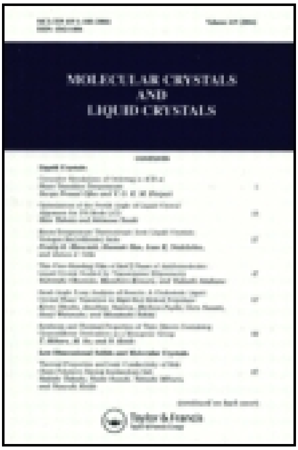

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Liquid Crystal Alignment on Photoinduced Species in Poly[methyl(phenyl)silylene] Film

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Liquid Crystal Alignment on Photoinduced Species in Poly[methyl(phenyl)silylene] Film

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The first observation of alignment of a liquid crystal deposited on a poly[methyl(phenyl)silylene] (PMPSi) film irradiated with linearly polarized light is reported. The effect seems to be controlled by the angular-dependent photodegradation caused by the photoinduced scission of the Si-Si bonds in the polymer backbone connected with the formation of other photoproducts preferentially oriented along the light polarization.

Keywords: poly[methyl(phenyl)silylene]; photoalignment; liquid crystal alignment; bond scission; photoselection

INTRODUCTION

Photopolymers are believed to allow the development of a "clean" contactless method of liquid crystal alignment important for the display operation, which permits the control of the azimuthal anchoring energy and the direction of an easy axis orientation over the aligning surface. Poly(organylsilylene)s with their uninterrupted chains of silicon atoms and with significant electron delocalization along the polymer chain [1] are a new class of photosensitive polymers with unusual properties.

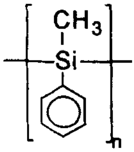
They possess promising photoconductive properties [2]. Upon strong UV irradiation at room temperature they also undergo a complex photodegradation process (photochemical cleavage of Si-Si bonds, oxidation to polysiloxanes, crosslinking, photoablation, etc.) Caused by this reason, polysilylenes have been studied as photoresists. One can expect that the interfacial properties are modified by these processes too. From the technological point of view, polysilylenes are materials soluble in many organic solvents, i.e., easy processability by conventional techniques, like spin coating and casting, is possible. In this paper a new phenomenon in poly[methyl(phenyl)silylene], consisting in the angular-dependent photoinduced cleavage of Si-Si bond and in the formation of other photoproducts preferentially within segments oriented along the light polarization, allowing liquid crystalline photoalignment, is described.

EXPERIMENTAL

Synthesis of Polymer

Poly[methyl(phenyl)silylene] (PMPSi) was prepared by the Wurtz coupling polymerization method described by Zhang and West [3]. The low-molecular-weight fraction was extracted with boiling diethyl ether. The residual polymer obtained in ca. 17% yield, possessed an unimodal but broad molar mass distribution, M_w being 4×10^4 g mol^{-1}. Glass transition temperature was determined by differential scanning calorimetry as 408 K.

Poly[methyl(phenyl)silylene]
(PMPSi)



Sample and Measurements

Thin films for flash photolytic experiments (thickness 0.1-0.3 μm) were prepared by casting toluene solution on quartz platelets. Before deposition, PMPSi was centrifuged (12 000 rpm, 15 min). After deposition, the films were dried at 0.1 Pa and 330 K for at least 4 h. The samples were irradiated with single 20-ns flashes (λ_{inc} = 347 nm) emitted from a ruby laser that was operated in conjunction with a frequency doubler.

A liquid crystal (LC) cell was fabricated from two parallel glass substrates with a gap of 60 μm (Fig. 1). One substrate was covered with rubbed polyimide layer producing a homogeneous planar LC orientation with a small tilt. The other one was covered with a PMPSi film which was illuminated with linearly polarized UV light (250 W high-pressure mercury discharge lamp, light intensity 8 mW/cm^2, polarization by Glan-Thompson polarizing prism) before cell assembling (the direction of UV light polarization was chosen at 45^0 with respect to the rubbing direction substrate). The cell was filled with an LC mixture (Merck, ZLI 4801-000) by capillary forces at room temperature.

