

POLY(METHYL-PHENYLSILYLENE) DERIVATIVES AS PHOTOCONDUCTORS

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Received March 22, 1993

Accepted May 14, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

The attachment of long wavelength absorbing π -conjugated chromophores to poly(methyl-phenyl-silylene) (PMPSi) via reactions of its formylated derivative is described. Some of the obtained polymers exhibit improved photostability in comparison with the parent polymer. Their spectral properties and photoconductivity are discussed. Ultrathin layers and multilayers were prepared from polar derivatives of PMPSi by the Langmuir-Blodgett technique and their photoconductive behaviour was studied.

The potential use of organic materials for photogeneration of free charge carriers in electrophotographic recording systems, light-sensitive devices and low-cost photovoltaic cells has stimulated considerable interest. Although significant advances have been made in understanding photoconductivity in organic molecular crystals such as anthracene, pentacene or triodomethane¹, the studies of the charge carrier photogeneration in organic polymers lagged behind. This was partly caused by the complexities of disordered states. Unlike crystalline substances polymers are further characterized by several material parameters such as molecular weight and its distribution, crystallinity, presence of end groups etc. On the other hand, polymeric photoconductors offer considerable advantages in comparison with molecular crystals, e.g. lower cost and easier processability by conventional techniques. The common feature of the photoconductive polymers studied in detail up to now is the presence of domains with conjugated π -electrons or aromatic systems. From the chemical point of view the known photoconductive polymers can be divided into two groups:

– Polymers with a high degree of conjugation in the main chain. In these materials the absorption extends well in the visible region of the spectrum.

– Polymers with large fused aromatic systems in the main chain or in pendant substituents. These polymers usually absorb only in the short wavelength region below 400 nm, in which they are photoconductive. Outside this region they often act as charge-carrier transport materials.

In many cases, an addition of low-molecular-weight compounds to the polymer matrix (“doping”) can bring about a considerable improvement in material photo-response².

Though many polymers with photoconductive properties have been prepared (see review articles²⁻⁴), the photogeneration mechanism was studied thoroughly for only few of them. It was found that in poly(*N*-vinylcarbazole), charge carrier photogeneration and, particularly, thermal dissociation of the electron-hole pair can be described by the Onsager theory of geminate recombination⁵. In other polymers such as polyacetylenes the exciton or soliton mechanism in a quasi-one-dimensional medium seems to be more probable⁶.

Several years ago, polysilylenes as a new class of polymeric photoconductors⁷ were reported. These materials with purely silicon backbone of a general formula $(\text{SiR}^1\text{R}^2)_n$ (R^1 and R^2 are alkyl or aryl groups) possess some unique properties, e.g., they show so-called σ -conjugation of electrons along the backbone⁸. In principle, this conjugation is caused by a greater overlap of two sp^3 orbitals located on adjacent silicon atoms than in the case of two carbon atoms. Owing to σ -conjugation, polysilylenes strongly absorb in the 300 – 400 nm region, depending on the nature of R^1 and R^2 substituents⁸. The high quantum efficiency of photogeneration of free charge carriers and the charge carrier drift mobility of the order of $10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, unusually high for organic polymers, stimulated the interest in both basic research and practical application. Since there is no apparent difference in charge-carrier mobility in poly(dialkylsilylenes) and poly(methyl-phenylsilylene) (PMPSi) it can be assumed that the charge-carrier transport proceeds predominantly along σ -delocalized Si backbone⁷.

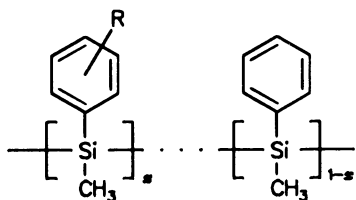
Although polysilylenes possess promising photoconductive properties, their practical use is precluded by their low stability against short-wavelength light: upon irradiation, all of them undergo homolytic scission of the main chain with the formation of silyl radicals and biradicals⁸.

