Measurement of the photobleaching kinetics of semiconducting polymer films by the pump–probe method

A.E. Ozimova, V.V. Bruevich, D.Yu. Paraschuk

Abstract. **A phenomenological model of the laser photobleaching dynamics of a semiconducting polymer in a dual-beam scheme for different wavelengths of the burning and probe beams is developed. An experimental method is implemented based on this model, which allows one to investigate materials with significantly different photodegradation rates. The photodegradation quantum yield in mixtures of a semiconducting polymer belonging to polyparaphenylene vinylenes (MEH-PPV) with a low-molecular electron acceptor 2,4,7-trinitrofluorenone (TNF) is measured at burning wavelengths of 488 and 514 nm for different component ratios of MEH-PPV : TNF. It is found that adding the acceptor decreases the polymer photodegradation quantum yield by at least four orders of magnitude in the MEH-PPV : TNF = 1 : 0.4 mixture; the photodegradation quantum yields are the same at both wavelengths. It is shown that the photodegradation rates of the MEH-PPV : TNF films measured by laser photobleaching and IR spectroscopy are in good agreement.**

Keywords: semiconducting polymer, photoluminescence, photodegradation, laser photobleaching, charge-transfer complex.

1. Introduction

Semiconductor (conjugated) polymers are of great interest as promising thin-film materials for different applications in photonics (for example, LEDs and solar cells). One of the general drawbacks of most semiconducting polymers is the low stability in environment under illumination [1, 2]. The best studied process of semiconducting polymer photodegradation is photooxidation [3, 4]. It is believed to be related primarily to the formation of long-lived triplet states, which interact actively with atmospheric oxygen [5].

It was established that the photooxidation rate of semiconducting polymers in their mixtures with organic molecules having a high electron affinity (electron acceptors) decreases significantly under illumination in the polymer absorption band. For example, it was found that the photooxidation rate of the semiconducting polymer belonging to soluble polyparaphenylene vinylenes (MDMO-PPV) in its mixtures with

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fullerenes decreases by an order of magnitude in natural atmosphere [6]. The measurements were performed by IR spectroscopy. Recent investigations by this method have revealed that the characteristic photooxidation rate of similar polymer MEH-PPV in a mixture with the electron acceptor 2,4,7-trinitrofluorenone (Fig. 1) decreases by a factor of more than 1000 [7]. This decrease in the photooxidation rate in the mixture was explained by switching off the channel of photoexcitation relaxation into the polymer triplet states.
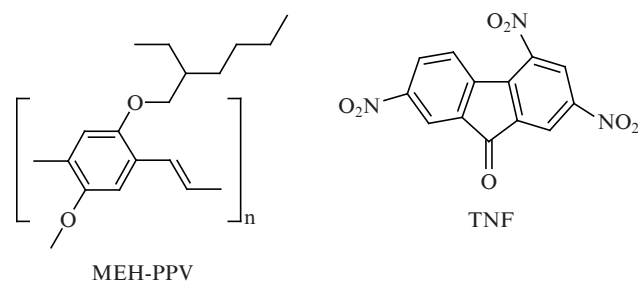
Figure 1. Structural chemical formulas of MEH-PPV and TNF.

At the same time, the photooxidative degradation of semiconducting polymers can be investigated by bleaching their fundamental absorption band in the visible range [8] (Fig. 2). To this end, it is convenient to use a simple method of laser photobleaching, which was proposed to study the degradation of organic dyes in a matrix [9]. This method is based on recording the sample-transmission kinetics under a burning laser beam; it was applied previously to study the photodegradation of polyparaphenylene vinylene (PPV) derivative [10]. It was shown that the photodegradation rate increases monotonically with increasing oxygen content in the atmospheric environment and, correspondingly, is related to photooxidation.

To identify the mechanisms of photooxidation in semiconducting polymers, it is important to determine the dependence of the photooxidation rate on the burning wavelength. Indeed, new energy relaxation channels affecting the photooxidation rate may arise under shorter wavelength excitation. For example, at a fairly high photon energy, a singlet exciton in the polymer may rapidly decay into two triplet states [11], through which photooxidation proceeds. In addition, a specific feature of semiconducting polymer photodegradation is that the longest chains, which correspond to long-wavelength chromophores, are generally the first to oxidise. In this case, the oxidation of long chains may lead to the formation of
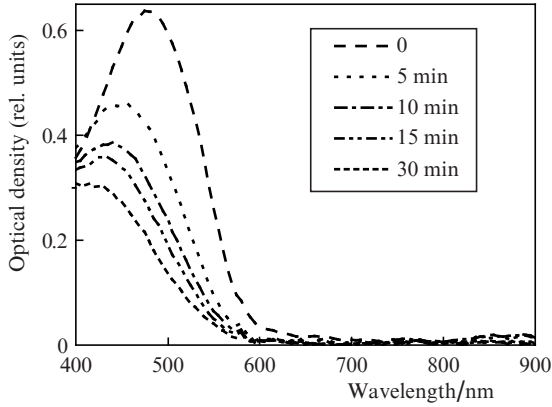
Figure 2. Absorption spectra of a 60-nm-thick MEH-PPV film on a glass substrate for different burning exposures.

