Journal of Optoelectronics and Advanced Materials Vol. 7, No. 3, June 2005, p. 1157 - 1168

Invited lecture

LIGHT-INDUCED PHENOMENA IN POLYMERIC THIN FILMS

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Photoprocesses in polymers are generally divided into two groups: (i) Photochemical processes resulting in a permanent chemical alternation of a macromolecule, like bond scission, crosslinking and oxidation. (ii) Physical (reversible) processes involving the distribution, relocation and ultimate fate of the excess energy associated with an excited molecule, following absorption of a photon, like photoluminescence, phosphorescence, photoinduced electron transfer and formation of charge-transfer states (excitons). The excitation is very often accompanied by charge redistribution and change of molecular conformation. An extreme case is the photochromic effect – photoreversible reaction of two forms of a single molecule. The changes in the molecular conformations lead very often to the formation of metastable electronic states. Similarly to semiconductors, electron-hole pairs or ion-pairs can be generated by the action of light in conjugated polymers. Their dissociation leads to the generation of free charge carriers. Photoconductive polymers with optical non-linear activity can be used for photorefractive and holographic memories.

(Received April 19; accepted May 26, 2005)

Keywords: Light-induced phenomena, Photodegradation, Photochromism, Photoconductivity

1. Introduction

Macromolecular materials have been of considerable interest both to scientists interested in purely academic problems and those carrying out applied research. At present, the number of applications based on polymers is very high. The susceptibility of organic systems to "molecular tailoring" has been known (and used) for decades, giving rise to a rapid increase in the number of synthesized organic compounds.

Interest in molecular solids has been enhanced by the discovery of materials exhibiting high, metallic-like conductivity and superconductivity, highly nonlinear optical properties, pyroelectricity and piezoelectricity, and other interesting electronic properties. The chemical flexibility of these materials allow information storage. Many physical processes result directly from the properties of the constituent molecules. Thus, one may envisage the possibility of constructing molecular-scale electronic devices; this field of molecular electronics is developing very fast at present. Important motive stimulating the research on synthetic polymers has been their similarity to materials of biological importance. Hence, in many cases synthetic compounds have been considered models for biomaterials.

The matter of interest of polymers is their sensitivity to light. After the photon absorption many effects can be observed in the excited state. Generally these processes can be divided into two groups: (i) unwanted ones, like photodegradation, bond scission, crosslinking and oxidation, (ii) active photoelectronic effects which can be utilized for the construction of optoelectronic devices.

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This article presents an overview of some optoelectronic properties of solid polymers. The photodegradation processes are also shortly mentioned.

2. Polymer photochemistry, degradation and stabilization

All organic polymers are sensitive to a greater or lesser extent to UV light-triggered free-radical photo-oxidation [1]. According to the first law of photochemistry, the photochemically induced changes are effective after the absorption of a photon resulting in electronically excited states [2]. Each absorbed photon activates only one macromolecule, present chromophore (Ch), photoactive impurity or additive in their ground state S_{0A}; thus, the excited singlet states (S_{iA}) are generated. The energies of the higher singlet states deactivates thermally very fast by vibrational relaxation and the lowest excited singlet (S_{1A}) state or, after the intersystem crossing (ISC), the first triplet state (T_{1A}) are formed. Both S_{1A} and T_{1A} are the starting species for following photophysical or photochemical processes encountering photodegradation. This differentiates photodegradation from thermal oxidation arising from the ground state S_{0A}.

Theoretically, polymers without inherent chromophores, such as most aliphatic polymers, polyolefins in particular, do not absorb light in the terrestrial UV range 295 to 400 nm. Aromatic polymers, such as aromatic polyamides, polyesters, polycarbonates, polyurethanes or epoxy resins include in their molecules chromophoric moieties making them inherently sensitive to direct photolysis and photo-oxidation. However, not even commercially available ‘chromophore-free’ polymers are any ideal systems and absorb actinic radiation due to structural inhomogeneities and light-absorbing impurities present mostly in trace amounts [3]. The level of structural inhomogeneities (unsaturation, oxygenated species), arising during fabrication and processing and sensitizing degradation, gradually increases during light exposure together with polymer branching and chain scission. The progressive degradation is enhanced by non-polymeric impurities such as metallic contaminants and photoactive pigments [3].

The photochemical reaction of a polymer taking place on a high-energy excited state potential level may result in generation of some high-energy products, free radicals. The electronic excitation is localized and restricted within a small number of atoms involved in the chromophore itself. The excitation energy can be, however, transferred to another part of the same macromolecule or can migrate intermolecularly [2] by an exciton (quantum of excitation energy) hopping mechanism. Some physically defined species can arise transiently, such as excimers (excited dimers, aggregates between aromatic moiety containing molecules in S_{1A} and S_{0A} states $[S_{1A}\cdots S_{0A}]$ arising from the exciton migration) or exciplexes (i.e., excited charge-transfer complexes existing in electronically excited states, for example between excited Ch and an acceptor of the energy (A), $[Ch\cdots A]^*$). This enhances the number of sites of polymer degradation by electronic energy transfer from the light-absorbing impurity to originally low- or non-absorbing groups in the polymer (tertiary C-H bonds, some peroxides). Electron delocalization also participates in energy deactivation contributing to enhanced polymer stability [4] and for physical interferences with photostabilizers.

