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A new visible light bimolecular photoinitiator system for free radical polymerization

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ABSTRACT

A new bimolecular photoinitiator system consisting of a ferrocenium salt (Fc) and N-methyl-2-pyrrolidone (NMP) is developed for free radical photopolymerization under visible light irradiation, which was delivered by a halogen lamp. Photopolymerization profiles of tripropylene glycol diacrylate (TPGDA) show that high conversion can be easily achieved. The processes associated with the Fc/NMP system are investigated by photochemical and electrochemical experiments. The results show that the photoinitiation mechanism of this bimolecular system could occur through charge transfers between Fc and NMP.

1. Introduction

Photopolymerization under the influence of visible light has recently been paid increased attention because of the less-harmful character of light at $\lambda > 400$ nm. Applications of the process in outdoor exposure conditions or in laser imaging science have been studied as well [1–3]. The photoinitiator, which is responsible for the absorption and transformation of light into chemical energy, is the key component in visible light-induced polymerization.

Camphorquinone (CQ)/tertiary amine (TA), functioning as a visible light curing photoinitiating system, is widely used in dental filling compositions [4,5]. CQ shows a broad absorption spectrum between 400 and 550 nm ($\lambda_{max} = 468$ nm). The disadvantages of CQ-TA photoinitiators, however, include toxicity of the amines used and yellowing of the cured materials caused by oxidation of amine impurities. A number of other visible light curing photoinitiators have been evaluated, for example, bisacylphosphine oxides [6,7], titanocenes [8], organic borates [9], and germanyl ketones [10]. Of these, only bisacylphosphine oxide has been partially used in industry applications. To increase the absorption in visible light regions, dye components are often included in most visible light photoinitiator systems as sensitizers. Therefore, visible light photoinitiators usually consist of two or three components, sometimes even four, to achieve high efficiency.

Fcs have been used as photoinitiators for cationic polymerization in visible light because they possess absorption capabilities in the middle region of the UV spectrum. The absorption and photoactivities of Fcs can be modified through structural changes of the ligands [11–14]. Photoinitiator systems of Fc/hydroperoxide and Fc/dye for free radical photoinitiation have been reported, and a possible mechanism for such has been proposed by Fouassier et al. [15–19]. According to reports, oxygen/hydroperoxide or dye is necessary for Fcs to photoinitiate free radical polymerization under visible light. In one report, a four-component system, consisting of a xanthenic dye, an Fc, a hydroperoxide, and an amine, was found to be effective in photoinitiating the radical polymerization of thick films.

In our laboratory, a great number of novel Fcs have been synthesized and studied as cationic photoinitiators. To promote the wide use of these Fcs, their ability to act as photoinitiators of free radical polymerization under visible light was investigated, and results showed that Fc/NMP bimolecular systems can efficiently photoinitiate the free radical photopolymerization of acrylic monomers under visible light even above 500 nm. This finding simplifies the photoinitiation system of Fcs as free radical photoinitiators and solves the problems inherent in using dye as a photosensitizer.

In this paper, the photoinitiating ability of Fc/NMP bimolecular photoinitiator systems is evaluated by near infrared (NIR) spectroscopy, and the photochemistry and electrochemistry involved in such systems are studied. The mechanism for this bimolecular photoinitiated free radical polymerization process is also discussed.

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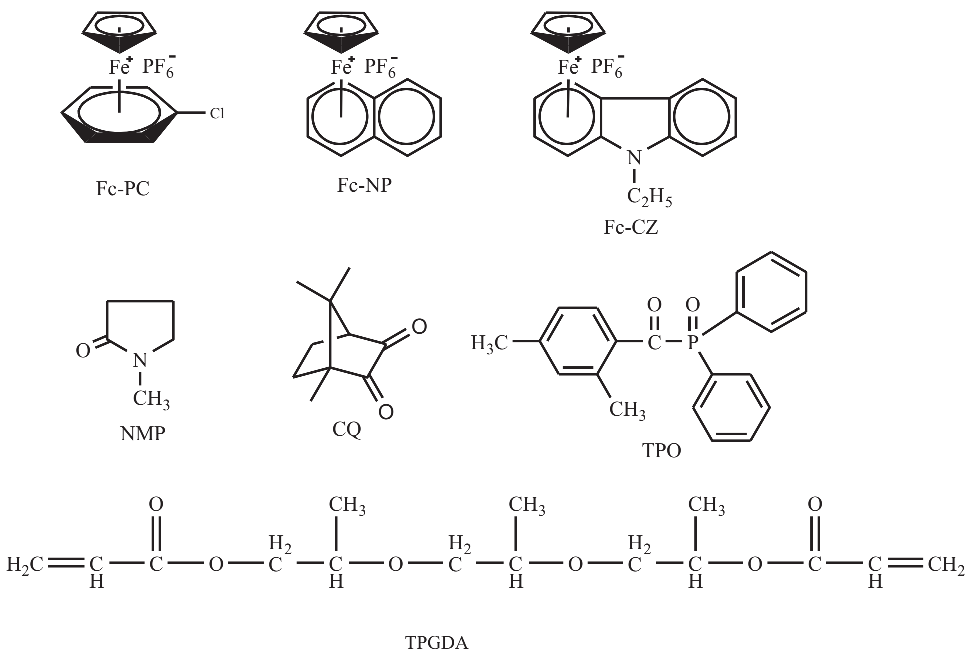