shorter chains, which absorb at short wavelengths. As a result, the polymer absorption band is bleached nonuniformly: the long-wavelength region is the first to disappear (Fig. 2). Therefore, to study the dependence of the photooxidation rate on the excitation wavelength, it is important to have a possibility of pumping and probing at different wavelengths. Moreover, one would expect that the maximum sensitivity to photobleaching can be implemented by choosing the probe wavelength near the maximum slope of the polymer fundamental absorption edge. At the same time, the laser photobleaching method was developed for one wavelength [9, 10]. In this study, the method is extended to different pump and probe wavelengths and used to study the photodegradation of mixtures of one of the best studied semiconducting polymers MEH-PPV with the electron acceptor TNF. It is shown that the photooxidation rate in the mixture of MEH-PPV with TNF decreases by four orders of magnitude.

2. Photobleaching model for different pump and probe wavelengths

To simplify the problem, we will neglect the distribution over the lengths of conjugated polymer segments and assume that there is one type of chromophores with a concentration decreasing under photobleaching. We will also assume that the degradation rate depends linearly on the excitation-beam intensity (this was observed for a PPV-type polymer [10]). To describe quantitatively photodegradation, we introduce the photodegradation quantum yield γ, defined as the inverse number of photons absorbed by a chromophore and causing its bleaching (destruction) [9]. Let a laser beam with a wavelength λ_0 (frequency ν_0) irradiate a sample (a film on a transparent substrate) for a time t, after which the sample transmission is measured by a laser beam with a wavelength λ_1. We will consider this problem in the one-dimensional geometry. The absorption coefficient $\alpha(z,t)$ is determined by the concentration of chromophores (conjugated polymer fragments) N at a depth z in the film:

$$\alpha_{0,1}(z,t) = \sigma_{0,1} N(z,t), \tag{1}$$

where $\sigma_{0,1}$ are the absorption cross sections at the wavelengths λ_0 and λ_1, respectively. The photobleaching-induced decrease in the concentration $N(z,t)$ with time can be written as

$$\frac{\partial N(z,t)}{\partial t} = -\gamma \sigma_0 N(z,t) \frac{I_0(z,t)}{h\nu_0}, \tag{2}$$

where the change in the photon flux $I_0(z,t)$ along the propagation direction z is determined by the formula

$$\frac{\partial I_0(z,t)}{\partial t} = -\sigma_0 N(z,t) I_0(z,t). \tag{3}$$

Let us write a similar expression for the change in the probe-beam intensity $I_1(z,t)$

$$\frac{\partial I_1(z,t)}{\partial t} = -\sigma_1 N(z,t) I_1(z,t). \tag{4}$$

and impose the boundary conditions

$$I_0(z=0,t) = I_{00}, \; I_1(z=0,t) = I_{10} \tag{5}$$

and the initial condition

$$N(z,t=0) = N_0. \tag{6}$$

The solution to this system of equations can be written as

$$I_1(L,t) = \frac{I_{10}}{\left\{ [\exp(\sigma_0 N_0 L) - 1]\left[\exp\left(-\sigma_0 \frac{I_{00}}{h\nu_0}\gamma t\right) + 1\right]\right\}^{\sigma_1/\sigma_0}}. \tag{7}$$

The transmittance of a film of thickness L, with allowance for the substrate transmittance $T_{1\infty}$, is determined by the expression

$$T_1(t) = [I_1(L,t)/I_{10}] \, T_{1\infty}. \tag{8}$$

Thus, the time dependence of the sample transmittance at the wavelength λ_1 has the form

$$T_1(t) = T_{1\infty}\left\{\left[\left(\frac{T_{1\infty}}{T_{10}}\right)^{\sigma_0/\sigma_1} - 1\right]\exp\left(-\sigma_0 \frac{I_{00}}{h\nu_0}\gamma t\right) + 1\right\}^{\sigma_0/\sigma_1}, \tag{9}$$

where $T_{1\infty}$ and T_{10} are, respectively, the sample transmittances at $t \to \infty$ (at the end of photobleaching) and $t = 0$.

Thus, the experimental kinetic dependences of the sample transmittance can be approximated by formula (9) to determine the photodegradation rate

$$k = \frac{\sigma_0 I_{00}\gamma}{h\nu_0} \tag{10}$$

and photodegradation quantum yield

$$\gamma = \frac{h\nu_0 k N_0}{\alpha_0 I_{00}}, \tag{11}$$

where $\alpha_0 = \sigma_0 N$.

