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Photodegradation of Poly[methyl(phenyl)silylene] in the Presence of Modifying Substances

Anna Kochalska, Juraj Nožár, Stanislav Nešpůrek, Jakub Peter*

Summary: Efficiency of the photodegradation of poly[methyl(phenyl)silylene] can be increased by electron acceptor additives with unstable anion radicals. The best chain degradation yield was obtained using benzoyl peroxide as an additive. The model for the photodegradation process is supported by quantum chemical calculations.

Keywords: lithography; photodegradation; polymer; poly[methyl(phenyl)silylene]; UV exposure

Introduction

Amorphous silicon is a member of the larger class of silicon-backbone solids which, in addition to crystalline phase, also contain silicon clusters, silane oligomers, poly(siloxanes), and poly(organylsilanes). The last mentioned backbone polymers are under considerable research interest because of their non-stability under UV and electron beam irradiation. The exposures lead to photobleaching and Si-Si bond scission, producing low-molecular-weight fragments. Thus, the interesting use of polysilanes is in area of photolithography[1] due to the fact that polysilanes can be easily changed to materials having completely disparate properties when exposed to radiation. The contribution of polysilanes to large scale integrated (LSI) circuit manufacturing technology is that silicon atoms included in the polymer chain are not recognized as impurities in silicon devices. Other metal atoms can cause contamination problems. For efficient photolithography process materials with high speed of photostimulated reactions are needed. Even though the photodegradation in polysilanes is quite fast, an enhancement is eligible.

In this paper we describe the results of experiments concerning the increase of the photodegradation efficiency in poly[methyl(phenyl)silylene] (PMPSi) by electron acceptor additives. It was assumed that during the UV illumination of PMPSi chain an electron is excited to antibonding state, electron-hole pair is formed and electron can be transferred to phenyl group. In this way, unstable charge-transfer exciton arises. It results in an electron deficit on the polymer chain and its unstability. However, after the exciton expire (its lifetime is about 36 μs which follows from flash photolysis measurements[2]) the electron can move back to the chain and recombine with delocalized hole (cation radical) which results in charge equilibrium and chain stabilization. If strong electron acceptor is present, the electron can be transferred to the additive. In the case of unstability of the anion radical of the acceptor, quantum efficiency of photodegradation increases. The idea is supported with quantum chemical calculations.

Experimental Part

Materials

Poly[methyl(phenyl)silylene] (PMPSi, see (i) in Scheme 1) was prepared by Wurtz coupling polymerization, as described by Zhang and West[3]. The low-molecular-weight fractions were extracted with boiling

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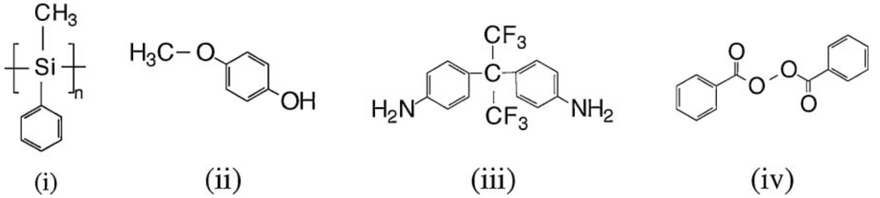
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v. v. i., Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
E-mail: kochalska@imc.cas.cz



Scheme 1.
(i) Poly[methyl(phenyl)silylene] (PMPSi) and electron acceptor additives used in the experiment: (ii) 2-methoxyphenol, ($C_7H_8O_2$), (iii) 4,4′-(hexafluoroisopropylidene) dianiline, (6FpDA) and (iv) dibenzoyl peroxide, ($C_{14}H_{10}O_2$)

diethyl ether. The residual polymer, obtained in c. 17% yield, possessed an unimodal but broad molar mass distribution, $M_W = 4 \times 10^4$ g mol^{-1}.

Electron acceptor additives (see (ii)-(iv) in Scheme 1) were obtained from Sigma-Aldrich. Materials (ii) and (iii) were used without further purification; (iv) was purified by crystallization.

Measurements

PMPSi was dissolved either in THF (for the experiments with additives (ii) and (iii)) or in toluene (for the experiments with additive (iv)). The concentration of PMPSi was 10 g l^{-1}. After an intensive shaking (at least 30 min) the solution of an additive was added (concentration was 8 mol% per PMPSi monomer unit). All the operations were performed in the dark.