Scheme 1. Structures of the photoinitiators and monomers.

2. Experimental

2.1. Materials

The Fcs (η6-chlorobenzene)(η5-cyclopentadienyl) iron hexafluorophosphate (Fc-PC) [20,21], (η6-naphthalene)(η5-cyclopentadienyl) iron hexafluorophosphate (Fc-NP) [22], and (η6-N-ethyl carbazole)(η5-cyclopentadienyl) iron hexafluorophosphate (Fc-CZ) [14] were all prepared in our laboratory and highly purified by column chromatography. The NMP was analytically pure, and water was removed by a molecular sieve. TPGDA obtained from Sartomer (Warrington, PA) was used as a monomer for free radical polymerization. CQ and (2,4,6-trimethylbenzoyl)diphenyl-phosphine oxide (TPO) were used as referenced long-wavelength free radical photoinitiators (Aldrich). Tetrabutylammonium hexafluorophosphate (NBu_4PF_6) was synthesized from tetrabutylammonium bromide (reagent grade, Beijing, China) by anion metathesis with HPF_6 (recrystallized in ethanol–water mixture and dried under vacuum) as a supporting electrolyte [23].

Scheme 1 summarizes the abbreviations and structures of all the materials employed in the polymerizations studied in this paper.

2.2. Instruments

FTIR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA). UV–vis absorption spectra were recorded on a Hitachi U-3010 UV-vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). Light intensity was recorded by a UV light radiometer (Photoelectric Instrument Factory, Beijing Normal University, China).

Fluorescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. The instrument directly provides corrected excitation spectra; fluorescence emission spectra were corrected for the characteristics of the emission monochromator and for the detection of the photomultiplier response.

Two kinds of optical filters were used: a wide passband filter, which can cut off light below 460 nm, and an interference filter, which only allows light at 540 nm to pass.

The electrochemical behavior of the bimolecular photoinitiator system was investigated by cyclic voltammetry with an LK3200A electrochemical workstation (Lanlike Chemistry and Electron High Technology Corporation, Tianjin, China).

2.3. NIR spectroscopy measurement

Near infrared (NIR) spectroscopy was used to measure the double bond conversion as a function of exposure time in the resins. All samples were photocured in 1.8 mm thick plastic molds with a 10 mm diameter. The molds were clamped between two glass slides, and samples were irradiated with a visible light source ($\lambda > 370$ nm, halogen lamp, 50 W, $I = 1–5$ mW/cm^2). Optical filters were also used for further investigations on free radical polymerization under special long-wavelength visible light. For each sample, RT-NIR runs were repeated three times. The specimens were irradiated at different time intervals by manually controlling the curing light. Upon collection of the uncured resin NIR spectrum, spectra were immediately obtained after each exposure interval. Double bond conversion profiles were calculated from the decay of the absorption band located at 6167 cm^{-1} as described by Stansbury and Dickens [24]. The double bond conversion was calculated using Eq. (1):

$$\text{DoubleBondConversion\%} = \left[1 - \frac{S_t}{S_0}\right] \times 100 \qquad (1)$$

where S_t is the area of the C=C characteristic absorbance peak and S_0 is the initial area of the C=C characteristic absorbance peak.

