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Conjugated Silicon–Based Polymer Resists for Nanotechnologies: EB and UV Meditated Degradation Processes in Polysilanes

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The comparison of the susceptibility of aryl-substituted polysilanes to the photodegradation by electron beam (EB) and UV radiation is examined on the prototypical material, poly[methyl(phenyl)silylene] (PMPSi). The main purpose of this paper is to compare the photoluminescence (PL) and cathodoluminescence (CL) after major degradation, predominantly in the long wavelength range of 400–600 nm, studying the disorder due to dangling bonds, conformational transformations and weak bonds created by the degradation process. The UV degradation was a completely reversible process, whereas the EB degradation process was only reversible, provided certain material specific level of degradation was not exceeded. This observation supports different paths and final states in both UV and EB degradations. The results serve for the optimization of polysilane nanoresists. [doi:10.2320/matertrans.MC200925]

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1. Introduction

Several important papers on both positive and negative electron beam (EB) resists exist (e.g., Ref. 1) and references there) where both scission and crosslinking were declared as predominant mechanisms of resists formation, with no direct influence of conformation transformations (CTr) or weak bonds (WB) on the resist properties.

This paper deals with the elucidation of the differences of EB and UV radiation mediated degradation processes, metastability and CTr and WB creation. The second major topic of the paper is the information content of cathodo luminescence (CL) compared to phtoto luminescence (PL) examined on prototypical polysilanes, poly[methyl(phenyl)-silylene] (PMPSi). In this respect we extend the scope of our latest papers.[2,3)]

2. Experimental Details

The details about the PMPSi films preparation, PL and IR absorption measurements were given elswhere.[3)] For the CL measurements the rebuilt transmission electron microscope TESLA BS 242 was used with the EB energy from 1 to 60 keV and EB current 0–1.6 nA mm^{-2}. The sample was placed in a special temperature controlled sample holder provided with the beam deflecting system and a blanking diaphragm for the measurements in the synchronous mode. For the CL signal measurements served photomultiplier Hamamatsu R943-02 with 51 mm diameter head-on type synthetic silica window, GaAs photocathode and the lock-in amplifier Unipan 232 B. This combination allows for high sensitivity over a wide spectral range from UV to near IR (160 to 930 nm).

3. Experimental Results

The EB and UV mediated degradation processes, differ, depending on both the excitation mechanism and their parameters.

Figure 1 shows the normalized spectral dependences of PL after the excitation at 330 nm, part a), and CL after 10 kV/ 0.16 nA mm^{-2} EB excitation, part b), (curves 1 show virging material). In the Figures are also depicted the plots after 10 min (60 min) degradation (curves 2) and 60 h (480 h) relaxation (curves 3) (for PL and CL, respectively), showing metastability of the degradation process. The spectral dependences show typical excitonic PL bands (situated at 356 ± 5 nm). We used information about the decrease of the PL band intensity during UV irradiation for the adjustment of the time and parameters of the experimental procedure, as the diminishing of the excitonic band served as the label of the degree of the polymer degradation.[4)]

The corresponding kinetics of the degradation process is shown in Fig. 2. In part (a) is depicted the degradation kinetics for the excitation wavelength 266 nm (curve 1) and 355 nm (curve 2), in part (b) is the degradation kinetics for the EB 10 kV and current densities of 0.016 (curve 1), 0.16 (curve 2) and 1.6 (curve 3) nA mm^{-2}, respectively. From the comparison of the two sets of curves it is obvious that the kinetics, and thus mechanism of PL and CL, are basically different. The PL exhibits dependence of two parabolical segments of the type $I \sim t^{-n}$ for $t < t_T$ and $I \sim t^{-m}$, for $t > t_T$, where t_T is the transition time between these two regions in accordance with Ref. 5) and t is the time.

