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Cyclopentadienyl(iron)arene-bis-(*p*-*N,N*-dimethylaminobenzylidene)-cyclopentanone Photoinitiated Polymerization of Methyl Methacrylate and Styrene

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CYCLOPENTADIENYL(IRON)ARENE-BIS- (*p*-*N,N*-DIMETHYLAMINO BENZYLIDENE)- CYCLOPENTANONE PHOTOINITIATED POLYMERIZATION OF METHYL METHACRYLATE AND STYRENE

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ABSTRACT

Polymerization of methyl methacrylate and styrene can be effectively photoinitiated by a binary photoinitiator system consisting of cyclopentadienyl(iron)arene hexafluorophosphate salt and bis(*p*-*N,N*-dimethylaminobenzylidene)cyclopentanone in the spectral range of 400–500 nm. The amine-type radical formed from the exciplex of the binary photoinitiator system is probably responsible for the radical polymerization of vinyl monomers. A probable mechanism of initiation of polymerization is discussed.

INTRODUCTION

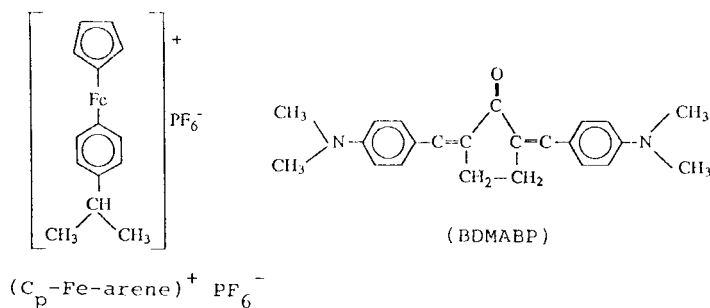
Organometallic photoinitiators are known to form radicals or cations which can initiate radical and/or cationic polymerization [1-3]. They are used for photopolymerization of a number of monomers on a commercial scale for surface coatings, printing inks, photoresists materials, protective coatings of electronic parts, stereolithography, can coatings, etc. However, their application for photocuring polymeric dental composites has not yet been considered. Most common photoinitiators undergo photofragmentation with the formation of free radicals when exposed to UV radiation below 400 nm. Application of this type of UV radiation is restricted in the oral cavity because of carcinogenic, photoallergic, mutagenic effects and the risk of oral tissue burning [4]. The only light irradiation allowed for application in the oral cavity is at wavelengths over 400 nm [5]. Commercially produced irradiation lamps for restorative dentistry operate with blue light at a maximum of 470 nm. This causes a number of problems in finding a photoinitiating system effective in this spectral region, i.e., which absorbs blue light [6]. Vinyl monomers are used as diluents for high viscous di- and trifunctional monomers in dental polymeric composite materials [7].

Organometallic photoinitiators are considered for future use in curing dental materials because they allow for photocuring of thick layers and are bleached during photopolymerization. Furthermore, photocuring of nontransparent dental polymeric formulations has become possible. The absorption bands of iron-based photoinitiators extend into the visible region of the spectrum.

Iron(II)arene salts exhibit intense absorption in the 400-500 nm region. However, the low molecular extinction coefficient is a serious disadvantage for these complex photoinitiators [8]. Therefore, it is necessary to use a sensitizer (or cophotoinitiator) which can enhance the sensitivity of iron(II)arene salts toward light absorption. Bis(*p*-*N,N*-dimethylaminobenzylidene)ketone has been reported in the patent literature [9] to be an effective sensitizer for iron(II)arene salts. However, the mechanism of this photosensitization reaction has not been elucidated. The aim of the present work was to investigate the mechanism of sensitization of photoinitiation by the above-mentioned system.

EXPERIMENTAL

A commercially available photoinitiator iron(II)arene complex, IRGACURE 261 (η^5 -2,4-cyclopentadien-1-yl)[(1,2,3,4,5- η)-(1-methyl)-benzene]-iron(II)-hex-



afluorophosphonate(1-) (CIBA GEIGY), was additionally purified by crystallization from nitromethane $(C_p\text{-Fe-arene})^+PF_6^-$ ($C_p = \eta^5\text{-cyclopentadienyl}$).

The sensitizer, bis(*p*-*N,N*-dimethylaminobenzylidene)cyclopentanone (BDMABP), was prepared according to the literature [10].