2.4. Electrochemical measurement

Reduction and oxidation potentials were determined by cyclic voltammetry (CV) in acetonitrile solutions containing 0.1 M NBu_4PF_6 as a supporting electrolyte. The reference electrode was a saturated calomel electrode (SCE); the electrode was connected to the sample solution through a fritted glass bridge containing the supporting electrolyte solution. The three-electrode system employed was based on an LK3200A Electrochemical station. A platinum electrode was used as working electrode, and a glassy carbon counter-electrode completed the setup.

3. Results and discussion

3.1. Free radical polymerization photoinitiated by the ferrocenium salt/NMP bimolecular system

To study the ability of Fcs to act as photoinitiators of free radical polymerization under visible light, Fc-PC, Fc-NP, and Fc-CZ were selected. The Fcs were unable to photoinitiate the polymerization of acrylic monomers when used as single photoinitiator components. When these Fcs were used with peroxide, no photoinitiating ability was also observed. However, when NMP was added to the photopolymerization system, the Fcs efficiently photoinitiated the free radical photopolymerization of acrylic monomers. Thus, the photoinitiating abilities of the Fc/NMP bimolecular systems were evaluated in the photopolymerization of TPGDA under halogen lamp irradiation. For comparison, CQ/triethanolamine (TEA) and TPO were also tested as photoinitiators.

Fig. 1(a) shows results directly obtained from the photopolymerization systems under the halogen lamp ($\lambda > 370$ nm). The Fc/NMP bimolecular systems exhibited good photoinitiating ability. Photopolymerization profiles showed that polymerization rates and final double bond conversion of TPGDA photoinitiated by the Fc/NMP photoinitiator systems were significantly higher than those of two commonly used long-wavelength visible photoinitiators, CQ and TPO, under the same experimental conditions.

Fig. 1(b) shows results obtained from the use of a wide pass-band filter ($\lambda \geq 460$ nm) under the halogen lamp. While TPO did not show photoinitiating ability and the ability of CQ/TEA significantly decreased, the filter had little effect on the photoinitiating ability of Fc/NMP, especially on those of the Fc-CZ/NMP and Fc-PC/NMP systems.

Fig. 1(c) shows results obtained from the use of an interference filter ($\lambda = 540$ nm) under the halogen lamp. CQ/TEA and Fc-PC/NMP showed no photoinitiating ability under this filter. In contrast, the Fc-CZ/NMP and Fc-NP/NMP systems showed obvious photoinitiating ability.

The results obtained in Fig. 1 are related to the UV–vis absorption of the photoinitiators in dichloromethane, as shown in Fig. 2. All three Fcs had weak absorption above 460 nm due to d–d transitions. CQ also showed some weak absorption above 460 nm due to *n*–π transitions, and TPO showed no absorption above 460 nm. Above 540 nm, only Fc-NP and Fc-CZ possessed some absorption.

3.2. Photolysis of ferrocenium salts in the presence of NMP

The NIR results show that the Fc/NMP bimolecular systems exhibit good visible light-cured free radical polymerization performance. Thus, it is very interesting to determine how Fc and NMP interact to understand the photoinitiation mechanism of such bimolecular photoinitiator systems. The UV–vis spectra of Fc-NP and Fc-NP/NMP in dichloromethane are compared in Fig. 3, and the photolysis of Fc and Fc /NMP under visible light was also studied. The absorption spectrum of NMP is also given as a reference.

Fig. 3 shows that the introduction of NMP significantly enhances the absorbance of Fc at the ground state. This is believed to be caused by Fc/NMP generation of a ground state complex, and this complex may show higher absorbance than Fc alone.

