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A chemiluminescence and fluorescence spectroscopy study: An investigation of photocrosslinking processes in polymer systems

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ABSTRACT

Chemiluminescence emission is shown to be a valuable method for the analysis and monitoring of the photochemical transformation process in BZMA-*co*-S copolymers. BZMA-*co*-S copolymer films are synthesized and irradiated at λ > 400 nm, in order to induce the phototransformation of benzyl (BZ) to benzoyl peroxide (BP) pendant groups, resulting in thermal decomposition and crosslinking. The chemiluminescence emission increases with irradiation time, and is shown to be related to the benzoyl peroxide moieties generated during irradiation. The increase in chemiluminescence intensity is interrupted at longer periods of irradiation, when the concentration of these species tends to a nearly constant value. In this case, others factors are considered to influence the chemiluminescence emission, for example the increasing crosslinking on irradiated samples, which would restrict the mobility of radicals to recombine due to crosslinking of the network.

A good correlation between fluorescence, FTIR and CL measurements during photochemical formation and thermal decomposition of peroxides is found. In this work, an intramolecular excimer forming fluorescent probe, DiPyM, is also used to analyse the crosslinking process. The results obtained contribute significantly to the development of chemiluminescence as a highly sensitive methodology for assessing the photocrosslinking of a polymeric material in the early stages of the process and is due to its sensitivity in comparison to that of fluorescence analysis.

1. Introduction

Benzil (BZ) derivatives are well-known Type II photoinitiators with benzil/amine systems having been used as photoinitiators for vinyl free radical polymerisation for many years. Some 1,2-dicarbonyl functionalised compounds are also industrially important as photoactive compounds for use in photoresists and photographic materials [1–3]. It has been shown previously, that the photochemistry of BZ was dependent on both, the employed irradiation wavelength and the absence or presence of molecular oxygen. The hydrogen atom abstraction by the lowest excited triplet state of benzil takes place in the absence of oxygen, leading to the formation of ketyl radicals from BZ and radicals from the hydrogen donor. However, it was recently reported that in the presence of oxygen, BZ could be converted almost quantitatively to benzoyl peroxide (BP) upon irradiation at λ > 400 nm, in solid polymer matrices such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). The later thermal decomposition of BP groups will then lead to the crosslinking of the polymer, Scheme 1. In fact, the vast majority of BP-based polymer chains were cross-linked even after irradiation without heating. This observation allows the application of polymers bearing covalently attached BP pendant groups for the preparation of photosensitive materials [4].

The aim of this work is to study the photochemical transformation of benzil carbonyl pendant groups in polystyrene copolymers, BZMA-*co*-S, to benzoyl peroxides carbonyl moieties, by using chemiluminescence and fluorescence spectroscopy. Recently, chemiluminescence (CL) has become a useful technique for the study of polymer degradation [5], oxidation mechanisms [6] and kinetics [7,8], as well as stabilizer efficiency [9,10]. This fact is due to its advantages with respect to other well-established techniques [11] especially its sensitivity. It is well known [12,13], that the chemiluminescence from polymers is due to the light emission that accompanies the recombination of secondary alkyl peroxy radicals. This bimolecular reaction promotes ketone products to its lowest triplet state and the radiative deactivation gives chemiluminescence emission in the visible region. The generation of peroxy radicals depends on the peroxide concentration, and the chemiluminescence emission can be related to the hydroperoxide (POOH)

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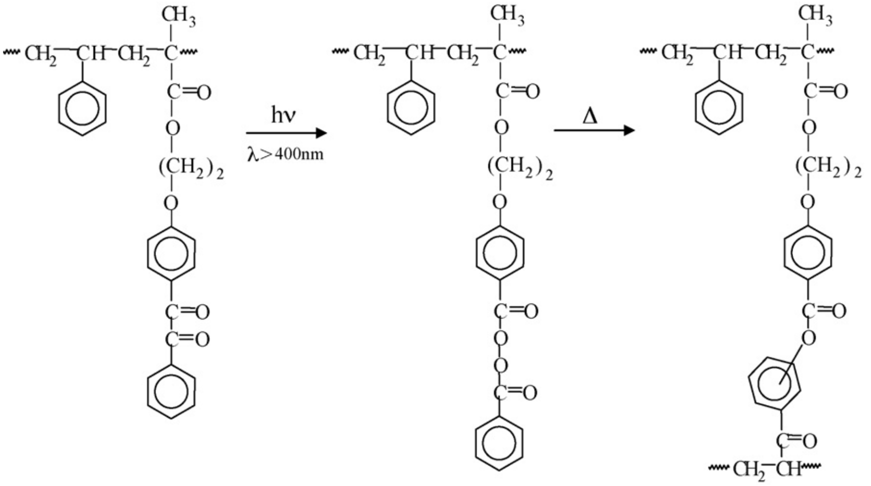

