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Observation of room-temperature afterglow in Polyamide-6 under UV excitation

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Abstract. We report on the observation of time-delayed luminescence of bulk Polyamide-6 polymer material under the room temperature and liquid nitrogen temperature conditions. The excitation was taken from low power diode laser operating at the wavelength 407 nm. The afterglow duration amounts up to several seconds and the decay function was found to coincide with the Becquerel hyperbolic law. The conclusion that we have made with account of the results obtained is the charge-recombination origin of this effect.

Keywords: luminescence, afterglow, polymer materials.

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1. Introduction

The interest to photophysics of soft matter materials is growing due to the prospects of organic photonics and molecular electronics [1, 2]. However, the microscopic processes of excitations and charge transport in soft materials are not studied yet on a level comparable to the solid state science [3]. In this sense, direct experimental treating of polymer material luminescence can give important information to the issue. For instance, recent research discovered the presence of narrow exciton-like emission lines in the luminescence spectrum of polyethylene and polytetrafluoroethylene [4].

For the first time to our knowledge, we report on a persistent afterglow observation at liquid nitrogen temperature as well as at the room one in bulk Polyamide-6 (C-6) excited by 407-nm UV radiation from a diode laser.

Polyamide-6 is a mass product common in everyday use. A bulk sample is nontransparent milky colored rigid material which can be mechanically processed for different purposes. The color is defined by the strong light scattering caused by the polycrystalline structure [5]. We note the earlier reports on the polyamide luminescence exploited UV excitation within the range 200…300 nm [6]. An interesting feature of this material luminescence is a noticeable dependence on the microscopic structure (crystalline or amorphous resin).

The choice of Polyamide-6 for this study was predetermined by detection of unique ability of time-delayed emission at room temperature distinct from other treated polymer materials.

2. Observation of the effect

Fig. 1a shows the image of a glowing C-6 sample taken in the darkness after UV diode laser illumination (407-nm wavelength). The exposure time was 5 s until total disappearance of the emission. The spatial scale of a bright zone exceeds noticeably the focused laser spot, as represented in Fig. 1b where laser illumination was registered separately by using the UV glass filter blocking the luminescence light and, *vice versa*, the visible luminescence image was taken without UV excitation radiation. While the laser spot is rather small and illumination is intensive, the luminescence area occupies broad zone with a smooth envelope.

Cooling the sample to the liquid nitrogen temperature (77 K) considerably increases the magnitude and visual duration of the afterglow. The measured afterglow is in the range of seconds, as seen in Fig. 2 for the room temperature (RT) and liquid nitrogen one (LNT). Both fast fluorescence response signal (with rectangular shape repeating the pump pulse) and time-delayed luminescence "tail" are clearly seen. The

