



Perylene derivatives as photoinitiators in blue light sensitive cationic or radical curable films and panchromatic thiol-ene polymerizable films

Pu Xiao^a, Frédéric Dumur^{b,c,d}, Michel Frigoli^e, Bernadette Graff^a, Fabrice Morlet-Savary^a, Guillaume Wantz^{c,d}, Harald Bock^f, Jean Pierre Fouassier^g, Didier Gignes^{b,*}, Jacques Lalevée^{a,*}

^a Institut de Science des Matériaux de Mulhouse IS2M, UMR CNRS 7361, UHA, 15, rue Jean Starcky, 68057 Mulhouse Cedex, France

^b Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire, UMR 7273, F-13397 Marseille Cedex 20, France

^c Univ. Bordeaux, IMS, UMR 5218, F-33400 Talence, France

^d CNRS, IMS, UMR 5218, F-33400 Talence, France

^e Institut Lavoisier de Versailles, UMR CNRS 8180, UVSQ, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France

^f Centre de Recherche Paul Pascal, CNRS & Université de Bordeaux, 115 Avenue Schweitzer, 33600 Pessac, France

^g Formerly, ENSCMU-UHA, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France

ARTICLE INFO

Article history:

Received 21 December 2013

Received in revised form 14 January 2014

Accepted 21 January 2014

Available online 30 January 2014

Keywords:

Photoinitiator

Perylene derivative

Blue light

Cationic photopolymerization

Radical photopolymerization

Thiol-ene photopolymerization

ABSTRACT

The perylene derivatives (PTCTE, BPTI and DPPDI) combined with an iodonium salt or an amine (and optionally an additive) are used as photoinitiating systems to initiate the cationic polymerization (CP) of epoxides, the free radical polymerization (FRP) of acrylates, or the thiol-ene polymerization (TEP) of a Trithiol/divinylether mixture under different irradiation sources i.e. very soft halogen lamp or laser diodes at 473 nm or 457 nm (blue light). Upon a blue light exposure, the PTCTE based systems are very efficient for CP and FRP and better than the camphorquinone (CQ) based reference systems. Interestingly, the combination of PTCTE with previously studied green light and red light sensitive perylene derivatives and an iodonium salt ensures the manufacture of a panchromatic thiol-ene polymerizable film (400–650 nm) usable under various household LED bulbs irradiations (i.e. blue, green, yellow or red lights). The photochemical mechanisms are studied by steady state photolysis, fluorescence, cyclic voltammetry, laser flash photolysis and electron spin resonance spin-trapping techniques.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Dyes with interesting long wavelength light absorption properties and high molar extinction coefficients find marvelous applications in photoinitiating systems (PISs) for various photopolymerization reactions: through interactions with suitable additives under specific light irradiations, different initiating species can be generated i.e.

radicals for free radical polymerization (FRP) or thiol-ene polymerization (TEP), cations or radical cations for cationic polymerization (CP) or free radical promoted cationic polymerization (FRPCP). It is of great interest to develop novel high performance dyes sensitive to different wavelengths for photopolymerization reactions usable in radiation curing, material elaboration, microelectronics, nanotechnology, medicine, or imaging and optics technologies [1–5]. Camphorquinone (CQ) is well known as a photoinitiator for polymerization reactions with blue lights [1]. We have recently developed a series of dyes (i.e. benzophenone [6], naphthalimide [7], indanedione [8,9], and

* Corresponding authors.

E-mail addresses: didier.gignes@univ-amu.fr (D. Gignes), jacques.lalevee@uha.fr (J. Lalevée).

thiophene derivatives [10], indoline dye [11], BODIPY [12], chromone [13], barbituric and acid derivatives [14], Michler's ketone [15], pyrene derivatives [16], pyrromethene dyes [17], anthracene derivatives [18], etc.) sensitive to wavelengths up to 500 nm. One fascinating challenge remains on the design of more efficient derivatives within a given scaffold.

In our recent research, perylene derivatives have been proposed and used in PISs under green light [19] or red light [20] irradiations. Perylene has also been found as a photosensitizer for the photolysis of sulfonium salts [21,22], *N*-ethoxy-2-methylpyridinium hexafluorophosphate [23], phenacylanilinium salt [24], or iodonium salts [25], at long-wavelength UV light irradiations and thus initiate the photopolymerization. Herein, we use novel blue light sensitive perylene derivatives **Pers** (Scheme 1; two previously studied compounds D_1 and Per1 will also be considered, and their chemical structures are given in the Scheme S1 in the Supporting information SI) as photoinitiators incorporable in PISs with other additives. The photoinitiating abilities of these PISs towards different types of polymerization reactions as well as irradiation sources (blue lights for CP and FRP, blue to red lights for TEP) are studied. The photochemical mechanisms involved in the initiation species formation are investigated by steady state photolysis, fluorescence, cyclic voltammetry, laser flash photolysis and electron spin resonance spin trapping techniques.

