2.15	8.11	NP7MI	2.69	8.10
NM23MI	2.28	8.06	K	1.59	7.65
NM4MI	2.06	8.16	NMK	1.80	7.60
NM5MI	2.09	8.20	NEK	1.65	7.65
NMI6MI	2.15	8.19	NPK	1.71	7.70
NM7MI	2.39	8.15	Py	1.97	8.28
NEI	2.49	8.22	NMPy	2.13	8.35
NE2MI	2.57	8.17	NEPy	2.24	8.55
NE3MI	2.34	8.07	NPPy	2.30	8.60
NE23MI	2.47	8.02	NE2MPy	2.36	8.50
NE4MI	2.31	8.14	NE3MPy	2.19	8.37
NE5MI	2.34	8.15	NE23MPy	2.23	8.35
NE6MI	2.40	8.16	NE24MPy	2.47	8.47
NE7MI	2.64	8.10	NE25MPy	2.49	8.40
NPI	2.55	8.22	NE34MPy	2.21	8.55
NP2MI	2.62	8.15	NE234MPy	2.31	8.41
NP3MI	2.44	8.07	NE2345MPy	2.27	8.23
NP23MI	2.51	8.03			

It is easy to verify that the computed values ip = 8.28, 7.85 and 7.65 eV reported for pyrrole (Py), indole (I) and carbazole (K), respectively, agree rather well with the 8.20, 7.76 and 7.57 eV experimental figures of ref. [21], obtained by different

methods in the gaseous phase. Similar considerations can be made for the edm values. The validity of the computed results seems to be further sustained by the computed ip values obtained for the 3- and 2,3-methyl derivatives of indole (e.g., NE3MI and NE23MI). The values reported in Tab. 1 show that the ip values of 8.07 and 8.02 eV, respectively, are the lowest ones. These figures fit very well the experimental data plotted in the following Fig. 1 that reports the wavelength λ_2^{\max} of the maximum of the optical absorptions of the charge-transfer complexes. It is well known that λ_2^{\max} shifts towards the infrared part of the spectrum when the ionization potential of the donor counterpart of the complex becomes lower and lower, as it happens in our experimental results.

NM23MI must be read as *N*-methyl-2,3-dimethylindole, NE234MPy as *N*-ethyl-2,3,4-trimethylpyrrole etc. *N*-Methylindoles can be used as plasticizers and actually we have used *N*-methylindole to this purpose. *N*-Ethylcarbazole has been extensively used as plasticizer in many carbazole-containing blends. In addition, both *N*-ethyl and *N*-propyl derivatives of indole and carbazole can be considered as model molecules of the parent moiety appearing as active centre in the side chains of poly-*N*-vinyl and polysiloxane macromolecules, respectively. Pyrrole derivatives have been considered here as potential starting molecules for different classes of photoconductive polymers, the electroconductivity of poly-*N*-vinylpyrrole having already been studied [24]. The overall self-consistence of the computed figures suggests that they can be assumed as sufficiently reliable, especially when the trends are considered rather than their absolute value.

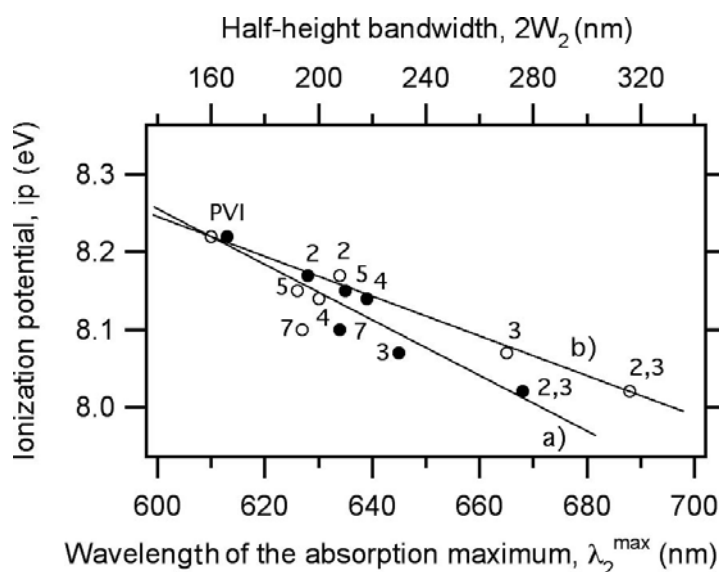


Fig. 1. Linear relationship of the ionization potential *ip* of the different methyl derivatives of indole with a) the wavelength λ_2^{\max} corresponding to the maximum of the absorptions in the optical spectra of the charge-transfer complex, and with b) the bandwidth $2W_2$ of the same absorptions. The numbering shows the positions of the methyl substituent on the indole moiety. Lines are meant only as a visual aid for the reader