Methyl methacrylate (Aldrich) and styrene (Aldrich) were carefully purified by standard methods and distilled under reduced pressure in a nitrogen atmosphere before use.

Absorption and fluorescence spectra were recorded using Hitachi 330 UV/Vis and Hitachi MPF-4 fluorescence spectrometers, respectively.

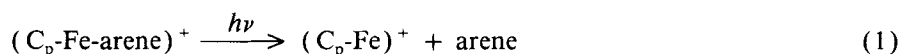
The kinetics of formation of isopropylbenzene during the photolysis of $(C_p\text{-Fe-arene})^+$ was monitored by a Shanghai Analytic 102-G chromatograph.

Light irradiations of samples were carried out using two types of xenon lamps (equipped with cut-off filters at 514 nm): SW 150 W (for photolysis study) and CSX 2000 W (for polymerization).

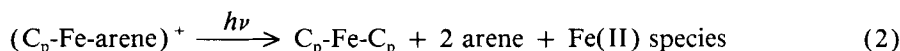
Polymerizations were carried out in a photoreactor under a nitrogen blanket at room temperature. After a given time of irradiation, the polymer was precipitated with a nonsolvent and dried at 60°C to constant weight. The monomer conversion was determined gravimetrically.

RESULTS AND DISCUSSION

UV/Vis absorption spectra of cyclopentadienyl(Fe)isopropylbenzene hexafluorophosphonate salt $(C_p\text{-Fe-arene})^+$ (Fig. 1) and bis(*p*-*N,N*-dimethylaminobenzylidene)cyclopentanone (BDMABP) (Fig. 2) overlap in the spectral region 350–550 nm. Both these compounds are slowly photolyzed under light irradiation; however, $(C_p\text{-Fe-arene})^+$ (Fig. 1) bleaches much faster than BDMABP (Fig. 2). It has been proposed that $(C_p\text{-Fe-arene})^+$ is photolyzed according to the mechanism [11]:



On the other hand, photolysis of $(C_p\text{-Fe-arene})^+$ in acetonitrile solution yields ferrocene ($C_p\text{-Fe-}C_p$), arene, and an Fe(II) species [12, 13]:



Irradiation of $(C_p\text{-Fe-arene})^+$ in aprotic solvents in the presence of the ligands also results in the formation of ferrocene, arene, and iron(II)hexafluorophosphonate [14].

The photolysis of BDMABP has not been reported in the literature.

During photolysis of the binary $(C_p\text{-Fe-arene})^+$ -BDMABP system, the following observations were made:

1. Addition of $(C_p\text{-Fe-arene})^+$ to BDMABP in dichloroethane accelerates the photolysis of the latter (Fig. 3).
2. Addition of BDMABP to $(C_p\text{-Fe-arene})^+$ enhances its photolysis and the formation of isopropylbenzene (Fig. 4). The differences in these two curves suggest that at least two processes are operative, a rapid process which is affected by the presence of BDMABP and a slower process which may or may not be

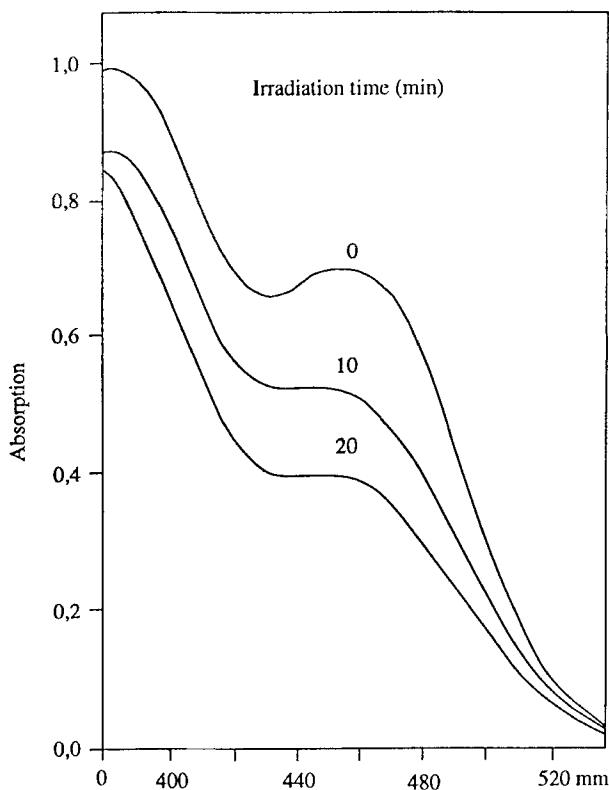
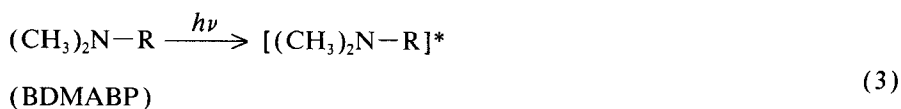


