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Atmospheric Aging of Poly[methyl(phenyl)silanediyl] Monitored by FTIR Spectroscopy

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Summary: Poly[methyl(phenyl)silanediyl] films were irradiated in ATLAS Weather-O-Meter Ci 3000+ for ca 3 h. Changes in the region of siloxane, carbonyl, hydroxyl, and C-H (aromatic) bands were monitored by FTIR. Main attention was paid to changes in siloxane formation, which could be reduced in the presence of phenolic UV absorber **1** and oxalanilide **3**.

Keywords: formation of siloxane groups; photooxidation; poly[methyl(phenyl)silanediyl]

Introduction

Poly[methyl(phenyl)silanediyl] (PMPSi) is a typical representative of polysilanes (PSi), a group of substituted σ-conjugated polymers with homoatomic backbone made exclusively of Si atoms. Cumulation of the Si atoms allows an extensive electron delocalisation, resulting in unusual electronic and photochemical properties[1-4]. The PSi chain arrangement may be linear, cyclic, branched or crosslinked. PSi with various substituents such as alkyls, cykloalkyls, aralkyls, aryls, functionalised aryls and heterocycles were prepared. PSi consists of Si chains with interacting sp^3 orbitals. Rezonance integral between two sp^3 orbitals localized on the adjoining Si atoms, β_{vic}, is responsible for the formation of Si-Si σ bond. Electron delocalization along the Si chain is a result of an interaction of sp^3 orbitals on the neighbouring Si atoms. The degree of electron delocalization in the chain is a function of the β_{vic}/β_{gem} ratio, where β_{gem} is the resonance integral between two sp^3 orbitals localized on one Si atom. The electron delocalization is optimal when the ratio is unity. The ionization energy of the Si-Si bond is lower in comparison with π-electrons in olefins. Hence the character of PSi is similar to unsaturated carbon polymers[2,5]. Various applications of PSi were published. Among others, they are β-SiC precursors, impregnating agents for strengthening ceramics, photoresists, waveguides and heat sensors. In the last couple of years, a remarkable attention was paid to the use of Psi-based systems as photoconductors, charge transport media

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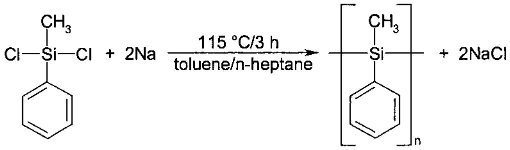
materials, charge-dissipating coatings components, non-linear optical materials and photoinitiators of radical and cationic reactions[1-3].

Phototriggered degradation (photolysis and photooxidation) of the PSi backbone during aging, accounting for breaking the σ-conjugation and formation of secondary reaction products[6,7] is considered as a negative effect on electric properties of PSi. Irreversible formation of oxygenated moieties, such as siloxane (Si-O-Si), hydroxy (OH) and carbonyl (>CO) functions in aged PSi was monitored in this study.

Materials and Methods

Polymer: Poly[methyl(phenyl)silanediyl] (PMPSi) was synthesized by Wurtz coupling of purified dichloro(methyl)phenylsilane in a mixture with sodium dried (reflux, 8 h) toluene and 15 % of *n*-heptane[8]. A sodium metal dispersion was prepared by vigorous stirring and heating of sodium at 110-115 °C (mild reflux) in the solvent mixture.



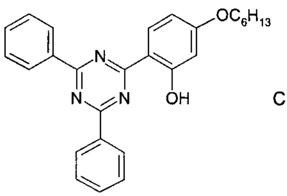
The reaction was carried out in an inert atmosphere (dry nitrogen) in a three-necked 1000 ml flask equipped with an electromagnetic stirrer and reflux condenser. At the reflux, the monomer was added dropwise to the sodium dispersion and the temperature was kept at 110-117 °C for 3 h. At the end of the reaction the color of the reaction mixture was dark violet and its viscosity increased. After cooling to room temperature, excess of sodium metal was decomposed by successive addition of isopropyl alcohol, methanol and water. The organic layer containing PMPSi was separated, washed with distilled water and dried with anhydrous magnesium dichloride for 24 h. Purification: Insoluble part (crosslinked PMPSi) was separated by centrifugation (10000 rpm, 2 h), PMPSi was precipitated with excess of methanol, filtered off and dried in vacuum (room temperature, 24 h, and 40 °C, 2 h). Low-molecular-weight portion (mostly cyclic oligomers) was removed by boiling PMPSi in diethyl ether (2 h), PMPSi was filtered off and dried in vacuum (room temperature, 24 h).

