

Luminescence of Polyamide-6 α and γ forms

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Abstract — We report the results of an experimental study of polymer bulk material Polyamide-6 luminescence properties. A new effect of persistent time-delayed luminescence was revealed at room temperature. Detailed inspection of the effect has shown strong dependence on the microscopic crystalline structure of the polymer. Two morphological forms were recognized with the aid of X-ray Bragg reflection treating. The afterglow with the decay time exceeding 10 seconds was found to appear at about 150 K for the γ -form and is observed at room temperature for the α -form. The temporal dependence of time-delayed luminescence was found to satisfy hyperbolic Becquerel law, thus indicating the recombination origin of the effect. Also, emission realized with the excitation by third optical harmonics of a femtosecond Ti:Sapphire laser (267 nm) at room temperature was examined. The registered luminescence spectra were found quite different for these forms. While γ -form samples exhibit spectrum at the visible region, the α -form emits a pronounced luminescence output in the near UV (340 nm).

Keywords—Polyamide-6 α and γ forms; room-temperature time-delayed luminescence; afterglow.

I. INTRODUCTION

Our study is devoted to bulk solid Polyamide-6 material with particular attention to its photophysics properties. Recently we reported on the effect of a persistent afterglow observed at room temperature with Polyamide-6 illuminated in UV region [1]. Surprisingly, morphological modifications of the polymer crystalline structure (α and γ forms) demonstrate quite different luminescent properties.

Figure 1 illustrates the afterglow effect as observed by eye. A sample of Polyamide-6 was illuminated by UV radiation from UV LED (374 nm wavelength) through a razor blade opening taken as a stencil. Then, 1 s after the illumination was switched off the picture is clearly seen in a dark room.

However, some Polyamid-6 samples did not exhibit any visible afterglow at room temperature (but at the liquid nitrogen temperature the effect was bright for them as well as for samples glowing at room temperature). To understand the origin of the difference in the time-delayed luminescence we applied X-ray diagnostics. The reason is that in Polyamide-6 two different crystalline modifications exist (α and γ forms) [2,3] which are different morphological realization of the polymer molecules packing.

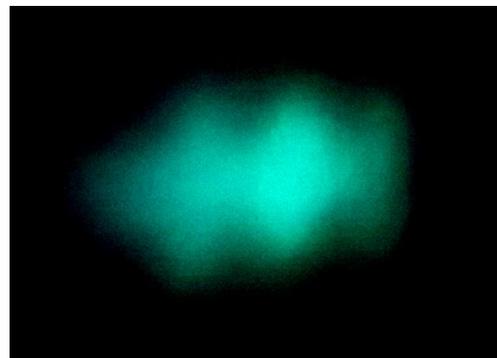


Fig. 1. Imprinted image of a projected to a sample face a razor blade opening. The picture was taken 1 s after switching off the illumination.

The influence of the crystalline form on the optical properties could probably explain the observed difference as we have supposed. The results of wide-angle X-ray diffraction treating are shown in Fig. 2.

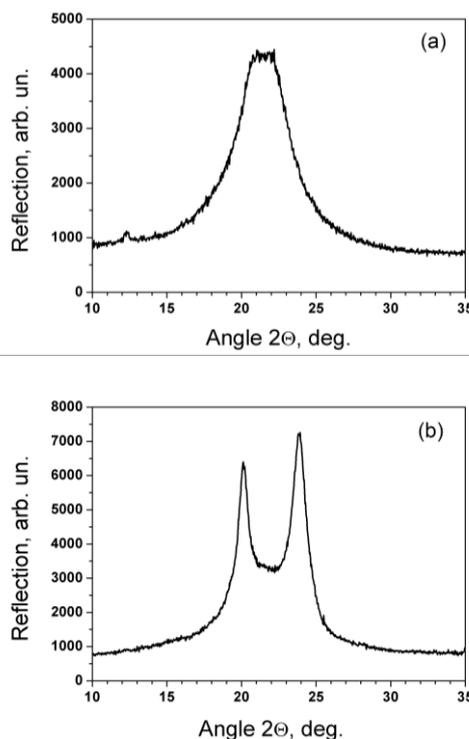


Fig. 2. Wide-angle X-ray diffraction pattern of polyamide-6 samples in γ (a) and α (b) forms.

Samples of the γ -crystalline phase possess well defined single reflection peak at about 21.5° (Fig. 2(a)), whereas the samples of the α -crystalline phase show two sharp reflection peaks at 20.13° and 23.85° (Fig. 2(b)).

The correlation between the crystalline form of a sample and its luminescence properties was detected: α -form samples do exhibit time-delayed luminescence at room temperature but γ -form samples do not.

II. LUMINESCENCE EXAMINATION

Generally, Polyamide-6 luminescence spectrum occupies the region from 300 to about 800 nm. To observe the whole spectrum we used third optical harmonics (267 nm) of a femtosecond pulse Ti:Sapphire laser operating at 800 nm wavelength as a source of UV radiation. The spectrum shape recorded at room temperature for α -form sample is presented in Fig. 3 (a). A strong pronounced maximum is observed in the near UV region (340 nm).