There exists no information concerning photoconductive behaviour of polysilylenes with substituents other than alkyl or aryl. We focussed our attention, therefore, on the preparation of new derivatives of PMPSi with pendant substituents absorbing in the long-wavelength region. We expected that a proper substitution might improve photoconductivity of these materials, decrease their photodegradability and bring new properties, such as photochromism and non-linear optical and electrooptical properties. A change in the optical spectrum upon doping or substitution can also bring about some additional advantages for practical application: such systems can be irradiated with the light of wavelengths outside the polysilylene main absorption, which might completely

prevent the photodegradation. For some applications, e.g. for photovoltaic cells, the possibility of preparing very thin polysilylene layers is desirable. Since some of our new PMPSi derivatives bear polar and hydrophilic groups, we tried to prepare ultrathin layers and multilayers of these materials using the Langmuir–Blodgett technique. The results of our effort are briefly described below.

Syntheses

The functionalization of aromatic polysilylenes seems to be a method of choice for the synthesis of new polysilylenes, since not many organic groups can withstand drastic conditions of the Wurtz coupling polymerization⁸. Our attention has been devoted to the chloromethylation and formylation of PMPSi and subsequent condensation reactions of the aldehyde derivative. The formulae of the new derivatives of PMPSi we have actually obtained are shown below, together with those of the starting materials *I* and *II*.



| R | R |
|------------------------------|-------------|
| <i>I</i> H | <i>VIII</i> |
| <i>II</i> CH ₂ Cl | <i>IX</i> |
| <i>III</i> | <i>X</i> |
| <i>IV</i> | <i>XI</i> |
| <i>V</i> | <i>XII</i> |
| <i>VI</i> CH=O | <i>XIII</i> |
| <i>VII</i> | |

Poly(methyl-phenylsilylene) *I* was prepared by standard Wurtz coupling polymerization⁸. Its M_w varied between 50 000 and 150 000. Chloromethylation⁸ of *I* using $\text{CH}_3\text{OCH}_2\text{Cl}/\text{SnCl}_4$ proceeded smoothly, but with some degradation of the main chain (usually to M_w between 20 000 and 30 000).

Attempts to convert *II* into *VI* directly, using either oxidation with dimethyl sulfoxide or the Sommelet reaction resulted only in ill-defined, oligomeric or crosslinked products. Therefore, we turned our attention to the Kroehnke procedure, used in the past for the syntheses of chemically sensitive aldehydes⁹. *II* was first converted to quaternary salt *III* using pyridine. This intermediate reacted with 4-nitroso-*N,N*-dimethylaniline yielding nitron *IV* which was smoothly hydrolyzed in acidic media to aldehyde *VI*. This method was found to be feasible for *II* with a degree of chloromethylation up to 0.25. M_w of polymeric aldehyde *VI* was always between 15 000 and 30 000.

Condensation reactions of *VI* with amines leading to Schiff bases *VIII*, *IX*, *X*, *XII* and *XIII*, as well as reduction of *VI* to *V* and preparation of 2,4-dinitrophenylhydrazone *VII*, proceeded smoothly and practically without degradation of the main chain. High degree of conversion was checked by IR, UV and visible spectra and, in some cases, also by elemental analysis. On the other hand, the Wittig reaction of *VI* did not proceed satisfactorily and about half of the originally present aldehyde groups was still present even after long reaction times.

All new polysilylenes, except *III*, are soluble in tetrahydrofuran (THF), chloroform and aromatics. They can be easily casted to transparent films with satisfactory mechanical properties.

UV and Visible Spectra

Whereas the absorption spectra of *II*, *III*, and *VI* are nearly identical with that of starting PMPSi (*I*), those of polysilylenes *IV*, *V*, *VII* – *XIII* exhibited an additional absorption band at higher wavelengths for which the attached chromophore group was responsible. Some examples are shown in Fig. 1. Notably, the attachment of π -conjugated chromophore does not lead to a detectable shift of the UV absorption band of the σ -conjugated backbone ($\sigma \rightarrow \sigma^*$ transition) of PMPSi.