Absorption spectra were measured by UV/VIS spectrophotometer Perkin Elmer LAMBDA 950. Photodegradations of solutions were performed by 200W Hg-Xe arc discharge lamp (Hamamatsu LC6) with interference filter 365 nm (Melles Griot EDC 03 FIM 028). The samples were illuminated (80 mW cm^{-2}) at room temperature on air, the total irradiation time was not longer than 60 min.

Quantum chemical calculations were performed by B3LYP method (basis 6-31G*, program G03[4]).

Results and Discussion

The long wavelength band of PMPSi $\lambda^0_{\max} = 336$ nm is composed mainly of (σ–σ^*) transitions. The energy of the delocalized (σ–σ^*) transition is conformation dependent and depends strongly on the length of macromolecule[5].

PMPSi is not stable under UV illumination. Optical absorption decreases and long wavelength maximum is shifted to higher energies during the photodegradation. It means that bonds scission of polysilane chain takes place. The example of the decrease and shift of the absorption maximum of neat PMPSi is shown in Figure 1. These two parameters were monitored during the measurements.

The dependence of the absorbance on illumination time (Figure 1b, curve 1) shows some saturation at long times. It results from the fact that (π–π^*) band (maximum at 276 nm, mainly phenyl ring absorption) is very broad and influences the value of (σ–σ^*) absorbance. Thus, the wavelength shift was generally taken into account for the determination of the degradation level (cf. curve 2 in Figure 1b).

The shape of the kinetic curves can be expressed by stretched exponential function[6]

$$\lambda^i_{\max} - \lambda^0_{\max} = \lambda_0 \exp(-(t/\tau)^\alpha) \tag{1}$$

where $\lambda^0_{\max}$is the wavelength of band maximum of neat PMPSi, $\lambda^i_{\max}$is the wavelength of band maximum of PMPSi after photodegradation, λ_0 is a constant, t is the time of sample illumination, τ is the time constant and α is the parameter describing the deviation from a pure exponential decay $(0.5 \le \alpha \le 1)$. In the case of neat PMPSi α was 0.8. Decay rate of the degradation process depended on light intensity. If the light intensity was lower photodegradation process was slower and

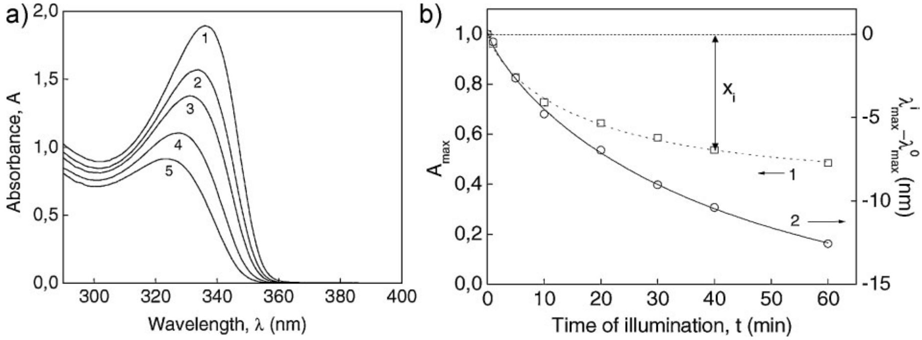


Figure 1.

(a) Change of the absorption spectrum of PMPSi during UV illumination (365 nm light). Curve 1 – before the polymer degradation, curves 2, 3, 4 and 5 – after 5, 10, 30 and 60 min of illumination, respectively. (b) PMPSi photodegradation detected by the blue shift (○) and decrease of the maximum of absorbance (□) during UV illumination.

the dispersion parameter α was higher. Parameter α changed from 0.8 to 0.9 when light intensity decreased from 100% to 20%.

Some additives can increase the photodegradation efficiency (Figure 2) and influence both the decay rate and the value of the α parameter, which varied from 0.7 to 0.8.

The fastest photodegradation of PMPSi was obtained using benzoyl peroxide (see (iv) in Scheme 1). After 40 min of UV illumination the absorption maximum was blue-shifted of 6.6 nm and the band maximum absorbance decreased (see x_i value in Figure 1b and in Table 1). The characteristics of the photodegradation process are summarized in Table 1. The increase of the blue-shift and higher x_i value indicates that shorter polymer segments are formed.

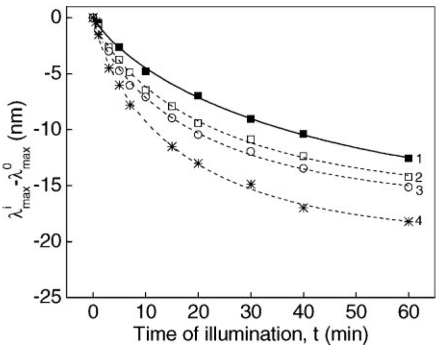


Figure 2.