FIG. 1. Change of absorption spectra of $(C_p\text{-Fe-arene})^+$ (1×10^{-3} M) in dichloroethane under light irradiation (SW 150 W).

affected by the presence of BDMABP. Furthermore, these results may indicate an additional reaction arising from energy transfer from BDMABP to $(C_p\text{-Fe-arene})^+$.

3. Addition of $(C_p\text{-Fe-arene})^+$ to BDMABP in dichloroethane strongly quenches its fluorescence and causes a red shift of the fluorescence peak wavelength (Fig. 5). The quenching results obtained cannot be directly fitted to the Stern-Volmer relationship because both $(C_p\text{-Fe-arene})^+$ and BDMABP are simultaneously photolyzed.

These observations support the following mechanism of the photolysis of the binary $(C_p\text{-Fe-arene})^+$ -BDMABP system:



or

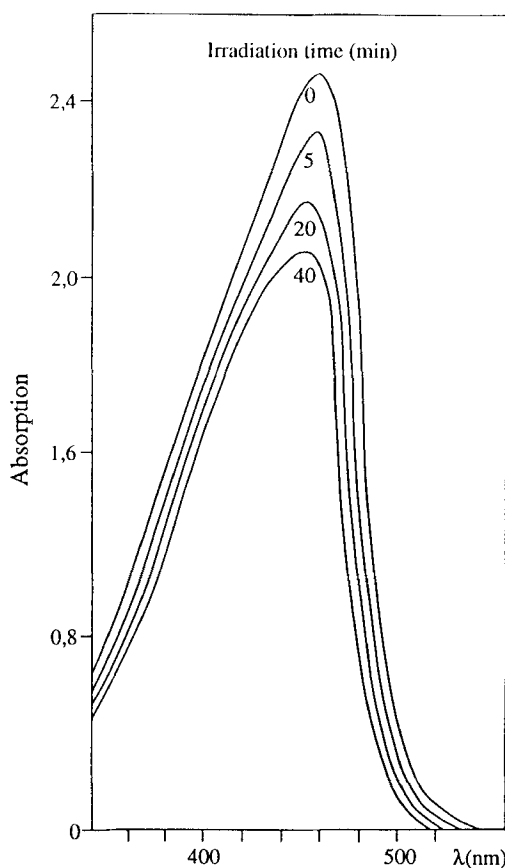
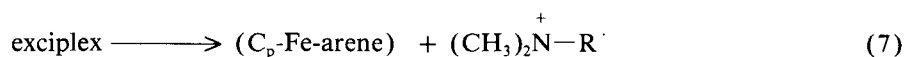
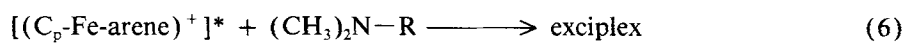
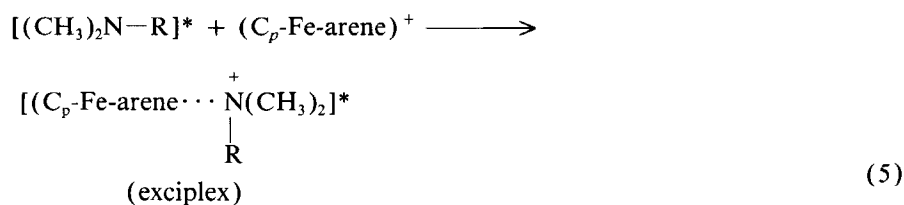
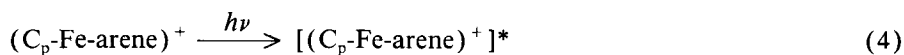


FIG. 2. Change of absorption spectra of BDMABP (1×10^{-4} M) in dichloroethane under light irradiation (SW 150 W).