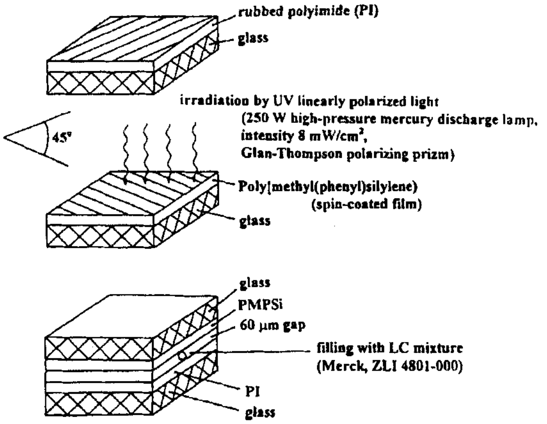


FIGURE 1. Sample for the experiment of photoinduced liquid crystal alignment.

Thermostimulated luminescence (TSL) measurements were performed in the fractional heating regime which allowed to determine the trap depth and frequency factor [4]. PMPSi samples (thickness about 3 μm) were after cooling irradiated with UV light (a high-pressure 500 W mercury lamp with optical filters). No sample photodegradation was detected during UV irradiation at low temperatures.

Photodegradation experiments were carried out in air using a xenon lamp (XBO 450 W, Osram). The wavelength of incident light (330 nm) was selected with aid of a monochromator (Polytech, model GM 252). Measurements for THF solutions were made with 1 cm quartz cells under stirring. Films were irradiated on quartz slides under the same conditions.

The irradiation procedure to induced dichroism was carried out using monochromatic (333 nm) and polychromatic light of a HBO lamp (100 W, Osram) under the action of a Glan-Thomson prism. The dichroism was measured using a Lambda 19 spectrometer (Perkin Elmer) and a photodiode spectrometer XDAP (Kontron) combined with computer driven polarizer (Glan-Thomson prism).

RESULTS AND DISCUSSION

Poly[methyl(phenyl)silylene] chain, with methyl and phenyl groups on every silicon atom, behaves as one-dimensional system with weak intermolecular interactions. The molecular feature of the material is reflected in the energy diagram of electronic states. It has been shown [5] that the first longest-wavelength absorption band with the maximum at λ_{max} = 338 nm (absorption coefficient $\alpha = 7.6 \times 10^4$ cm^{-1}) is formed mainly by the delocalized (σ - σ^*) transitions in the Si backbone. The (π - π^*) aryl-like excitations are responsible for the short wavelength absorption with the maximum at 276 nm ($\alpha = 5.2 \times 10^4$ cm^{-1}).

During the (σ - σ^*), i.e. Si-Si bond, excitations, a bonding electron is promoted from the bonding to an antibonding orbital followed by electron transfer on the chain. Thus, an electron-hole pair is formed. However, the pairs generated at the same chain segment, very often recombine geminately with a very fast decay rate, due to the electron delocalization in the Si backbone. An intrachain or interchain electron jump is necessary for the stabilization of the charge transfer state. During the (π - π^*), i.e. the phenyl, excitations, a Frenkel exciton is formed. For both types of the excitations, the intrachain electron transfer from the main Si chain to phenyl group is very probable [6]. Thus, the charge transfer (σ, π^*) state and a more stable ion-pair is formed. The electron in the phenyl radical-anion is localized whereas the hole in the radical-cation state is delocalized over the silicon main chain. However, the electron transfer is responsible for the chain instabilities during UV irradiation.

Irradiation of PMPSi at λ_{inc} = 347 nm yields a transient absorption with a strong maximum around 375 nm and two weaker maxima at about 410 and 450 nm (solid state, Fig. 2, [7]). The 375 nm maximum is ascribed to the poly(silylene) radical cation [8]. According to conclusions arrived at in earlier works [9,10] the transient absorption spectrum formed during the flash should be mainly composed of the spectra of the silyl radical and silylene biradical (SCHEME 1).

