

Long-lasting photoluminescence in polymers

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Abstract

Several solid polymers of technical importance like polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), ethylene-tetrafluoroethylene-copolymer (ETFE), polyetheretherketone (PEEK) and polypropylene (PP) show a long-lasting, spectrally broad luminescence after irradiation with ultraviolet light of low intensity. With a sensitive photo detection system the luminescence decay is registered for several hours. The decay curves can be approximated by an inverse power law with fractional exponent, partly showing a pronounced temperature dependence. Qualitatively, the luminescence emission can be understood as arising from radiative recombination of trapped charges that diffuse under thermal activation.

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1 Introduction

Many solids exhibit a low level of transient luminescence that may persist for hours after a temporally limited excitation process has been terminated. Light, ionising radiation, electric fields, mechanical pressure or other perturbations may separate charges that can diffuse and may become trapped. Depending on the depth of the trap, they may relax or recombine under the emission of light only after a considerable delay or after external activation via heat, light or other stimuli. Especially thermoluminescence, initiated by ionising radiation and activated by heat, has found widespread applications in dosimetry and in archeological and geological dating [1]. Here we study long lasting isothermal photoluminescence in some polymers of technical importance, initiated by irradiation with low-intensity ultraviolet or visible light at room temperature.

A comprehensive study of photoluminescence in 98 commercial solid polymer materials was published in 1987 by Mendenhall and Agarwal [2]. An incandescent lamp, spectrally filtered to the wavelength range 300–1000 nm, was used as the excitation light source. Luminescence decay curves were recorded up to 600 s for some samples. Under these conditions, 62 of the 98 materials were reported not to show luminescence. Here we show that some of those materials – including the widely applied fluoropolymers PTFE and PVDF – exhibit significant levels of photoluminescence after excitation with ultraviolet light. A sensitive photo detection setup allowed us to follow some decay curves for many hours. Table 1 lists the names and abbreviations of the polymer materials that are studied here.

The long temporal delay that is observed between photo-excitation and the emission of light rule out any process where energy is stored in metastable excited molecular states. In studies of photoluminescence in polymers complicated, non-exponential decay characteristics have been observed, for example due to triplet recombination, on timescales below 1 s [3, 4, 5]. Without attempting a detailed study of the processes underlying the long-lasting luminescence in the present experiments, one may assume that the ultraviolet radiation that is used here leads to ionisation and possibly also to breaking of the polymer chain and the creation of radicals. Electrons may diffuse on the polymer chain or even between chains and may become trapped. For the unordered polymer materials a wide distribution of trap depths and diffusion lengths may be assumed that the electron has to overcome before finally recombining. This leads to a wide distribution of electron lifetimes. We will show that thermal activation plays an important role in determining the rate of luminescence emission.

Table 1: Abbreviations and names of polymers studied in this work. m -values: fractional exponent for the isothermal luminescence decay at room temperature (cf. Sec. 3). If applicable, two values for m are given: m_1 for the temporal range from 500-10000 s and m_2 for the long-term behaviour beyond 20000 s.

Abbr.	Name	m_1	m_2
ETFE	ethylene-tetrafluoroethylene-copolymer	0.3	0.8
PEI	polyetherimide	0.7	
PES	polyarylethersulfone	0.6	
PEEK	polyetheretherketone		1.0
POM	polyoxymethylene	0.7	
PP	polypropylene	1.2	0.8
PSU	polysulfone	0.9	
PTFE	polytetrafluoroethylene	1.0	
PVDF	polyvinylidene fluoride	0.5	0.9