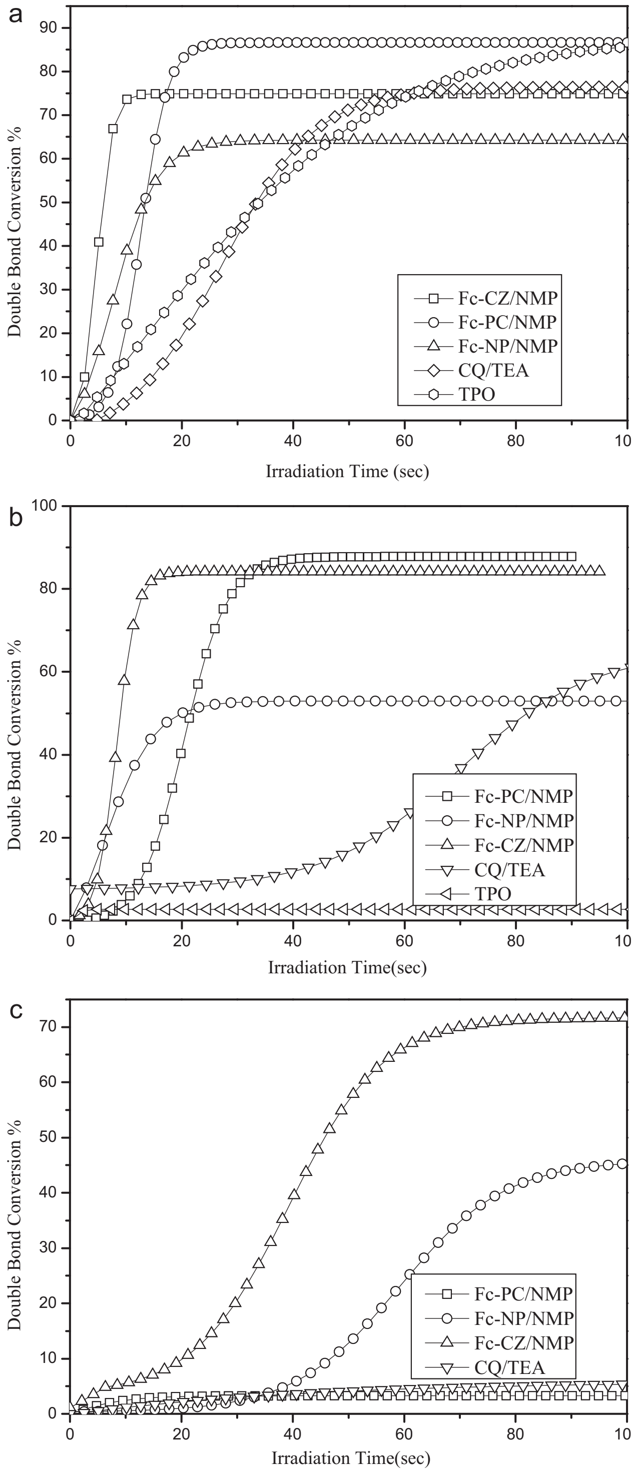


Fig. 1. Double bond conversions of TPGDA photoinitiated by ferrocenium salt/NMP bimolecular systems, comparing with CQ/TEA and TPO. The concentration of photoinitiator is 0.6 mol% and the molar ratio of ferrocenium salt to NMP is 1:50. (a) In the absence of filters, $I = 1$ mW/cm^2; (b) in the presence of a filter ($\lambda \geq 460$ nm), $I = 2$ mW/cm^2; (c) in the presence of a filter ($\lambda = 540$ nm), $I = 5$ mW/cm^2. TEA was used as amine co-initiator for CQ and the molar ratio of CQ to TEA is 1:50.

Fig. 4 shows the photolysis of Fc-NP as an example of an Fc at a concentration of 10^{-3} M in the absence and presence of NMP. The absorbance of Fc-NP gradually decreased with increasing irradiation time. The absorbance of Fc-NP/NMP was completely different from that of Fc-NP, and exhibited a higher photolysis rate under visible light. Therefore, it can be concluded that Fc first combines with NMP to form a ground state complex. When directly irradiated by the halogen lamp, the complex is excited and then photodecomposed with high efficiency with increasing irradiation time.

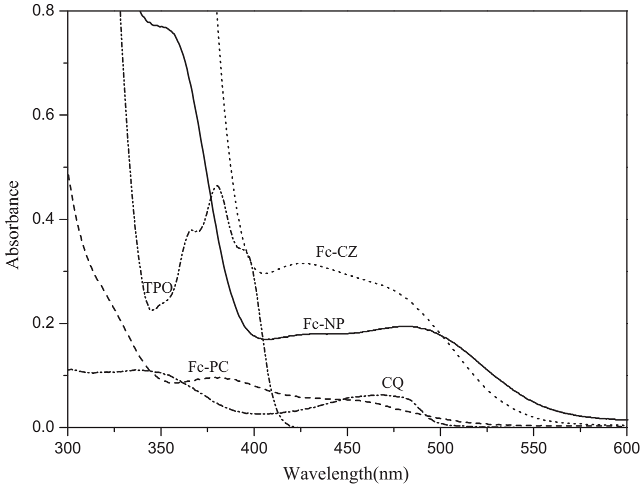


Fig. 2. UV–vis spectra of 10^{-3} M Fc-PC, Fc-NP, Fc-CZ, CQ and TPO in dichloromethane.

