

New Visible-Light Photoinitiating Systems for Free-Radical and Cationic Photopolymerization

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In this paper, we discuss visible-light photoinitiating systems that are developed for free-radical photopolymerization (FRP) and free-radical promoted cationic photopolymerization (FRPCP). In the former case, the use of a pyromethene dye was found to yield a high rate of polymerization as well as a high final conversion when combined with an amine and a redox additive (such as a triazine). The mechanism of reaction was investigated by laser flash photolysis, providing useful information to determine the mechanism of reaction. In the case of FRPCP, the outstanding properties of silyl radicals as a reactant for the decomposition of iodonium salt are described. It is shown that efficient FRPCP can be carried out under visible light using camphorquinone as a light-absorbing species.

Introduction

Photopolymerization has become a technology of prime importance that can be applied in very different fields, ranging from the coating industry to microelectronics, graphic arts or optics.¹ Many different photoinitiating systems are commercially available, covering a wide range of applications. Although the photopolymerization under UV light is based on a large

choice of commercially available photoinitiators exhibiting high performance at low cost, the situation is more tricky when one has to deal with visible-light photopolymerization. Indeed, besides the rare photoinitiators absorbing in the visible region, there is a painful lack of commercial systems. Therefore, there is a need for visible-light photoinitiating systems for both FRP and FRPCP. This is particularly true in the laser-imaging applications that require more photosensitivity, shelf-life properties and bleaching capability.²

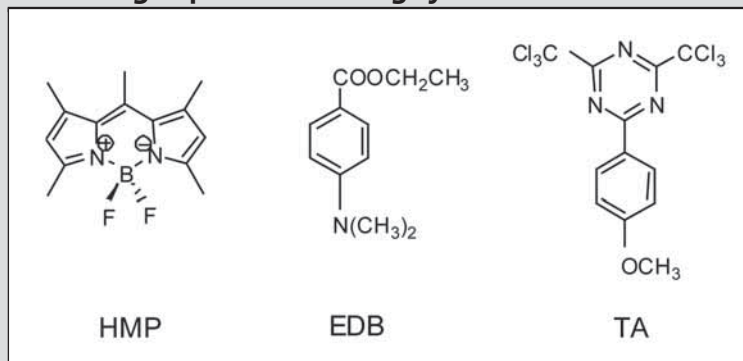
In this paper, both FRP and FRPCP initiated under visible light are addressed. Pyromethene dyes are shown to yield very good polymerization efficiency in a three-component system for FRP using an amine as coinitiator and triazine A as a redox additive. For FRPCP, new photoinitiating systems based on silyl radicals are shown to exhibit a good ability to sensitize the iodonium salt decomposition in FRPCP.

Experimental

Photopolymerizable samples were prepared using an ethoxylated bisphenol A diacrylate (SR 349 from Sartomer) for FRP or a dicycloaliphatic epoxide monomer (Cyracure 6110 from Dow) as an epoxy resin. All

FIGURE 1

Visible-light photoinitiating system for FRP



the compounds used in the different photoinitiating systems are later described in the respective parts.

The polychromatic light of a Xenon arc lamp (Hamamatsu L8253, 200 W) for FRP or a Hg-Xe lamp (Hamamatsu, L8252, 150 W) for FRPCP was used to irradiate the sample. The evolution of the double-bond content was continuously followed by real-time FTIR spectroscopy (Nexus 870 from Nicolet or Vertex from Bruker) as described elsewhere.³ The rates of polymerization R_p were calculated from the early times of the conversion curves followed at 1637 cm^{-1} in the case of acrylate and 800 cm^{-1} for the epoxide resin.

