New visible light photoinitiating systems for free radical and cationic photopolymerization

X. Allonas*, C. Ley, J. Lalevée, O. Tarzi, A. Ibrahim, M.A. Tehfe, J.P. Fouassier

Department of Photochemistry,
University of Haute-Alsace, ENSCMu,
3, rue Alfred Werner 68093 Mulhouse Cedex, France

Abstract

In this paper, visible light photoinitiating systems are developed for Free Radical Photopolymerization FRP and Free Radical Promoted Cationic Photopolymerization FRPCP. In the former case, the use of a pyrromethene dye was found to yield high rate of polymerization as well as 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 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 light absorbing species.

I. Introduction

Photopolymerization is nowadays a technology of prime importance that is 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 performances at low costs, the situation is more tricky when one has to deal with visible light photopolymerization. Indeed, beside the rare photoinitiators absorbing in the visible region, there is a painful lack of commercial systems. Therefore, there is a need of visible light photoinitiating systems for both free radical polymerization FRP and free radical promoted cationic polymerization FRPCP. This is particularly true in the laser imaging applications that requires more and more photosensitivity, shelf-life properties and bleaching capability.[2]

In this paper, both FRP and FRPCP initiated under visible light are addressed. Pyrromethene 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 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.

II. Experimental part

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 the compounds used in the different photoinitiating systems are described below 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 were 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 Rp 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.

III. Free Radical Photopolymerization FRP

Pyrromethene dyes were first synthesized at the end of the 80s and are strongly used as laser dyes due to their high fluorescence quantum yield.[4] Beside 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 chemically amplified process.[5,6] Recently, we found that pyrromethene dyes exhibited good performance in three-component photoinitiating systems.[7]
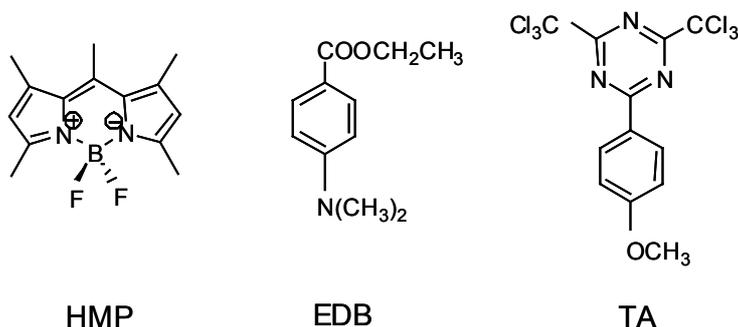
Scheme 1: Visible light photoinitiating system for FRP.

This is illustrated in Figure 1 showing that 1,3,5,7,8-pentamethyl pyrromethene difluoroborate complex (HMP, Scheme 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 from Figure 1 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) has clearly a beneficial effect on the photopolymerization. It is worth noting that the best efficiency is achieved at low EDB/TA ratio.
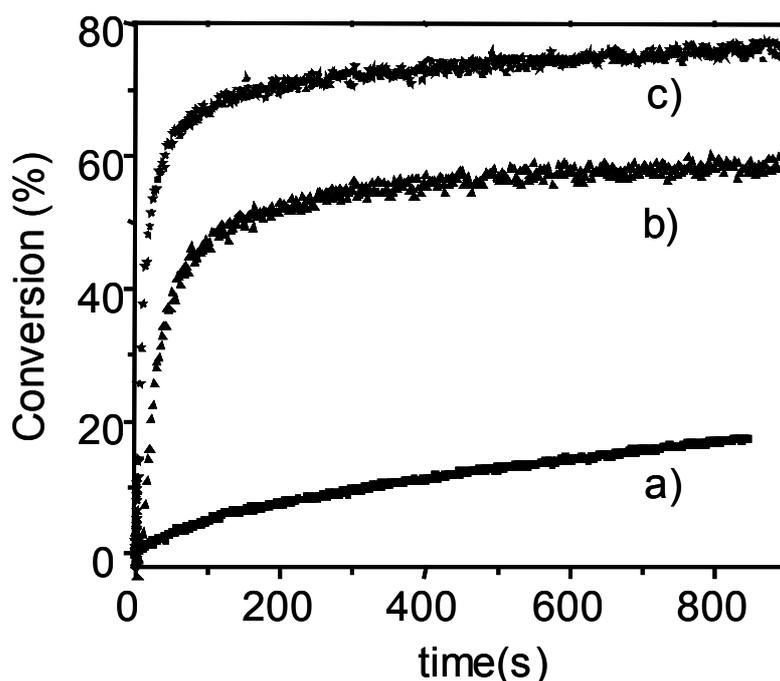
Figure 1: Photopolymerization of an ethoxylated bisphenol A diacrylate under visible light using: a) HMP, and HMP / coinitiators with molar ratio of EDB:TA of b) 5:1 and c) 1:5.