The absorption of a quantum of UV radiation by a chromophoric impurity does not always result in photodegradation, although enough energy is available to dissociate chemical bonds in a polymer PH and generate macroalkylradicals P· by direct or sensitized photolysis, thermolysis or metal (M) catalysis. This is due to photophysical processes encountering excited states [2]: conversion to thermal energy, conversion between electronic states (ISC), energy transfer or radiative dissipation (luminescence), schematically described in the Yablonski diagram (Fig. 1). The first triplet state (T_{1A}) of the chromophore is generated from S_{1A} by non-radiative intersystem crossing. Triplet state T_{1A} loses a part of its energy by a radiative process, phosphorescence, and radiationless intersystem crossing to the singlet ground state S_{0A}.

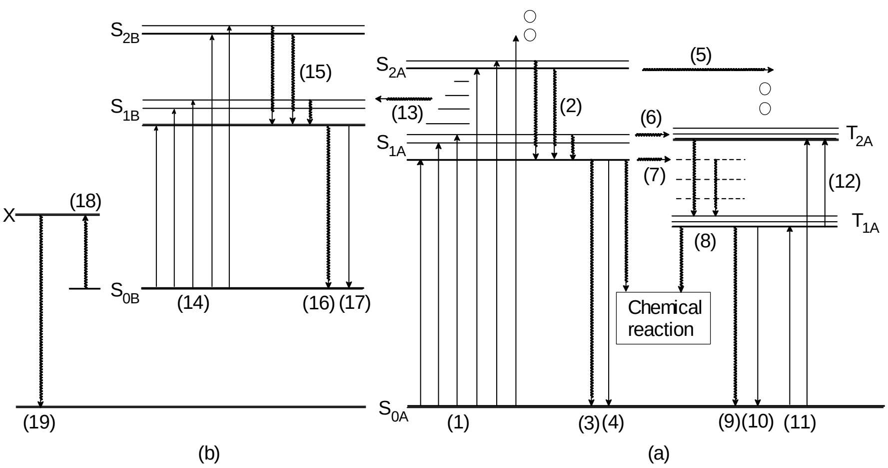


Fig. 1. (a) Simplified energy (Yablonski) diagram characterizing physical pathways and sites of chemical transformation of an excited organic molecule. S_{0A} – ground singlet electronic state; S_{1A}, S_{2A} – excited singlet electronic states; T_{1A}, T_{2A} – triplet electronic states. Processes: (1) – electronic excitation; (2) – relaxation of higher singlet states into the first singlet state including vibrational decay; (3) – internal conversion; (4) – fluorescence; (5) – autoinitiation of the excited state; (6) and (7) – intersystem crossing; (8) – relaxation of the second triplet state into the first triplet state including vibrational decay; (9) – internal conversion; (10) – phosphorescence; (11) – singlet-triplet absorption (at high light intensity only); (12) – triplet-triplet absorption. (b) Energy diagram of coloured form B. S_{0B} – ground singlet electronic state, S_{1B}, S_{2B} – excited singlet electronic states (triplet states are not included), X – transition state for bleaching reaction. Process: (13) – photochemical transformation of the molecule A into its B form; (14) – electronic excitation; (15) – relaxation of higher singlet states into the first singlet state including vibrational decay; (16) – internal conversion; (17) – fluorescence of coloured molecule; (18) and (19) – bleaching processes into the ground state S_{0A} of the initial state.

The photochemical reaction occurs, as mentioned above, from both photoexcited S_{1A} or T_{1A} states. The probability of a chemical reaction in the excited state increases with their lifetime. The long-living triplet state provides usually 10^5 times more time for photodegradation than S_{1A} state and is more liable to primary photochemical conversions. If thermodynamically or kinetically possible, chemical reactions *via* S_{1A} occur as well. The initiating process resulting in primary radicals is mostly vaguely defined, because most polymers are rather complex systems and contain various inherent or adventitious initiating or sensitizing species. The resistance of polymers to photodegradation is related to the ease of formation of the primary radicals by abstraction of hydrogen from the activated C–H bonds (formation of intrachain radicals) or by breaking weakened C–C bonds in the backbone (formation of terminal radicals). Polymer-bound moieties such as $\sim CH_2NH\sim$, $\sim CH_2O\sim$, $\sim CH_2CH=CH\sim$ or $\sim COCH=CH\sim$ are more oxidation-sensitive and enhance radical formation [2]. On the contrary, fluorinated or silicone-based polymer segments are more resistant in the initiation phase.