2. Experimental

2.1. Materials

The Chemical structures of the studied perylene derivatives **Pers** i.e. perylene-3,4,9,10-tetracarboxylic tetraethyl ester (PTCTE), benzo[ghi]perylene-1,2,4,5,10,11-hexacarboxylic tris(2-ethylhexyl) imide (BPTI) and 1,7-dipiperidinyl-perylene-3,4,9,10-tetracarboxylic dioctyl imide (DPPDI), and other studied compounds are shown in Schemes 1 and 2. PTCTE and BPTI were prepared according to published procedures [26,27]. DPPDI was prepared according to a procedure described in detail in the SI.

Diphenyliodonium hexafluorophosphate (Iod), *N*-vinylcarbazole (NVK), methyl diethanolamine (MDEA), 2,4,6-tris(trichloromethyl)-1,3,5-triazine (R'-Cl), tri(ethylene glycol) divinyl ether (DVE-3), trimethylolpropane tris(3-mercaptopropionate) (Trithiol), and the other reagents and solvents were purchased from Sigma-Aldrich or Alfa Aesar and used as received without further

purification. (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) and trimethylolpropane triacrylate (TMPTA) were obtained from Cytec and used as benchmark monomers to characterize the photopolymerization efficiency of the photoinitiating systems.

2.2. Computational procedure

Molecular orbital calculations were carried out with the Gaussian 03 package. The electronic absorption spectra of the different **Pers** were calculated with the time-dependent density functional theory at B3LYP/6-31G* level on the relaxed geometries calculated at UB3LYP/6-31G* level; the molecular orbitals involved in these transition can be extracted [28,29]. The geometries were frequency checked.

2.3. Irradiation sources

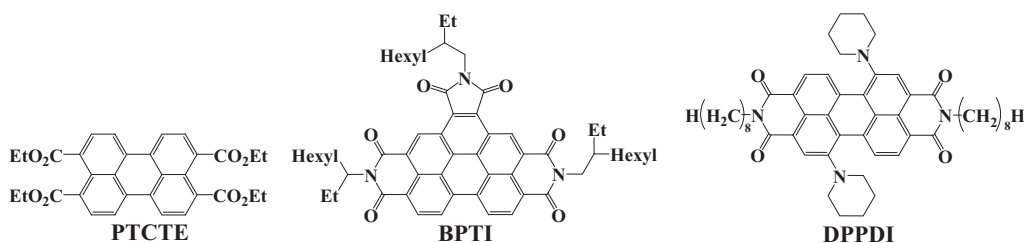
Different irradiation sources were used for the photopolymerization experiments: polychromatic light from a halogen lamp (Fiber-Lite, DC-950; incident light intensity: $I_0 \approx 12 \text{ mW cm}^{-2}$ in the 370–800 nm range); laser diodes at 457 nm (100 mW cm^{-2}), 473 nm (100 mW cm^{-2}) or 635 nm (100 mW cm^{-2}) and household blue LED bulb at 462 nm ($\sim 10 \text{ mW cm}^{-2}$), green LED bulb at 514 nm ($\sim 10 \text{ mW cm}^{-2}$), yellow LED bulb at 591 nm ($\sim 10 \text{ mW cm}^{-2}$) or red LED bulb at 630 nm ($\sim 10 \text{ mW cm}^{-2}$).

2.4. Photopolymerization experiments

The experimental conditions of the photopolymerization reactions are given in the figure captions. The photosensitive formulations were deposited on a BaF₂ pellet under air or in laminate (25 μm thick) for irradiation with different lights. The evolution of the epoxy group content of EPOX, the double bond content of TMPTA, the double bond content of DVE-3 and the thiol (S–H) content of Trithiol were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) [30,31] at about 790 cm⁻¹, 1630 cm⁻¹, 1620 cm⁻¹ and 2580 cm⁻¹, respectively.

2.5. Fluorescence measurements

The fluorescence properties of the studied perylene derivatives were studied using a JASCO FP-750 spectrometer. The interaction rate constant k_q between **Pers** and Iod was extracted by classical Stern–Volmer treatments [32] ($I_0/I = 1 + k_q\tau_0[\text{Iod}]$), where I_0 and I stand for the fluorescent intensity of **Pers** in the absence and the presence of the Iod



Scheme 1. Chemical structures of PTCTE, BPTI and DPPDI.

Download English Version:

<https://daneshyari.com/en/article/7806482>

Download Persian Version:

<https://daneshyari.com/article/7806482>

[Daneshyari.com](https://daneshyari.com)