Characterization of PMPSi: (a) Molecular weight was determined by GPC [modular arrangement: Constametric 3500 pump (LDC Analytical), RIDK 101 and UV-VIS LCD 2563 detectors (Laboratory Instruments Praha), 8x600 mm, SDV 10^4 Å column, (PSS Mainz), PS standards (Merck), THF Chromasolv as the mobile phase, DATAAPEX hardware and software for the data calculations]: M_w = 23240, M_n = 4557. (b) UV spectral characterization with UV/VIS spectrophotometer Perkin Elmer LAMBDA 20 (1 cm quartz cell), the data were calculated using UV-WINLAB software. (c) For the measurement of IR spectra of neat and aged PMPSi, an FTIR spectrometer Bruker IFS 55 was used and the results were calculated using Opus 3.0 software. The characteristic absorption bands selected according to[9] are listed in Table 1.

Table 1. Characteristics IR absorption bands.

Wavenumber [cm^{-1}]	1122	1111	1098	1800-1650	3725-3100	3100-3000, 800-600	3000-2700
Assignment	Si-O-Si	Si-O-Si	Original skeleton	C=O	OH	C-H aromatic	C-H aliphatic

Additives: UV absorbers were used as delivered. 2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)phenol (**1**, Tinuvin 1577, Ciba Specialty Chemicals, CAS 147315-50-2), dimethyl [(4-methoxyphenyl)methylidene]propanedioate (**2**, Hostavin PR 25, Clariant, CAS 7443-25-6), *N*-(5-*tert*-butyl-2-ethoxyphenyl)-*N*'-(2-ethylphenyl)oxalamide (**3**, Sanduvor EPU, Clariant, CAS 35001-52-6). Characteristic UV absorption spectra of these absorbers were measured in tetrahydrofuran (THF) and are given in Figure 1.



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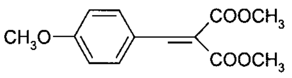

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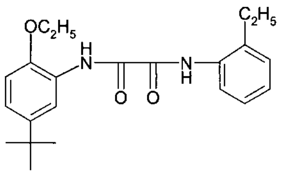

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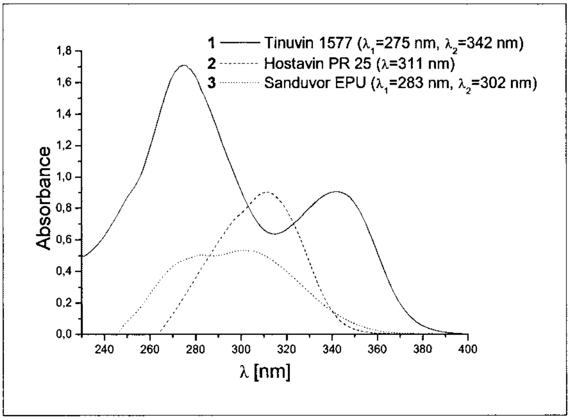

Figure 1. Absorption spectra of the used UV absorbers measured in THF at concentration of $2.10^{-4} mol.l^{-1}$

Preparation of PMPSi samples: a 10 wt.% solution of PMPSi was prepared by dissolving the PMPSi powder in toluene under intensive shaking for 60 min and subsequent centrifugation (8000 rpm, 45 min). Thin films of PMPSi on dry crystalline potassium bromide backings were prepared by spin-coating (400 rpm, 5 s and 800 rpm, 60 s) and dried in air (room temperature, 24 h) and in vacuum (45 °C, 4 h). The samples were protected from direct light during all the manipulations. Film thickness varied between 20 and 60 μm.

Preparation of PMPSi samples with UV absorbers: all doped samples were prepared by the method described above, adding stabilizers **1-3**, dissolved in toluene to the polymer solution before spin-coating. For stabilizer **1,** two concentrations of 1.5 wt.% a 5 wt.% were used. After interpretation of the effect of UV absorber **1**, only the samples with 5 wt.% of stabilizers **2** and **3** were prepared. This concentration was decided to be the upper limit for all further experiments.