Scheme 1.

content, which are formed during processing or in-service life of the material under ambient conditions [6,14]. In previous work [15] the chemiluminescence emission has been shown to be sensitive to the morphology of polymer samples, which exhibit a strong dependence on the crystallinity. Therefore, chemiluminescence has been used to study relaxation processes in semicrystalline polymers. The chemiluminescence emission for example, decreases for poly(ethylene terephthalate) annealed samples with respect to the initial sample. In this work it was related to the enhanced crystallinity of annealed samples, which would restrict the mobility of hydroperoxides to react due to the higher rigidity of the medium.

The study of the chemiluminescence arising in the thermal decomposition of benzoyl peroxide in various polymers has been undertaken by a number of authors [16–18]. The recombination of benzoyloxy radicals or induced decomposition of benzoyl peroxide by benzoyloxy radicals has been proposed as chemiluminescence source, and the influence of factors such us composition, molecular weight and structure of polymers has been determined.

In the last decade, fluorescence analysis has also become a powerful technique for studying the properties of homopolymers, copolymers and blends by means of luminescent probes, which were incorporated, free or covalently attached, to the polymer matrix [19–22]. The emission of the fluorescent guest is sensitive to their microenvironment since the emission of the molecular luminescent probe depends on both their intrinsic photophysical properties and their interactions with the surrounding polymer matrix [5,6]. Thus, monitoring the UV curing of polymers [23], early stages of their photooxidation [11] as well as the swelling [24,25] gelation [25], crosslinking [26] and structure of interpenetrating polymer networks [24] are all processes in which the fluorescence technique has been successfully employed during the past few years.

For this purpose, an intramolecular excimer forming fluorescent probe, DiPyM, has been used to analyse the crosslinking process of BZMA-*co*-S films irradiated at λ > 400 nm, in order to follow the phototransformation of benzyl to benzoyl peroxide pendant groups, and their thermal decomposition and subsequent crosslinking. The fluorescence technique was also employed for monitoring excimer formation of DiPyM in cyclohexane, which was released from BZMA-*co*-S films on swelling. A range of cross-link densities was achieved through thermally treatment at different times of BZMA-*co*-S irradiated samples. In this way, copolymer films of different cross-link density may be characterised.

FTIR spectroscopy was used to measure the benzoyl peroxide moieties generated during irradiation and their decomposition upon thermal treatment and used to correlate the crosslinking results with those obtained by chemiluminescence and fluorescence analysis.

2. Experimental

2.1. Materials and sample preparation

The copolymer of 1-(4-(2-methacroyloxyethoxyphenyl))-2-phenyl-1,2-ethanedione (BZMA) and styrene (S), BZMA-*co*-S (M_n = 109,000 g/mol and M_w = 215,000 g/mol), was prepared as previously described in Ref. [27]. Films of BZMA-*co*-S were prepared via casting from chloroform solutions as described earlier [4].

The fluorescent probe di(1-pyrenylmethyl)ether (DiPyM) was synthesized as previously described in Ref. [28]. The structure of the probe used in this work is shown in Fig. 1. BZMA-*co*-S films doped with DiPyM were prepared by casting from chloroform solutions of the fluorescence probe (10^{-3} M).

BZMA-*co*-S films were irradiated (λ > 400 nm) using medium pressure mercury (or xenon) arc or in merry-go-round apparatus as described [2]. Thermal decomposition of the formed benzoyl peroxide structures was carried out in an oven chamber with air circulation at 91 ± 0.1 °C.

2.1.1. Chemiluminescence

Chemiluminescence spectra of film samples were obtained using an earlier described CL400 ChemiLUME apparatus from Atlas Electric Devices Co [29]. The film samples (4 mm diameter) were held in aluminium pans in the sample cell under a continuous flow of dry nitrogen (50 ml/min). The cell is temperature-controlled and was heated up with a pre-test ramp (10 °C/min) at 100 °C. During dynamic experiments, material samples are heated up to 200 °C with a heating rate (5 °C/min).

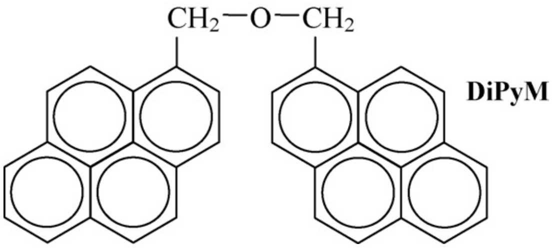

Fig. 1. Structure of di(1-pyrenylmethyl)ether (DiPyM).