Photochemically induced free radicals eventually react to form final products through dark (secondary) reactions. In oxygen-deficient atmosphere, carbon-centered radicals undergo self-reactions: disproportiation (resulting in two molecular fragments and enhanced in-chain unsaturation) and recombination (responsible for branching or crosslinking). However, in the presence of oxygen, oxidation chain reaction is triggered preferentially [2,3]. It involves propagation, Eq. (1) and Eq. (2), chain branching, Eq. (3) and Eq. (4), and termination steps, Eq. (5).

$$P\cdot + O_2 \rightarrow POO\cdot \tag{1}$$

$$POO\cdot + PH \rightarrow POOH + P\cdot \tag{2}$$

$$POOH \xrightarrow{\Delta,\, h\nu,\, M} PO\cdot + HO\cdot \tag{3}$$

$$PO\cdot\,(HO\cdot) + PH \rightarrow P\cdot + POH\,(HOH) \quad (4)$$

$$P\cdot, PO\cdot, POO\cdot, HO\cdot \rightarrow \text{non-radical products} \quad (5)$$

The role of free migrating radicals HO· is underrated. They are active reactants yielding hydrogen peroxide and are involved in initiation of photodegradation [2]. The alkoxy radicals PO· undergoe β-scission resulting in carbonyl species. Hydroperoxides and carbonyls are dangerous chromophores [2,3]. Hydroperoxides, more depleting species than carbonyls due to an easy photolysis, Eq. (3), were intensively studied as initiating species in polyolefins and polystyrene. Excited carbonyls (Ch^*) are involved in their triplet states in sensitized formation of macroalkyls, in formation of singlet oxygen by energy transfer to ground state oxygen, Eqs. (6) and (7), and in sensitized homolysis of alkylhydroperoxides *via* an exciplex, Eq. (8), (the exciplex increases absorption of alkylhydroperoxide in the near UV).

$$Ch \xrightarrow{h\nu} {}^1Ch^* \rightarrow {}^3Ch^* \quad (6)$$

$${}^3Ch^* + {}^3O_2 \rightarrow Ch + {}^1O_2 \quad (7)$$

$${}^3Ch^* + ROOH \rightarrow [Ch\cdots ROOH]^* \rightarrow Ch + RO\cdot + HO\cdot \quad (8)$$

The energy transfer from excited chromophore may take place intermolecularly or intramolecularly, attacking in the latter case non-excited segments of the molecule and enhancing locally the level of oxidation products, one of reasons of photodegradation heterogeneity.

Photodegradation of polymers deteriorates their material properties [2, 5, 6].To prevent from attacking UV radiation, light screening pigments and UV absorbers (UVA) are used. Photoantioxidants deactivate peroxidic species arising in photo-oxidation. Quenchers (Q) deactivate excited species in polymers, by collision energy transfer within a distance 10-15 Å or by resonance transfer over extensive regions of space (50-100 Å) as a result of Coulombic interactions [7]. Quenchers dispose the energy as heat or fluorescent and phosphorescent radiations. The discussion of the photostabilization is not the main subject of the paper. The reader can find more information in special articles [5,6,-10].

However, not all effects related to the polymer degradation and singlet oxygen production are unintentional processes. As examples we can mention photoresists and liquid crystal alignment on phototreated polymer surfaces which are used in optoelectronics and singlet oxygen production whichcan be exploited in photodynamic therapy.

3. Exploitation of photodegradation-based processes

3.1. Polymer resists

Planar microelectronic components can be patterned using photolithography. A surface is first covered with a light-sensitive photoresist and then exposed to UV light through a mask. Either the exposed photoresist (positive resist) or the unexposed regions (negative resist) can subsequently be washed away to leave a positive or negative image of the mask on the surface. Photodegradation processes and crosslinking play here an important role. Conventional photolithography has feature sizes about 100 nm. Structures of less than 10 nm may be fabricated by using techniques of shadowing and edge-step deposition [11].

3.2. Alignment of liquid crystals on polymer surfaces treated with polarized UV light

Photopolymers are believed to allow the development of a "clean" non-contact method of the liquid crystal (LC) alignment important for the display operation, which permits control of the direction of the easy axis of orientation and the anchoring energy of LC over an aligning surface

[12]. We will demonstrate the photoalignment process on the example of polysilanes, but similar processes were found also on other photosensitive polymers.

Polysilanes with their uninterrupted chains of silicon atoms and with significant electron delocalization along the polymer chain [13] are a new class of photoconductive [14-16] polymers with unusual properties. Upon UV irradiation they undergo complex photodegradation processes, like photochemical cleavage of Si-Si bonds, oxidation to polysiloxanes, crosslinking, photoablation, formation of quasi-stable electron-hole pairs and metastable electronic states. For these reasons, polysilanes were also studied as photoresists [13].