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 1, one can observed 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 radial anion of TA which is known to dissociate into initiating radical. EDB is then involved in secondary reaction taking place with the radical cation of the dye which leads to the recovery of the initial dye and the radical cation of EDB. The latter radical cation yields new initiating species after a deprotonation process (Scheme 2).
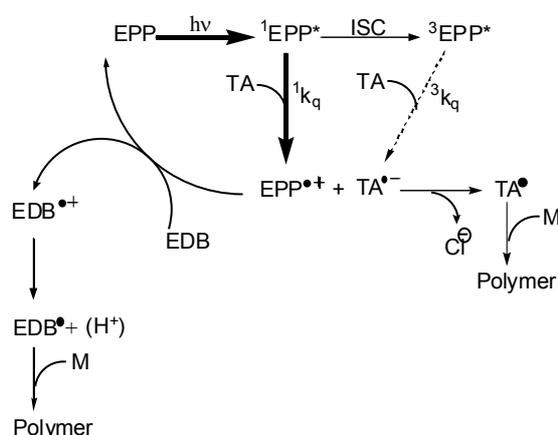

Scheme 2: photochemical mechanisms involving the HMP/EDB/TA photoinitiating system.

Therefore, the three-component system HMP/EDB/TA exhibits a high reactivity due to i) fast dissociation process of the radical anion of TA into initiating radical, ii) recovery of the starting dye from a secondary redox reaction, and iii) formation of additional initiating radical from EDB in the later redox reaction.

IV. Free Radical Promoted Cationic Photopolymerization FRPCP

The development of cationic photopolymerization reactions has been limited by the low absorption of the aryl iodonium salts in the UV range (λ < 300 nm).[8] Free radical promoted cationic polymerization FRPCP was proposed as an interesting alternative for the use of longer wavelength.[9,10] Recently, silyl radicals also revealed a pretty good ability to sensitize the decomposition of iodonium salt (IS) in free radical promoted photopolymerization.[11,12] A series of silanes that produce silyl radicals after hydrogen abstraction by camphorquinone (CQ) was investigated to sensitize iodonium salt and polymerize a dicycloaliphatic epoxide monomer (Scheme 3).

In these FRPCP experiments, camphorquinone (CQ) was used at a concentration of 3 wt % to absorb the visible light. Silanes as well as iodonium salt are added at a concentration of 1 wt %. The experimental set up was fitted with a cut off filter to select wavelengths higher than 300 nm. The absorbance of the epoxy group was continuously followed by real time FTIR spectroscopy at about 800 cm^{-1}.
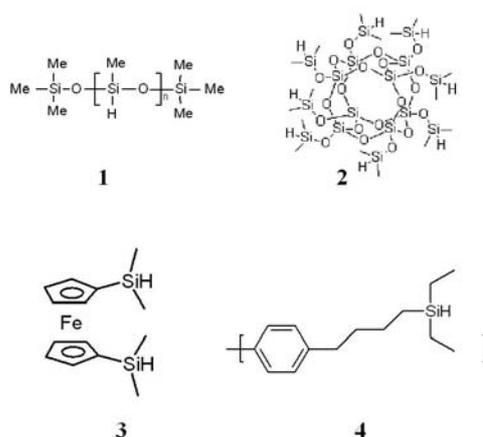
Scheme 3: Structure of the molecules used in the FRPCP photoinitiating systems

Figure 2 shows the performance of the different systems investigated (CQ/silanes/IS). For silanes 2-3, the polymerization kinetics are almost similar to that observed using CQ/IS. For 1 and 4, both the polymerization rates and the final conversion are enhanced.
These results can be explained by the hydrogen abstraction reaction between ^{3}CQ and the silane forming the silyl radical. As previously demonstrated, the silyl radical is then oxidized by IS, the generated cations R_3Si^+ being the initiating species.[11,12] The interest of using 1 and 4 also lies in their polymeric structure. Since the polymerization is initiated from the Si center, grafted polymers are obtained.
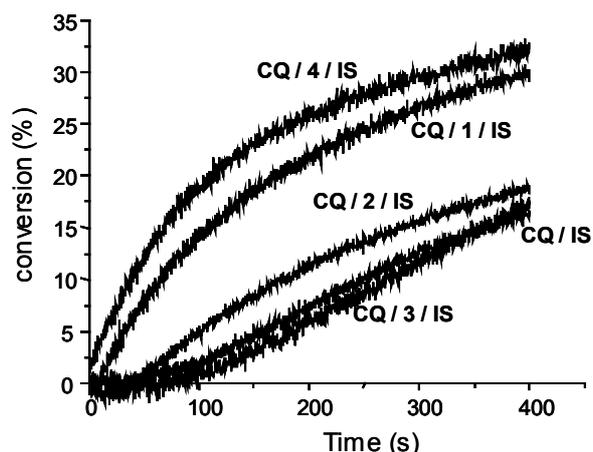
Figure 2. Photopolymerization of Cyracure 6110 using CQ as the absorbing species, silanes as the radical sources and diphenyl iodonium hexafluorophosphate (IS) as a cationic photoinitiator.

Silyl radicals are also demonstrated to be effective sensitizing radicals for the decomposition of iodonium salts in FRPCP. Their low ionization potential is likely the main parameter driving the observed high reactivity.

V. Conclusion

In this paper, a couple of photoinitiating systems absorbing in the visible region and for Free Radical Photopolymerization FRP and Free Radical Promoted Cationic Photopolymerization FRPCP were investigated. It is shown that the knowledge of the photochemical reaction involved in three-component system 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.

VI. References

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