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ARTICLE TYPE

ESR spectroscopy for monitoring photochemical and thermal degradation of conjugated polymers used as electron donor materials in organic bulk heterojunction solar cells

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It was shown that ESR spectroscopy represents very useful technique for monitoring photochemical and thermal degradation of conjugated polymers commonly used in organic solar cells. Relative stability of materials can be quantified by comparing the rates of trap accumulation (dC_R/dt) estimated from their ESR profiles.

The efficiency of organic fullerene/polymer bulk heterojunction solar cells has been increased substantially during the last few years mainly due to the design and implementation of novel electron donor materials with advanced optoelectronic properties.¹ However, major concerns regarding their stability have appeared.²

It is known that even simple and robust non-conjugated polymers such as polypropylene, polystyrene or PMMA require special stabilizing additives to sustain simultaneous action of light, oxygen and moisture.³ Conjugated polymers are rather fragile substances and it is clear that they will require special protection in aggressive environment. Therefore, most probably, organic solar cells can be applied practically only in combination with appropriate barrier layers which can prevent (or at least diminish substantially) penetration of oxygen and moisture in the active layer of organic solar cells. However, the action of light and elevated temperatures cannot be avoided under the real solar cell operation conditions. This is a reason why investigation of photostability of conjugated polymers and fullerene/polymer blends under anaerobic conditions attracts more and more attention.⁴

Here we have applied ESR spectroscopy for monitoring photochemical and thermal degradation of several different conjugated polymers in the absence of oxygen and moisture. The light-induced ESR (LESR) spectroscopy was used previously for investigation of the photoinduced charge separation in the fullerene/polymer blends,⁵ charge recombination kinetics,⁶ distribution of trap states in conjugated polymers⁷ and their accumulation during aging of P3DDT/[60]PCBM blends.⁸ The ESR spectra obtained in the absence of light (dark ESR) were used to study degradation of conjugated polymers in air⁹ and determination of defects in inorganic semiconductors.¹⁰ The ESR spectroscopy was also

used previously for monitoring the photodegradation of cellulose and natural (or artificial) skin.¹¹ Recently we have applied ESR spectroscopy for assessment of electronic quality of conjugated polymers designed for photovoltaic applications¹² and investigation of their photostability.¹³ More recently similar approach was used to investigate photodegradation of PCDTBT/PCBM blends.⁴ Here we report results of a comparative study of seven different conjugated polymers whose molecular structures are shown in Fig. 1.

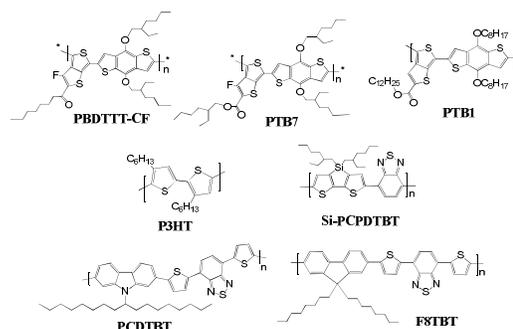


Figure 1. Molecular structures of investigated polymers

Our initial hypothesis was based on the assumption that some minor fraction of excitons generated in the polymer films under illumination undergo non-radiative quenching leading to the rupture of some chemical bonds and formation of novel species. Some of these species might represent stable radicals which could be detected by ESR spectroscopy. We have shown previously that such radical species behave as deep traps for mobile charge carriers and affect severely the performance of different conjugated polymers in organic solar cells.¹² Therefore, continuous illumination of polymer samples is expected to result in accumulation of radical species and degradation of their photovoltaic properties.

To investigate the photostability of conjugated polymers (Fig. 1), their thin films were deposited inside the ESR sample tubes and sealed in the atmosphere of extra pure helium. The sealed tubes were constantly illuminated with except for a time when the ESR spectra were measured (see more details in Electronic Supplementary Information, ESI).

Indeed, the performed experiments have revealed that

conjugated polymers undergo degradation under illumination with visible light resulting in gradual accumulation of free radical species. This behavior is clearly illustrated by exemplary sets of the ESR spectra obtained for conjugated polymers PTB7 and PBDTTT-CF (Fig. 2, Fig. S1, ESI).