Electrooptical behaviour

By considering the above edm and ip data, it is now possible to attempt a better rationalization of the already reported experimental results [10] obtained from the

optical study of the charge-transfer complexes of the indolyl groups in poly-*N*-vinylindoles. The optical spectra were obtained in dilute CH₂Cl₂ solution of the polymer complexed with 1 wt.-% of 2,4,7-trinitrofluorenylidene malonitrile (TNFM), the sensitizer. In particular, new absorption bands of the complex formed by the intermolecular interaction between donor D (the indolyl group) and acceptor A (TNFM) were recorded. Two new bands were particularly relevant. The former one corresponds to the transition from the second highest occupied molecular orbital HOMO(2) to the LUMO: this is the highest energy transition. The corresponding wavelength λ_1^{\max} of the maximum of the absorption remained nearly constant for all complexes (about 500 nm). A similar behaviour characterized the bandwidth (about 100 nm at half-height). The latter band corresponds to the transition from the HOMO to the LUMO. Its energy is lower than that of the first transition and the corresponding λ_2^{\max} values strongly depend on the values of the physico-chemical parameters of the D molecule involved in the charge-transfer complex. Computed values of i_p reported in Tab. 1 give a fairly linear dependence [25] on the values of λ_2^{\max} for all the studied [10] poly-*N*-vinylindoles (Fig. 1).

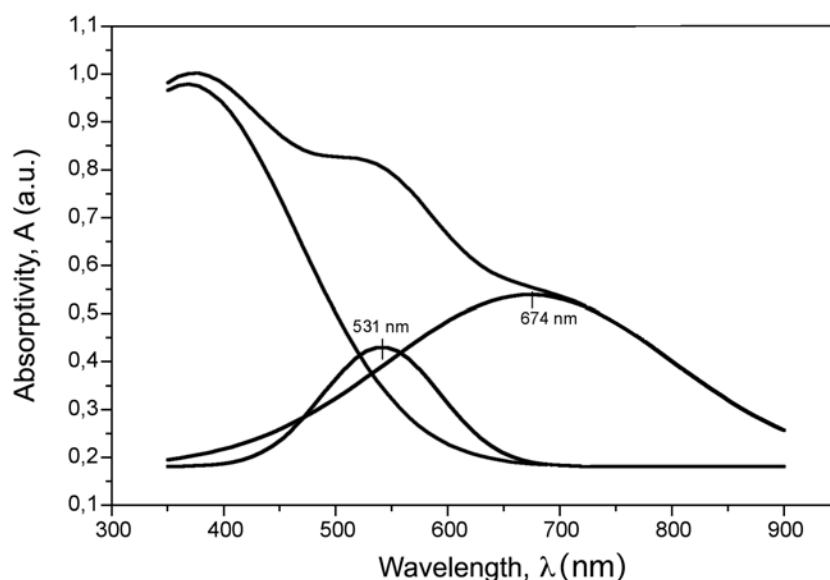


Fig. 2. Optical spectrum of a 100 μm thick film of the 2,3-dimethylindole derivative of polysiloxane in the region of its charge-transfer complex transitions, together with its deconvolution. The high absorptivity A in the near infrared and green regions, besides that in the red region, must be remarked

Trend a) in Fig. 1 clearly shows that the energy of the second transition shifts towards the infrared part of the spectrum when the 2,3-dimethyl derivative with the lowest i_p value is employed. The shift corresponds to 55 nm with respect to poly-*N*-vinylindole (PVI) itself while the 2-methyl and 3-methyl derivatives contribute to the linear trend with shifts equal to 15 and 32 nm, respectively. The methyl group in 4-, 5- and 7-position modifies to a lesser extent the i_p value with respect to PVI and their shift seems to merge at about 635 nm; their contribution to the linear trend seems to be a lower one. From these data it can be inferred that the substituents on the heterocyclic ring of indole exert a stronger influence on the i_p value, suggesting that it is more involved than the benzene ring in the formation of the charge-transfer complex. Totally similar considerations can be made for the trend b) of the band-

widths $2W_2$ of the same polymers. Also in this case a linear trend for the 2-, 3- and 2,3-methyl derivatives is observed. The effect of the substituents can be put in relation with the hyperconjugative behaviour of the methyl groups through which they release electron charge to the ring that consequently results electronically enriched. This makes the D molecule a stronger electron donor by decreasing its ip value [26,13]. When the optical spectra of the indolyl derivatives of polysiloxane are considered, it is found that the λ_2^{\max} values are totally similar to those of the corresponding poly-*N*-vinyl derivatives. Actually, this result could be foreseen from the computed ip values of the *N*-propyl derivatives (model molecules for polysiloxanes), which match closely those computed for the *N*-ethyl derivatives (model compounds for poly-*N*-vinyl derivatives). Optical spectra directly recorded from 100 μm thick films give optical parameters totally similar to the values obtained from dilute solutions. As an example, we report the spectrum of the charge-transfer complex of the *N*-allyl-2,3-dimethyl derivative of polysiloxane (PSDMI) (Fig. 2).

By inspection, it can be easily verified that the relevant parameters λ_2^{\max} and $2W_2$ do not change appreciably with respect to those reported in Fig. 1. Fig. 2 allows also appreciating that the absorptivity A of PSDMI is still relevant in the near IR region of the spectrum.

