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End capped polyenic structures as visible light sensitive photoinitiators for polymerization of vinylethers

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A B S T R A C T

Nine new photoinitiating systems based on a combination of new and established dyes (having an end capped polyenic structure) with an iodonium salt have been synthesized and tested for the polymerization of divinylether and epoxy monomers upon a visible light exposure. They exhibit a strong absorption in the 350–650 nm range which well matches the visible light emission of different convenient visible light sources. Interestingly, very soft irradiation conditions can be employed. Excellent polymerization profiles have been obtained from selected dye iodonium salt combinations using a halogen amp or a laser diode à 457 nm. The chemical mechanisms associated with these novel photoinitiating systems are investigated by steady-state photolysis and ESR experiments.

1. Introduction

Dye photosensitized polymerization reactions (DPPR) occur in the presence of a colored molecule ("dye") incorporated into a visible light absorbing photoinitiating systems (vPIS) and being able to act as a photoinitiator (PI) or a photosensitizer (PS) [1,2]. DPPRs play an important role in many industrial applications within e.g. the radiation curing and imaging area [1,2] as they allow a rapid cure of a multifunctional monomer/oligomer matrix under exposure to visible light delivered by high intensity sources or soft irradiation devices. These DPPRs have been largely known for many years (see e.g. in Refs. [1,3]) in free radical polymerization (FRP) and, to a lesser extent (indeed, until the recent years, the available cationic (vPISs) were rather limited), in cationic polymerization. The search of colored molecules and visible light absorbing photoinitiating systems (vPISs) is continuously carried out and the proposal of novel systems still remains an exciting topic. In particular, there is still a need in (CP) and (FRPCP) as the synthesis of polymers based on cationic formulation can avoid the detrimental shrinkage of the film observed during FRP reactions.

Solvent-free formulations are based on acrylate monomers which are known to undergo a rapid FRP [4]. Vinyl ether monomers (VEs) (low-odor and non-irritating) have recently appeared as an environment friendly alternative to the widely used acrylate monomers which show a strong odor and may cause skin and eye irritation [5]. VEs are very reactive monomers and exhibit a fast cationic polymerization [6,7]. They are encountered in various UV-curing applications (in particular as protective coatings) where a

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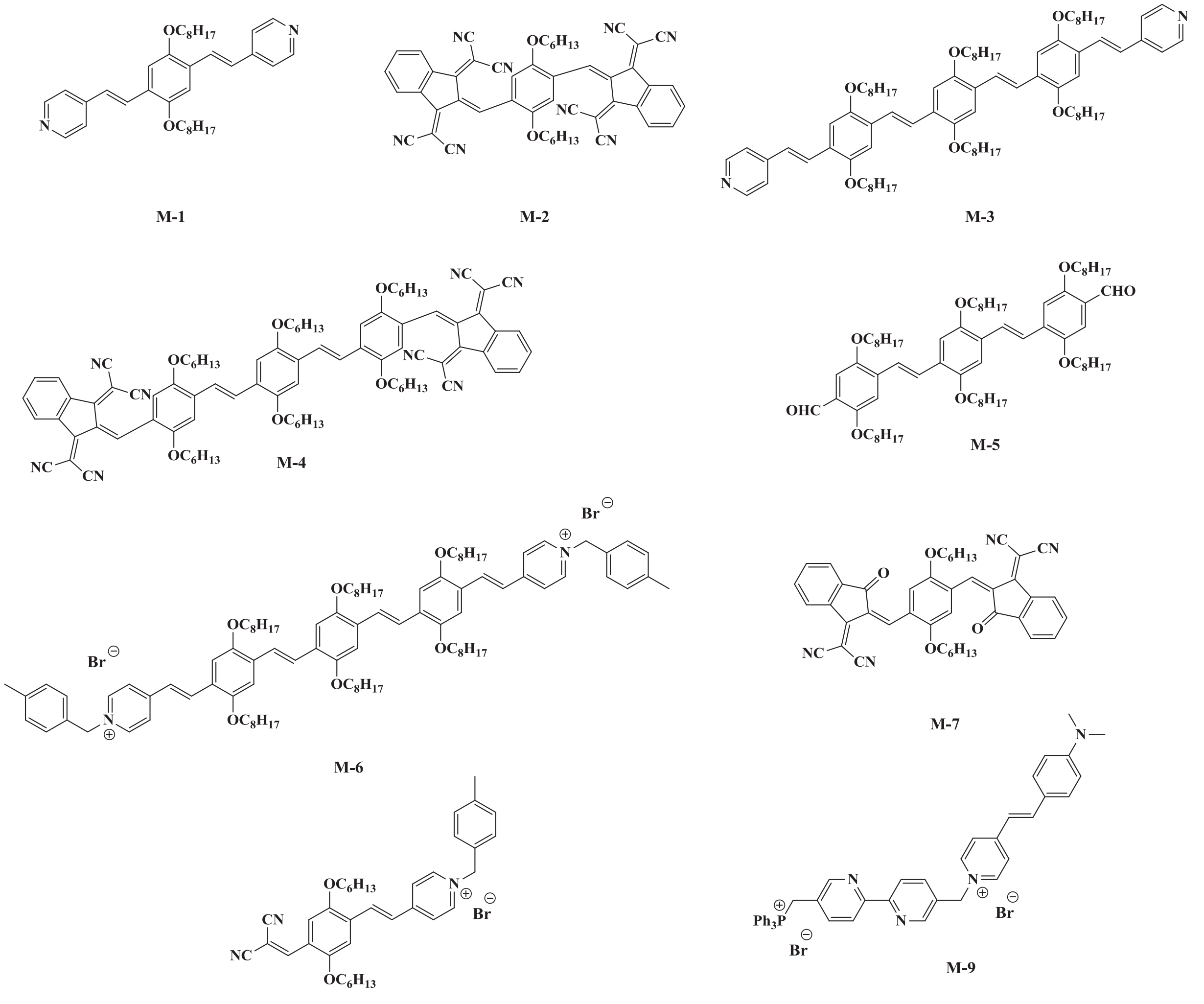
high speed and an extensive cure are desired, together with low shrinkage, great impact strength and high adhesion of the UV-cured polymer. They can also be used to reduce the formulation viscosity.

