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Effect of UV-irradiation on fluorescence of poly(methyl methacrylate) films with photosensitive organic compounds



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ABSTRACT

The simple way of physical modification of poly(methyl methacrylate) (PMMA) for the purpose of formation its photoactivity and fluorescence properties has been described. It was found that aromatic carbonyl compounds (2,2-dimethoxy-2-phenylaceto-phenone, benzoyl peroxide and *tert*-butyl perox-ybenzoate) dispersed in PMMA matrix changed its optical properties, which was studied by absorption and emission spectroscopy. Modified PMMA exhibits fluorescence upon excitation of 220 or 270 nm. The intensity of emission band decreases after samples exposure to short wavelength UV-irradiation, which is evidence of component photolysis. The fluorescence decay is slightly smaller for the irradiated initiators in PMMA matrix, but the trend is similar to that for pure initiators exposed to UV. The protective effect of PMMA on the studied compounds after UV-irradiation, however, is accompanied by photodegradation reactions occurring in the polymer, which was confirmed by viscometric measurements.

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1. Introduction

Photoactive polymeric composites attract much attention because they are potential materials for the new technologies in the fields such as electronics, optics, biotechnology, medicine, pharmacy etc.

Poly(methyl methacrylate)(PMMA) is a valuable raw material for the production of photosensitive plastics. The physical and chemical modification of this polymer can lead to obtaining fluorescent or photoconductive materials [1–4]. Moreover, acrylate polymers are also used as a matrix for low-molecular organic or inorganic compounds [5,6]. For example, PMMA doped with fluorescent probes (amino aromatic species) has been successfully obtained by pulsed laser deposition. Such material can act as a sensor for detection of environmental impurities [7]. In other interesting work, the switching properties of fluorescent photochromic PMMA copolymerized with spironaphthoxazine and D- π -A type pyran-based dye have been reported [8].

Atactic and syndiotactic PMMA with anthracene fluorophores attached to the end of side chains or embedded in the polymer backbone has been studied by time-resolved fluorescence spectroscopy. Additionally, isotactic PMMA without anthracene fluorophore was prepared to mix it with labeled PMMA. It was found

that stereocomplexes between the syndiotactic and the isotactic PMMA in dimethylformamide were formed due to the local conformational motion of polymer segments [9].

Studies of anthracene-labeled PMMA gels by fluorescence anisotropy decay were the subject of the article by Aoki [10]. It was concluded that the local motion of PMMA gel at crosslinks was governed by the segment density of the network chains in the vicinity of crosslinks.

Furthermore, it was found that nanocarbon-PMMA composites, prepared by pulsed laser ablation technique, exhibited fluorescence. Spectroscopic studies revealed interactions between nanocarbon particles and polymer matrix due to transfer of π electrons from the carbonyl groups of PMMA to nanocarbon [11].

The possibilities of other applications of modified PMMA and its copolymers in fabrication of nanodevices, in which the photoactivity is demanded, have been reported in numerous publications [3,4,12–18].

Moreover, experimental emission techniques appeared useful in evaluation of component miscibility in polymer blends by means of excimer fluorescence and fluorescence microscopy [19,20].

Recently, PMMA was modified by the addition of small amount of different photosensitive low-molecular weight compounds such as aromatic or aliphatic ketones and peroxides [21–24]. It was found that PMMA doped with these photoinitiators undergoes accelerated photodegradation compared to the unmodified polymer, which is important in designing photodegradable

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polymers. Moreover, the thermal resistance of modified polymer was lower than that of unmodified, whereas the surface properties of PMMA with or without additives did not change significantly.

The aim of the present work was to study the fluorescence of PMMA physically modified with three organic compounds: 2,2-dimethoxy-2-phenylaceto-phenone (**Irg**), benzoyl peroxide (**BP**) and *tert*-butyl peroxybenzoate (**tBPB**). Physical mixing of photosensitive compounds with polymers is much simpler and cheaper method of preparing fluorescent materials than the complex, often multi-step and long-term synthesis of polymer-based photoactive compounds. In this way it is possible to prepare photosensitive plastics for potential applications because of easy processing and possibility of modification of mechanical properties in a wide range.

An important objective of the work was to check whether the fluorescent properties of the photosensitive compounds still remained in the polymer matrix and to what extent these properties changed under the influence of UV radiation.