Photodegradation

It is well known that molar absorptivity of polysilylenes is reduced and the longest wavelength absorption maximum is significantly blue-shifted as a consequence of chain scission⁸. Photodegradation of some new polysilylenes was therefore investigated by measuring their UV and visible spectra after irradiation of either THF solutions or solid films at 330 nm. Some results of these experiments are summarized in Table I, where the drop in the normalized absorbance at λ_{max} after irradiation is listed.

One can see that the new PMPSi derivatives are less photodegradable than the parent *I*. In solution, this stabilization effect is very distinct for polymers *VII* – *IX*. A similar photostabilization was also observed with films. Apparently, the chromophores of the polysilylenes mentioned above are able to quench electronically excited states which

TABLE I

Photodegradation of poly(methyl-phenylsilylene)s as measured by the relative absorbance A/A_0 (%) at λ_{\max} after UV irradiation ($\lambda = 330$ nm, photon flux = $9.8 \cdot 10^{17}$ photon $\text{m}^{-2} \text{s}^{-1}$)

| Polymer | THIF solution ^a | Solid film ^b |
|-------------|----------------------------|-------------------------|
| <i>I</i> | 12 | 56 |
| <i>VI</i> | 25 | 69 |
| <i>VII</i> | 89 | 90 |
| <i>VIII</i> | 97 | 95 |
| <i>IX</i> | 96 | 96 |

^a 5 min irradiation; ^b 40 min irradiation.

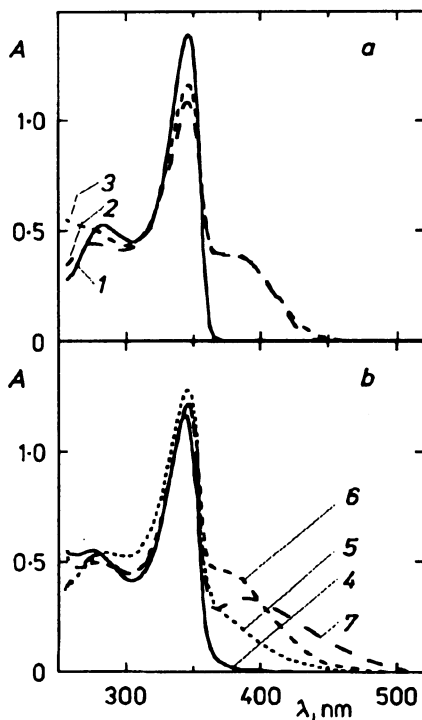


Fig. 1
UV and visible absorption spectra of polysilylenes in THIF solutions. *a*: 1 *I*, 2 *IV*, 3 *V*; *b*: 4 *VI*, 5 *IX*, 6 *VIII*, 7 *VII*

are formed in the polysilylene chain upon absorption of light and which would lead to homolytic main-chain scission⁸. The improved photostability of the new PMPSi derivatives shows that these materials might be promising as photoconductors.

Emission Spectra

In the fluorescence spectrum of the parent polymer *I*, a narrow unstructured band ($\lambda_{\text{max}} = 354 \text{ nm}$) was observed⁸. An examination of the new polysilylenes showed that the emission band is efficiently quenched by the substituent. This effect is even more pronounced in the case of films. Notably, the emission spectra of *IV* – *VII* and *XI* also exhibit weak maxima at long wavelengths: in solution between 500 and 520 nm and in films between 480 and 580 nm. A long lifetime (about 1 μs) of this emission suggests phosphorescence to occur.

It is interesting to note that fluorescence quenching is associated with a decreased photolability of *IV*, *VII*, *VIII*, and *XI*. Since there is a good overlap of the emission spectrum of *I* and the absorption spectra of the chromophoric groups, resonance energy transfer from the polysilylene to the chromophoric groups via the excited singlet states seems to be feasible and might explain the stabilizing effect of the chromophores. This explanation is supported by the experiments, in which both the fluorescence quenching and photostability were increased by mere admixing the low-molecular-weight compounds corresponding to the chromophores bound to PMPSi.