In this laboratory, we have recently launched a series of work aiming at designing vPIS for radical and cationic polymerizations. In the present paper, we look for compounds presenting an extended delocalization and being able, as part of vPISs, to initiate the cationic polymerization of vinyl ethers and epoxides upon visible light exposure under a soft irradiation source (e.g. household halogen lamp) or laser diodes. Nine new dyes (based on an end capped polyenic structure containing one or more 2,5-dioctyloxyphenyl units (**M-1** to **M-8**) or a pyridinium unit (**M-9**) in the main chain; see Scheme 1) will be synthesized and their polymerization initiation ability checked. The chemical mechanisms will be investigated by steady state photolysis and ESR experiments.

2. Experimental section

i) Synthesis of the different photoinitiators:

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peak DMSO-d_6 (2.49 ppm), $CDCl_3$ (7.26 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak DMSO-d_6 (39.5 ppm), $CDCl_3$ (77 ppm). (*E,E*)-2,5-Dioctyloxy-1,4-*bis*(2-[4]pyridyl-ethenyl)benzene **M-1**, 2,2′,2″,2‴-(((2,5-*bis*(hexyloxy)-1,4-phenylene)*bis*(methanylylidene))bis(1*H*-indene-3,2,1 (2*H*)-triylidene))tetramalononitrile **M-2**, 1,4-*bis*[2-(4-([4]pyridyl-ethenyl))-2,5-dioctyloxy-phenyl)ethenyl]-2,5-*bis*(octyloxy)benzene **M-3**, oligo(*p*-phenylene)vinylenes **M-4** and **M-6**, 2,2′-((2*Z*,2′*Z*)-((2,5-*bis*(hexyloxy)-1,4-phenylene)*bis*(methanylylidene))*bis*(3-oxo-2,3-dihydro -1*H*-indene-2,1-diylidene))dimalononitrile **M-7** were synthesized as previously reported [8]. 4,4′-((1*E*,1′*E*)-(2,5-*bis*(octyloxy)-1,4-phenylene)*bis*(ethene-2,1-diyl))*bis*-(2,5-*bis*(octyloxy)benzaldehyde) **M-5** was synthesized by a two-step formylation of 1,4-*bis*[2-(4-bromo-2,5-dioctyloxyphenyl) ethenyl]-2,5-*bis*(octyloxy)benzene [9] consisting in the lithiation



Scheme 1. Investigated compounds.