Photodegradation of PMPSi with various additives characterized by the wavelength shift of the band maximum. 1 – neat PMPSi, 2 – PMPSi + $C_7H_8O_2$ (ii), 3 – PMPSi + 6FpDA (iii), 4 – PMPSi + benzoyl peroxide (iv).

Quantum Chemical Calculations

Two possible models were elaborated for the interaction of PMPSi and an additive (see Scheme 2). In both cases an electron is transfered (after the photoexcitation) from bonding to antibonding state (step (i)). Electron in antibonding state can move to electron acceptor additive (step (ii)). At this state two cases are possible:

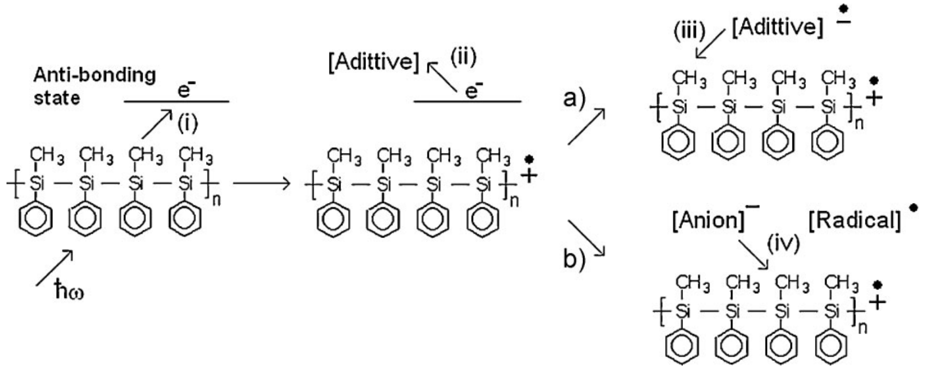
Table 1.

Blue-shift and decrease of the maximum of absorbance of PMPSi with different additives after 40 min of UV illumination (reference to the degradation of neat PMPSi).

	Blue-shift of the absorption maximum	Absorbance decrease
	$\lambda^i_{max}-\lambda^0_{max}$ [a]	x_i [b]
neatPMPSi	0	0.46
PMPSi + $C_7H_8O_2$	−2.0 *nm*	0.50
PMPSi + *6FpDA*	−3.0 *nm*	0.54
PMPSi + $6FpDANH_3^+Cl^-$	−4.0 *nm*	0.55
PMPSi + *benzoylperoxide*	−6.6 *nm*	0.60

[a] $\lambda^i_{max}-\lambda^0_{max}$, the shift of the position of the absorption maximum.

[b] x_i, absorbance decrease after 40 min of UV illumination by light 365 nm.



Scheme 2.
Photodegradation model for PMPSi in the presence of an additive. (i) Excitation of Si chain and transfer of electron from bonding to anti-bonding state; (ii) transfer of the electron in anti-bonding state to electron acceptor additive; (a) electron localizes on the additive for a significant time and then relaxes back to polymer chain (iii); (b) non-stable bond of the additive undergoes a scission in the presence of excess electron; created radical and nucleophilic anion can attack positive charged polymer chain (step (iv)). In the figure e^{-} indicates an electron.

(a) In the first one, the electron is localized on the additive for a significant time. During the localization silicon bonding of the main chain is weakened and chain can undergo bond scission. However, the electron relaxation back to polymer (step (iii)) limits the efficiency of the photodegradation.