2 Experimental

The polymers studied here (cf. Table 1) are in the form of bulk plastics of typical dimensions $4 \times 4 \times 1 \text{ cm}^3$ ¹ While PEEK is of beige color and opaque, PEI and PSU are amber and transparent, PES is brownish and translucent, whereas POM, PP, ETFE, PTFE, and PVDF are whitish and translucent. Some of the materials show detectable luminescence already after exposure to indirect sunlight, most notably PEEK, and also PSU, PEI, PES, POM, and PP. For quantitative experiments, ultraviolet excitation with a low-pressure mercury discharge lamp is used with an intensity of approximately 5 mW/cm^2 and a spectrum that consists essentially of the two resonance lines of Hg atoms at 254 nm and 185 nm. Less than 7% of the intensity of the lamp is emitted as visible light. Samples were exposed to the uv light for typically 60 s. The low intensity illumination does not lead to any noticeable heating of the sample. In some of the experiments forced venting with air was employed to avoid oxidation of the polymer from the ozone produced by the lamp. No difference in the luminescence properties is detected when this measure was not taken. Because only the long-term behaviour of the luminescence is of interest here, the samples were manually transferred from the illumination area into a light-tight box that houses the detection system. Detection typically started 20–30 s after the excitation had been terminated. The photon detector is a photomultiplier tube (PMT) with bialkali photocathode that is sensitive in the spectral range from 185 nm to 680 nm (quantum efficiency $> 1\%$) and reaches a maximum quantum efficiency of nearly 25% for blue and ultraviolet photons. The PMT is operated in the photon counting mode and shows a dark count rate of less than 3 s^{-1} . In order to obtain stable PMT gain and a constant dark count rate for the low-level fluorescence measurements, the high voltage is applied to the PMT at least one hour before the start of the measurement. The PMT housing can be closed off from the sample compartment with a light-tight shutter so that the PMT is not blinded while the sample is mounted. Light from the sample is collected with an off-axis spherical concave reflector of 80 mm diameter, ensuring that about 10% of the photons emitted from the polymer surface reach the photocathode.

3 Photoluminescence decay curves

Figure 1 shows representative photoluminescence decay curves of the polymer materials studied here, plotted on a double-logarithmic scale. With the exception of PP and PEEK, all materials were measured at room temperature (20–22° C) after excitation with the mercury lamp. The PP sample was also excited with the Hg lamp but the sample temperature was actively stabilized at 30° C. In the case of PEEK, activation was by exposure to standard work place illumination from white fluorescent tubes for 10 minutes and the temperature was stabilized at 30° C. The signal background due to photomultiplier dark counts was subtracted from all curves.

¹High purity commercial plastics supplied by the companies Ensinger, Gehr and Thyssen-Krupp-Schulte were used. The samples are specified as being of natural composition, i.e. free from additives.

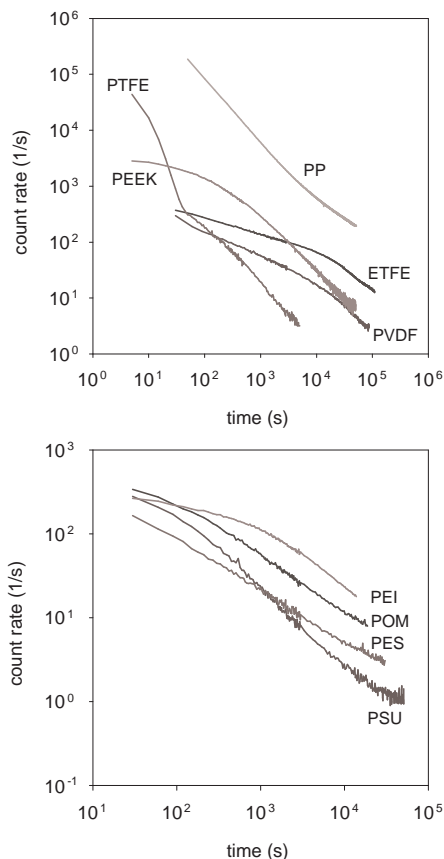


Figure 1: Isothermal photoluminescence decay curves for several polymer materials at room temperature (see text for experimental details).

A characteristic feature of these luminescence signals is the slow temporal decay. The curves of luminescence intensity $I(t)$ versus time cannot be fitted by an exponential $I(t) \propto \exp(-t/\tau)$, neither by a $I(t) \propto 1/t^2$ dependence. The latter would be characteristic for the so-called “bimolecular” decay of the density of luminescence centers N , governed by a $dN/dt \propto -N^2$ differential law. The double logarithmic plot of $I(t)$ shows that for most of the polymers and for significant fractions of the observation time the decay can be described by a function $I(t) \propto 1/t^m$ where m is a fractional exponent in the range $0.3 < m < 1.2$. A decay law of this type was introduced by Debye and Edwards [6] and is often used heuristically in the description of luminescence decays of phosphors. Table 1 lists the m -values for the different polymers and for two different temporal ranges of validity. The range of m -values measured here is consistent with that observed in the photoluminescence decays of other polymers [2]: 0.6 – 1.2. Exponents $m = 1.175$ for PP and $m = 1.029$ for PTFE have been reported for isothermal luminescence decay after excitation with X-radiation [7], in good agreement with our result for uv excitation. In the case of PTFE, an initial exponential decay with a time constant $\tau = 5.4 \pm 0.3$ s can clearly be distinguished from the long-term behaviour that follows quite closely a hyperbolic $I(t) \propto 1/t$ dependence, i.e. $m = 1$. Sintered PTFE and a thin PTFE film produced from a dispersion was also investigated and showed a somewhat smaller m -value of 0.8.

