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Photoreactivity of poly(*p*-phenylphenylenevinylene)

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Summary

In films of poly(para-phenylphenylenevinylene) a photoreaction has been observed. The significant feature is a decrease of the fluorescence emission intensity during irradiation. It is assumed that a cycloaddition between C=C- double-bonds leads to crosslinks in the material.
Under similar conditions of excitation a photoreaction has not been observed in poly(p-phenylenevinylene) prepared via the precursor-route.

Introduction

Photoreactivity of polymers has been studied extensively. Typical reactions are degradation, dimerization and isomerization (1). Photosensitive polymers are technically important, e.g. as negative photoresists (1).
Special attention has been paid to polymers containing C=C-double-bonds. Well known examples are poly(vinylcinnamate) and polyesters based on para-phenylenebis(acrylic acid). The first contains the unsaturated group in the side chain, the second in the main chain (2 - 5). These materials are capable of being crosslinked by photoreaction, which is a $(2\pi+2\pi)$-cycloaddition between two C=C-double-bonds leading to a cyclobutane ring (1, 5, 6). The dimerization forms a crosslink when the double-bonds belong to different polymer chains.
A repetitive cycloaddition in diolefinic monomers leads to polymerization (7), e.g. for distyrylbenzene (8).
The cycloaddition can also be induced thermally (9). This has been observed for various polymers with chromophores based on para-phenylenebis(acrylic acid), para-carboxylic cinnamic acid (5) or para-distyrylbenzene (10). In polymers containing stilbene units in the main chain, crosslinking only occurs during irradiation at elevated temperatures (5).

Polymers with a conjugated backbone, e.g. poly(p-phenylenevinylene) and its derivatives, have received much interest during the last years (11 - 14).
Conjugation of the main chain can be interrupted by geometrical distortions or chemical defects. This leads to a description of those polymers by a chain consisting of a distribution of oligomeric segments (15, 16). Recently, one of the authors (17) has described a solidification of the melt of various derivatives of poly(p-phenylenevinylene). It was concluded that crosslinking via vinylene-units is responsible for this effect.

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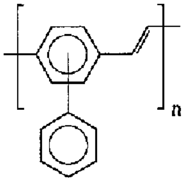
The aim of this note is to report photoreactivity of poly(p-phenylphenylenevinylene) in comparison with poly(p-phenylenevinylene) and an oligomeric model compound.
To our knowledge, photoreactivity has not been described for phenylene-vinylene polymers: Meier (18) reported a long-term-stability for derivaties of PPV when irradiated with λ = 436 nm; Rentsch et al. (19) observed no degradation of poly(phenylenearylvinylene) while performing photoinduced absorption mesasurements at an excitation wavelength of 351 nm.

Experimental

Poly(p-phenylphenylenevinylene) (PPPV, **1**) was synthesized via a Heck reaction (17). The polymer has all-trans configuration with respect to the C=C-double-bonds and a molar mass of M_W = 7100 g/mol (20). Spin-coated films of PPPV on glass plates were prepared with a thickness of about 0.2 µm from solution in tetrahydrofuran. Extinction of these films was between 0.1 and 0.2 at the long wavelength maximum (410 nm). In addition, dilute solutions of PPPV in polystyrene films and in tetrahydrofuran were prepared.
Poly(p-phenylenevinylene) (PPV) was synthesized by M. Lux, Bayreuth, via the precursor-route (21) and was received as a film, 10 µm thick.
The polymers were compared with an oligomeric model compound, trans-trans-p-distyrylbenzene (DSB, **2**), which was received from H. Meier, Mainz.



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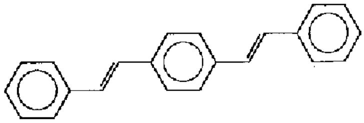

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Fluorescence experiments were carried out on a Spex-Fluorolog spectrometer with usual 90°-geometry between excitation and emission, double grating monochromators and a 450 W xenon-lamp for excitation.
Irradiation of the samples was performed in the spectrometer using just the exciting light needed for creating fluorescence. The angle of incidence was 60°.