The CL kinetics exhibits for low level of the EB current densities the first order dependence $I = I_o \exp(-t/\tau_{deg1})$, whereas for high EB current densities the transfer to two time constants process $I = I_{o1} \exp(-t/\tau_{deg1}) + I_{o2} \exp(-t/\tau_{deg2})$ is observed. Supposing the reservoir of the segments concentration, their "defect pool", to be N_{Co} at $t = 0$ s, then the time evolution of $N_C(t)$ is given by the formula

$$N_C(t) = N_{Co} e^{-\frac{t}{\tau_{deg1}}}, \tag{1}$$

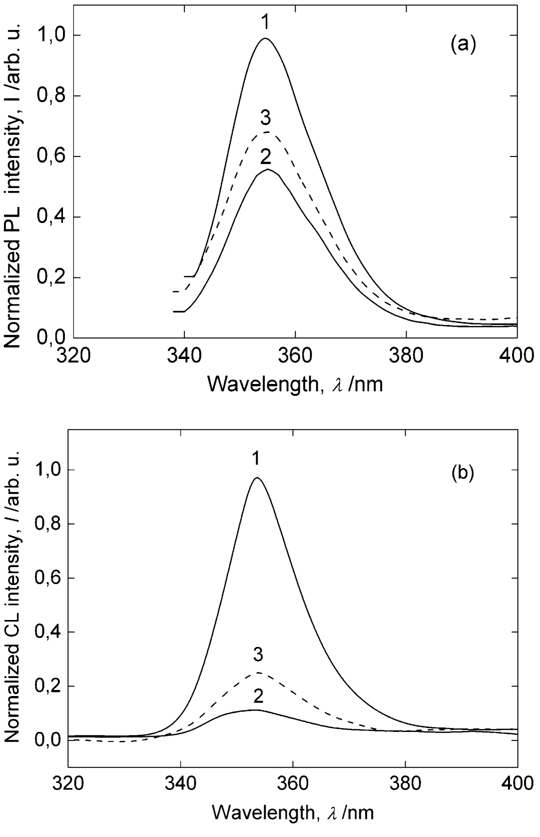

Fig. 1 Comparison of UV and EB stimulated degradation and metastability spectra: Normalized spectral dependences of PL after the excitation at 330 nm, part (a), and CL after 10 kV/0.16 nA mm^{-2} EB excitation of the virgin sample, part (b), (curves 1), after 10 min (60 min) degradation by UV and EB radiation, respectively (curves 2), and 160 h (480 h) relaxation at room temperature (curves 3), showing metastability of the degradation process.

where $\tau_{\rm degl} = 1/[\sigma_{abs} IA \exp(-E_{\rm degl}/kT)]$, σ_{abs} is the absorption crosssection for the electon by a segment, I is the current of the EB and the term $A \exp(-E_{\rm degl}/kT)$ expresses the Arrhenius term with overall activation energy of the thermally activated scission of Si-Si bonds.[6)]

In Table 1 are given the dependences of the time constants $\tau_{\rm degr\ 1}$ and $\tau_{\rm degr\ 2}$ on the current I of EB.

The degradation-metastability relaxation kinetics of the intensity of CL is shown in Fig. 3, part (a). It is worth mentioning that the recovery process is completely reversible, provided the degradation process does not exceed 50% of the original value of the PL intensity at 356 nm even at room temperatures, following the kinetics

$$I = I_{\rm oo}(1 - e^{-\frac{t}{\tau_{\rm rec}}}), \qquad (2)$$

where $\tau_{\rm rec} = \tau_{\rm orec} \exp(-E_{\rm arec}/kT)$ and $E_{\rm arec}$ is the activation energy of the recovery process. After the degradation to more than 50% of the original value, an irreversible degradation was found. This is clearly visible in Fig. 3, part (b), where the degradation process progressed to different levels of the original value of the PL intensity at 356 nm. The metastability relaxation process rate after 450 h in vacuum at 20°C showed the final values, depending on the previous prehistory of the degradation process. The activation energy for the recovery process was evaluated to be $E_{\rm arec} = 0.61$ eV from the temperature dependence of the recovery process.