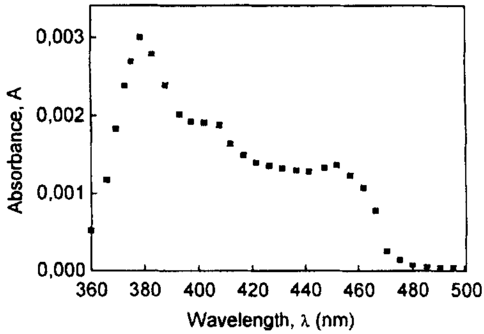
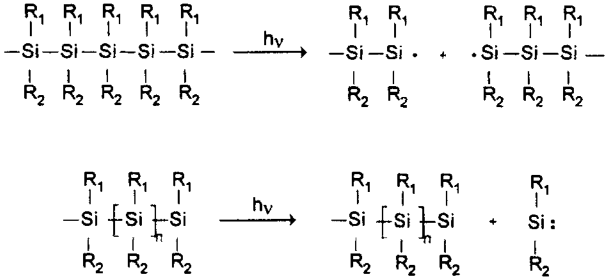


FIGURE 2. Flash photolysis transient optical absorption spectrum of thin rigid PMPSi film.



SCHEME 1.

Schematic picture of Si-Si bond scission and formation of silyl radical and silylene biradical.

The Si-Si bond scission leads also to the formation of charge carrier traps, as it follows from the thermostimulated luminescence (TSL) measurements. The TSL glow curve of non-degradated sample is given in Fig. 3 as dashed line. Detailed analysis [4] leads to the conclusion that a quasicontinuous tail-states distribution exists in PMPSi films. The activation energy and frequency factor in the maximum of the TSL glow curve is $\langle E_m \rangle = 0.19$ eV and $S \cong 10^{10}\ s^{-1}$, respectively. The high-energy wing of the TSL low temperature peak can well be approximated by a Gaussian distribution of states with the half-with $\sigma = 0.094$ eV. Structural changes induced by UV light in PMPSi at temperature $T \geq 100$ K lead to the modification of the TSL spectra: (i) the quantum yield of TSL slightly decreases, and (ii) an additional high-temperature shoulder at the main TSL peak in the temperature region of 150-200 K appears (Fig. 3, curve 1). The drastic changes in TSL glow curve occurred when the polymer was preliminarily irradiated with UV light at room temperature. In that case, a new TSL peak with a maximum at about 190 K appeared (Fig. 3, curve 2); its relative intensity became comparable to the intensity of the main TSL peak. The quantum yield of TSL strongly decreases simultaneously with the appearance of new TSL peak. The activation energy and frequency factor in the maximum of the new TSL peak was estimated as 0.45 eV and 2×10^{10} s^{-1}, respectively. It should be mentioned that photochemical traps, 0.5 eV deep, were also detected by thermally stimulated current studies [11] and by current post-transient analysis [12]. Annealing of these traps seems to be interesting [13]. The annealing at room temperature is demonstrated in Fig. 3: the relative intensity of the new peak becomes twice lower after storing the sample in cryostat at room temperature for several days (curve 3). The quantum yield of TSL increased concurrently. The effect of the trap formation is associated with the Si-Si bond scission as demonstrated in Inset of Fig. 3 where the reciprocal value of the molar mass (determined by gel permeation chromatography) vs. irradiation ($\lambda = 350$ nm) time is presented. The molar mass decreases with irradiation time. At the same time optical absorbance decreases as shown in Fig. 4. Thus, the UV irradiation of PMPSi film at room temperature leads to: (i) Si-Si bond scission accompanied with the formation of silyl radicals, silylene biradicals, and charge carrier traps, and (ii) the formation of ion-pairs which after their dissociation in external electric field contribute to free charge carriers; the contribution of such charged species to modify the surface properties for a longer time and on the alignment on liquid crystals is on further investigation.