Results and discussion

For dilute solutions of both, DSB and PPPV, the fluorescence intensity at a chosen pair of excitation (λ_{ex}) and emission (λ_{em}) wavelengths (360/415 nm and 400/480 nm, respectively) remains unchanged during an one hour illumination. No photochemical processes are observed that change the number of emitting chromophores. This is in contrast to the behaviour of trans-stilbene, where an intramolecular trans-cis-isomerization leads to a decrease of the absolute fluorescence quantum yield (9). Silbene is a subunit of the model compound DSB.

For a pure film of PPPV a significant decrease of the fluorescence intensity is observed, as demonstrated in figure 1 with λ_{ex} = 400 nm and λ_{em} = 530 nm.

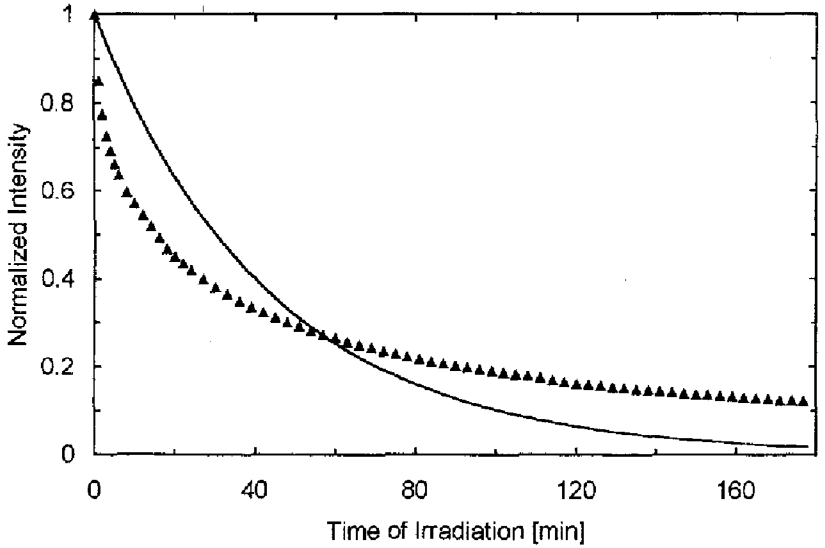

Figure 1: Normalized fluorescence intensity versus time during irradiation of a PPPV-film on a glass plate (▲, λ_{ex} = 400 nm, λ_{em} = 530 nm, slit width excitation 3.6nm / emission 1.8 nm). The full line represents a least-square mono-exponential fit.

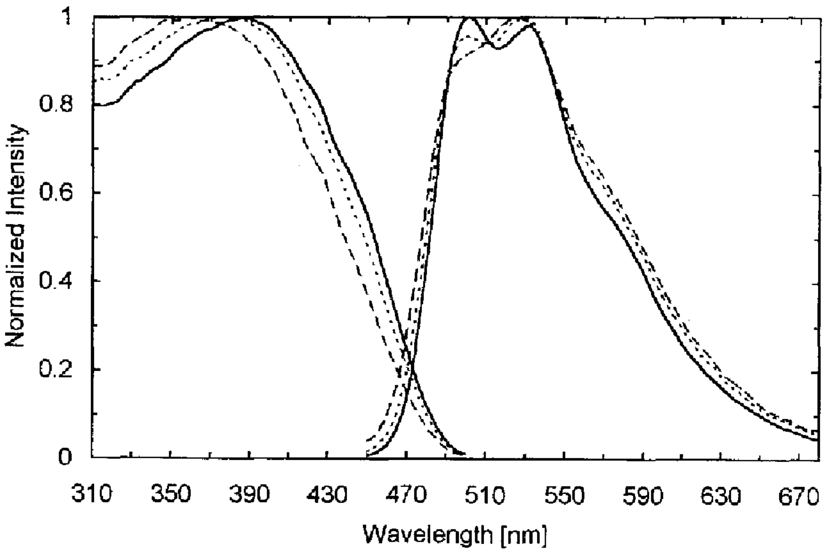

Figure 2: Normalized excitation (λ_{em} =520 nm) and emission spectra (λ_{ex} = 400 nm) of a PPPV-Film on a glass plate at various degrees of photoreaction (slit width 1 nm/3 nm). Irradiation was performed at a slit width of 3 nm (λ_{ex} = 400 nm). The ratio I/I_0 (see text) is 1 (———), 0,65 (· · · · ·), 0,38 (– – –).