FRP

Pyrromethene dyes were first synthesized at the end of the 1980s and are strongly used as laser dyes due to their high fluorescence quantum yield.⁴ Besides their use as laser dyes, pyrromethenes have also shown very good performance as sensitizing dyes, either in free-radical photopolymerization of acrylates or together with a photoacid generator in a chemically amplified process.^{5,6} Recently, we found that pyrromethene dyes exhibited good performance in three-component photoinitiating systems.⁷

This is illustrated in Figure 2 showing that 1,3,5,7,8-pentamethyl pyrromethene difluoroborate complex (HMP, Figure 1) alone is hardly capable to initiate the photopolymerization. By contrast, in the presence of ethyl-4-dimethylaminobenzoate (EDB) and 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TA), high polymerization rates and high final conversion were noted upon visible irradiation. It can be seen in

Figure 2 that the addition of EDB and TA with respective content of EDB:TA of 2.5:1 wt% (i.e., a molar ratio of 5:1, curve b), and 0.4:5.5 wt% (i.e., a molar ratio of 1:5, curve c) clearly has a beneficial effect on the photopolymerization. It is worth noting that the best efficiency is achieved at low EDB/TA ratio.

In order to understand more deeply the mechanism involved, laser flash photolysis experiments were performed. It turns out that all the photochemical reactions are diffusion controlled in the acrylate resin. Therefore, the excited states of the dyes will predominantly react with the additive (EDB or TA) found with the highest concentration. From Figure 2, one can observe that the most efficient photopolymerization occurs when the dye reacts first with TA. This leads to the formation of the radical cation of the dye and the radical anion of TA, which is known to dissociate into an initiating radical. EDB is then involved in a secondary reaction taking place with the radical cation of the dye which

FIGURE 2

Photopolymerization of an ethoxylated bisphenol A diacrylate under visible light

Using (a) HMP and HMP/coinitiators with molar ratio of EDB:TA of (b) 5:1 and (c) 1:5 were used

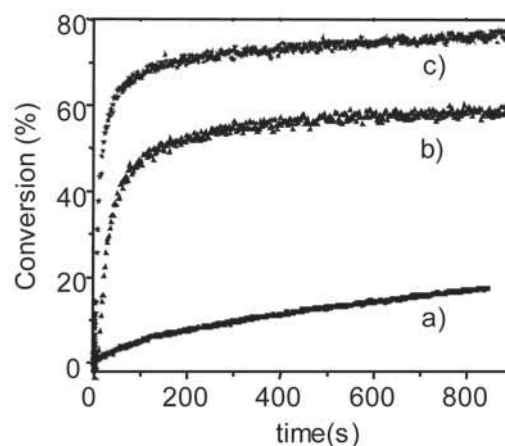
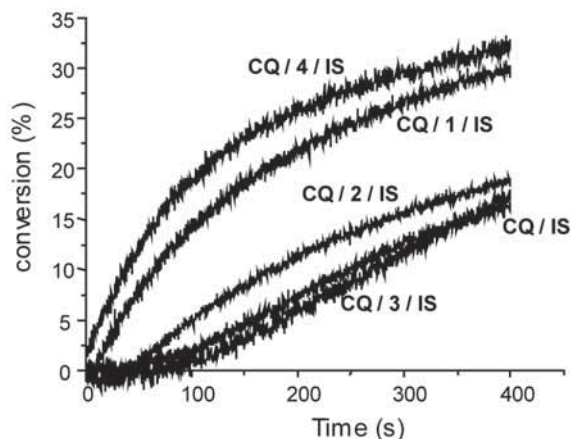


FIGURE 5

Photopolymerization of Cyracure 6110

CQ is used as the absorbing species, silanes as the radical sources and diphenyl iodonium hexafluorophosphate (IS) as a cationic photoinitiator.



Conclusion

In this paper, a couple of photoinitiating systems absorbing in the visible region and for FRP and FRPCP were investigated. It is shown that the knowledge of the photochemical reaction involved in three-component systems explains quite well the efficiency of dye-based systems for free radical polymerization. In the case of FRPCP, the outstanding properties of silyl radical can open new opportunities to sensitize the decomposition of iodonium salt. This could lead to the development of new photosensitive systems for cationic polymerization. ■

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