3. Experimental

Films of mixtures of MEH-PPV with the acceptor TNF were deposited on glass substrates by spin-coating at 1500 rpm from a solution in chlorobenzene with a characteristic polymer concentration of 5 g L^{-1}; the films were no more than 50 nm thick. The molar donor/acceptor ratio in the mixture varied from 1:0.0001 to 1:0.4.

The sample was placed on a diaphragm 0.43 mm in diameter so that to ensure incidence of laser beam on the sample from the side of the film. The radius of the focused pump

beam exceeded significantly the diaphragm radius. A pump source was an argon laser working at wavelengths of 488 and 514 nm. A probe 532-nm laser beam passed through the sample to fall on a silicon photodetector, the output signal of which arrived at a lock-in detector. The probe beam was modulated by a mechanical chopper of the lock-in detector with a frequency of 75 Hz. The pump- and probe-beam intensities were 2.4 – 3.5 and 0.2 mW cm^{-2}, respectively.

4. Results

We measured the kinetic dependences of the transmittance of MEH-PPV : TNF films. Because different films had different optical thicknesses, we report the dependences for the normalised transmittance. These dependences on the exposure time, obtained with a 514-nm burning beam, are shown in Fig. 3 for different ratios of the MEH-PPV : TNF mixture components. One can see that the transmittance increases with increasing exposure time. Note that the kinetic dependences are different for different molar fractions of the acceptor in the mixture. In the mixtures with a low acceptor content (below 0.004) the transmittance increases more rapidly than in the mixtures with a high acceptor content. Thus, the mixtures with a higher molar content of the acceptor are bleached more slowly; i.e., they are more photostable.
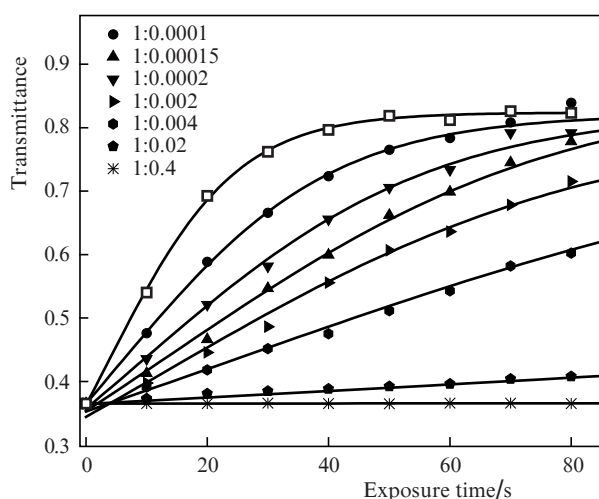
Figure 3. Kinetic dependences of the transmittance of MEH-PPV : TNF films for different ratios of mixture components (closed symbols) at a burning wavelength of 514 nm. The lines are the results of approximation according to formula (9) with the following parameters: $T_{1\infty} = 0.82$, $T_{10} = 0.37$, and $\sigma_0/\sigma_1 = 1.22$. The dependence of the MEH-PPV film transmittance is shown by open symbols.

Based on the experimental data obtained, we calculated the photodegradation quantum yield. The obtained experimental kinetic dependences of the transmittance were approximated by the theoretical dependence (9) for each molar fraction of the acceptor. Similar results were obtained for burning at 488 nm.

Figure 4 shows the dependences of the photodegradation quantum yield γ, calculated from the data in Fig. 3 according to formula (10), as functions of the TNF molar fraction in the film at pump wavelengths of 488 and 514 nm. One can see that adding TNF reduces the degradation quantum yield of MEH-PPV by at least four orders of magnitude (to approxi-

mately 2×10^{-8}, a value determined by the experimental error). These measurement errors are due to the error in approximating the kinetic curves in Fig. 3. The spread of the experimental data in Fig. 4 is also caused by fluctuations (which are difficult to control) of the degradation rate of the samples prepared under nominally identical conditions. The behaviour of the curves in Fig. 4 suggests that the photodegradation quantum yield coincides for two used burning pump wavelengths within the experimental error.
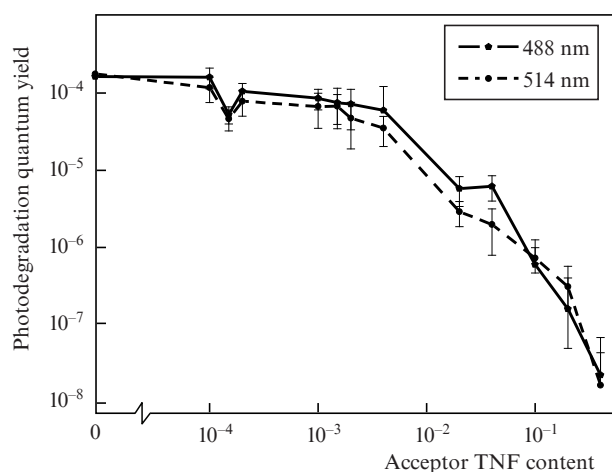
Figure 4. Dependence of the photodegradation quantum yield on the TNF content in MEH-PPV : TNF films for two burning wavelengths. The photodegradation quantum yield was calculated from formula (11) for $N_0 = 10^{21}$ cm^{-3} and $\alpha_0 = d^{-1}(T_{1\infty}/T_{10})$, $(d = 50$ nm).