Obviously, the decrease in fluorescence intensity indicates that the number of emitting chromophores is reduced. We assume that this is mainly caused by a reduction of the number of absorbing chromophores. This is confirmed by UV/vis-absorption spectra showing significant differences before and after the experiment: the long wavelength maximum at about 410 nm of PPPV disappears during irradiation. Additionally, a change in fluorescence quantum yield may also happen; one is not able to separate this effect from the decreasing concentration of chromophores.
The plot intensity versus time (fig. 1) is obviously not mono-exponential, because not only the number, but also the reactivity of the remaining sites suitable for photoreaction is reduced. Egerton et al. (6) investigated this point in detail for poly(vinylcinnamate).

Figure 2 displays normalized fluorescence spectra consecutively recorded for one film of PPPV at various steps of the photoreaction in progress. This is expressed by the ratio I/I_0. I_0 is the fluorescence intensity at the start of irradiation and I the intensity at the start of recording the corresponding spectra. The respective irradiation time for the spectra in fig. 2 can be approximately estimated applying fig. 1 for the given ratios I/I_0.
During irradiation excitation spectra shift to shorter wavelength. In the emission spectra the ratio of the two peaks changes in favour of the one at longer wavelength. A photoreaction takes place that appears to be intermolecular, because it is not observed in dilute solutions.
The fluorescence spectra of the emitting chromophores does not change dramatically: photoproducts may not absorb at λ_{ex} = 400 nm or may transfer their excitation energy to remaining PPPV-segments.

For distyrylbenzene, casted on a glass plate from solution, we also observe a decrease of the fluorescence intensity during illumination. In this system the decay in the corresponding plot is not as fast as for PPPV. It is concluded that the decrease results from the photopolymerization based on a $(2\pi+2\pi)$-cycloaddition, similar to the mechanism reported by Oelkrug et al. (8) for concentrated solutions of this compound.
We assume that a similar reaction takes place in PPPV, too. This would lead to crosslinks in the material, with a loss of conjugation at these sites. Tests, whether the irradiated area shows a decreased solubility in tetrahydrofuran as an effect of crosslinking, were not conclusive so far.
A shorter effective conjugation length is responsible for the blue shift of the excitation spectra. Emission spectra are only slightly changed, because energetically favoured chromophores, not influenced by crosslinking, are populated by excitation energy transfer prior to emission.

Within this interpretation, the photoprocess is similar to the thermally induced crosslinking of PPPV described earlier (17), i.e. the cycloaddition can be induced thermally and photochemically.

It could be expected that the described photoreaction should also be possible in PPV. Actually, however, no significant changes in fluorescence intensity during irradiation of PPV at an excitation wavelength of 350 nm (slit width 4.5 nm) were observed.

One possible explanation for this result might be that the distance between adjacent C=C-double bonds is too far in the crystalline regions of PPV; this is also known from trans-stilbene, which shows no dimerization in the crystalline state(18).
Another possible reason could be that during preparation the PPV material has already been crosslinked at the reactive sites. This may happen during the process of thermal elimination of the precursor polymer.

In summary, a photoreactivity in poly(p-phenylphenylenevinylene) as determined by a decrease in fluorescence intensity, has been observed. This is in contrast to the behaviour of poly(p-phenylenvinylene) prepared by the precursor route.
A more detailed investigation is necessary, especially concerning the exact nature of the process and its dependence on the wavelength of irradiation.

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