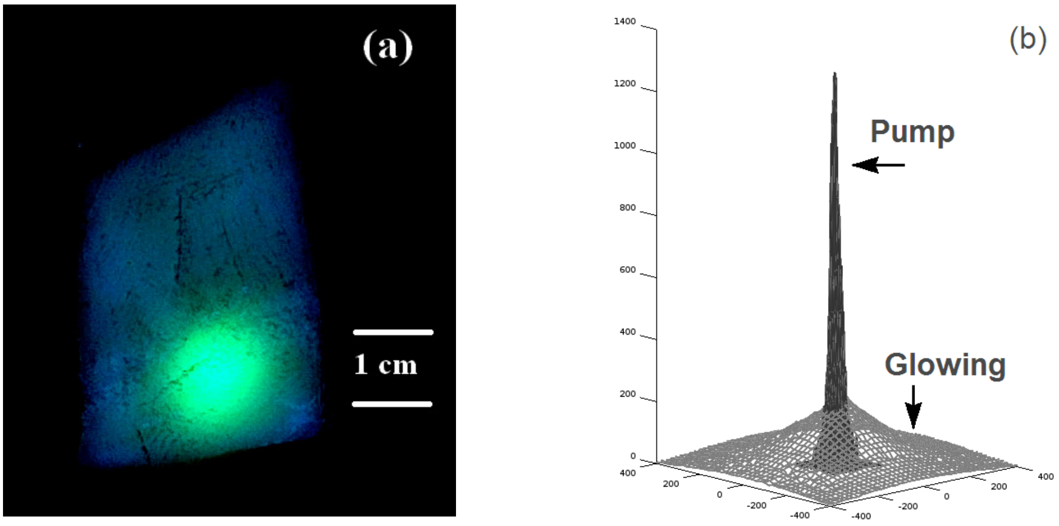

Fig. 1. (a) Image of the glowing C-6 sample after excitation with the UV diode laser. (b) Evaluation of the laser-illuminated spot and the luminescence emerging zone. Transversal dimension is 8×8 mm. Vertical intensity scale differs for the pump and glowing distributions, the pump is in 30 times reduced.

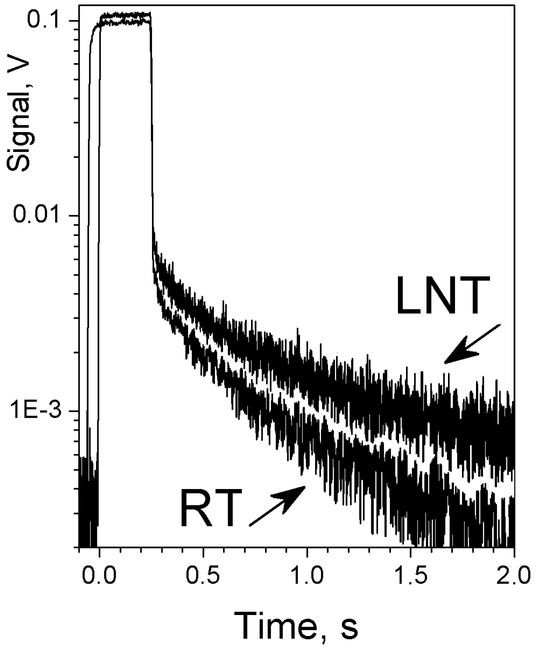

Fig. 2. Single-pulse response of the luminescence from Polyamide-6 sample, at room temperature and liquid nitrogen temperature (note the logarithmic scale). To excite the luminescence, CW low-power diode laser was used with the emission line 407 nm.

logarithmic scale indicates definitely non-exponential decay function and permits to compare the afterglow signals.

To accurately measure the characteristics of the time-delayed luminescence, we applied a technique that permits to eliminate the strong fluorescence signal as described below.

3. Experiment

The UV diode laser used as the excitation source can operate in CW regime or in the regime of periodic pulses of variable duration (usually about 100 ms). Under laser illumination, we observed bright luminescence in the blue-green visible spectrum range, as seen in Fig. 3a (room temperature measurements). The broad contour occupies the range from 450 to 650 nm. We did not detect any narrow spectral lines that could be assigned to some impurities like metal ions. Cooling the sample down to LNT did not influence noticeably on the spectrum shape.

We note, however, that the spectral maximum and the whole contour position depend on the excitation source wavelength. With short-wave UV excitation at 267 nm from the third harmonic of femtosecond-pulsed Ti-sapphire laser (fundamental emission wavelength 800 nm), we observed the spectrum shifted closer to the excitation wavelength with the maximum close to 350 nm, as seen in Fig. 3b.

The principal experimental setup is shown in Fig. 4. Laser-illuminated C-6 sample placed into the cryostat emits strong fast fluorescence signal (nanosecond response time range) and weak time-delayed afterglow. Optical system composed from two silica lenses L_1 and L_2 focuses radiation to the photomultiplier window. Interference filter placed in front of the window cuts off the scattered UV pump and separates the necessary range from the luminescence spectrum.

To isolate relatively small (with respect to the bright fluorescence) signal of the time-delayed emission, we used a chopper that blocks the input to the photomultiplier at the moments of the pulse pump. Then the chopper opens the window between laser pulses and, therefore, the only afterglow signal can be registered.