Tab. 2. Physical and electrooptical data of the studied polymers (T_g' : with plasticizer)

Polymer	T_g in $^{\circ}\text{C}$	T_g' in $^{\circ}\text{C}$	i_{ph} / A	$\sigma / \Omega^{-1}\text{cm}^{-1}$	η in %
PVK / NEK	220	35	$1.23 \cdot 10^{-6}$	$3.41 \cdot 10^{-11}$	$1.22 \cdot 10^{-1}$
PSK	44	–	$1.80 \cdot 10^{-7}$	$5.01 \cdot 10^{-12}$	$2.02 \cdot 10^{-2}$
PVI / NMI	172	26	$3.14 \cdot 10^{-9}$	$8.71 \cdot 10^{-14}$	$6.51 \cdot 10^{-4}$
PVI / NEK	172	23	$9.20 \cdot 10^{-9}$	$2.55 \cdot 10^{-13}$	$1.91 \cdot 10^{-3}$
PSI	-18	–	–	–	–
PSIK	23	–	$4.50 \cdot 10^{-8}$	$1.25 \cdot 10^{-12}$	$5.03 \cdot 10^{-3}$
PVDMI / NMI	181	31	$1.27 \cdot 10^{-8}$	$3.52 \cdot 10^{-13}$	$1.24 \cdot 10^{-3}$
PVDMI / bisBI	181	51	$4.25 \cdot 10^{-8}$	$7.67 \cdot 10^{-13}$	$4.38 \cdot 10^{-3}$
PSDMI	30	–	$1.03 \cdot 10^{-9}$	$2.86 \cdot 10^{-14}$	$1.56 \cdot 10^{-4}$

Photoconductivity measurements

In the frame of the geminate recombination model (electron-hole pair) in organic amorphous materials [13], the photogeneration and transport of the charges in the polymer matrix depend essentially on a three-step process. The first step is represented by the transition to the excited state of the charge-transfer complex, the second one by an electron transfer from the donor D to the HOMO of the complex when the complex decays from its excited state, and finally by the migration of the charges generated by the dissociation of the electron-hole pair. The charge transport can be thermally activated and favoured by the presence of an electric field E across the polymeric film; the invoked mechanism sustaining the transport is usually a hopping one among the active centres present in the material. The measured values of photocurrent i_{ph} , of photoconductivity σ , and of the photogeneration efficiency η for some representative samples at $E = 51 \text{ V}/\mu\text{m}$ are reported in Tab. 2 and the trend of i_{ph} as a function of $E^{1/2}$ in Fig. 3 [27]. The reported data should help in comparing the behaviour of the same active centre in poly-*N*-vinyl (PV) or polysiloxane derivatives

(PS) - the D donors - namely carbazole (PVK, PSK), indole (PVI, PSI) and 2,3-dimethylindole (PVDMI and PSDMI). All PV derivatives contain about 30 wt.-% of a plasticizer, necessary to lower the glass-transition temperature T_g of the polymer, cf. Tab. 2. PVK is usually plasticized with *N*-ethylcarbazole (NEK) while *N*-methylindole (NMI) is preferred for PVI and PVDMI. When such low T_g values are achieved, it is easy to squeeze the blends between two ITO-coated glasses at only 130°C to obtain the film. The use of higher temperatures for the preparation of the cell is not dangerous for the polymer itself, as confirmed by TGA measurements showing that all polymers taken into consideration can withstand temperatures up to about 450°C without decomposition. However other components, chiefly the sensitizer and the plasticizer, tend to quit the blend at a lower temperature. The PS derivatives do not require a plastifier because the T_g values of the polymers (Tab. 2) are already sufficiently low.