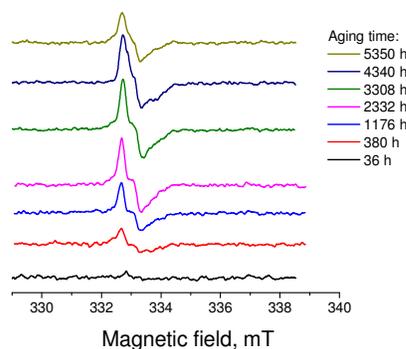


Figure 2. Evolution of the ESR spectra of PTB7 sample in the course of photothermal aging

Both polymers contained initially very low concentrations of radical species. However, aging resulted in the appearance of strong and unsymmetrical signals in the ESR spectra suggesting simultaneous formation of few different radical species. Interpretation of these spectra in terms of defining structural localizations of the radical centers in the polymer chains is not possible at the present stage. It is notable that intensity of the signals in the ESR spectra of PTB7 and PBDTTT-CF decreased when the aging time approached 4000-5000 hrs. We believe that continuous structural degradation of conjugated polymers at some point starts to affect stability of radical species and the rate of their quenching becomes higher than the generation rate. The conjugated polymers PTB1, F8TBT and Si-PCPDTBT demonstrated very similar trends as compared to PTB7 and PBDTTT-CF (Fig. 3).

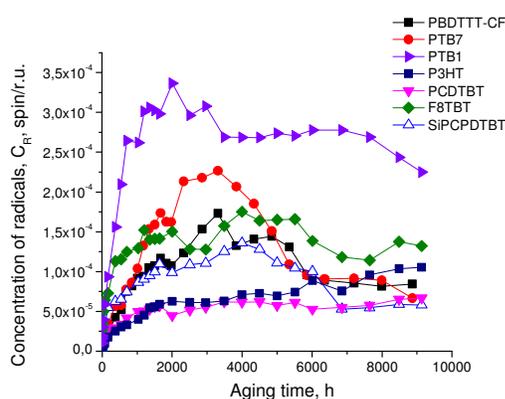


Figure 3. Degradation profiles of conjugated polymers under photothermal aging conditions obtained using ESR spectroscopy. The concentration of the radical species is expressed as a number of spins per one repeating unit (r.u.) in a polymer chain.

On the contrary, P3HT and PCDTBT have revealed rather different behavior. The contents of the radical species in P3HT and PCDTBT films were considerably lower compared to all other investigated polymers. Moreover, the

concentrations of radicals did not decrease even at long aging time of 9000 hrs. Both observations support a preliminary conclusion about superior stability of P3HT and PCDTBT.

In order to compare the stability of the investigated conjugated polymers, we have analyzed their degradation profiles revealed using ESR spectroscopy (Fig. 3). It should be noted that concentrations of the radical species depend almost linearly on the aging time for all conjugated polymers in the time frame between ~100 and 1000-1300 h (Fig. 4a). The slopes of the linear fits presented in Fig.4a define the initial rates of accumulation of radicals R_{in} . The values of R_{in} estimated for each polymer are given in Table S1, ESI. Alternatively, one can also calculate average rates of accumulation of radicals R_{av} defined as $C_R(max)/T(max)$, where $C_R(max)$ is a maximal concentration of radical species observed for a certain polymer, while $T(max)$ is a time when this maximal concentration was reached (Table S1, ESI).

It should be emphasized that comparison of R_{in} and R_{av} values obtained for different conjugated polymers leads to very similar conclusions regarding the relative stability of these materials (Fig. 4b). It is reasonable to assume that the least stable materials are characterized by the highest R_{in} and R_{av} values and *vice versa*. The experimental data presented in Table S1 and Fig. S4 strongly suggest that P3HT and, especially, PCDTBT are the most stable conjugated polymers. On the contrary, PTB1, PTB7 and PBDTTT-CF comprising thieno[3,4-b]thiophene units in their molecular frameworks demonstrated the lowest stability.