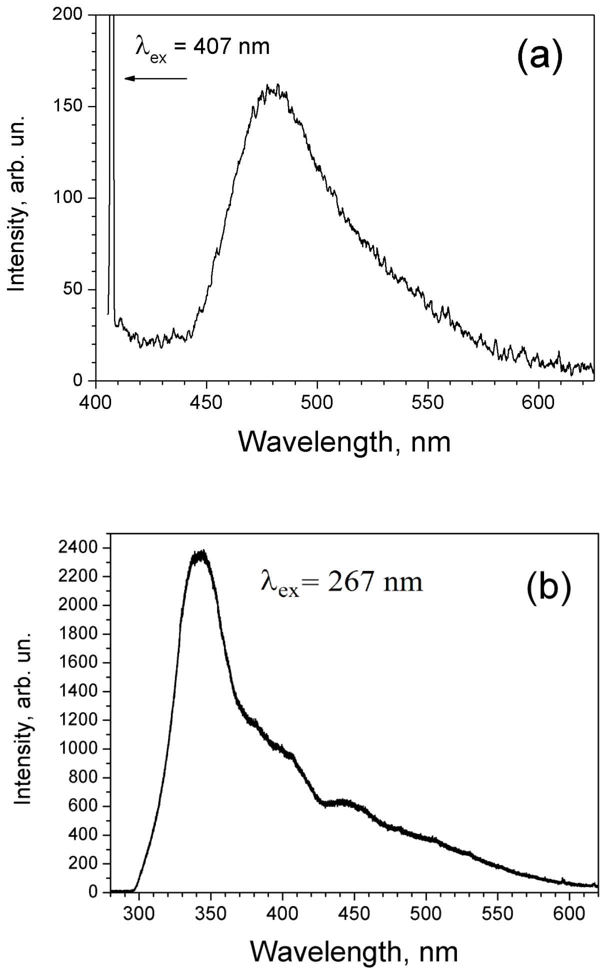

Fig. 3. Luminescence spectrum of C-6 polymer sample at room temperature. (a) The maximum position is detected at 480 nm with excitation at 407 nm. (b) Excitation wavelength 267 nm, the contour maximum is close to 350 nm. The pump wavelength is blocked with a polymer (PMMA) plate cutting off the spectrum shorter than 294 nm wavelength.

Thus, instead of the fluorescence peaks we will detect pure afterglow in the intervals between the excitation pulses. The resulting oscilloscope trace is shown in Fig. 4b. The rise of the dark signal is seen as well as the decay after switching the pump off. The quality of the experiment permits to resolve with accuracy the temporal function of the afterglow decay.

The registered afterglow temporal dependence can be fitted with the Becquerel law function [7]

$$S(t) = \frac{S_0}{(t + t_0)^{\kappa}}, \tag{1}$$

where S_0 and t_0 are experimental parameters and the experimentally determined $\kappa \approx 1.1$, the example is shown in Fig. 4c. Cooling the sample to LNT increases the signal and, therefore, enlarges the visually observed afterglow duration. In contrast the factor κ was found to have subtle dependence on the temperature.