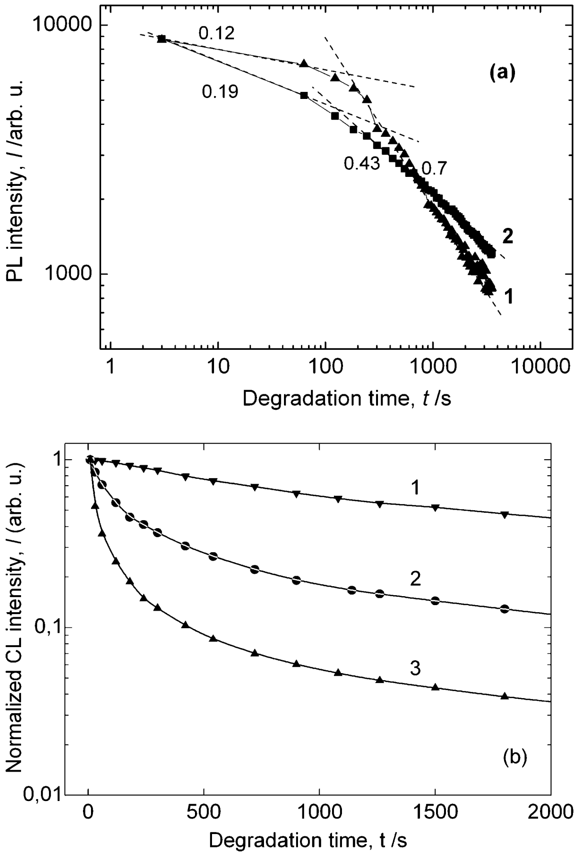

Fig. 2 Comparison of UV and EB stimulated degradation kinetics: The excitation wavelength 266 nm (curve 1) and 355 nm (curve 2), part (a). The degradation kinetics for the EB 10 kV and current densities of 0.016 nA/mm^2 (curve 1), 0.16 nA mm^{-2} (curve 2) and 1.6 nA mm^{-2} (curve 3), part (b).

Table 1 EB degradation time constants for 10 kV acceleration voltage.

I (nA mm^{-2})	$\tau_{\rm degl}$ (s)	$\tau_{\rm deg2}$ (s)
0.016	1981	—
0.16	190	2440
1.6	19	298

The main difference in PL and CL spectra are their long wavelength parts broadly distributed in several pronounced bands, spread in the interval 400–600 nm. These bands are sometimes called the white luminescence region, as they are responsible for the white light emission, prospective for applications. In Fig. 4 is the comparison of the white light luminescence emissions in PMPSi, CL induced by EB 10 kV/0.16 nA mm^{-2} (curve 1), PL induced by the photodegradation light $\lambda = 330$ nm (curve 2) and that induced by heating at 120°C (curve 3). The existence of two ill defined broad bands with maxima at about 420–470 (CL) nm and 480–520 nm (PL) are visible, similar to our previous results,[2,3)] where we ascribed the first band to CTr defects and the second band to the WB formation. Curve 3, and the corresponding changes in the photoluminescence spectra could be caused by conformation changes and by heating (to 120°C).[7)] In Fig. 5(a), the time evolution of PL emission intensity of the 480–520 nm band during the photodegradaion