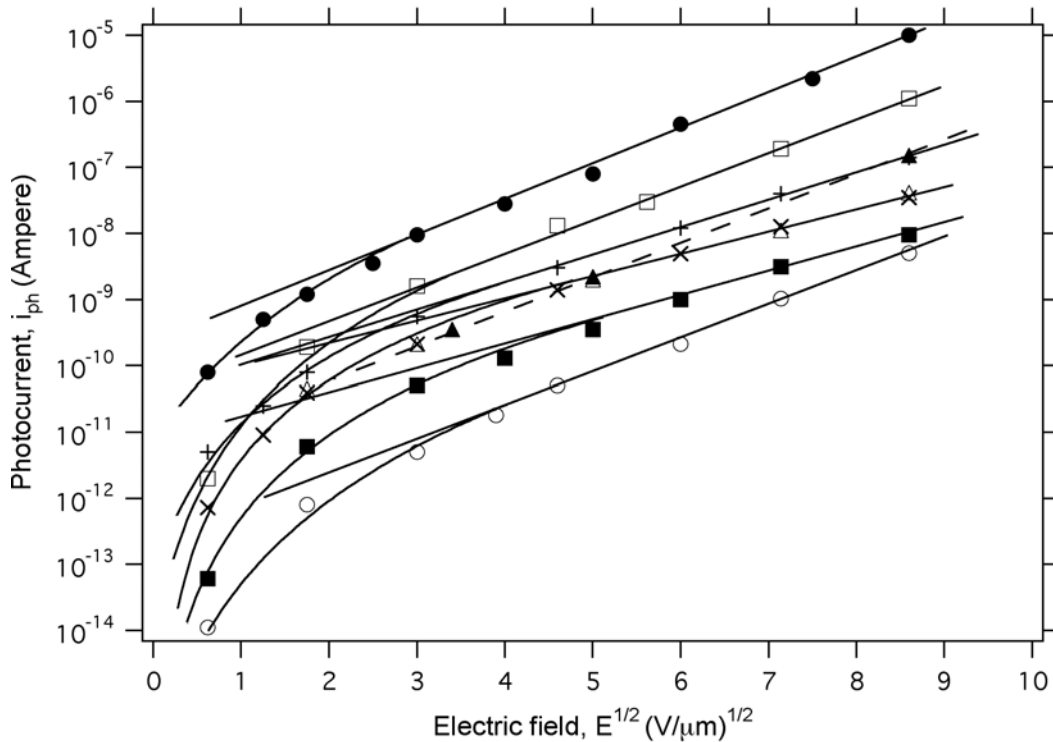


Fig. 3. Measured photocurrent i_{ph} , at constant laser power $P = 5$ mW, as a function of the square root of the applied electric field E , for the different polymeric films. ● PVK/NEK; □ PSK; + PSIK; × PVDMI/NMI; △ PVI/NEK; ■ PVI/NMI; ○ PSDMI; ▲ PVDMI/bisBI (dashed line) (see text). Lines are meant only as a visual aid for the reader

From Tab. 2 one can see that PVK/NEK has the highest value of $\sigma = 3.41 \cdot 10^{-11} \Omega^{-1} \text{cm}^{-1}$. This result agrees with the lowest value of the ionization potential $i_p = 7.65$ eV computed for NEK (Tab. 1). The low i_p enhances the charge generation efficiency as experimentally confirmed by the value of the photoconductivity efficiency $\eta = 1.22 \cdot 10^{-1} \%$ reported in Tab. 2 and obtained from $\eta(E) = (2 h\nu/eP) (i_{ph}/A)$, in which ν is the laser frequency, A is the absorptivity of the photoconductive film at that frequency, e is the electron charge and P is the laser power applied on the film. The value of σ reported for PVK can be directly compared with that of PSK that amounts to $0.501 \cdot 10^{-11} \Omega^{-1} \text{cm}^{-1}$. Since the computed value $i_p = 7.70$ eV for *N*-propylcarbazole

(NPK) is very similar to $i_p = 7.65$ eV of NEK, the difference in σ should be ascribed to the distance parameter R among the active centres that is known to condition both the photogeneration efficiency and the rate of the hopping transport mechanism [13,15]. An increase of R lowers in both cases the photoconductivity through an exponential dependence. A rough estimate of the variation of the average distance R in the different materials studied can be obtained by assuming that they are characterized by an average specific gravity $d = 1.0$ g/cm³. The volume V of the laser-irradiated material is the same for every film, corresponding to the volume of the cylinder with a radius $r = 0.15$ cm (the radius of the laser beam) and a height $l = 10^{-2}$ cm (the thickness of the film). Hence, $V = 7.07 \cdot 10^{-4}$ cm³. At this point, $wt = V \cdot d = 7.07 \cdot 10^{-4}$ g being the weight of the irradiated polymer, the number of moles n_i present in that volume can be easily obtained from $n_i = wt/mw$ where mw is the molecular weight of the repeating unit of each polymer. The result is: $n_{PVK} = 3.7 \cdot 10^{-6}$ mol; $n_{PSK} = 2.6 \cdot 10^{-6}$ mol; $n_{PVI} = 7.6 \cdot 10^{-6}$ mol; $n_{PSI} = 4.3 \cdot 10^{-6}$ mol; $n_{PVDMI} = 5.8 \cdot 10^{-6}$ mol and $n_{PSDMI} = 3.6 \cdot 10^{-6}$ mol. A shorter distance R corresponds to a higher value of n_i . PSK has a n_{PSK} value that is lower than the value n_{PVK} for PVK; therefore, this should justify the lower photoconductivity of PSK, as originating only from a higher value of R . Anyway, it has been shown [15] that in a description of the hopping mechanism, the electric dipole moment (edm) of the active donor group cannot be ignored. The interactions of the migrating charges (holes) with the edm's inside the material leads to the Poole-Frenkel-like equation for the mobility:

$$\mu(E) = \mu(0) \exp(S \cdot E^{1/2}) \quad (1)$$

as a function of the square root of the applied electric field E [27]. In semilogarithmic representation, $\mu(0)$ is the intercept at $E = 0$ and S represents the slope of the linear function when $E^{1/2}$ is reported on the abscissa. It can be shown, for instance in the frame of the Gaussian disorder model (GDM) [14], that to a higher value of $\mu(0)$ corresponds a lower value of the energetic disorder due to the dispersive interactions of the migrating charges with the D molecules. Such a disorder relates to the density of the states (DOS) whose width increases with the disorder. Even the slope S is sensitive to the energetic disorder and also to a geometrical disorder connected to a random distribution of the intermolecular distances and orientations. S is higher for higher disorder. Now, coming back to the initial comparison between the behaviour of PVK and PSK, the good parallelism of the trends reported in Fig. 2 demonstrates that disorder should be similar inside the two materials independent of the introduction of NEK as a plastifier in PVK and not in PSK. Actually, it has been verified that a modification of the content of NEK from 30 to 40 wt.-% lowers the T_g ' of PVK, but does not influence at all the slope leaving nearly unchanged the value of σ . Going now to examine the behaviour of the polymers containing the indolyl groups, it can be verified from the data of Tab. 2 that PVI has a value of $\sigma = 8.71 \cdot 10^{-14}$ $\Omega^{-1}\text{cm}^{-1}$, well lower than that of PVK. This result originates mainly from a lower photogeneration efficiency due to the value $i_p = 8.22$ eV computed for NEI that is higher than that for NEK with an increase of 0.57 eV (Tab. 1). Anyway, a not negligible contribution to the lowering of the photoconductivity is certainly given by the higher value of edm = 2.49 D for NEI with respect to edm = 1.65 D for NEK (Tab. 1). The higher value of edm corresponds to an increasing energetic interaction of the lattice with the migrating charges with a consequent lowering of the photoconductivity. A positive contribution to the photoconductivity might come from the shorter distance among the active centres as deduced from $n_{PVI} = 7.6 \cdot 10^{-6}$ mol previously calculated for PVI. Unfortunately, photoconductivity measurements were not possible on PSI due to its very low $T_g = -18^\circ\text{C}$. This low T_g is not surprising since it matches the lowering of T_g of about

50 - 60°C when going from PVK to the various indolyl derivatives [10]. However, at room temperature the too low viscosity of PSI produced large current spikes when photoconductivity measurements were attempted on the film. A similar situation has been reported to happen during photorefractive studies on nematic liquid crystal systems. The 'busy' response was attributed to hydrodynamic instabilities related to charge injection from the electrodes and to ionic current flow between the two electrodes [28]. The trend for PVI/NMI reported in Fig. 3 shows a value of S that is lower and a $\mu(0)$ value that is comparatively higher than the corresponding values for PVK/NEK.

This result clearly suggests, on the basis of the considerations previously made for PVK, that the disorder acting on the hopping migration is lower when the indole group is present inside the blend. Moreover, it seems that it is the indole group directly bound to the polymer backbone that is controlling the degree of disorder. Indeed, the replacement of NMI with NEK to study PVI/NEK instead of PVI/NMI, increases the extent of photogeneration efficiency but leaves unchanged the values of slope S and $\mu(0)$ and hence the disorder of the system. With the aim of getting some more information on PSI, we have synthesized the mixed polymer PSIK in which both indole and carbazole groups are connected to the polysiloxane chain in a 45 to 55 ratio. The photoconductivity markedly increased to $\sigma = 1.25 \cdot 10^{-12} \Omega^{-1} \text{cm}^{-1}$ becoming higher than those of both PVI/NMI and PVI/NEK and approaching that of PSK (Tab. 2 and Fig. 3). This is evidently due to the beneficial effect of the lower ip of NPK present in PSIK on the photogeneration efficiency. Anyway, it is interesting to note that the value of S increases with respect to that of both PVI samples, the slope of the trend becoming intermediate between that of PVK (PSK) and PVI. The two indole and carbazole groups seem now to exert a balanced control on the disorder degree.

Coming now to the polymer blends containing the 2,3-dimethylindole group, the data of Tab. 2 put in evidence that PVDMI/NMI has a value of $\sigma = 3.52 \cdot 10^{-13} \Omega^{-1} \text{cm}^{-1}$ that is distinctly higher than that of PVI/NMI, $\sigma = 8.71 \cdot 10^{-14} \Omega^{-1} \text{cm}^{-1}$, and similar to that of PVI/NEK, $\sigma = 2.55 \cdot 10^{-13} \Omega^{-1} \text{cm}^{-1}$. The higher σ value is in agreement with a better photogeneration efficiency due to the computed ip = 8.02 eV (Tab. 1) of *N*-ethyl-2,3-dimethylindole (NE23MI) that is lower than ip = 8.22 eV of NEI. The analogous polysiloxane derivative, PSDMI, has $\sigma = 2.86 \cdot 10^{-14} \Omega^{-1} \text{cm}^{-1}$, which is lower than that of PVDMI/NMI. As the computed ip = 8.03 eV for 1-propyl-2,3-dimethylindole (NP23MI) matches almost exactly that of NE23MI, it can be concluded that the lowering of the photoconductivity has to be ascribed to the higher distance R among the active centres as argued from the calculated mole numbers $n_{\text{PVDMI}} = 5.8 \cdot 10^{-6} \text{ mol}$ and $n_{\text{PSDMI}} = 3.6 \cdot 10^{-6} \text{ mol}$. Even the calculated edm values for NE23MI and NP23MI suggest that the photoconductivity of PSDMI should be slightly lower than that of PVDMI. From the trends of Fig. 3 it seems clear that, contrary to what was deduced for PVI, NMI conditions the disorder degree even when it is used as a plastifier. Indeed, the slope S for PVDMI/NMI is the same of both the studied PVI blends. The value of S corresponds to a lower disorder degree than that found for PSDMI that seems to be, from this point of view, more disordered and more similar to the behaviour of PVK and PSK. As observed previously [12], when *N,N'*-(1,4-butandiylo)-bisindole (bisBI) is used instead of NMI as a plastifier, the photoconductivity slightly increases and, most important, the slope S increases giving a more disordered system similar to PVK and PSK, cf. Fig. 3. The presence of the indole group, both connected with the polymer backbone or used as a low-molecular-weight plastifier, seems then to favour the formation of a less disordered material. An overall careful

examination of the trends represented in Fig. 3 allows to put quantitatively in evidence the competition between the recombination rate and the dissociation rate of the electron-hole pair to give back the charge-transfer complex or to dissociate in charges participating in the hole-hopping transport mechanism. The applied voltage at which the trends become linear should represent the threshold at which the dissociation process prevails upon the recombination one. This threshold for the carbazole and 2,3-dimethylindole polymers (about 900 V) is much lower than for the indole-containing polymers (about 3500 V), thus confirming that a lower i_p value controls the photogeneration efficiency by influencing the competition between the two processes.