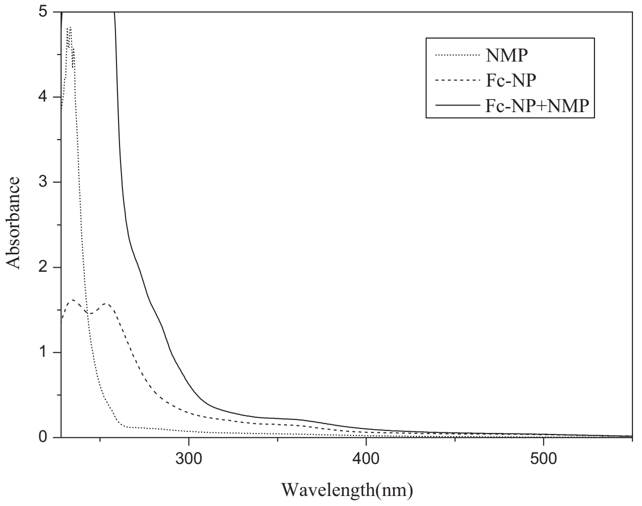


Fig. 3. UV–vis spectra of 10^{-4} M NMP, 10^{-4} M Fc-NP with and without NMP in dichloromethane.

3.3. Electrochemical studies

As we consider the photoinitiation mechanism of Fc/NMP photoinitiation systems, electron transfer is the main process by which these bimolecular systems generate active free radicals to initiate the polymerization of acrylate monomers. Therefore, cyclic voltammograms (CVs) were carried out to demonstrate the possibility of an electron transfer (ET) process between an Fc and NMP.

The free energy change (ΔG_{el}) is an important parameter for the ET process. If ΔG_{el} is negative, the ET process is thermodynamically allowed [25,26]. In this paper, the ΔG_{el} for the ET reaction between the excited state of an Fc as an electron acceptor and NMP as an electron donor was calculated based on the Rehm–Weller equation (Eq. (2)) [26]:

$$\Delta G_{\text{el}} = E_{\text{ox}}\left(\frac{D}{D^{\bullet+}}\right) - E_{\text{red}}\left(\frac{A^{\bullet-}}{A}\right) - \frac{Ze^2}{\varepsilon a} - E_{00} \quad (2)$$

In this paper, $E_{\text{ox}}(D/D^{\bullet+})$ is the oxidation potential of the electron donor and $E_{\text{red}}(A^{\bullet-}/A)$ is the reduction potential of the electron accepter. E_{00} is the singlet excited state energy of the electron-accepting molecule obtained by Eq. (3) [27]. $Ze^2/\varepsilon a$ is Coulombic energy and considered negligible with respect to the overall magnitude of ΔG_{el}.

$$E_{00} = \frac{hcN}{\lambda} \quad (3)$$

The oxidation potential of NMP ($E_{\text{ox}} = 1.121$ V) as an electron donor in the bimolecular photoinitiated system was measured in a separate experiment. The oxidation and reduction potentials of three Fcs and the calculated ΔG_{el} for all photoredox pairs are presented in Table 1. The excitation spectra and emission spectra of the Fcs are measured by fluorescence spectrometer, as given in Fig. 5.The negative ΔG_{el} values of the Fc-PC/NMP, Fc-NP/NMP,