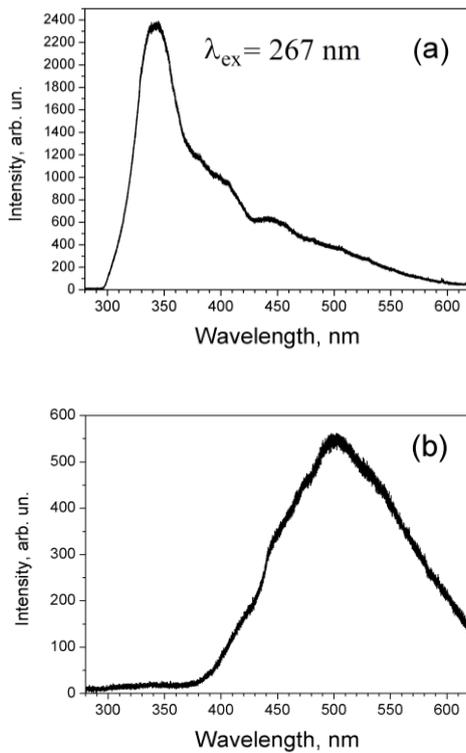


Fig. 3. Comparison of the luminescence spectra of the Polyamide-6 samples in the crystalline form α (a) and γ (b).

Surprisingly, with Polyamide-6 samples possessing γ -form crystallization, the registered spectrum has quite different shape which is shown in Fig. 3(b). The spectrum does not exhibit any maximum in the near UV, instead the maximum is located in the visible part at about 500 nm.

We note that this difference is hardly detectable with an excitation source with the output wavelength longer than 400 nm. The example of a luminescence spectrum registered with CW excitation by violet radiation (diode laser, $\lambda_{ex} = 407$ nm) is shown in Fig. 4. Irrespectively on the crystalline form the

spectrum at the Stokes side possesses the maximum at about 480 nm. Even with the use of green (532 nm) excitation laser line the corresponding luminescence is observed in the orange-red range.

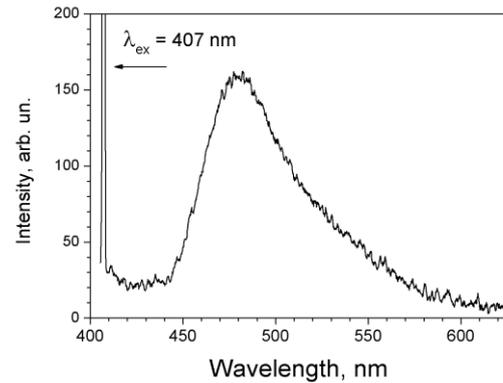


Fig. 4. Polyamide-6 luminescence with the excitation from diode laser at 407 nm.

We can conclude from here that the origin of luminescence is not caused by specific molecular excited energy levels but more likely is a result of excitations disseminated in a polymer network with continuum spectrum.

III. TEMPORAL RESPONSE OF POLYAMID-6 ON PULSE EXCITATION

In order to measure the temporal characteristics of the afterglow which signal accounts to about 1% on the fast response (fluorescence) we elaborated a scheme which closes the detector (photomultiplier) window at the time of excitation pulse and opens it between the pulses. The sketch of the scheme is shown in Fig. 5. Low power (10 mW) 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). Laser-illuminated sample placed in a cryostat emits strong fast fluorescence signal (nanosecond response time range) and weak time-delayed afterglow [1]. Optical system composed from two quartz lenses L_1 and L_2 focuses the radiation to the photomultiplier window. Glass filter placed in front of the window cuts off the scattered UV pump and separates the necessary range from the luminescence spectrum.

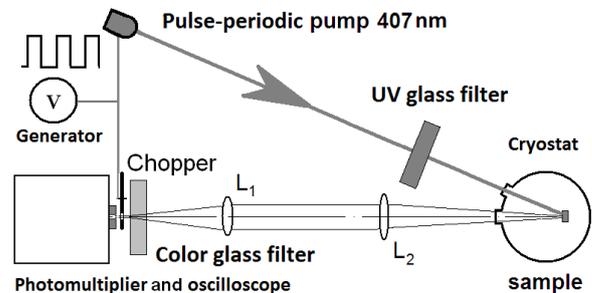


Fig. 5. Experimental scheme composed from the excitation laser diode (407 nm) operating in a pulse-periodic regime, sample in a cryostat and a detector (photomultiplier). The chopper closes the photomultiplier window at the moments of the excitation pulses and opens it in the interval between the pulses.

This technique is quite reliable and very suitable for detection of a relatively low signal on a background of fluorescence response. An example of the accumulation and following relaxation of time-delayed luminescence is shown in Fig. 6. As seen, the afterglow signal comes to saturation for less than 1 s and after switching the pump off the decay time exceeds 2 s.