The irradiation of poly[methyl(phenyl)silylene] (PMPSi) film at the region of the first absorption band (λ_{inc} = 347 nm) causes a transient absorption [17] with strong maxima around 460 and 370 nm. These peaks are attributed to chain radicals and/or delocalized cation radicals [18] (II and III in Figure 2). It follows from kinetic studies that the life-times of these radicals are about 4 and 260 μs, respectively, but long-lived species exist depending on the morphology distribution of polymer chains. The kinetics of the radicals suggests that they can recombine but products based on photoinduced Si–Si bond scission can also occur. An irradiation in air can cause the formation of siloxane species (IV in Fig. 2) as it follows from IR spectrum where additional peaks at 1122 and 1111 cm^{-1} were found [19]. During these (σ–σ*) excitations (I, Fig. 2), i.e. the excitations of Si–Si bonding electrons, the electron is promoted from the bonding to an antibonding orbital. This process can be followed by electron transfer on the polymer chain (V, Fig. 2). Thus, an electron-hole pair is formed. However, the pairs generated in the same chain segment very often recombine geminately with a very fast decay rate, due to the electron delocalization in the backbone. An interchain or intrachain (VI, Fig. 2) electron transfer to phenyl moieties is necessary for the stabilization of the charge transfer state. A similar situation exists during the (π–π* transition), i.e. the phenyl group excitations, when a Frenkel exciton is formed. A positive hole from the excited phenyl group is transferred to the Si–Si main chain and a main chain cation-radical is formed. In the external electric field the ion-pairs can dissociate and free charge carriers (polarons) are generated. This effect will be discussed in detail latter on.

During the photodegradation with UV light some changes in the absorption spectrum were detected (Fig. 3a). The intensity of the long wavelength band, which arises from the delocalized (σ–σ*) electronic transitions, decreased with the level of the photodegradation and its maximum was shifted to the short wavelength region. Because the energy of this transition is conformation-dependent and depends on the molar mass and conjugation length of the macromolecule, the excitation energy is effectively deposited almost in the longest all-trans segments. Thus, the blue shift of the peak suggested that Si–Si bond scission occurred and conjugation length becames smaller. This was demonstrated by the measurement of the decrease in molar mass during the PMPSi photodegradation [20] and by photoluminescence experiments. It was also found that during UV irradiation with 254 nm a photovoltatilization occurs [21].

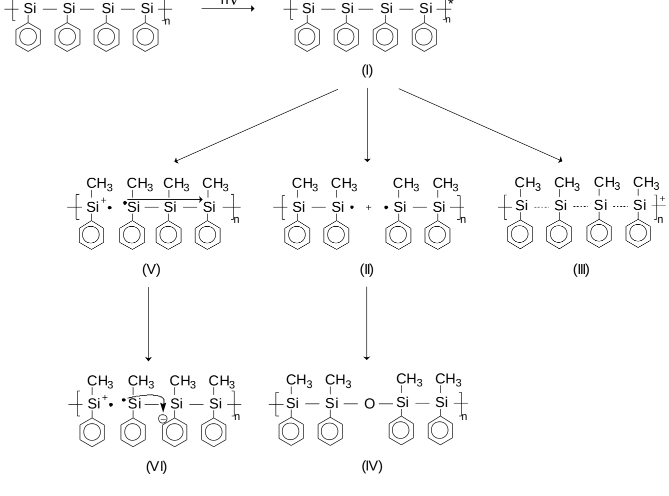
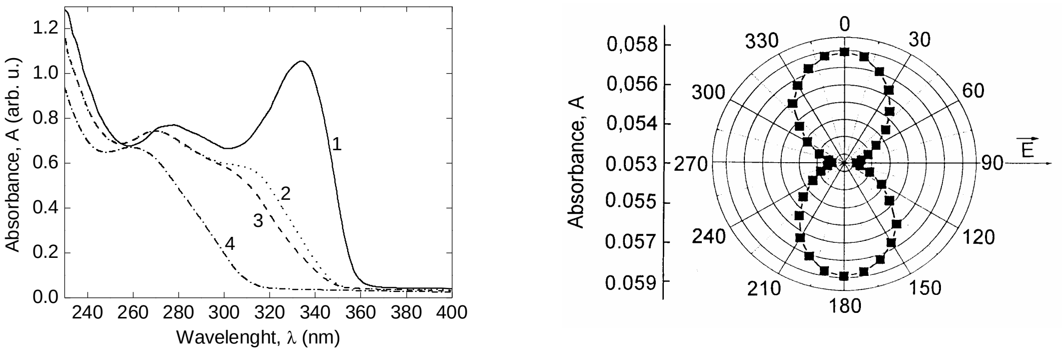


Fig. 2. Formation of photospecies during the (σ–σ*) excitation of PMPSI.



(a) (b)

Fig. 3. (a). Changes in polarized UV spectra of PMPSi film on irradiation with linearly polarized light of He-Cd laser (λ = 325 nm, P = 10 mWcm^{-2}): (1) spectrum of as-prepared film; (2) spectrum parallel to the polarization of the exciting light after the exposure dose 0.2 Jcm^{-2}; (3) spectrum perpendicular to the polarization of the exciting light after the exposure dose 0.2 Jcm^{-2}; (4) spectrum measured after the exposure dose 12.0 Jcm^{-2}. (b) 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 visualizes the electric field vector of the incident light.