5. Discussion

The obtained dependence of the photodegradation quantum yield of MEH-PPV on the TNF content shows that adding the acceptor to the mixture decreases significantly this parameter (up to four orders of magnitude). It follows from these results that the conjugated polymer MEH-PPV in a mixture in natural atmosphere can absorb no less than 10^8 photons without any noticeable photodegradation.

We compared the obtained dependences of the photodegradation rates of MEH-PPV:TNF films with the results of [7], where MEH-PPV : TNF films were investigated by IR spectroscopy at a burning wavelength of 532 nm. Figure 5 shows the photodegradation rates of MEH-PPV:TNF films determined by two methods. Note that IR spectroscopy was performed on much thicker films, prepared by the drop-casting technique (the characteristic thickness was several hundreds of nanometers). The differences in the photodegradation rates of the films can also be related to the difference in their preparation conditions [12]. For example, the longer time of solvent removal in the case of drop-cast films is known to facilitate the acceptor aggregation, which, in turn, may decrease the local concentration of the acceptor dispersed in the polymer matrix. This circumstance explains the higher photodegradation rate found by IR spectroscopy. Nevertheless, the photodegradation rates of MEH-PPV:TNF films obtained by laser photobleaching and IR spectroscopy are in good correlation.

As was noted in the Introduction, a possible cause of the photodegradation of a conjugated polymer is that the absorption of a photon leads to the formation of long-lived triplet
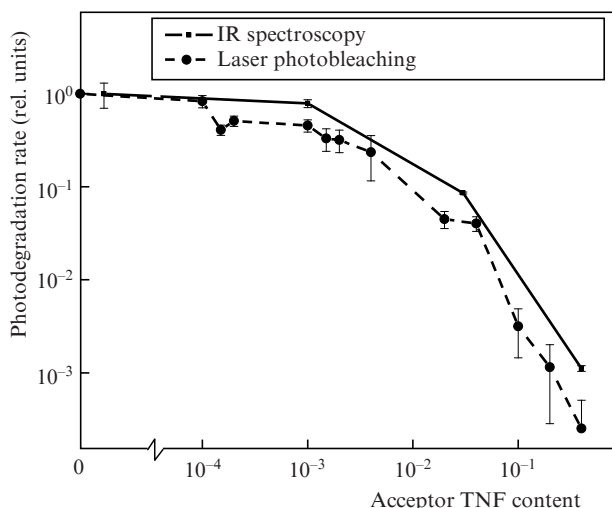
Figure 5. Dependences of the photodegradation rate of MEH-PPV films on the TNF content, obtained by IR spectroscopy and laser photobleaching.

states [1], which are involved in the polymer photooxidation [5]. The experimental results show that the polymer photodegradation rate is reduced significantly after adding acceptor to polymer, which can be explained by the decrease in the occupation rate of the polymer triplet states. This explanation is confirmed by the observed correlation between the photodegradation rate and the photoluminescence quenching efficiency [13].

The decrease in the occupation rate of triplet states can be caused by the formation of fast nonradiative channel of polymer singlet-state relaxation. The formation of this channel is evidenced by the high efficiency of photoluminescence quenching in MEH-PPV:TNF [14] films; this efficiency is due to the formation of complex with polymer–acceptor charge transfer. The photoexcitation energy can be efficiently transferred from the polymer singlet state to the acceptor for a time that is much shorter than the characteristic times of photoluminescence (several hundreds of picoseconds) and intersystem crossing (~1 ns).

6. Conclusions

The phenomenological model of photobleaching dynamics of semiconducting polymer films was developed for different pump and probe wavelengths. The transmittance kinetics was investigated for thin films of semiconducting polymer MEH-PPV doped with a low-molecular acceptor TNF, subjected to laser irradiation at wavelengths of 488 and 514 nm in a natural atmosphere. The photodegradation quantum yield was calculated based on the obtained experimental dependences. For the MEH-PPV:TNF = 1:0.4 mixture, this parameter is at least four orders of magnitude smaller than that for pure polymer.

It was shown that the photooxidative degradation rate is the same for the two wavelengths used. Thus, the developed method allows one to investigate the materials with significantly different photodegradation rates. The results obtained indicate that MEH-PPV:TNF composite films are promising for various photonic devices.

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