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

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n this paper, we discuss visiblelight 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 pyrromethene 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 silvl 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 lightabsorbing 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. 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. 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 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

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. 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.

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.

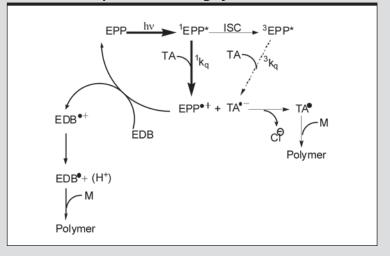
In order to understand more deeply the mechanism involved, laser flash photolysis experiments were performed. It turns out that all the photochemical reactions are diffusion controlled in the acrylate resin. Therefore, the excited states of the dyes will predominantly react with the additive (EDB or 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 radial 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 80 c) 60 Conversion (%) b) 40 20 a) 200 400 600 800 time(s)

FIGURE 3

Photochemical mechanisms involving the HMP/EDB/TA photoinitiating system



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 (Figure 3).

Therefore, the three-component system HMP/EDB/TA exhibits a high reactivity due to (i) the 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.

FRPCP

The development of cationic photopolymerization reactions has been limited by the low absorption of the aryl iodonium salts in the UV range $(\lambda < 300 \text{ nm}).^8 \text{ FRPCP was proposed}$ as an interesting alternative for the use of longer wavelengths. 9,10 Recently, silyl radicals also revealed a 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 (Figure 4).

In these FRPCP experiments, CQ was used at a concentration of 3 wt % to absorb the visible light. Silanes and iodonium salt are added at a concentration of 1 wt%. The experimental setup was fitted with

a cutoff 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.

Figure 5 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 3CQ and the silane forming the silyl radical. As previously demonstrated, the silyl radical is then oxidized by IS, the generated cations R₃Si⁺ 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.

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.

FIGURE 4

Structure of the molecules used in the FRPCP photoinitiating systems

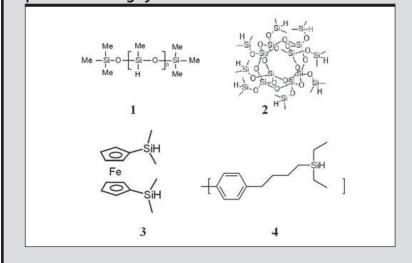
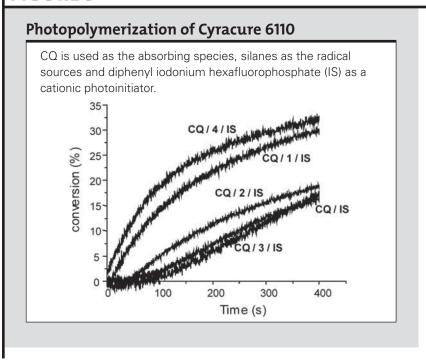


FIGURE 5



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.

References

- J.P. Fouassier, "Photoinitiation Photopolymerization and Photocuring," Hanser Publishers, Munich, New York, (1995)
- X. Allonas, C. Croutxe-Barghorn, J.P. Fouassier, J. Lalevée, J.P. Malval, F. Morlet-Savary, in "Lasers in Chemistry, Vol 2. Influencing Matter," M. Lackner Ed., Chap. 35, Wiley, (2008).
- J. Lalevée, X. Allonas, S. Jradi, J.P. Fouassier, Macromolecules 39 (2006) 1872.
- A. Costela, I. Garcia-Moreno, C. Gomez, R. Sastre, F. Amat-Guerri, M. Liras, F. Lopez Arbeloa, J. B. Prieto, I.Lopez Arbeloa, J. Phys. Chem. A 106 (2002) 7736.

- S. Blaya, P. Acebal, L. Carretero, A. Fimia, Opt. Com. 228 (2003) 55.
- S. Suzuki, X. Allonas, J. P. Fouassier, T. Urano, S. Takahara, T. Yamaoka, J. Photochem. Photobiol. A: Chem. 181 (2006) 60.
- 7. O. I. Tarzi, X. Allonas, C. Ley, J.-P. Fouassier, submitted
- 8. J.V. Crivello, J.H.W. Lam J. Polym. Sci. Polym. Chem. Ed. 17 (1979) 1059.
- 9. J.V. Crivello, M. Sangermano J. Polym. Sci. Part A: Chem 39 (2001) 343.
- Y. Bi, D.C. Neckers, Macromolecules, 27 (1994) 3683.
- J. Lalevée, M. El-Roz, X. Allonas, J. P. Fouassier, J. Polym. Sci. A Pol. Chem., 46 (2008) 2008.
- 12. N. Arsu, G. Hizai, Y. Yagci, Macromol. Reports (1995) 1257.

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