Photoconductivity

The measurements of the photogeneration efficiency were carried out using the technique of emission-limited photoinduced discharge¹⁰. In this technique, the surface of a polymer film spin-casted on a gold electrode is charged to the initial voltage by a corona and then discharged upon irradiation. The surface potentials were measured using a rotary electrodynamic condenser electrometer with the time resolution of 20 ms. To ensure the emission-limited conditions, the discharge was measured with photon fluxes as low as possible ($10^{17} - 10^{18} \text{ photon m}^{-2} \text{ s}^{-1}$). The photogeneration efficiency was measured using 254 nm, 355 nm and 405 nm irradiation incident upon a positively charged surface. It is noteworthy that the UV and visible spectra of all samples recorded after photoconductivity measurements were unchanged, indicating no or negligible photodegradation.

Sandwich-type samples were used for measurements of the drift mobility of free-charge carriers. They consisted of a transparent conductive ITO (indium tin oxide) glass substrate, through which irradiation was performed, a spin-casted polymer film (thickness typically in the range of 1 to 5 μm), and an upper gold or aluminium electrode deposited in vacuum. The samples were irradiated with the frequency-doubled flash of a ruby laser ($\lambda_{\text{ex}} = 347 \text{ nm}$, pulse duration 20 ns) or with a 5 μs flash of a xenon

lamp (using band filter, λ_{\max} 365 nm, halfwidth 60 nm). The photogenerated charge was detected with the aid of an electrical circuit consisting of a voltage source, sample and resistor connected in series.

The values of photogeneration efficiency are given in Table II. An increase in photogeneration efficiency was observed in polysilylenes *VI*, *VII* and *IX*, in comparison with PMPSi. The greatest photogeneration efficiencies were found in polysilylenes *VII* and *IX*, about a half order of magnitude higher than that in PMPSi; also an extension to visible region (405 nm irradiation) was observed. The increase in the photoelectric sensitivity is probably caused by the presence of nitro groups in the chromophore, which act as electron acceptors. On the other hand, amino groups in polymers *IV* and *V* should act as electron donors and form hole trapping energy levels. The photogeneration efficiency in polysilylenes *IV* and *V* was about one order of magnitude lower than that in PMPSi. The electric field strength dependence of photogeneration efficiency in the range $10^7 - 10^8$ V m⁻¹ can be described by the Onsager theory of geminate recombination.

Figure 2 shows typical kinetic curves of the transient photocurrent in polymer *VII* (M_w 10 000, substitution degree 0.17), measured with the irradiated electrode positively biased, at electric field strength $F = 3 \cdot 10^7$ V m⁻¹ and at various temperatures. A similar behaviour was found for polymers *I*, *IV* – *VI*, *VIII*, and *IX*. Both the shape and amplitude depended on the electric field strength and on temperature. It appears that shortly after photoexcitation the photocurrent is determined by very fast trapping and charge recombination in the vicinity of the irradiated electrode. At room and higher temperatures the transport is Gaussian as follows from the shape of the transient photocurrent; at lower temperatures the transport is dispersive. The mobility value $\mu = 2 \cdot 10^{-9}$ m² V⁻¹ s⁻¹ for holes was found at $T = 340$ K and $F = 3 \cdot 10^7$ V m⁻¹. The electron transients (the irradiated electrode was negatively biased) were influenced by

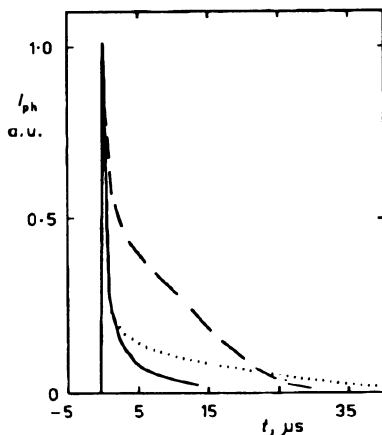


Fig. 2
Transient photocurrent measured in polymer *VII* at $F = 3 \cdot 10^7$ V m⁻¹ and 212 K (full), 314 K (dotted), 345 K (dashed line)

a fast recombination and trapping, and no transit time of the electrons could be determined. The electron lifetime was too short to allow a measurable number of electrons to be collected at the opposite electrode, even at higher temperatures. As in the case of parent polymer⁷ *I*, holes are the majority charge carriers in the new polysilylenes.