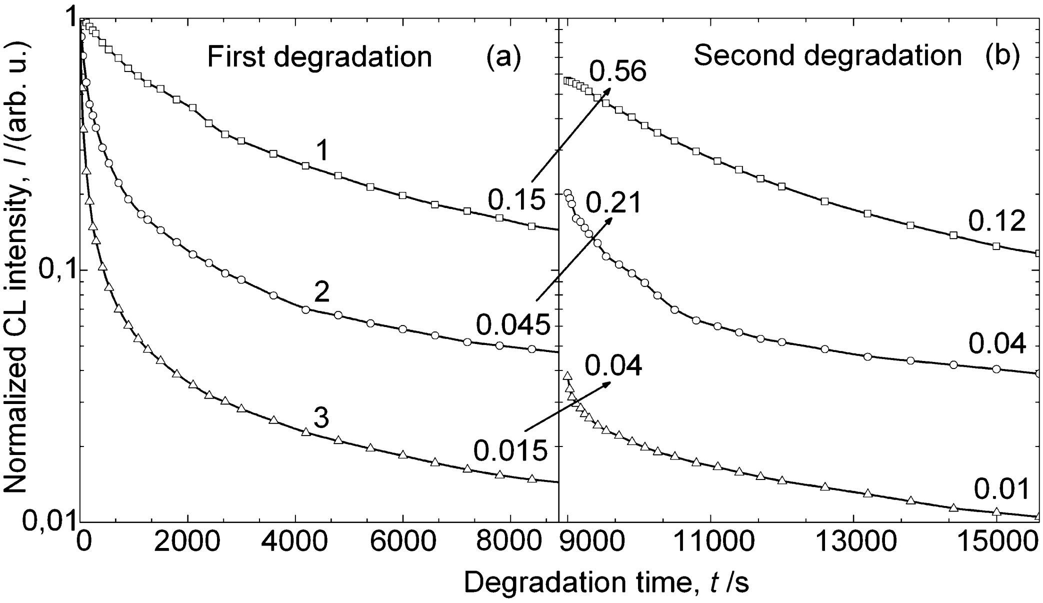

Fig. 3 Degradation–relaxation kinetics of CL: degradation (left panel)–recovery kinetics (right panel) of the CL signal (for small degradation less than 50%) (EB 10 kV and the current density of 0.16 nA mm^{-2}, temperature 20°C), part (a) three subsequent degradations separated by relaxation for 20 h at 20°C; sample exposed by EB 0.016 nA mm^{-2} (curve 1), 0.16 nA mm^{-2} (curve 2) and 1.6 nA mm^{-2} (curve 3), part (b). The arrows mean a spontaneous relaxation when the sample is kept in vacuum and in the dark.

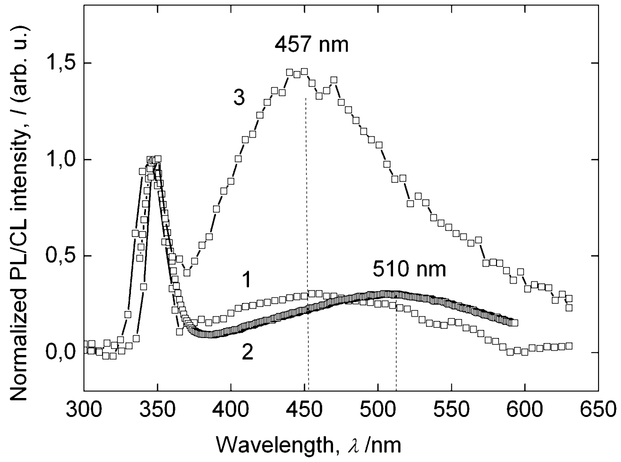

Fig. 4 Spectral dependence of the luminescence: CL after the degradation for $t = 600$ s by EB 10 kV, 0.16 nA mm^{-2} (curve 1), PL after the degradation for $t = 600$ s by light $\lambda = 330$ nm (curve 2), CL after heating to 125°C and measured at 20°C (curve 3).

by light $\lambda = 266$ nm (curve 1) and $\lambda = 355$ nm (curve 2) is shown. In Fig. 5(b) is depicted a similar process due to CL degradation by EB 10 kV/0.16 nA mm^{-2}.

4. Discussion

In spite of the fact that CL is a very efficient tool for the study of polymers, their electron structure and prospective applications, it is very rarely used.[8] Recently Wellman *et al.*[9] introduced CL as an important tool for the investigation of materials for organic electroluminescence devices (OLEDs), as the mechanisms for electron interactions and exciton creation (75% triplets, 25% singlets generation) with