The long-wavelength absorption band is influenced by the all-trans main chain segments separated by gauche conformations. Thus, a polysilane film is an assembly of energetically different, weakly coupled Si-Si chain segments. The exposure with the linearly polarized light results in the angularly dependent excitation of the main chain segments, which are oriented parallel to the electric field vector of the exciting light. Fig. 3b shows the polar diagram of the absorbance at 333 nm after irradiation with linearly polarized light of 335 nm. An anisotropic distribution of species is clearly visible. When liquid crystal (LC) is applied on PMPSi surface treated in this way, a LC alignment is observed. The dependence of azimuthal energy on the exposure dose is shown in Fig. 4. Another possibility for liquid crystal alignment represent photochromic polymers (see Chapter 5).

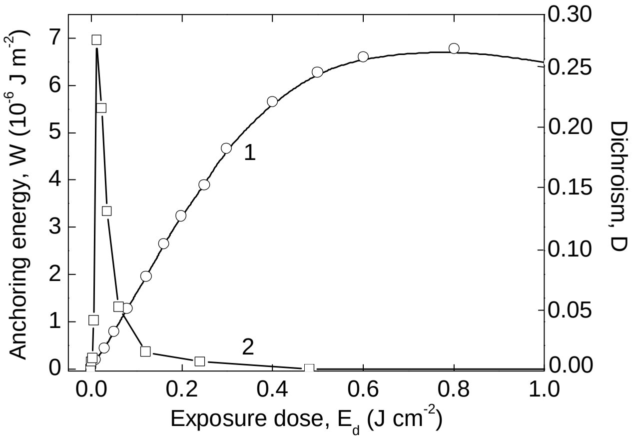
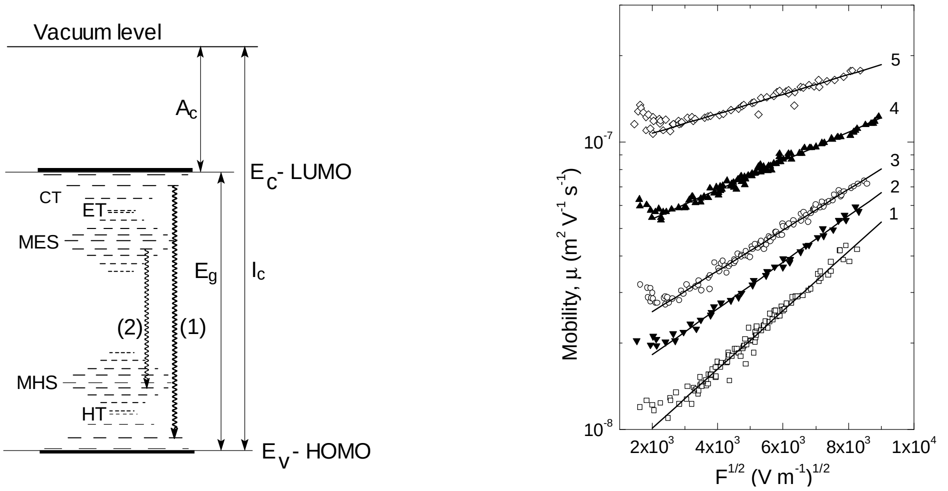


Fig. 4. Changes of azimuthal anchoring energy of liquid crystal (Merck, LC 2 LT-4801) (1) and dichroism calculated at 333 nm (2) on irradiation of PMPSi film with linearly polarized light of He-Cd laser (λ = 325 nm, P = 10 mVcm^{-2}).

4. Metastable states

Fig. 5 shows the energy diagram of ionized states of solid polymer. It consists of several levels: E_v – HOMO level (edge of the valence band) which is characterized by the ionization potential I_c and in one electron approximation it is given by the energy of highest occupied molecular orbital (HOMO); comparing with the position of neutral electronic states it is located close to the ground singlet state in the solid. E_c – LUMO level (edge of the conduction band) which is characterized by the electron affinity A_c and in one electron approximation it is given by the energy of lowest unoccupied molecular orbital (LUMO). Energy gap E_g is spread between E_c – LUMO and E_v – HOMO. Tail states for holes and electrons, respectively, exist above the E_v and below the E_c and are responsible for charge carrier hopping transport. Their background is given by the dispersion of the polarization energy due to the molecular geometrical disorder. Electron transitions between electron and hole tails states ((1) in Fig. 5a) are usually responsible for luminescence. Deeper levels represent localized states for electrons (ET) and holes (HT).