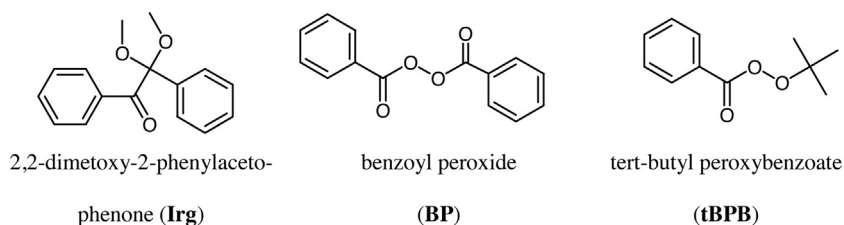
The emission properties of modified PMMA-based materials are important in the case of using such plastics as selective sensors, fluorescent markers as well as the substances for lithography, optics or electronics.

2. Experimental

2.1. Materials

Poly(methyl methacrylate), IUPAC name: poly(methyl 2-methylpropenoate), PMMA, has been purchased from Sigma–Aldrich. The average molecular weight of polymer was 120,000.

Photoinitiators: (2,2-dimethoxy-2-phenylaceto-phenone); trade name: Irgacure 651 (**Irg**), benzoyl peroxide (**BP**) and *tert*-butyl peroxybenzoate (**tBPB**) were supplied by Ciba, Basel, Switzerland; Sigma–Aldrich. The formula of these compounds and their abbreviations are shown below:



Acetonitrile (ACN) and tetrahydrofuran of high purity (Sigma–Aldrich) were used as solvents.

2.2. Sample preparation

2% (w/v) solutions of polymer and organic compounds in tetrahydrofuran were prepared. The solutions were mixed in a proper volume ratio to obtain the mixtures of PMMA with 5 wt.% of modifier content. Thin films (thickness of 20 μm) of pure PMMA and PMMA with photoinitiators were obtained by casting method. After solvent evaporation, films were carefully dried in a vacuum oven at 30 °C for one week. The purity of dried films was checked by spectroscopic analysis.

2.3. Fluorescence measurement

Fluorescence measurements were performed on a Hitachi F-7000 Fluorescence Spectrophotometer at room temperature using a Xenon lamp source for excitation and the 1 cm quartz cell.

Excitation and emission slit widths were 5 nm for the wavelength response of the system. The response time was 0.1 s while a data interval—1 nm. Individual and three-dimensional spectra were recorded in the range of 200–900 nm at a rate of 60 000 nm/min. The spectra were evaluated with the PC software package supplied with spectrophotometer (FL-Solution 2.1 for F-7000).

Emission spectra of UV-irradiated samples were recorded directly after exposure. To compare the UV influence on different samples, the relative changes of fluorescence intensity has been calculated:

$$\Delta I_{\text{rel}} = \frac{I_0 - I_t}{I_0} \quad (1)$$

where I_0 and I_t are fluorescence intensity of unirradiated sample before and after t time of irradiation, respectively

All fluorescence measurements were performed for samples in a solid state.

2.4. UV-vis spectroscopy

Absorption spectra in UV-vis range have been recorded using UV-1601PC spectrophotometer (Shimadzu, Japan). The measurements were performed in acetonitrile solutions (pure initiators) and in a solid state (thin films of photoinitiator-doped PMMA). The molar absorption coefficients, $\epsilon_{\lambda_{\text{max}}}$, for photoinitiators in dilute solutions have been calculated from Beer-Lambert law.

2.5. Ultraviolet exposure

Polymeric films were UV-irradiated using a low-pressure mercury vapor lamp TUV30W, Philips, Holland. This source emits radiation of 254 nm wavelength. The intensity of the incident light, measured by HD 9021 radiometer, was 32.2 W/m². The irradiation was carried out at 30 °C and at ambient atmosphere. Fluorescence

spectra of UV-irradiated films were systematically measured.

2.6. Viscosity measurements

Unirradiated and UV-irradiated films of PMMA and PMMA with photoinitiators have been dissolved in acetonitrile. Viscosity of these diluted solutions was measured at 25 ± 0.01 °C using Ubbelohde capillary viscometer. From the flow times of the solvent and the solutions, relative (η_r) and specific (η_{sp}) viscosities were determined for 4–5 concentrations. The flow time of liquid was measured with accuracy of 0.01 s. Intrinsic viscosity (limiting viscosity number, LVN, dl/g) has been calculated by extrapolation of reduced viscosity (η_{sp}/c) to zero concentration ($c=0$). The relative percentage changes of LVN of various samples have been calculated according to the formula:

$$\Delta(\text{LVN}) = \frac{(\text{LVN})_0 - (\text{LVN})_t}{(\text{LVN})_0} \times 100\% \quad (2)$$

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