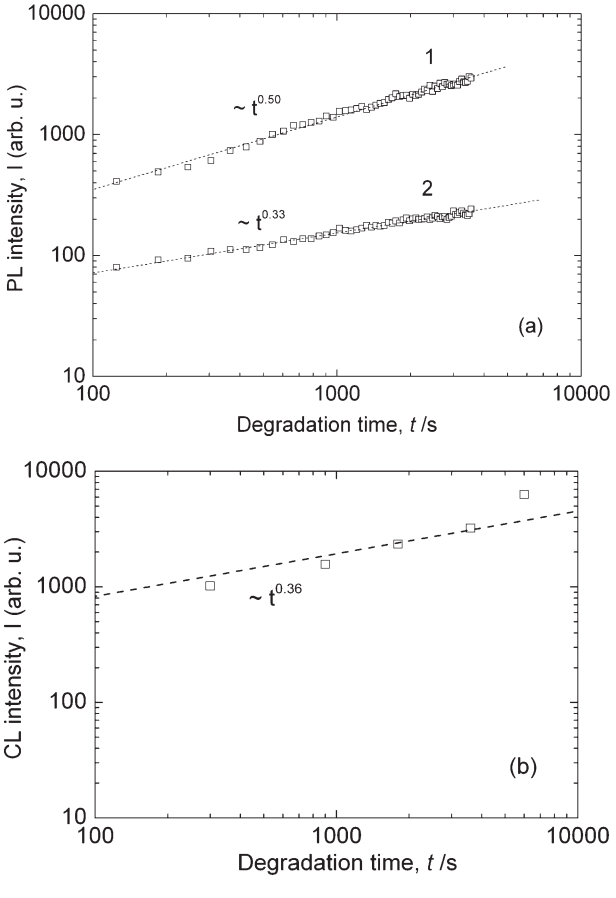

Fig. 5 Defect luminescence kinetics after PL/CL degradation: part (a) Time evolution of PL emission intensity of the 480–520 nm band during the photodegradation by the radiation of $\lambda_{\mathrm{deg}} = 266$ nm (curve 1) and $\lambda_{\mathrm{deg}} = 355$ nm (curve 2); part (b) Time evolution of CL emission intensity of the 420–470 nm band during the photodegradation by EB 10 kV, 0.16 nA mm^{-2}.

strong enhancement of triplet phenomena and intersystem crossing are also operative in CL induced by EB. This is identical with OLEDs injection generation mechanisms. Sharma *et al.*[10] mentioned out the complex electroluminescent (EL) spectrum with some substantial differences compared to PL spectra. They pointed out, on the basis of a weak or absence of visible emission in PL, the possibility of defect formation by other mechanisms. They also point out that the mechanism of forming EL excited states is different, through injection of electrons and holes. The holes could be trapped at the defect sites and the arrival of electrons could lead to the recombination or the formation of excitonic states on the defect sites. So, CL may become a strong tool for the investigation of EL in polymers without the need of the building a functioning EL device like it was presented in Ref. 11), or for the investigation of triplet harvester organic solar cells.[12]

As the polysilanes are an important group of materials with prospective applications, the comparison of PL and CL and disclosing similarities and differences in the excitation, degradation and metastability is an important question. The excitation by EB is different and in consequences similar to injection of a pair of carriers, where excitons are generated after coupling in an electron-hole pair.[9] The spectral courses of the principal excitonic bands induced by PL and CL, as it is shown in Fig. 1 part (a) and part (b) are identical, without any substantial differences both in the shape, position and metastability. In general, degradation due to UV absorption or EB irradiation may be caused by (i) breaking of the Si-Si bond, resulting in the nonabsorbing/nonemitting shorter segment or (ii) creation of a defect/trap site providing a nonradiative pathway.[10]

The comparison of UV and EB degradation in Fig. 2 part (a) and part (b), respectively, show some similarities. The degradation is in both cases composed of two different temperature activated degradation processes with substantially different kinetics. The PL corresponding to the degradation kinetics, see Fig. 2, part (a), is formed by two parabolical segments of the type $I \sim t^{-\mathrm{n}}$ for $t < t_{\mathrm{T}}$ and the region with $I \sim t^{-\mathrm{m}}$, where t_{T} is the transition time between these two regions in accordance with Ref. 5), whereas the CL exhibits one time constant of the first order kinetics dependence for low level EB current densities, whereas for high EB current densities transfer to two time constants is observed, (see Table 1). Partially, the differences may be accounted for by the differences in penetration depths of UV excitation which is more or less surface effect,[13] whereas the excitation mechanism by EB may be considered as a bulk effect. The penetration depth of UV light, which is used for PL stimulation, is in PMPSi in the range of 50 nm,[14] whereas in CL for 10 kV EB may be approximately 1–2 μm, depending on the density of the organic material as Monte-Carlo simulations show.[8]