The m -value is convenient to characterize the temporal decay of the luminescence intensity, but it cannot be considered an intrinsic property of these polymers. For this reason we give only one significant figure for most of the results listed in Table 1. In many cases a strong temperature dependence is observed (cf. Sec. 5) and a dependence on the concentration of charges is probable. The luminescence decay in PEEK at times shorter than about 3000 s depends on the spectrum of the light that is used for the excitation. Short wavelengths from the mercury lamp or sunlight lead to luminescence components with faster initial decay, i.e. higher m -value, than excitation from

an incandescent lamp. This indicates that different electron distributions are initially populated. In PVDF with excitation from the Hg lamp, a dependence of m on the thickness of the sample is observed, probably due to the wavelength dependence of the transmission of this translucent material. The thinner sample – with higher relative uv transmission – shows a faster initial decay of the luminescence.

Unlike an exponential decay that is described by a single time constant, the Debye Edwards decay law does not possess a characteristic time scale. If the exponent m fulfills $m < 2$ the distribution of the lifetimes of the electrons before recombination does not even possess a finite mean value. This has led to the notion of “fractal time” [8], related to anomalous diffusion and Lévy distributions. If electrons are trapped and have to be released, either by tunneling or by thermal activation, the trapping time before recombination will depend on the depth of the trap. In an amorphous solid or in crystals with randomly distributed defects, the trap depths may show a wide distribution. Consequently, the ensemble of trapped charges that is created in the photoexcitation is subject to “aging”, with the electrons in the deeper traps leading to luminescence with longer delay time. Several models have been proposed to relate the m -value or other characteristics of nonexponential luminescence decay curves to either the spatial [6, 9] or the energetic distribution [10, 11, 12, 13] of the charges. But, as will be discussed below, none of these models is directly applicable to describe the complex behaviour observed here.

4 Luminescence spectra

The spectral distribution of the luminescence of PTFE, ETFE, PVDF, PEEK and PP was investigated by sequentially placing a series of long-pass filters in front of the photomultiplier during the observation of the luminescence decay curve. The long-pass filter series was chosen with cut-off wavelengths (50% transmission) at 320 nm, 370 nm, 418 nm, 470 nm, 550 nm, and 610 nm ². Measurements were taken in the time interval of 150 s to 700 s after the excitation. Comparison of the first and a second sequence of filter measurements showed that in the cases of PTFE and PVDF emission at shorter wavelengths decays faster so that the center of the emission spectrum slightly shifts towards longer wavelengths with increasing time after the excitation. Quite generally, temporal changes in the shape of the emission spectrum can be expected if the radiative recombination proceeds from a distribution of charges that is subject to “aging” [9, 11] and if different luminescence centers contribute to the spectrum.

Figure 2 shows the distributions of the detected luminescence photons over seven wavelength intervals, as determined from the difference of the filter transmissions. The upper and lower wavelength limits of 190 nm and 680 nm are determined by the sensitivity range of the PMT. Significant emission at wavelengths below 320 nm is only observed from PVDF. The decrease of the signals at long wavelength may partly be due to the decreased sensitivity of the photomultiplier: its quantum efficiency is essentially constant over the wavelength interval 250–450 nm but falls off to about 10% of its peak value at 650 nm. The shape of the spectra of ETFE, PVDF and PP is similar, with the strongest emission in the wavelength region of 470–550 nm. In comparison, the spectrum of PTFE has its center shifted towards shorter wavelength and from PEEK a strong luminescence signal is detected at red wavelengths. Because PEEK is opaque this emission must essentially originate from the surface of the sample. For PTFE, measurements at short delay time show that the wavelength of the exponentially decaying emission with $\tau = 5.4$ s is between 400 and 500 nm. Phosphorescence spectra of polypropylene have been reported previously for excitation by X-radiation [7] and by ultraviolet light [14, 15, 16] and – in agreement with our result presented in Fig 2 – emission was mainly detected in the wavelength range 400–550 nm. In [14] a phosphorescence spectrum of PTFE at the temperature of liquid nitrogen is presented, showing emission in the same range 400–550 nm.