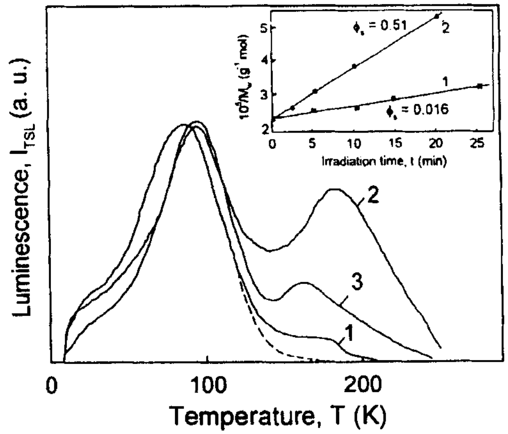


FIGURE 3. Normalized TSL spectra of PMPSi after a preliminary irradiation with unfiltered light of Hg lamp for 5 min at 150 K (curve 1), at 290 K (curve 2), and evolution of TSL spectra after the annealing the previous sample at room temperature for several days (curve 3). TSL spectrum of PMPSi without preliminary irradiation (dashed curve). Inset: Reciprocal value of the molar mass vs. irradiation time (λ = 350 nm). Solid PMPSi, line 1; PMPSi in tetrahydrofuran solution, line 2. Φ_S are the quantum efficiencies of the polymer main chain scission.

Anisotropic UV-light absorption by conjugated Si-segments results in photoinduced scission of the Si-Si chain segments preferentially oriented along the light polarization. The long-wavelength absorption band is mainly caused by the all-trans main chain segments separated by gauche conformations. Thus, a polysilylene film represents an ensemble of energetically different, week coupled Si-Si chain segments. The exposure with linearly polarized light results in the angular dependent excitation of main chain segments which are oriented parallel to the electric field vector of the incident light. Fig. 4 shows the change of the UV-VIS spectra caused by photodegradation on irradiation with linearly polarized light of 333 nm. In this way, an anisotropic photodegradation is induced resulting in an anisotropic orientational distribution of the still intact polysilylene segments and of photoproducts such as polysiloxane segments.

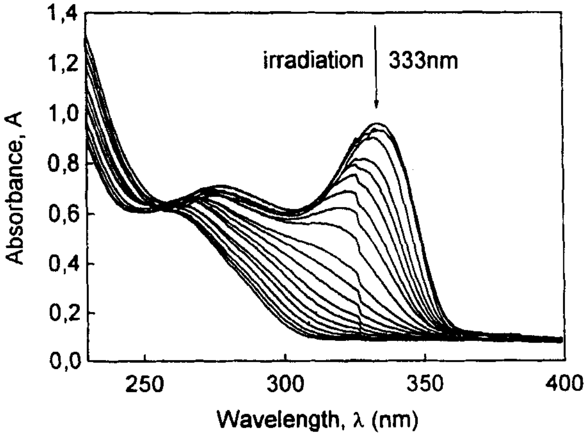


FIGURE 4. Absorption spectra of PMPSi film during the photodegradation. Irradiation was done with linearly polarized light from HBO 100 W lamp; λ_{inc} = 333 nm. Curves from the top are spectra for non-degradated film and films gradually photodegradated for up to 120 min.

In Fig. 5 the preferred photodegradation parallel to the electric vector of the electromagnetic radiation E is visualized by the photoinduced dichroism at 333 nm. Initially the dichroism increases with the conversion of the polysilane measured at 333 nm, where the long all trans chain segments absorb. It goes through a maximum if the most these chain segments are converted and on subsequent irradiation it goes to zero. The polar plot of Fig. 6 shows the maximum of the dichroism at 333 nm (0.20) after the irradiation with linearly polarized light of 333 nm.

Thus, using linearly polarized UV light, an anisotropic distribution of species is generated in the polymer film by angular dependent photoselection. Using the cell geometry described above and filling the cell with liquid crystal, a twisted director distribution of the LC was observed. The direction of the easy axis was parallel to the UV light polarization.

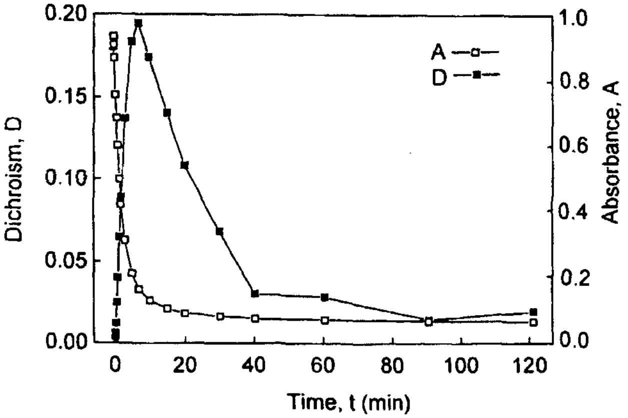


FIGURE 5. Decrease of absorbance and induction of dichroism at 333 nm upon irradiation with linearly polarized light (333 nm, 1.5 mW cm^{-2}) corresponding to Figure 4.