The fact, that electron acceptor groups increase the efficiency of charge photogeneration is favourable to the applications of polysilylenes in electronic devices. However, for such applications also a relatively high charge mobility is usually required. The hole mobility decreased when PMPSi was modified with the acceptor substituents even at a low degree. For example, the time-of-flight method gave, at 293 K and $F = 3.6 \cdot 10^7 \text{ V m}^{-1}$ for polymer *VII* with substitution degrees 0.0, 0.0055, 0.0088, 0.013, and 0.10, the mobility values 2.3, 1.2, 0.78, 0.26, and $0.11 \cdot 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The transient photocurrents measured in the polymers of higher substitution degree did not show the characteristic kink at room temperature, from which the mobility could be determined. Experiments on mixtures of PMPSi with low-molecular-weight compounds were performed to gain a better understanding of the effect of electron acceptors on the hole mobility in polysilylenes. The increase in quantum generation efficiency of charge in these doped PMPSi films followed the increasing electron affinity of the dopant. The hole mobility was decreased most progressively by doping PMPSi with phenanthrene-quinone, the oxidation potential of which (0.484 V) was lower than that of PMPSi (1 V). In this case the mobility was reduced by the repeated trapping of transported holes by the dopant and their release thermally activated with activation energy 0.18 eV ($F = 3.6 \cdot 10^7 \text{ V m}^{-1}$). The effect of the other dopants depended on their dipole moments. Acceptors with large dipole moments, including low-molecular-weight analogs of the substituents in the modified PMPSi, reduce the mobility due to an increase in the geometrical and energetic disorder in the host polymer matrix. On the other hand, an increase in the mobility was observed with chloranil, a strong electron acceptor of a

TABLE II
Photogeneration efficiencies (charge per photon) in polysilylenes at various wavelengths ($T = 300 \text{ K}$, $F = 4 \cdot 10^7 \text{ V m}^{-1}$)

| Polymer | 254 nm | 355 nm | 405 nm |
|-------------|--------|--------|--------|
| <i>I</i> | 0.019 | 0.005 | — |
| <i>IV</i> | 0.0025 | 0.0005 | — |
| <i>V</i> | 0.0025 | 0.0005 | — |
| <i>VI</i> | 0.046 | 0.019 | — |
| <i>VII</i> | 0.046 | 0.025 | 0.010 |
| <i>VIII</i> | 0.038 | 0.003 | 0.0003 |
| <i>IX</i> | 0.072 | 0.038 | 0.012 |

zero dipole moment. The field dependence of the mobility observed in polymers *VII* corresponded with the model^{11,12} of charge hopping through a manifold of states with superimposed energetic and positional disorder.

Ultrathin Films

The charge-carrier mobility in polysilylenes is high enough for some practical applications such as electrographic devices but it may not be sufficient for their use in photovoltaic cells. In this case, the preparation of very thin photoconductive polymer film might be the way of compensating high serial resistance of the cell.

A method of choice for the preparation of the polymer films with thicknesses in nanometer scale is the Langmuir–Blodgett (LB) technique. Polymers suitable for LB technique are roughly of two types: those containing proper amount of polar or hydrophilic groups which tend to make a contact with a water surface, or having a rigid rod-like structure, which makes possible a regular arrangement of their molecules on water surface. Up to now, the only polysilylenes successfully employed with LB technique have been some rod-like poly[bis(alkoxyphenyl)silylenes] (ref.¹³).