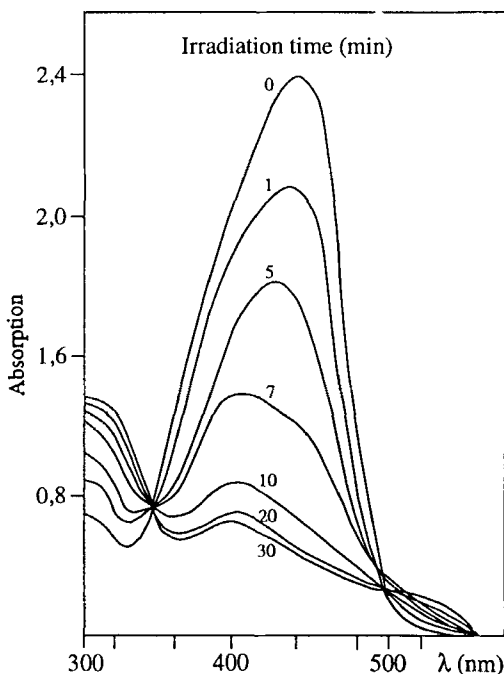
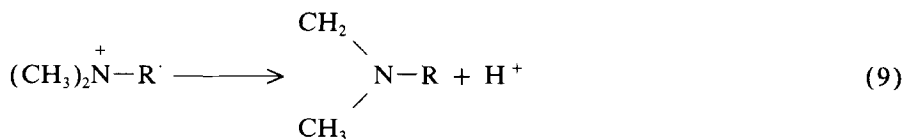
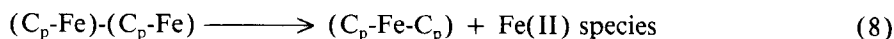
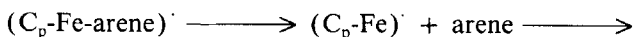


FIG. 3. Change of absorption spectra of $(C_p\text{-Fe-arene})^+$ (1×10^{-2} M)-BDMABP (1×10^{-4} M) in dichloroethane under light irradiation (SW 150 W).



The red shift of the fluorescence peak wavelength (Fig. 5) can be a result of the formation of an exciplex between the excited state of $[(BDMABP)]^*$ or $[(C_p\text{-Fe-arene})^+]^*$ and its counterpart in the ground state. Because both components absorb in the same spectral range, it is difficult to estimate the mechanism of exciplex formation. Decomposition of the exciplex produces the amine-group radical (of BDMABP) (Reaction 9), ferrocene, and arene (isopropylbenzene) (Reaction 8).

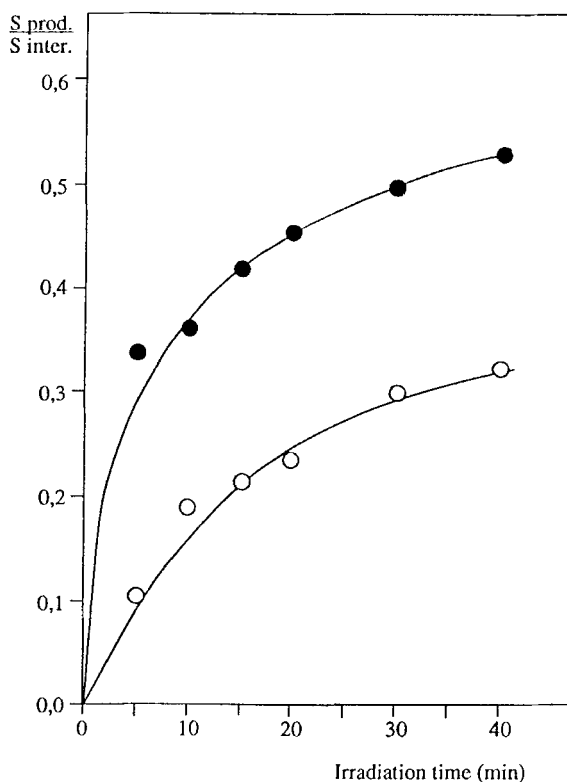


FIG. 4. Kinetic of formation of isopropylbenzene during light irradiation of (○) $(C_p-Fe-arene)^+$ and (●) $(C_p-Fe-arene)-BDMABP$ ($1 \times 10^{-2} M$).