(a) (b)

Fig. 5. (a) energy diagram of ionized state of solid film. E_v-HOMO – edge of the valence band, E_c-LUMO – edge of the conduction band, CT – charge transfer states, ET and HT – electron and hole trap levels, respectively; MES and MHS – electron and hole metastable states, respectively, A_c – electron affinity, I_c – ionization potential, E_g – energy gap, (1) – usual photoluminescence, (2) – photoluminescence via metastable states. (b) Electric field dependence of the mobility of PMPSi parametric in temperature: T = 295 K (curve 1), 312 K (curve 2), 325 K (curve 3), 355 K (curve 4), and 358 K (curve 5).

It has followed from the energy transfer experiments [22] that during the excitation a stretching of chemical main chain bonds occur. A similar situation is expected during the polaron formation [23]. This effect is more pronounced in polymers with heavy atoms in the main chain (Si, Ge, Te), even that this effect can be expected also in carbon-chain polymers. However, only few information is available. Thus, we will present the explanation of the metastable states formation on example of polysilanes. The stretching of the bonds and the shrinking of the chain conformation leads to the formation of electronic states in the HOMO-LUMO gap. On the other hand, the extension of chain conformation leads to the formation of electronic states outside the gap. These in-gap states follow from the weakened Si bonds (WB) and are expected to be metastable. It could be mentioned that this situation can be realized during weak chain excitations when the polysilane chain is not degraded yet but when the chain deformation occurs after the radical or ion-pair formation. Electronically, the band-edge states are changed by the formation of weakened bonds in the following way [24]. The local Si skeleton-bond stretching weakens the pσ bonding character of the highest occupied valence-band (HOVB) state, which is formed from the pσ bonding state between the skeleton Si $3p_x$ atomic orbitals, and destabilizes this state. Therefore, the original HOVB state energetically shifts upwards forming a hole-gap state localized around the WB site. Conversely, a reduction in the spσ* antibonding character (the lowest unoccupied conduction band state, LUCB, is formed from the spσ* antibonding state between the skeleton Si 2s and $3p_y$ atomic orbitals) stabilizes the LUCB state energetically, shifting the original LUCB state downwards, and an electron-gap state is formed. The appearance of WBs thus interrupts the chain σ-conjugation of the band-edge states and creates the tail states. According to quantum chemical calculations [24] holes are localized in the position of the WB cutter, whereas the tail-state electrons tend to localize at two Si atoms on this weakened bond.

Because these gap (tail) states for electrons and holes conserve original orbital symmetries of the delocalized band-edge states, optical transitions between them (see transitions (2) in Fig. 5a) are possible. Thus, these WBs can act as radiative centres if the excited electron and hole do not separate spatially. This was observed experimentally using photoluminescence. The spectrum measured at 4.2 K with 313 nm excitation consists of two bands with maxima at 354 and 420 nm. The irradiation of the film by ‘photodegradation light’ (366 nm) at room temperature caused the shift of the main fluorescence peak to the shorter wavelengths from 354 nm to $\lambda \cong 344$ nm. This suggested backbone scission and formation of shorter polymer segments or formation of chain disturbances, which limited the effective conjugation length. However, some increase in photoluminescence (PL) at ca. 520 nm occurred. This photoluminescence intensity increased with the formation of weakened bonds. Visually, the luminescence colour shifted from blue (for the non-degraded PMPSi sample) to light-green (for sample after “photodegradation”). It should be pointed out that the photoluminescence band at 520 nm manifested good reversibility in the case of moderate excitation of the polymer; it nearly disappeared during the annealing procedure and the light-green colour of the PL at 4.2 K returned to blue one.

5. Photochromism

The photochromic phonomenon may be schematically written as a photoreversible reaction between two forms, A and B, of molecule with absorption at wavelengths λ_1 and λ_2, respectively. In general, $h\nu_1$, which is the radiation which causes the conversion of system A to system B is associated with electromagnetic energies lying mainly in the UV region. Reversibility is an important feature of photochromic reactions. In many cases, the reversal to A may be accelerated by $h\nu_2$, radiation which is generally located in the visible or IR region of the spectrum.

$$\mathrm{A}\ (\lambda_1)\ \underset{\substack{h\nu_2 \\ \text{and/or heat}}}{\overset{h\nu_1}{\rightleftarrows}}\ \mathrm{B}\ (\lambda_2)$$

The photochromic reaction is controlled by energy levels of the colourless molecule A and its colour form B (Fig. 5b). The new ground state has mostly higher energy content than the original ground state; the latter is thermodynamically less stable and spontaneously reverts to A thermally through the transition state X. The colour of the photochromic material is given by electron transitions from S_{0B} to S_{1B}. The fact that molecules can switch between two alternative forms may provide a phenomenological entrée into the desired novel technology of optical memories, switches and holographic media.

Photochemical processes which require excited singlet or triplet states to produce new molecular system B involve a rearrangement of the atoms of the original system A. Many photochromic materials have been described in several review articles and monographs [25,26]. The basic photochromic mechanisms include:

(a) trans – cis isomerization
(b) Homolytic bond scission
(c) Heterolytic bond scission and ring opening
(d) Hydrogen tautomerism
(e) Photodimerization

Excimers are formed very often during the excitation of organic materials . When bonding energies are high enough stable chemical dimers can be formed as, for example, in the case of anthracene molecules. Bleaching reaction has to be usually activated optically.