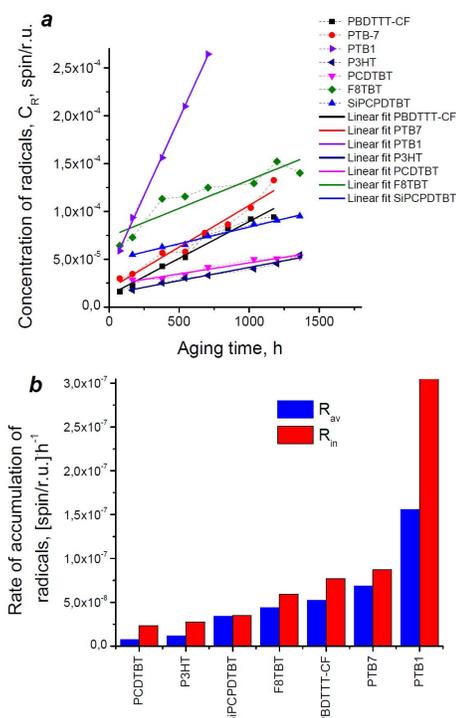


Figure 4. Selected linear part of the degradation profiles of different conjugated polymers and corresponding linear fits (a). Comparison of the relative initial (R_{in}) and average (R_{av}) rates of accumulation of radical species by different conjugated polymers (b).

It is notable also that the presence of fluorine atoms in the

thieno[3,4-b]thiophene units of PTB7 and PBDTTT-CF results in a substantial stabilization of these two polymers as compared to PTB1 possessing no fluorine atoms.

Discrimination of the degradation effects induced either by illumination or by heating is another important issue. It is rather challenging to realize the conditions when illumination of the polymer samples with high power light does not lead to increase in the temperature (at least local) of the analyzed material. On the contrary, it is easy to exclude the light and maintain the required temperature in a chamber with the test samples. We have incubated the samples of the investigated conjugated polymers (prepared in sealed ESR tubes as described above) in dark at the temperature of 88-90 °C in order to observe heat-induced degradation effects. The obtained degradation profiles are shown in Fig. S2 (ESI). It is seen from the fig. S2 and Table S1 that conjugated polymers PTB1 and PBDTTT-CF undergo facile thermal destruction resulting in a massive accumulation of radical species. PBT7 was found to be much more stable compared to PTB1 and PBDTTT-CF; however, it also degrades within 10000 h. Some minor degradation was observed also for F8TBT and P3HT (not shown). In the latter case the initially formed trace amounts of radical species have disappeared after 2000-3000 h. Such behavior suggests that the observed radicals originate most probably from a trace impurity (e.g. oxygen) in the P3HT sample rather than from thermal degradation of the polymer itself. Finally, no signs of the thermal degradation were revealed for PCDTBT and SiPCPDTBT.

In conclusion, we have demonstrated that ESR spectroscopy represents very useful technique not just for controlling the quality of organic semiconductor materials (our recent report¹²), but also for monitoring their photochemical and thermal degradation and comparing the stability of different materials designed for photovoltaic applications.

The obtained results imply that light is the most crucial factor inducing degradation of polymers PCDTBT, SiPCPDTBT, F8TBT and P3HT, while heat along leads to very minor effect (F8TBT) or has no influence at all (PCDTBT, SiPCPDTBT). On the contrary, thermal degradation of polymers PTB1 and PBDTTT-CF proceeds with comparable rates to photochemical degradation.

Conjugated polymers comprising thieno[3,4-b]thiophene units (PTBT1, PTB7, PBDTTT-CF, PBDTTT-CT, and etc.) are extensively studied nowadays by many research groups around the world as promising electron donor materials providing high efficiencies (7-9%) in organic solar cells.^{1,14} However, the results presented in this work strongly suggest that this type of materials can hardly find any practical applications due to their inferior thermal and photochemical stability. More stable materials resembling the behavior of conjugated copolymer PCDTBT (and also P3HT to some extent) have to be designed to meet long-term stability criteria required for real outdoor implementation of organic photovoltaics.

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- [†] Electronic Supplementary Information (ESI) available: detailed description of the experimental procedure; the ESR spectra of PBDTTT-CF; the thermal degradation profiles revealed for conjugated polymers; the numerical data on the degradation rates of the analyzed conjugated polymers. See DOI: 10.1039/b000000x/
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