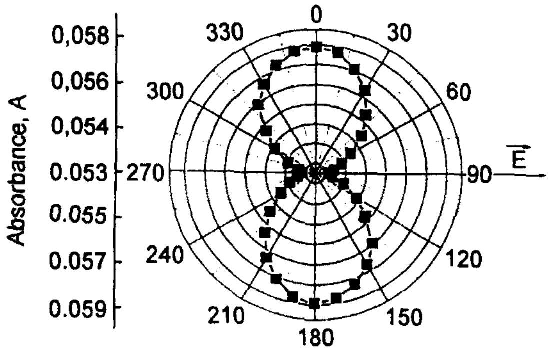


FIGURE 6. Polar diagram of the absorbance at 333 nm after the irradiation with linearly polarized light of 333 nm (HBO 100 W, 7 min). Electric field vector visualises the electric field vector of the incident light.

The dependence of the twist angle on the exposition time is given in Fig. 7. The twist angle increases with the exposure time; the saturation for t = 20 ÷ 100 s exposure implies that the anchoring energy on the surface is equal or higher than the elastic energy of the twist deformation. Longer expositions led to a decrease in the twist angle. The dependence of the anchoring energy of the alignment on the illumination time showed a rather steep maximum in comparison, for example, with poly(vinyl cinnamate). PMPSi produced a good-quality of planar alignment with a zero pretilt, which was thermostable up to 100 °C and did not show any fatigue at least for several months. The LC orientation on the PMPSi film was not reversible, i.e., the direction of the easy axis could not be changed several times by the illumination with another polarization of the light.

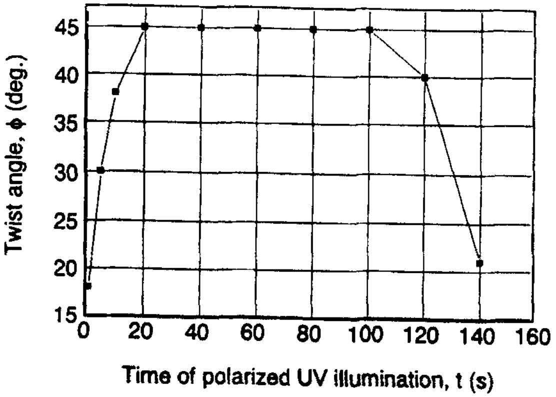


FIGURE 7. Dependence of the twist angle on the time of illumination (easy axis direction at 45° to the rubbing direction).

At the moment it is not clear which of the photochemical modifications of the surface is really responsible for the LC alignment. The fact that a further change of the primary director orientation can not be generated by the change of the electric field vector with respect to the initial samples in the second irradiation procedure can be interpreted in terms of an anisotropic and irreversible photochemical modification of the initially polysilylene film as reason for the LC alignment.

CONCLUSION

Irradiating with linearly polarized UV light, an anisotropic distribution of some species is generated in the polymer film by angular dependent photoselection. This anisotropy causes an planar alignment of the LC mixture ZLI 4801 without any tilt angle. The photoalignment ability of films was found to be of a good quality and thermal stability. The mechanism of the photoalignment is probably connected with anisotropic UV-light absorption by the conjugated Si-segments which result in photoinduced angular-dependent photodelection by the scission of the Si-Si chain and in formation of described photoproducts, such as polysiloxane species, preferentially within segments oriented along the light polarization. The fact that a further change of primary director orientation cannot be generated by the change of the electric field vector with respect to the initial sample in a second irradiation procedure can be interpreted in that way that the irreversible photochemical modification of the polymer chain is very probable.

Acknowledgements
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