In order to look for correlations between emission and absorption, measurements of the transmission spectra were performed for the translucent materials PTFE, ETFE, PVDF, and PP. In the wavelength range 300–800 nm the transmission of all these samples shows a steady decrease towards shorter wavelengths, indicating that it is limited by nonresonant scattering. The lowest photon energy that is strongly absorbed in PTFE is around 8 eV for a state that is delocalized over the chain and the ionization threshold is 10.6 eV [17], significantly above the highest photon energy

²Schott filters WG 320, KV 370, KV 418, KV 470, KV 550, and RG 610 were used.

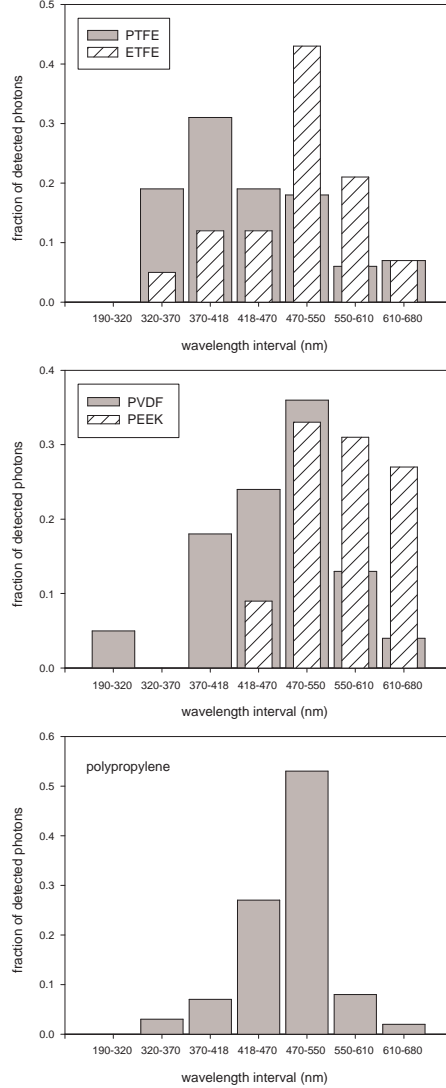


Figure 2: Spectral distributions of the photoluminescence from PTFE, ETFE, PVDF, PEEK and PP measured in seven wavelength intervals as transmission differences through a series of long-pass filters. Measurements were taken in the time interval from 150 s to 700 s after the uv excitation.

of 6.7 eV from the Hg lamp. Ionization and luminescence in the fluoropolymers must therefore be related to defects like unsaturated main chain groups or carbonyl groups, as it was suggested in [14].

5 Temperature dependence of the decay curve

In order to further elucidate the luminescence process, the temperature dependence was studied in the five polymers where luminescence was still detected after the longest delay times: PTFE, ETFE, PVDF, PEEK, and PP. When the samples were exposed to indirect sunlight and mounted in the detection system at room temperature, a significant increase in the luminescence intensity is observed from all of these polymers upon mild heating to 340 K. One may expect that an increase in temperature will lead to faster release of trapped charges and enhanced diffusion.