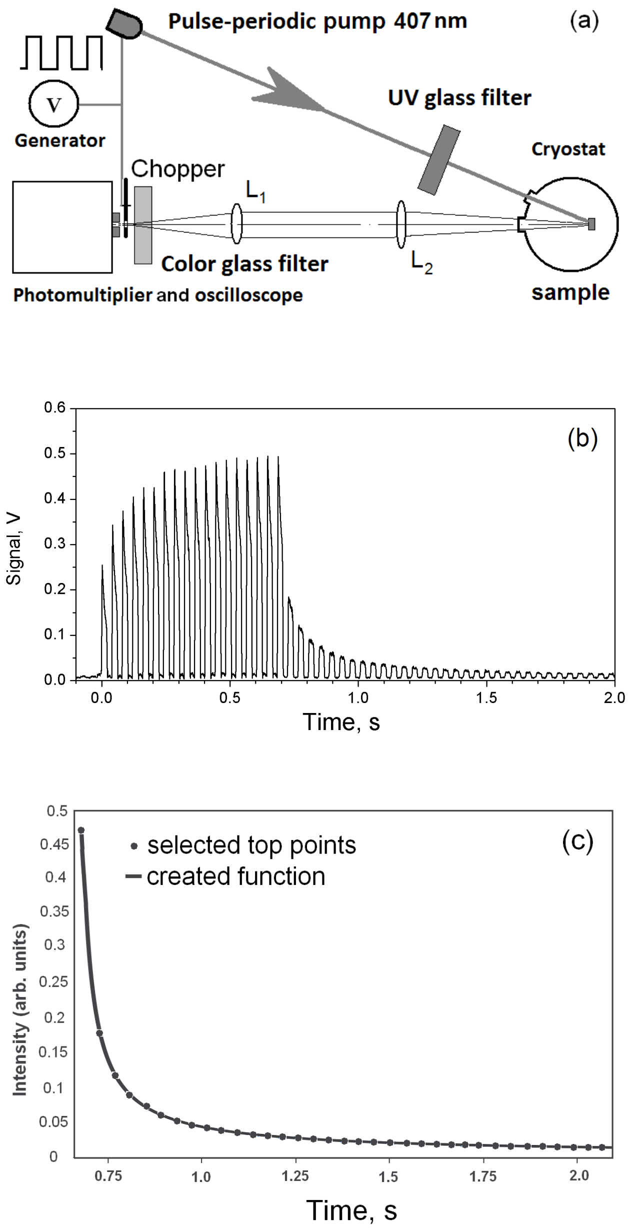

Fig. 4. (a) Experimental setup. The source of UV radiation is a diode laser operating in pulse-periodic regime. The emission is rectified by an UV glass filter cutting off the visible spectrum content. The illuminated sample placed in a cryostat emits both fast fluorescence signal and time-delayed afterglow. Optical system composed from two silica lenses L_1 and L_2 focuses the radiation to the photomultiplier window. The glass filter before the window cuts off the scattered UV pump. The chopper is able to close the window at the moments of laser pulses and, therefore, the only afterglow signal can be registered. (b) Evolution of the afterglow signal taken in the intervals between the excitation pulses. Pulse-periodic excitation (the repetition rate is 25 Hz) longs till 0.7 s, the afterglow signal relaxation is observed in the interval from 0.7 to 2 s in the trace. (c) Fitting of the relaxation with the Becquerel compressed-hyperbola function. Points are selected maxima of the trace (b), the fitting program finds the corresponding hyperbola.

4. Discussion of the results and conclusions

We report on a new effect of a persistent afterglow of a polymer material observed at room temperature. While the origin is not clear yet, some important conclusions can be made even now. The broad luminescence spectrum observed is hardly assigned to some molecular electronic transitions but more likely is the result of random distribution of energy release in the charge recombination. We tested the afterglow effect also with a set of LED emitting in blue range and found the threshold at about 474 nm (2.6 eV photon energy).

In a bulk sample, the dimension of luminescence area exceeds noticeably the laser-illuminated spot, and explanation of this feature is based on the material excitation inside the sample by strongly scattered laser beam with relatively small absorption. This gives an evidence of the light emerging from a bulk sample body, not a surface effect.

The temporal characteristic of the afterglow decay gives the witness to the favor of the charge-recombination process responsible for light emission. However, there is a noticeable difference between samples of high pressure production and samples obtained from a melted polymer resin. Probably, the microscopic structure of this material influences on the charge transport and, therefore, on duration of the recombination process. The profound difference caused by the material structure is seen also in the luminescence spectra registered with UV excitation at the wavelength 267 nm. While the tested Polyamide-6 sample exhibits strong near-UV luminescence response at 340 nm (Fig. 3b), resin material does not.

Comparison of the relaxation function at room temperature and liquid nitrogen temperature shows the relaxation process rate does not depend strongly on the temperature.

In addition, we note the afterglow effect is very common not only for polymer materials but also for amorphous materials of very different nature, *e.g.*, inorganic synthetic opal [8] or organic natural cellulose [9].

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