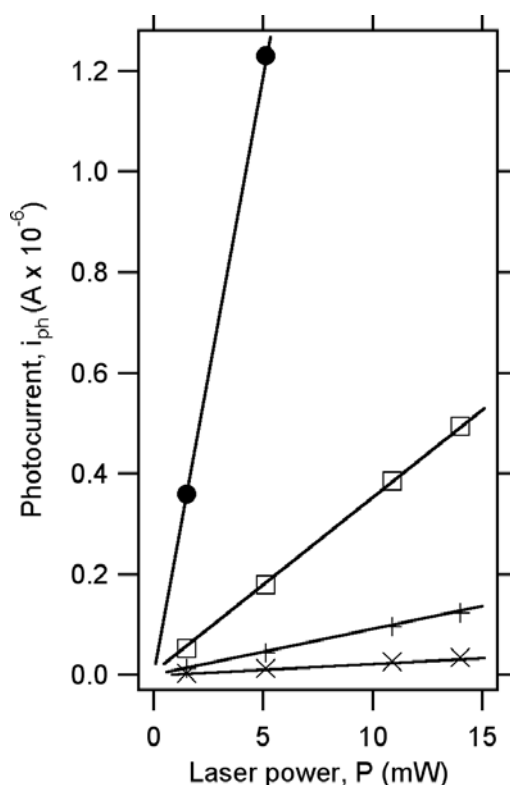


Fig. 4. Linear dependence of the photocurrent i_{ph} on the applied laser power P spanning from zero to 15 mW for some of the studied 100 μm thick polymeric films. The electric field was held constant at 51 V/ μm . Same symbols as in Fig. 3. Lines are meant only as a visual aid for the reader

Disorder and traps

The presence of so-called ‘traps’ is of essential importance for a material to show photorefractivity. Indeed, it is on these traps that part of the migrating charges stops to give origin to the inner lattice of charges that modulates the point value of the refraction index through the Pockel and/or Kerr effect. A trap can be seen, in general, as a point site of the material where a migrating hole can be favourably energetically stabilized. The probability of formation of a trap is higher where the width of the density of states (DOS) is higher, i.e., when the previously considered disorder is higher [23,29]. This proposition seems to be sustained by the results of our measurements. When a carbazole-containing material is irradiated, a very high spike of photocurrent appears just after the firing of the laser radiation. After a given (usually short) time, depending on the material, the photocurrent decreases by an exponential-like

law towards the measured stable value. Polymers containing the 2,3-dimethylindole group behave similarly, at least qualitatively. On the contrary, all polymers containing the unsubstituted indole group show no hint of a spike, the photocurrent going rather slowly from its 'dark' value to the measured one. The existence of that initial spike has been frequently ascribed to the easy formation of traps [30]. Significantly, the materials that we have classified as the more disordered ones gave constantly a well-defined spike [11]. A second argument is provided by the trend of the photocurrent for a film containing an increasing amount of photosensitizer when it is irradiated at constant laser power [11,12]. When the content becomes higher than 1 wt.-%, the photocurrent stops to increase and already at a content of 2 wt.-% it decreases markedly. This happens for all carbazole- and 2,3-dimethylindole-containing polymers. In the case of indole-containing polymers no saturation exists and the photocurrent continuously increases at least up to a content of 2 wt.-% of photosensitizer. This behaviour remains unchanged at both 1000 and 5100 V applied voltage. The saturation can also be explained as a consequence of the presence of a larger amount of traps in the more disordered systems. On the other hand, for all studied polymers a linear dependence was found of the photocurrent i_{ph} as a function of the laser power P applied to the films (Fig. 4). This dependence can be of the linear type only if the photogeneration efficiency η is independent of the value of P , as shown by the relationship:

$$i_{ph} = e A \eta / (2 h \nu) \quad (2)$$

Therefore, saturation of the photocurrent cannot be correlated to the first steps of the photogeneration process like, e.g., the excitation of the electron-transfer complex or the electron transfer to give back the initial complex in its fundamental energy state.