Low-molecular-weight photochromic molecules represent very sensitive labels and probes for the study of polymer motion, free volume distribution, phase transitions, etc. The incorporation of molecularly dispersed chromophores into polymer matrices is a useful method for the study of both the characteristics of a photochromic reaction and polymer dynamics.

Thermal bleaching process in solution, B → A, can usually be described by the first order kinetics. However, in the solid phase a time-extended exponential, $[M]_t = [M]_0 \exp(-(vt)^{\alpha})$, where $0 < \alpha \leq 1$ measures the deviation from pure exponential behaviour, v is the decay rate constant, $[M]_t$ is the reactant concentration at the time t,describes better the experimental data. This shape may be represented, in principle, by a superposition of several exponentials, but the use of a statistical distribution of thermodynamic reaction parameters (activation energies, free volume) seems to be more sensible [27,28]. Optical properties of disordered materials can be understood as resulting from a set of individual processes with different rates, weighted by distribution parameters. If the kinetics are of the first-order at each site, a superposition of time-independent rates will cause the overall rate of the process to be time-dependent.

6. Photoconductivity

Change in electrical conductivity with sample illumination is defined as photoconductivity; it usually arises from a change in the density of free carriers. If the light intacting a photoconductor creates g carriers per second per unit volume, then the steady-state value of Δn equals $g\tau$, where τ is the lifetime of a charge carrier. g can be written as a product $g = \eta\alpha\Phi$, where η is the quantum photogeneration efficiency, α is the absorption coefficient and Φ is the total absorbed radiation (photons per square metre per s). In the electric field the photocurrent passes the sample. Under the assumption that charge carrier mobility, μ, is unaffected by light excitation the photocurrent of the solid with ohmic contacts is given by the formula:

$$i_{ph} = \sigma_{ph} F = \eta \Phi \tau e \mu F / L \tag{9}$$

where F is the electric field strength, L is the sample thickness. Thus, the photocurrent consists of two main terms: the quantum efficiency η and the range of the charge carriers $\mu\tau F$.

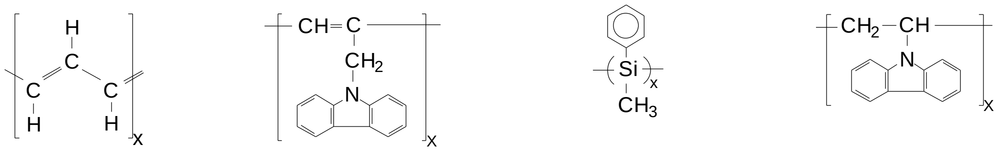
From the chemical point of view photoconductive polymers can be divided into four groups (see Fig. 6):

(1) Polymers with π-conjugated main chain (e.g. polyacetylene, 1).

(2) Polymers with a high degree of conjugation in the main chain with chemically attached π-conjugated pendant light groups (e.g. poly[N-(2-propinyl)carbazole], 2). These polymers absorb in the visible and, in some cases, in the near infrared region, especially when certain electron-withdrawing groups are present.

(3) Polymer with a σ-cojugated backbone, like polysilanes with catenated Si–Si bonds (e.g. poly[methyl(phenyl)silylene], 3).

(4) Polymers with pendant polynuclear aromatic groups having a π-conjugated system (e.g. poly(N-vinylcarbazole), 4). These polymers usually absorb only short wavelength light below 400 nm.



(1) (2) (3) (4)

Fig. 6. Chemical structures of photoconductive polymers.

The process of charge carrier photogeneration is quite complicated and very often includes several mechanisms. Here, we will discuss only two basic mechanisms, viz., charge generation due to HOMO-LUMO transitions and that via autoionization process. We will not discuss the processes like exciton dissociation at electrode/semiconductor interface, exciton dissociation due to the interaction of excitons and trapped charge carriers, exciton dissociation due to the interaction of excitons and impurities, and direct excitation of trapped carriers into the conduction or valence bands. The first step of charge carrier photogeneration is the photon absorption. It can be realized on the main polymer chain or on side groups. Optical absorption in the main polymer chain is associated with HOMO-LUMO excitations – here, there is some similarity to band-to-band transitions in inorganic semiconductors. The excitations of side groups usually lead to the formation of Frenkel excitons. The excitations of the main chain results in formation of "on-chain" electron-hole pairs that usually undergo a fast geminate recombination to a significant extent. The remaining portion of the pairs escape the fast geminate recombination presumably due to the fact that the chain conjugation extents only over a limited number of chemical bonds. The remainder of electron-hole pairs relaxes to the ion-pair charge-transfer states. This implies a transfer of the electron from the backbone to the pendant side group (intramolecular charge-transfer (CT) state) or to another polymer chain (intermolecular CT state). Similarly, during the excitation of the pendant group an intermolecular CT state, based on electron transfer to another macromolecule or some impurity molecule (oxygen), can be formed. From the point of energy structure, the CT states are polar states localized below conduction band (LUMO level, electron) and above valence band (HOMO level, hole). Electron and hole in the CT state is bound by Coulomb interaction and can move by stochastic hopping through polymer bulk.