Whereas the parent polysilylene *I* is unsuitable for the LB technique, we were able to prepared LB films from polymers *VII* and *XIII*, which contained polar groups. Owing to their improved photostability these polymers do not require a special handling during the LB film preparation, which was the case of poly[bis(alkoxyphenyl)silylenes].

Substrated for the LB film deposition were glass slides hydrophobized with dimethyldichlorosilane or transparent ITO glass. An aluminium strip of thickness of 30 nm was deposited on the hydrophobized glass in vacuum as a substrate electrode for the electrical measurements. Monomolecular films were spread on water surface from toluene solutions at 16 °C and transferred onto the substrates using a Lauda FW 2 film balance. A semitransparent gold electrode was deposited in vacuum on the top of the LB film so that a glass/Al/PSi/Au sandwich sample of an area of $5 \cdot 10^{-6} \text{ m}^2$ was prepared. Electric and photoelectric properties of the sample were measured using a Keithley 616 electrometer and a Keithley 240 power supply. Samples were illuminated through the gold electrode with a monochromatic light source consisting of a xenon lamp and monochromator.

Surface pressure-area isotherms of *VII* and *XIII* monolayers spread on the air–water interface at 16 °C are shown in Fig. 3. Polymers *VII* and *XIII* provided on water surface optically homogeneous and stable monolayers. The layers spread from polymers *I* and *IX* were inhomogeneous and unstable. The limiting areas determined from the isotherms were 1.2, 7.8, 10.3, and 2.3 \AA^2 per one monomeric unit in the monolayers of *I*, *VII*, *IX*, and *XIII*, respectively. It was not possible to transfer the monolayers onto the solid substrates by the usual LB vertical dipping technique. LB films consisting of dozens of the monolayers were prepared by the repeated horizontal touching. The regularity of the deposition was checked by the linear increase in the optical absorbance of

the LB film at 338 nm with an increasing number of the transferred monolayers. UV and visible spectra of the LB film of *VII* and *XIII* were the same as spectra of the polymers in THF solutions. An average thickness of one monolayer of *VII* estimated interferometrically was about 6 nm. The high thickness and the low limiting areas of the monolayers suggested that polymer chains *VII* and *XIII* were not fully spread on water but folded, exposing to water only some of the chain units, probably those substituted with polar groups. Polymer *XIII* containing nitro and hydroxy groups formed a more spread monolayer than *VII* containing two nitro groups. Monolayers of the non-polar *I* and *IX* containing only one nitro group collapsed continuously during compression giving macroscopically inhomogeneous films.

The electrical resistance of glass/Al/PSi/Au sandwich samples increased with increasing number of monolayers in the LB film, n . (The resistance is the sum of the resistances of the LB film and the Al_2O_3 layer on the Al electrode surface in series.) Low resistances ($10^6 - 10^7 \Omega$) of the samples containing less than 6 monolayers of *VII* indicated the presence of conducting defects in the LB films. From this point of view the LB films of *XIII* were better providing the resistance of about $10^8 \Omega$ even for the sample containing a single monolayer. At $n = 12$ the resistance (above $10^9 \Omega$) of films of *VII* approached that of the films of *XIII*.

Under irradiation, the sandwich samples operated as photovoltaic devices generating negative photovoltage at the Al electrode. The photocurrent, higher by more than one order of magnitude than the dark current, was observed in the sample containing 12 layers of *XIII* at the bias voltage below 0.5 V. The power efficiency calculated for this photocell from the short circuit photocurrent, I_{sc} , and the open circuit photovoltage, U_{oc} , under illumination at 340 nm ($5 \cdot 10^{17} \text{ photon m}^{-2} \text{ s}^{-1}$) was about 0.02%. The spectral response of I_{sc} was symbatic with the absorption spectrum of the LB film