The explanation of different kinetics for UV and EB degradation may be provided by the model including the energy transfer to lower energy segments and the segment scission, combined with the introduction of the concept of Si-Si intersegment (the bond between two conjugated segments) and intrasegment (the bond located inside the conjugated segment) location, originally proposed in Ref. 13) and elaborated in Ref. 6). As we found[3] for high energy excitons the ratio of the efficiencies of both processes is in favor to either segment cutting and/or WB defect creation, whereas for low energy excitons the probability is in favor of the exciton transfer to lower energy segment (longer chain) and its subsequent cutting with a low probability of WB formation. We additionally claim, based on the presented results and in accordance with Ref. 6), the observation of two mechanisms of degradation and metastability, which is obvious from the results in Fig. 2, part (a) and part (b). The first mechanism, the faster one, is based on the existence of certain, material quality dependent, intrinsic CTr intersegment Si-Si sites (in Sharma[6] nomenclature type-1 segments) and their changes in the early stages of the degradation process due to the excitons diffusing along the chain, creating the defects diminishing and PL. Also a possibility exists that those intersegment Si-Si sites are scissored, diminishing the molecular mass but not the PL. These states are the main candidates for the complete PL metastability recovery observed in Fig. 3, part (a). The photophysical properties of the polysilanes are quite sensitive to the polymer conformation because the electronic states are strongly influenced by the overlapping of electron orbitals along the silicon chain. The absorption and fluorescence spectra show a thermochromism in some polysilanes supporting an idea about the order-disorder transitions on polymer backbone.[15] The conformation changes may induce localized states for excitons, resulting in the emergence of a new band in the PL spectrum. The change of local symmetry in the vicinity of the conformation defects could result in the allowance of the forbidden transitions with the energy of about 4.2 eV ($\lambda = 294$ nm).[16] This effect is not temperature dependent. The long-time degradation leads to the second, slower mechanism of the degradation, where the excitons attack the long intrasegments of the Si-Si chain (in Sharma[6] nomenclature type-2 segments). It results in the formation of the WB with radiative paths for luminescence (as we observed in Ref. 3)) or chain scission. This second prolonged degradation process leads to non-reversible processes, observed in Fig. 3, part (b). Similar observation of two types of DB was presented by Naito[17] and explained by two subsequent types of DB differeing in energy configurational diagram.

The differences in degradation processes due to UV and EB are visible in Fig. 4, part (a) with two distinct bands, the first, by EB degradation situated at 420–470 nm (curve 1) and the second, by UV degradation, at 480–520 nm (curve 2). In accordance with our previous results,[2,3] where we ascribed the first band due to the CTr defects and the second band to the WB formation, indicating the existence of two degradation mechanisms. For comparison, we present also in Fig. 4, part (a) as a curve 3, the PL band situated at identical wavelength of about 457 nm, due to CTr induced by thermochromic effect in accordance with Ref. 7). The PL of polysilanes, both their singlet excitonic bands (σ, σ^*), (σ, π^*), and their long wavelength bands are frequently discussed topics due to their potential applications in both LEDs[18] and in the connection to the triplet photon harvesting in solar cells,[12] though the latter one with some ambiguity in explanation.[19] The charge transfer (CT) exciton $^1(\sigma, \pi^*)^{\mathrm{CT}}$, branching points (BP) and phosphorescence from triplet excited state $^3(\sigma, \sigma^*)$ due to intersystem crossing (ISC), were suggested as the candidates for the observed PL on the basis of time resolved photoluminescence spectroscopy.20) We suggested3) a model based on the Frenkel type exciton, sensitive to the excitation wavelength, creating both DB and WB for short wavelength (266 nm), and removing defects at long wavelength (355 nm) of excitation. These observations were based on the firmly established facts that WB are the primary consequence of the glassy state and/or external fields excitation of any glassy solid state material in general and in polysilanes in particular. According to calculations, the DB and/or WB in polysilanes are created selectively depending on the wavelength of the radiation.21) As both electrons and holes in WB maintain their original orbital symmetries, the optical transition between them is possible, so WB act as a radiative centre with a strong PL, a DB, on the other hand, is non-radiative centre, suppressing PL.

5. Conclusions

The main conclusions may be formulated as follows.

(1) The differences in UV vs. EB degradation process were observed based on the differences in the generation-recombination process in PL vs. CL and the consequences for EL devices based on polysilanes discussed. The main step of both is the creation of $^1(\sigma, \sigma^*)$ excitons and their deexcitation, resulting in Si-Si cutting and DB creation.

(2) The obvious difference in both degradation processes is given by the different penetration depths of both radiations, and also might be influenced by the different proportion of singlet to triplet excitons in both excitation processes.

(3) The degradation process due to UV radiation creates predominantly the WB states with luminescence at about 550 nm band, whereas the EB degradation gives rise predominantly to the CTr and corresponding defects with luminescence situated at the band 420–450 nm, similar to thermochromic conformation changes. Both WB and CTr defects serve as defect pool for Si-Si scission by temperature activated processes.

(4) The observed metastability after UV and EB degradation differs in the reversibility, supporting the differences in the energies in the conformation energy diagram of ensuing states for both processes. The UV degradation was completely reversible, whereas the EB degradation process was reversible, provided certain material specific level of degradation was not exceeded. This observation supports different paths and final states in both UV and EB degradations.

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