Under the influence of the external electric field, ion-pairs can dissociate and free charge carriers are formed. The electric field dependence of the photogeneration efficiency is strong and can be described by the Onsager theory of geminate recombination of ion-pairs [29]. The presence of an acceptor supports the photoinduced electron transfer. Very often oxygen molecules present in the bulk of the polymer participate in the generation mechanism. Then, photoconductivity is mainly influenced by an extrinsic process via a nonrelaxed exciplex formed between singlet excitons D* and acceptor-like impurities or photooxidation products A. The following mechanism is proposed:

$$\mathrm{D}^* + \mathrm{A} \rightarrow (\mathrm{D}^* \cdots \mathrm{A}) \rightarrow (\mathrm{D}^+ \cdots \mathrm{A}^-)^* \xrightarrow{1} \mathrm{D}^+ \overset{r_0}{\cdots\cdots} \mathrm{A}^- \xrightarrow{2} \mathrm{D}^+ + \mathrm{A}^-$$

Here, $(\mathrm{D}^* \cdots \mathrm{A})$ represents an encounter complex, $(\mathrm{D}^+ \cdots \mathrm{A}^-)^*$ a nonrelaxed exciplex state, $(\mathrm{D}^+ \overset{r_0}{\cdots\cdots} \mathrm{A}^-)$ the CT state and $\mathrm{D}^+ + \mathrm{A}^-$ free charge carriers. The process $\xrightarrow{1}$ is a thermalization; $\xrightarrow{2}$ represents dissociation of the electron-hole pair that can again be described by the Onsager theory. Measurements performed with PMPSi and pyrromellitic dianhydride (PMA) indicate that both the lifetime and concentration of the ion-pairs increase. At the same time, the anion radical of PMA with its typical absorption maximum at about 660 nm was detected. This supports the idea of photoinduced electron transfer from the polymer donor to acceptor dopand.

To generate the photocurrent, the photogenerated charge must be transported to electrodes. Because polymers are disordered media the charge transport is usually influenced by hopping mechanism through gap tail states. Fig. 5b illustrates the dependences of the charge carrier mobility, μ, of a PMPSi sandwich sample (thickness ca. 2 μm) on F at different temperatures. In all cases, the mobility can be described by an exp $(\beta F^{1/2})$ dependence for $F > 10^7$ Vm^{-1}. At lower field strengths, $\mu(F)$ becomes constant or increases slightly upon reducing F. These types of dependences are usually treated in the framework of the hopping disorder concept. However, due to the strong electron-phonon coupling in polymers, a contribution of polarons can be expected. The essential difference between the polaron and disorder models is that the latter, at variance with the former, implies a sufficiently weak electron-phonon coupling and the activation energy of charge transport reflects the static energy disorder of the hopping sites. In contrast, the polaron model suggests a strong electron-phonon coupling and a negligible contribution of energy disorder to the activation energy of the carrier mobility. Since the structural distortion is an intramolecular process, polaron binding energy E_p is not subjected to meaningful variation. Small polaron model fails to account for the observed Poole-Frenkel-type field and non-Arrhenius temperature dependences of the thermal equilibrium carrier mobility. Thus, it was suggested [30] that the extrapolated value of zero-field activation energy of the mobility, $E_a^*(F \rightarrow 0)$, can be approximated for many polymers by the sum of the disorder and polaron contribution as

$$E_a^*(F \to 0) = E_a^{pol} + E_a^{dis} = \frac{E_p}{2} + \frac{4}{9}\frac{\sigma^2}{(kT)^2} \tag{10}$$

where E_a^{pol} and E_a^{dis} are the polaronic and disorder contributions, respectively, σ the energy width of the DOS distribution, *k* the Boltzmann constant, and *T* the temperature.

7. Conclusion

Polymers are usually quite sensitive to light exposure. The photoprocesses can be devided into two main groups: (i) Photochemical processes which result in a permanent chemical alternation of a macromole, like bond scission, network formation and oxidation; (ii) Physical reversible processes based mainly on the reversible change in the energy diagram of a macromolecule during the excitation, charge carrier photogeneration, photoluminescence, energy transfer, etc. The first group of the processes usually leads to polymer degradation accounting for loss of useful properties. Consequently, a lot of activities have been done for material stabilization. The second group of the processes represents positive contribution for the construction of macromolecular optoelectronic elements. From these the photochromism (concerning switching, memories, holography) and photoconductivity (concerning photodetectors and solar cells) play an important role.

Acknowledgements

The research was supported by the Ministry of Education, Youth and Sports of the Czech Republic (grant No. ME 700) and by the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. AV0Z40500505).

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