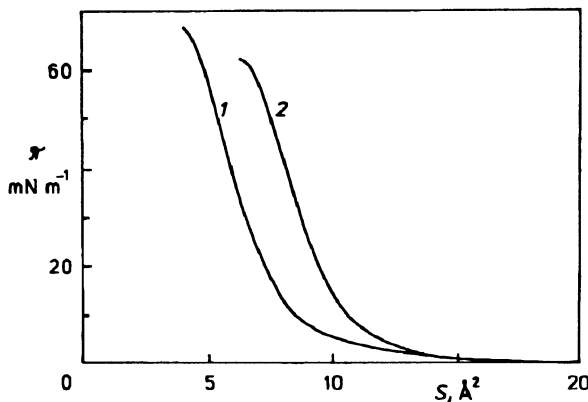


FIG. 3
The surface pressure (π) vs area per monomeric unit (S) isotherms of monolayers of polysilylenes *VII* (1) and *XIII* (2) at water-air interface at 16 °C

(Fig. 4). The charges were generated after the absorption of light both by the electron system of the PMPSi main chain (below 360 nm) and by the attached chromophores (at wavelengths longer than 360 nm).

With increasing number of monolayers in films of *VII* or *XIII*, I_{sc} increased; however, the apparent quantum efficiency of charge-carrier generation, η , decreased. Evidently, the first monolayer at the Al electrode is the most active in the photovoltaic effect. The less active upper layers decrease η by absorbing the photons before they penetrate into this layer and by increasing the passive resistance of the cell.

The observed linear dependence of I_{sc} on the incident photon flux indicated that there was no surface recombination of the photogenerated charges. It can be assumed, that the holes photogenerated at the Al contact migrate, due to their mobility, to the opposite electrode. However, in thick films (12 layers) I_{sc} decreased with increasing time of irradiation. Probably the electrical field of the space charge formed by trapping photo-generated charges was responsible for the photocurrent decrease. The release of the trapped charges was observed as a slow decay of the short-circuit hole photocurrent from the Al toward ITO electrode for about 5 μ s after the 20 ns irradiation of the ITO glass/*VII*/Al ($n = 12$) sample with a laser flash at 347 nm.

CONCLUSIONS

The preparation of some new poly(methyl-phenylsilylene) derivatives bearing chromophoric groups absorbing at long wavelength is reported. These materials exhibit an

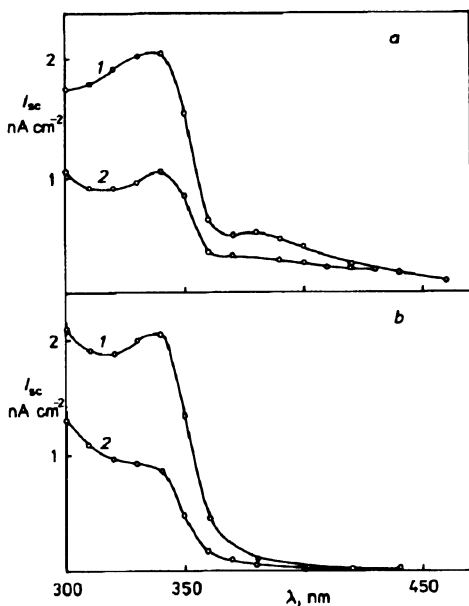


FIG. 4

The action spectra of the short-circuit photocurrent of Al/polysilylene/Au cells (incident photon flux $10^{13} \text{ cm}^{-2} \text{ s}^{-1}$) containing various numbers, n , of monolayers in the polysilylene film. *a* *VII*, *b* *XIII*; 1 $n = 4$, 2 $n = 1$

improved photostability and, therefore, they are more promising candidates for photo-electrical applications than other polysilylenes. The charge-carrier photogeneration efficiency in polymers bearing electron-acceptor nitro groups is significantly higher than that in the parent polysilylene. However, the hole drift mobility is lowered by a disorder in the polymer matrix caused by the substituents of high dipole moments. Owing to the polar nature of substituents attached, some of the new derivatives are also suitable for the preparation of ultrathin layers by the Langmuir–Blodgett technique, which might be of some advantage in potential applications such as photovoltaic cells.

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Translated by the author (I. K.).