The binary $(C_p-Fe-arene)^+-BDMABP$ system effectively photoinitiates polymerization of methyl methacrylate (MMA) and styrene (St) (Fig. 6). Polymerization reaction can be completely inhibited by addition of 0.01 g diphenylpicrylhydrazyl (DPPH) or 0.01 g 2,6-di-*tert*-butyl- α -(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-4-tolyloxy (Galvinoxyl radical), which are very effective radical scavengers. Oxygen (air) also inhibits polymerization. Radical polymerization of MMA and St is probably initiated by the amine-group radical (BDMABP) formed in Reaction (9). This type of amine radical is formed by the proton transfer mechanism during UV irradiation of a binary amine-aromatic ketone (e.g., benzophenone) system and can easily initiate polymerization of vinyl monomers [15]. Increasing the BDMABP content in the binary photoinitiating system from 0.1:1 to 1:1 enhances the percentage of MMA and St conversion (Fig. 6).

Photopolymerization of MMA and St does not occur when $(C_p-Fe-arene)^+$ or BDMABP are used separately. A strong Lewis acid (HPF_6) does not initiate polymerization, either. The $(C_p-Fe-arene)^+$ in the presence of CCl_4 and at a high concentration can photoinitiate polymerization of MMA but not of St. Ferrocene

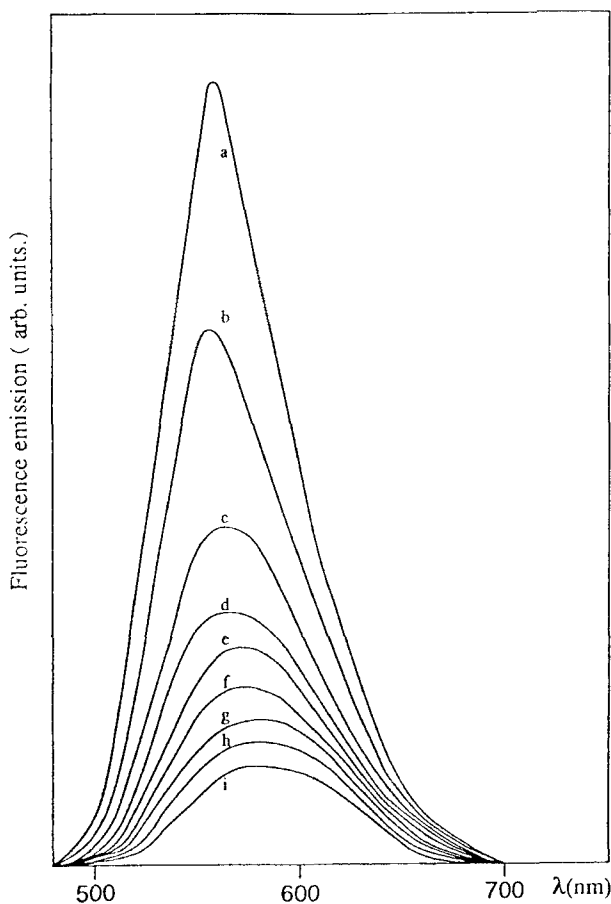


FIG. 5. Change of fluorescence emission spectra of BDMABP (1×10^{-5} M) ($\lambda_{\text{ex}} = 460$ nm) in the presence of $(\text{C}_p\text{-Fe-arene})^+$: (a) 0.0 M; (b) 5.0×10^{-5} M; (c) 1.0×10^{-4} M; (d) 1.5×10^{-4} M; (e) 2.0×10^{-4} M; (f) 2.5×10^{-4} M; (g) 3.0×10^{-4} M; (h) 3.5×10^{-4} M, and (i) 4.0×10^{-4} M.

$(\text{C}_p\text{-Fe-C}_p)$ is formed from the photolysis of $(\text{C}_p\text{-Fe-arene})^+$ and can be considered to be a rather weak photoinitiator of polymerization. $(\text{C}_p\text{-Fe-arene})^+$ in the presence of CCl_4 also causes the photoinitiated polymerization of pyrrole [16].