To conclude, we have tried to rationalize the electrooptical behaviour of the studied polymer-based materials putting in evidence how the different parameters characterizing the active centres can influence the overall behaviour. This has been possible by exploiting the unique feature of the materials taken in consideration that differ only in the polymeric chain by maintaining unchanged the nature of the active centres. Some indications have been gained on the relative availability of 'traps' that are so important in determining the photorefractivity efficiency. The higher edm and ip values of the indolyl derivatives lead to blends with lower photoconductivities. Despite this, we have verified that indolyl-based blends also containing the NLO molecule DMNPAA to obtain photorefractive materials are more stable over time, with respect to recrystallization, than the PVK-based blends, possibly because the different edm values positively influence the intermolecular interactions. This is particularly true for PVDMI and we hope that the same will be verified for PSDMI. It is worth recalling that PSK-based blends are more stable over time than the corresponding PVK-based ones [31,32]. Moreover, we believe that PVDMI- and PSDMI-based blends should be considered interesting materials on which photoconductivity and photorefractivity measurements are recommended also in the infrared and green regions. On these materials, tests will be made to evaluate the technological potentialities towards the possible building-up of blends sensitive to white light, see Fig. 2.

Experimental part

Syntheses and general information

The synthesis of 1-vinylindole derivatives and their polymerization to poly-1-vinylindoles has already been described [10,12]. Poly(9-vinylcarbazole) (PVK), was

purchased from Aldrich (USA) as a powder with $M_w \approx 63\,000$ and $T_g \approx 220^\circ\text{C}$. All methyl derivatives of indole have been obtained from Aldrich. ^1H NMR chemical shifts δ are given in ppm downfield from SiMe_4 .

1-(2-Propenyl)indole (1) (hereafter *N*-allylindole) was obtained using tetrabutylammonium hydrogen sulfate as catalyst in aqueous NaOH solution by reacting indole with allyl chloride. A three-necked 250 mL flask with mechanical stirrer and reflux condenser was charged with, in the order, 30 mL of a 50 wt.-% water solution of NaOH, indole (11.4 g, 100 mmol) in 65 mL of benzene solution, allyl chloride (11 mL, 150 mmol) and tetrabutylammonium hydrogen sulfate (TBAHS) (2.5 g, 7.3 mmol). After 24 h at room temperature and with mild stirring, the water phase was repeatedly washed with benzene. The combined benzene extract was washed with 10 wt.-% aqueous HCl followed by distilled water until neutral pH. The extract was dried over anhydrous MgSO_4 over night. Evaporation of volatiles under reduced pressure gave an oil that was purified by distillation over potassium at 67°C and 0.1 mmHg to give product (1) in 60% yield.

^1H NMR (CDCl_3 , 200 MHz): $\delta = 4.77$ (dt, $J = 1.5, 5.4$ Hz, 2H), 5.13 (dq, $J = 1.5, 17.2$ Hz, 1H), 5.25 (dq, $J = 1.5, 10.2$ Hz, 1H), 5.95 - 6.14 (m, 1H), 6.59 (d, $J = 3.4$ Hz, 1H), 7.15 (d, $J = 3.4$ Hz, 1H), 7.18 - 7.41 (m, 3H), 7.71 (d, $J = 7.0$ Hz, 1H) [18].

$\text{C}_{11}\text{H}_{11}\text{N}$	Calc.	C 84.04	H 7.05	N 8.91
	Found	C 83.92	H 7.03	N 8.88

1-(2-Propenyl)-2,3-dimethylindole (2) (hereafter *N*-allyl-2,3-dimethylindole), was obtained under similar conditions but using 18-crown-6-ether (1,4,7,10,13,16-hexaoxacyclooctadecane) as catalyst. A three-necked 250 mL flask with mechanical stirrer and reflux condenser was charged with, in the order, NaOH in pellets (4.6 g, 82 mmol), 2,3-dimethylindole (6.0 g, 41.4 mmol) in 30 mL of toluene solution and 18-crown-6-ether (1.08 g, 4.14 mmol). The solution was stirred for 30 min at room temperature: the colour changed from light yellow to orange. Allyl chloride (6.8 mL, 82 mmol) in 20 mL of toluene solution was dropped in 10 min. After 22 h stirring at room temperature, the reaction mixture was diluted with 50 mL of toluene and repeatedly washed with water. The organic phase was dried over anhydrous MgSO_4 over night. Evaporation of the volatiles under reduced pressure gave a crude light yellow solid. After column chromatography elution on silica with CHCl_3 , product (2) was obtained in 43% yield [19,20].

^1H NMR (CDCl_3 , 200 MHz): $\delta = 2.34$ (s, 3H), 2.39 (s, 3H), 4.73 (dt, $J = 1.8, 4.8$ Hz, 2H), 4.89 (dq, $J = 1.8, 16.8$ Hz, 1H), 5.16 (dq, $J = 1.8, 10.2$ Hz, 1H), 5.90 - 6.08 (m, 1H), 7.15 - 7.38 (m, 3H), 7.58 (d, $J = 7.0$ Hz, 1H).

$\text{C}_{13}\text{H}_{15}\text{N}$	Calc.	C 84.24	H 8.16	N 7.56
	Found	C 84.32	H 8.19	N 7.77

Indolyl derivatives of poly[(hydrogenmethyl)siloxane] (PHMS, Petrarch, $M_n = 2300$) were obtained by hydrosilylation reaction of PHMS with monomers (1) and (2). The synthesis of the carbazole derivative has already been described [7,8].