For quantitative measurements, polymer samples of 4 mm thickness were fixed on a heated aluminum plate. The temperature of the plate was stabilized before the illumination with the mercury lamp and was kept stable during the whole observation period. Experiments were performed

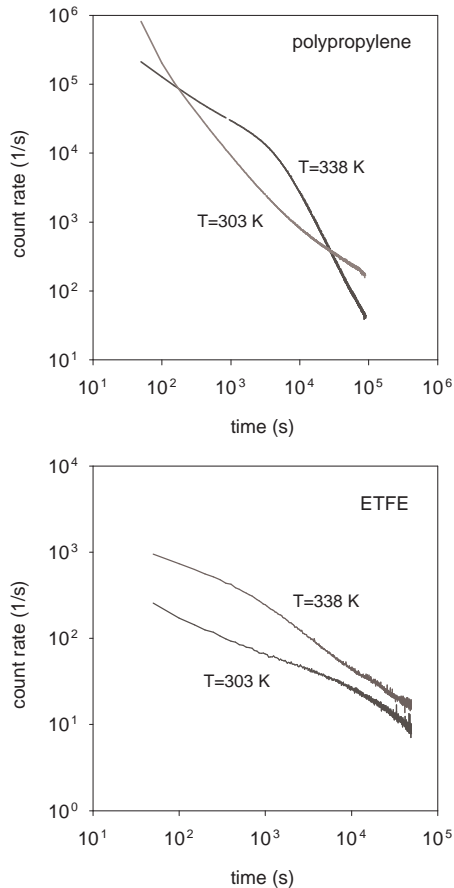


Figure 3: Isothermal photoluminescence decay curves from polypropylene and ETFE at two different temperatures: 303 K and 338 K.

at 303 K and at 338 K. In PEEK the long term m -value at 338 K is about 0.8 in comparison to 1.0 at 303 K. In ETFE and especially in PP strong changes in the temporal decay characteristics are observed at the higher temperature (cf. Figure 3). In ETFE the m -values for $t > 10000$ s are about the same for both temperatures. In PP the shape of the decay curve changes completely, with the higher temperature leading to slower luminescence decay at short times ($t < 1$ h) and to an acceleration afterwards.

Qualitatively, both, an increase as well as a decrease of the m -value upon a temperature rise can be understood in a diffusion and trapping scenario: Luminescence emission will increase if the higher temperature leads to the faster release of the trapped charge from a given trap depth. On the other hand, heating may also lead to enhanced diffusion and an “annealing” that will favor the occupation of deeper traps and will consequently lead to longer delay times before recombination.

A simple expression for the temperature dependence of m has been proposed in [12, 13]: Assuming that the temperature dependence of the trapping time τ_t in a trap of depth E is given by an Arrhenius law $\tau_t \propto \exp(E/k_B T)$, and assuming that the trap depths are distributed exponentially with $P(E) = (1/E_0) \exp(-E/E_0)$ it can be shown that the luminescence decay curve would follow a $I(t) \propto 1/t^m$ law with $m = 1 + k_B T/E_0$. Apart from the fact that most m -values observed here are smaller than 1, the observed temperature dependences are much more pronounced than predicted by this expression. In principle, one may try to reconstruct the shape of a spatial or energetic charge distribution from the observed luminescence decay curve, but the result would strongly depend on the model that is assumed for the recombination process.

6 Conclusion

We have shown that many solid polymers, including the fluoropolymers PTFE and PVDF that do not significantly absorb visible light, show long-lasting luminescence after irradiation with ultraviolet light of low intensity at room temperature. The luminescence emission has been characterized spectrally and temporally. It seems plausible that the underlying cause of the light emission is the thermally activated recombination of charges that were separated by the uv light. Additional information to corroborate this view may be obtainable from measurements of electrical properties like photoconductivity. Since optical transitions intrinsic to these molecules are not known it is possible that ionization and luminescence originate at defects of the polymer chain.

Originally, this study was motivated by the search for a suitable luminescence-free container material that should be chemically inert and mechanically stable for sensitive fluorescence experiments with acid solutions of radioactive isotopes. Because of the luminescence detected in most of the suitable materials, carbon fiber filled PEEK was finally selected for the application. In this material the black carbon fibers effectively absorb the intrinsic luminescence from the polymer.

If one wishes to use any of the polymer materials studied here in an optical system with sensitive photodetection, the uv-induced luminescence may be a nuisance and the purpose of this publication is partly to alert designers of this problem. PTFE, for example, is widely used as a diffuse reflector in radiometric systems and problems related to uv-induced fluorescence in diffuse reflectance standards made from sintered PTFE have already been reported [18, 19]. Positively, however, the study of anomalous diffusion and aging in soft matter that has been touched here is interesting in its own right. Here we have identified a new system that is easily accessible for further experimental studies.

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