It was reported that ferrocene photoinitiates the polymerization of acetonitrile (AN) but not of MMA and St. However, in the presence of CCl_4 , ferrocene is an effective photoinitiator of polymerization of MMA, AN, and isobutyl vinyl ether (IBVE) but not of St [17, 18]. The charge-transfer (CT) complex of ferrocene with CCl_4 [19, 20] was found to play an important role in the mechanism of photoinitiated polymerization of vinyl monomers [17, 18, 21, 22]:

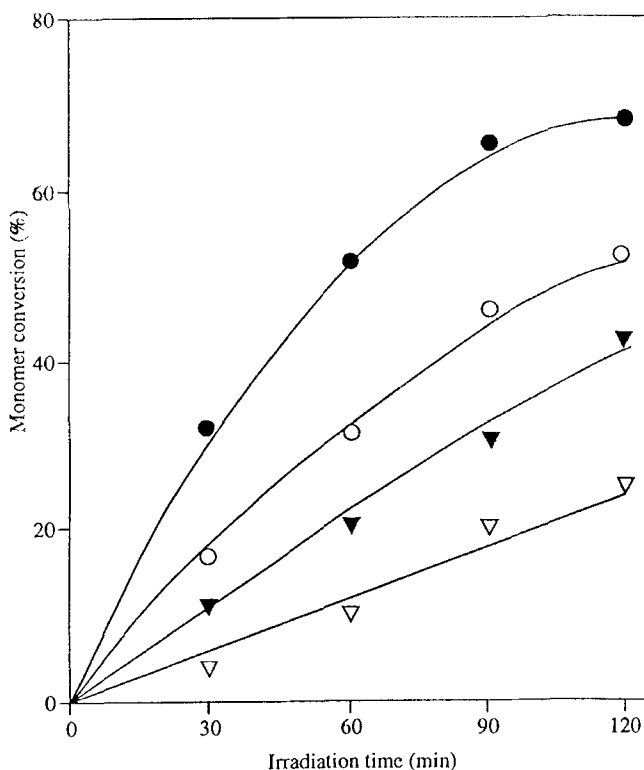
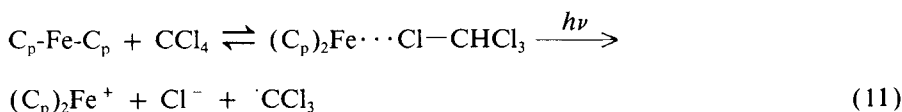


FIG. 6. Kinetic of polymerization of St (∇ , \blacktriangledown) and MMA (\circ , \bullet) in the presence of $(C_p\text{-Fe-arene})^+$ (10^{-3} M)-BDMABP (10^{-4} M) (∇ , \circ) and $(C_p\text{-Fe-arene})^+$ (10^{-3} M)-BDMABP (10^{-3} M) (\blacktriangledown , \bullet) during light irradiation (CSX 200 W).



It is most unlikely that ferrocene formed during photolysis of the binary system $(C_p\text{-Fe-arene})^+$ -BDMABP in the absence of CCl_4 would initiate the polymerization of MMA and St. The photolysis products of $(C_p\text{-Fe-arene})^+$ added to BDMABP and further irradiated do not initiate a polymerization reaction.

Chinese scientists have reported [23, 24] that $(C_p\text{-Fe})$ and C_p radicals are formed during photolysis of ferrocene, and they are easily detected by ESR spectroscopy. These radicals are probably not efficient for initiating the polymerization of vinyl monomers.

It was also found that the bimolecular-type photoinitiator system based on $(C_p\text{-Fe-arene})^+$ and 3,3',4,4'-tetrakis(*tert*-butyl-dioxy-carbonyl)benzophenone in the presence of an amine-type coinitiator such as di(4-diethylaminocumarino)ketone (KCD) causes very efficient photopolymerization (at 499 nm, argon laser

radiation) of pentaerythritol triacrylate for holograms [25]. A similar electron transfer with the formation of amine-type radicals was considered, since the excited triplet state of KDC is also effectively quenched by $(C_p\text{-Fe-arene})^+$.

CONCLUSIONS

Photoinitiated polymerization of methyl methacrylate and styrene by the binary cyclopentadienyl(iron)arene-bis(*p*-*N,N*-dimethylaminobenzylidene)cyclopentanone system is probably caused by the amine-type radical formed from photolysis of the photoinitiator system used. The primary photochemical reaction (i.e., formation of an exciplex), however, is still unclear. This photoinitiating system can be considered for application in visible light photocuring of di- and trifunctional (meth)acrylic monomers used widely in dental restorative polymeric composites, as well as in the photopolymerization of holographic recording materials.

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