Poly[methyl-3-(1-indolyl)propylsiloxane] (PSI): PHMS (0.9 g, 15 mmol) was added under argon to a 30 mL dry toluene solution of (1) (3.14 g, 200 mmol) contained in a 100 mL double-necked flask with reflux condenser and magnetic stirrer. After addition of dichloro(dicyclopentadiene)platinum (II) (3.4 mL of a $2.3 \cdot 10^{-3}$ M solution in dry toluene, $7.8 \cdot 10^{-6}$ mol), the mixture was stirred at 60°C for 22 h. The extent of functionalization of PHMS was followed by the progressive lowering of the intensity of the IR absorption band of the Si-H stretching of PHMS at 2168 cm^{-1} . Its total

disappearance was considered an indication of a high extent of functionalization of the polymeric chain. Addition of 1-octene (4 mL) and further 2 h of stirring ensured complete conversion of possible residual traces of unreacted Si-H groups. The mixture was allowed to cool down and poured into 800 mL of cold n-hexane. The obtained crude polymer was purified by two subsequent precipitations from a tetrahydrofuran/ n-hexane mixture. Column chromatography elution of the resulting brownish polymer with CH₂Cl₂ on neutral alumina (Merck, 0.06 - 0.2 mm) gave the colourless title product in 68% yield.

¹H NMR (CDCl₃, 200 MHz): δ = -0.45 - 0.00 (bs, Si-CH₃), 0.00 - 0.40 (bm, Si-CH₂), 1.35 - 1.70 (bm, Si-CH₂-CH₂), 3.6 - 3.8 (bm, CH₂-N), 6.30 - 6.50 (bm, H₃), 6.75 - 6.95 (bm, H₂), 6.95 - 7.35 (bm, 3H, Ar-H), 7.50 - 7.70 (bm, H₇).

The number-average molecular weight as determined by gel permeation chromatography (GPC) was $M_n = 8200$.

Poly[methyl-3-(2,3-dimethylindolyl)propylsiloxane] (PSDMI) was synthesized following the same procedure as described for PSI. Pure light yellow PSDMI was obtained in 63% yield.

¹H NMR (CDCl₃, 200 MHz): δ = -0.30 - 0.00 (bs, Si-CH₃), 0.00 - 0.40 (bm, Si-CH₂), 1.30 - 1.55 (bm, Si-CH₂-CH₂), 2.00 - 2.20 (2s, 6H, CH₃), 3.50 - 3.80 (bm, CH₂-N), 6.85 - 7.15 (bm, 3H, Ar-H), 7.30 - 7.50 (bm, H₇).

$M_n = 9100$ as determined by GPC.

Poly[methyl-3-(1-indolyl)propyl-co-methyl-3-(9-carbazolyl)propylsiloxane] (PSIK): This copolymer, containing both indole and carbazole groups, was obtained according to the same synthetic route as described before. An appropriate mixture of *N*-allylindole (0.585 g, 3.7 mmol) and *N*-allylcarbazole (1.00 g, 4.8 mmol) was used to obtain a product having a 45/55 ratio of randomly distributed indole and carbazole groups as verified by ¹H NMR. The yield was 65%.

¹H NMR (CDCl₃, 200 MHz): δ = -0.55 - 0.00 (bs, Si-CH₃), 0.00 - 0.40 (bm, Si-CH₂), 1.20 - 1.80 (bm, Si-CH₂-CH₂), 3.40 - 4.00 (bm, CH₂-N), 6.20 - 8.20 (bm, carbazole and indole Ar-H).

$M_n = 9150$ as determined by GPC.

¹H NMR spectra were recorded at room temperature on a Varian Gemini 200 spectrometer by dissolving the sample in CDCl₃. TGA measurements were performed at 10°C/min under nitrogen flow on a Mettler TA 400 thermogravimetric analyzer equipped with a TG5/M3 balance. DSC measurements were accomplished on a Mettler Toledo 822 differential scanning calorimeter operating under nitrogen atmosphere and at 10°C/min. In and Zn standards were used for calibration. UV-vis spectra were obtained at room temperature in a range between 350 and 900 nm. Spectra deconvolution was accomplished by the Origin 5.0 program.

Cell fabrication and electrooptical measurements

Photoconductive cells were fabricated by squeezing the polymeric blend between two ITO-coated glass slides at about 130°C where the viscosity was sufficiently low to allow smooth polymer flow. Spherical glass-spacers having a diameter of $106 \pm 5 \mu\text{m}$ were put between the two slides and outside the polymer-filled measuring area to ensure its constant thickness. For the photoconductivity measurements, the cells were connected in a simple homemade apparatus [11] in which the current through

the film is measured by a Keithley Mod. 6514 electrometer and the voltage is applied by a Glassman Mod. ER15R20 dc high-voltage power supply (up to 15 000 V). The photocurrent was stimulated by a temperature-controlled laser diode operating in the single longitudinal mode (Mitsubishi Mod. ML1013R) and emitting at 685 nm. All the reported results have been standardized at an applied voltage of 5100 V and at a power laser output of $P = 5$ mW. In this way the intensity of the emitted radiation corresponds to $I = 70$ mW/cm². The diameter of the output beam was held fixed at 3.0 mm. The actual values of the laser power were measured by a Melles Griot Pocket Laser Power Meter.

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