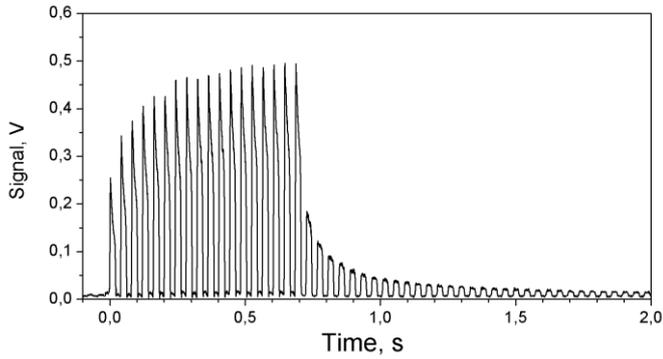


Fig. 6. Example of experimentally recorded time-delayed luminescence signal at room temperature. Excitation from a diode laser (407 nm) lasts to 0.7 s, then the relaxation of the afterglow signal is detected with a hyperbolic function.

The temporal dependence of the afterglow relaxation does not follow usual exponential decay function. Instead, the best fit was found with the compressed hyperbolic (Becquerel law) function [4]

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

where S_0 and t_0 are experimental parameters and the experimentally determined factor κ amounts to ≈ 1.1 . An algorithm was elaborated to evaluate the relaxation function along the Eq. (1), the example is shown in Fig. 7. Experimental points depicted are the determined tops of the trace (Fig. 6) and solid line corresponds to the fitting function (Eq. (1)). The algorithm also determines the background noise illumination.

The hyperbolic law provides infinite time of the afterglow, so we have to inspect very low signals on a noise background to verify the full relaxation function. In our estimations the afterglow becomes undetectable in 20 seconds.

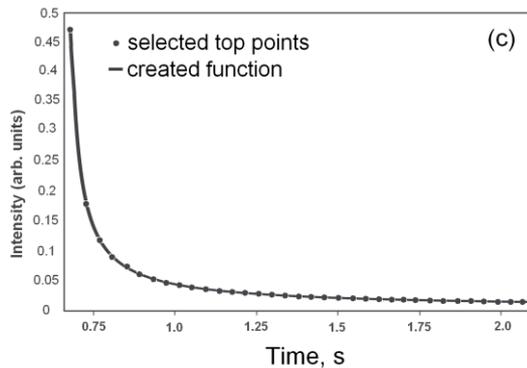


Fig. 7. Fitting of the afterglow relaxation function along the Becquerel law (Eq. (1)).

With the use of short-time pulse excitation from N_2 laser (9 ns pulse duration, 337 nm wavelength) we can inspect also an immediate response time of the material.

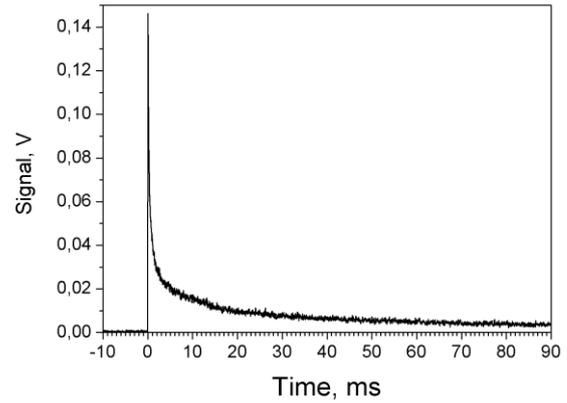


Fig.8. Luminescence response of Polyamide-6 sample (α -form) on UV pulse pump from N_2 laser (337 nm, 9 ns duration) at room temperature. The sharp peak is a direct response (fluorescence) spike. Long-time afterglow “tail” signal is seen.

Checking the temporal function of the time-delayed signal in the case of short-pulse excitation gave the result of the hyperbolic dependence along the formula (1) but with the factor $\kappa \approx 0.5$. This result is consistent with the theoretical consideration of the recombination luminescence [4].

Cooling a sample to liquid nitrogen temperature 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. Also we did not find substantial difference in the spectral shape with the temperature variations. With the increase of the temperature to about $50^\circ C$ we come to the disappearance of the afterglow for α -form samples, and for γ -form samples the temperature threshold amounts approximately 150 K.

IV. DISCUSSION 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. 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.

The temporal characteristic of the afterglow decay gives the witness to the favor of the charge-recombination process responsible for the light emission. There is a noticeable difference however between samples with α - crystalline form and γ -form. Probably microscopic structure of a material influences on the energy potential shape and therefore on the temperature dependence of the recombination process. The profound difference caused by the material microscopic structure is seen also in the luminescence spectra registered with UV excitation at 267 nm wavelength. While the tested α -

form Polyamide-6 samples exhibit strong near-UV (340 nm) luminescence response (Fig. 3 (a)), γ -form material does not.

We expect the results obtained will help to develop the model of excitation trapping and transport in polymer networks which look perspective for the tasks of molecular electronics [6,7].

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