Irradiation of PMPSi films: the Weather-O-Meter ATLAS Ci 3000+ device equipped with xenon lamp and external and internal borosilicate filters was used. The irradiation was carried out under dry conditions at 60 °C of the black panel temperature (bpt) in air atmosphere. The samples were irradiated in intervals increasing by 2 min from 1 min to 23-27 min. The total irradiation time was longer than 3 h in most cases. The IR spectrum was measured immediately after each irradiation and was compared with those of unstabilized PMPSi. The manipulation time between two irradiations was as short as possible and the samples were protected during this period from direct light.

Results and Discussion

Films of neat and UV absorbers containing PMPSi were irradiated in ATLAS Weather-O-Meter. Spectral changes in the photooxidized material were monitored by FTIR spectroscopy. Changes in characteristic absorption bands listed in Table 1 were monitored.

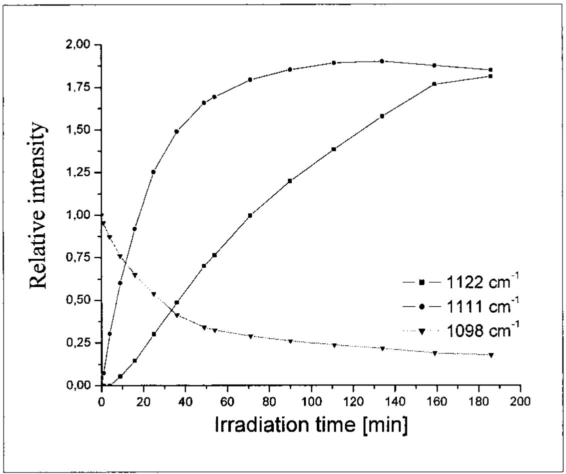

Figure 2. PMPSi without additives exposed in WOM. Formation and separation of three characteristic bands in the 1200-1000 cm^{-1} region.

Figure 2 shows an increase in intensity of the two absorption bands characteristic of Si-O-Si groups (1122cm^{-1}, 1111cm^{-1}) formed in the PMPSi backbone when irradiated in the absence of photostabilizers, and a decrease in intensity of the 1098 cm^{-1} band characteristic of the original skeleton destructed during irradiation. The time evolution of the overall intensity integral in the 1200-955 cm^{-1} region for the stabilized and unstabilized samples is shown in Figure 3.

Photodegradation of pure PMPSi and conversion to siloxane moieties was very rapid (Figure 2). PMPSi films containing 5 wt% of stabilizer **2** was quickly degraded as well (Figure 3). The rate of Si-O-Si groups formation was similar to that of additive-free PMPSi. Stabilizer 2 having absorption maximum at 312 nm was virtually ineffective as the degradation retarder (Figure 3). PMPSi film with 1.5 wt.% of stabilizer **1** degraded in the monitored region 1200-

955 cm^{-1} noticeably slower (Figure 3). The used concentration of **1** was assumed to be insufficient in PMPSi protection. The degradation was markedly retarded in the presence of 5 wt.% of stabilizer **1** in comparison with neat PMPSi and PMPSi with 1.5 wt.% of stabilizer **1** (Figure 3). This indicates an effective retardation of photodegradation by phenolic UV absorber **1** showing an absorption maximum in the UV-A region at 342 nm, i.e. close to that of PMPSi (332 nm). Degradation of the PMPSi film containing 5 wt.% of the non-phenolic stabilizer **3** showing λ_{max} at 302 nm (i.e., in the UV-B region) was characterized by increased intensity in the siloxane region. The increase in the oxygenated functions content was, however, retarded after prolonged irradiation (Figure 3). On the basis of this result, we assume that the photostabilization effect of UV absorbers in PMPSi is less dependent on the characteristic UV absorption maximum of the absorber than on its inherent durability in the substrate and, in particular, on the mechanism of activity. Involvement of the excited state intramolecular proton transfer mechanism[10] in **1** and probably in **3** as well plays certainly an important role. The elucidation of the stabilization mechanism is under study.