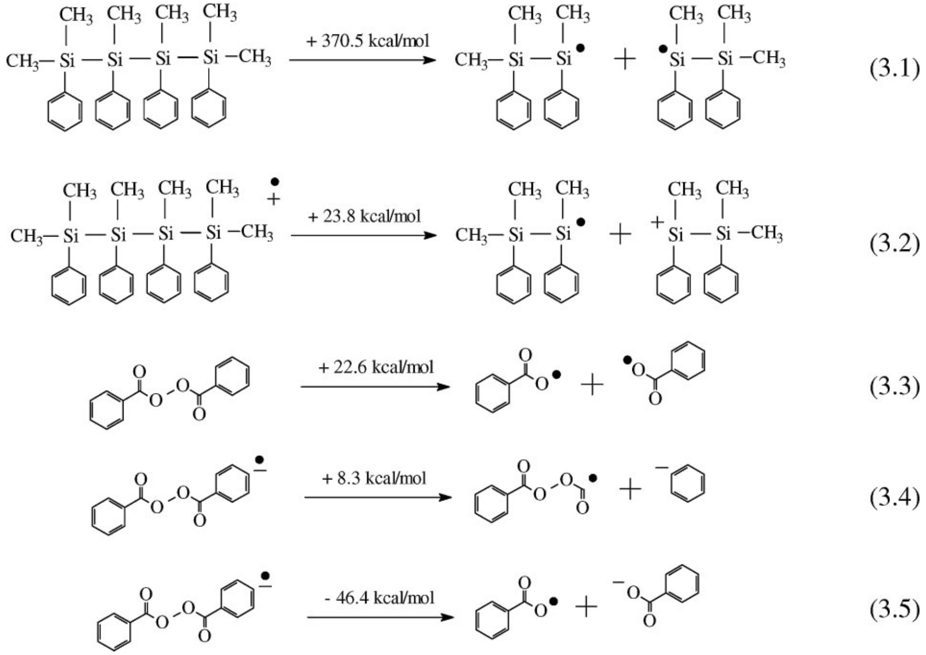
(b) The second case requires the existence of a non-stable bond in the additive[7]. The bond is expected to be not stable in the form of anion radical; thus, radical and anion (nucleophilic) group is expected to be formed. The later can subsequently attack positive charged silicon chain (step (iv)). The additive molecule must satisfy the condition that its energy in a separate state (nucleophilic anion and radical) is lower than the energy in a joint state (anion-radical).

Model (b) anticipates that electron additive molecule is unstable in the anion-radical case. To verify this requirement we optimized the molecule in the anion-radical state (charge $= -1$, multiplicity $= 2$) and then dissociated the bond that we expected to be labile. Two newly formed species were then optimized again. Since they originate from anion-radical, in order to conserve number of electrons one part has been optimized as an anion and the other one as a radical. Afterwards the sum of electronic energies of the anion and radical part were compared with the electronic energy of the anion-radical of the electron acceptor molecule. The instability condition for the additive molecule is expressed by Eq. 2

$$E_{anion-radical} > E_{anion} + E_{radical} \qquad (2)$$

where $E_{anion-radical}$ is the electronic energy of anion-radical of the electron acceptor, E_{anion} is the electronic energy of the optimized anion and $E_{radical}$ is the electronic energy of the optimized radical of the original molecule. Note, that at this point we do not examine the transition species and barriers between anion-radical state and separated anion and radical parts. We only focus on initial and final states.

For the theoretical modeling the additive (iv) (see Scheme 1) was selected. It contains peroxide bond which is expected to be unstable. The values of the formation heats during the transformations of PMPSi (i) and dibenzoyl peroxide (iv) are presented in Scheme 3.



Scheme 3.
Formation heats of PMPSi and dibenzoyl peroxide.

Scheme 3.1 and 3.2 presents formation heats of PMPSi (modeled as tetramer) molecules into two parts. One can see that cleavage of Si-Si bond in PMPSi in the ground state requires high amount of energy. If polymer chain is weakened by the missing electron, the energy required for Si-Si bond scission is much lower but still positive and system is stable. Schemes 3.3–3.5 refer to the decomposition of dibenzoyl peroxide in the ground and anion-radical state. The effective scission of the peroxide bond proceeds only from anion-radical state (low formation heat); thus, we expect this process to be most probable. Since the tentative energies of the reactions 3.2 and 3.3 are nearly the same and peroxides are known for their unstability under light exposure we assume that PMPSi decomposes by the process 3.2 if the additive is missing. Since the electron transfer from PMPSi to the dibenzoyl peroxide is probable (it acts as electron acceptor for PMPSi) we assume that the processes 3.4 and 3.5 are responsible for the acceleration of the photodegradation process.

Conclusion

The photodegradation of PMPSi can be accelerated by electron acceptor additives with unstable anion. We suggest, that along with the heterolytic bond scission of positive charged PMPSi chain, the following mechanism of the acceleration in the presence of an electron acceptor additive takes place: after the excitation of the polysilane chain an electron is transferred from bonding to antibonding state and then to the electron acceptor molecule. Thereafter the anion–radical of the additive dissociates into two parts, an anion and a radical. The nucleophilic anion attacks positive charged Si chain, leading to Si-Si bond scission. The most efficient material for the increase of the photodegradation efficiency was found to be dibenzoyl peroxide which, according to theoretical modeling, can spontaneously decompose from anion-radical state.

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