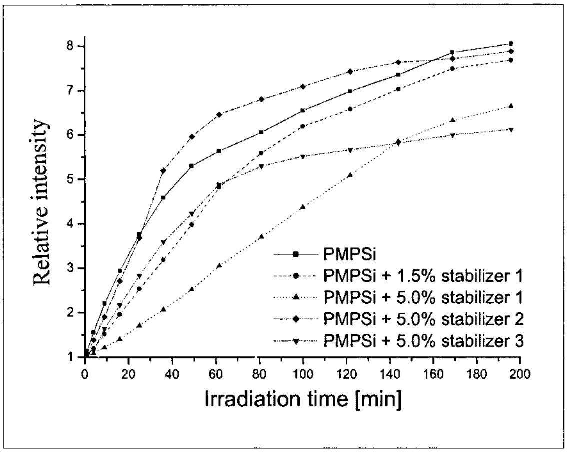

Figure 3. Comparison of the overall integrals of the bands in the 1200-955 cm^{-1} region.

In all samples a noticeable increase in the carbonyl intensity (Figure 4) and that of hydroxyl (Figure 5) group absorption was found. It is assumed that terminal silanol (Si-OH) groups and oxygenated transformations products formed on methyl groups accout for this absorption. Stabilized non-irradiated PMPSi films show non-zero values of the intensity of C=O and OH absorption bands. This may result either from the presence of these functional groups in the added UV absorbers, or from adventitious trace impurities or from occluded humidity.

Interesting changes were found in the 800-650 cm^{-1} region (aromatic C-H out-of-plain deformations). These changes are caused by structural changes in PMPSi due to the generation of Si-O-Si species in the Si backbone.

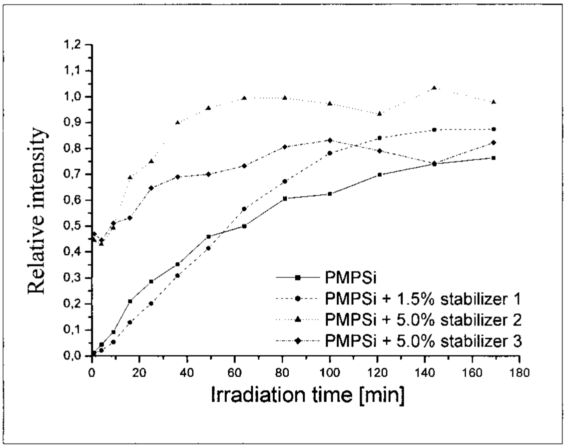

Figure 4. Increase in the intensity of characteristic carbonyl group band in the 1795-1640 cm^{-1} region.

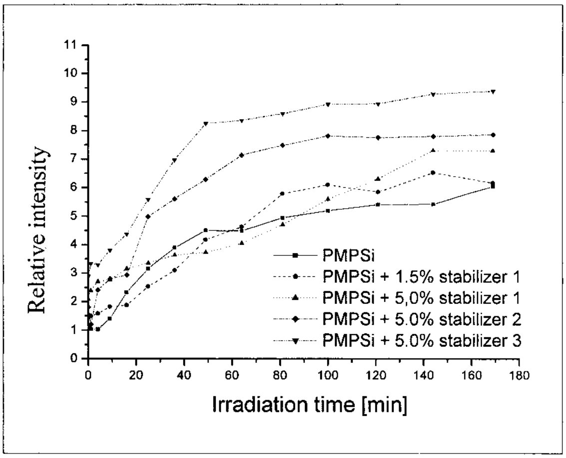

Figure 5. Increase in the intensity of characteristic hydroxy group band in the 3720-3100 cm^{-1} region.

Conclusions

Irradiation of poly[methyl(phenyl)silanediyl] films in ATLAS Weather-O-Meter Ci 3000+ changes the IR spectra in siloxane, carbonyl, hydroxyl and aromatic regions. IR spectral analysis indicates that the phototriggered irreversible degradation of PMPSi consists of several parallel chemical reactions, including dual photoprocesses - photolysis and photooxidation - followed by the conversion of the primary species. Elucidation of effects of environmental conditions and additives on PMPSi degradation is in progress. Main attention was paid to the formation of siloxane groups breaking the Si-Si conjugation. Their formation was retarded by phenolic UV absorber **1** and oxalanilide **3**.

Acknowledgement

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