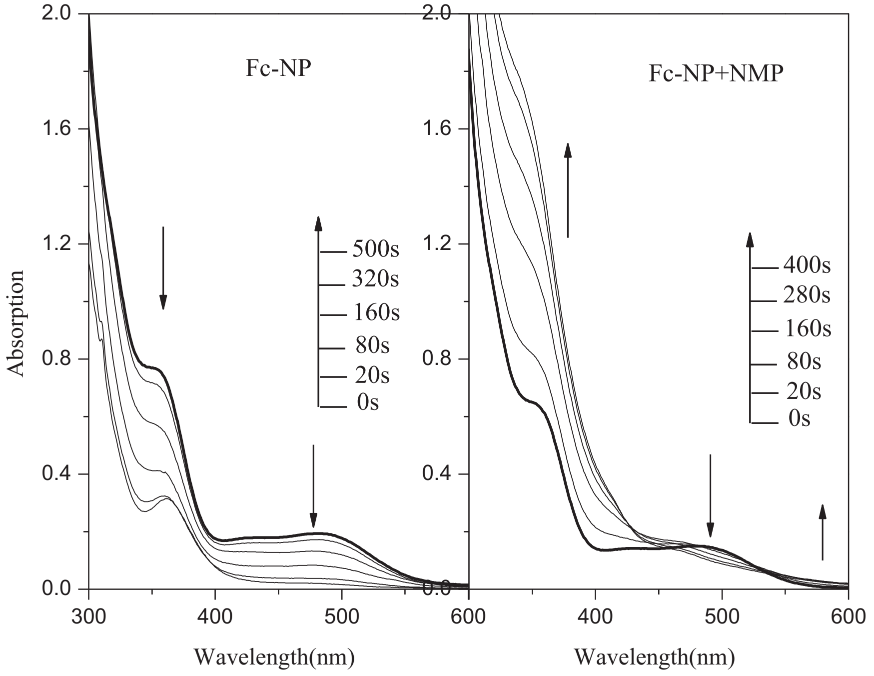
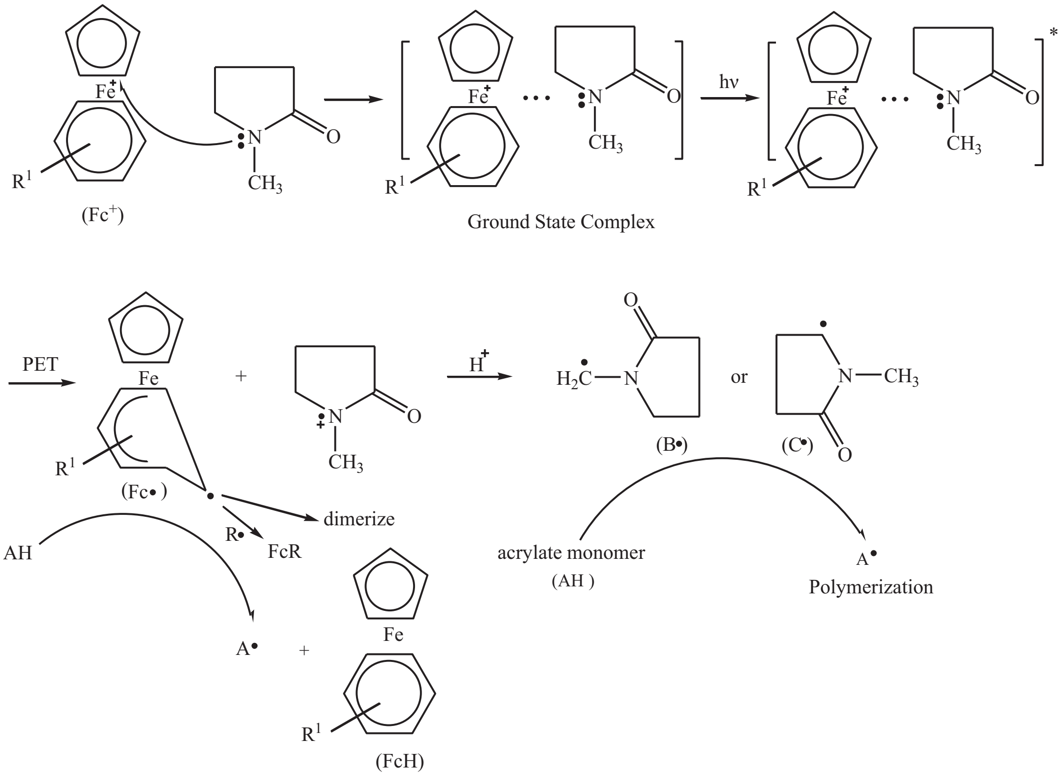


Fig. 4. (L) Photolysis of Fc-Naph in the absence of NMP, at *t*: 0, 20, 80, 160, 320, 500 s of illumination. (R) Photolysis of Fc-Naph in dichloromethane, in the presence of NMP, at *t*: 0, 20, 80, 160, 280, 400 s of illumination. The concentration of photoinitiator is 10^{-3} M ($I = 1$ mW/cm^2).

Table 1
Spectroscopic and electrochemical properties of Fc-PC, Fc-NP, Fc-CZ.

No.	λ^{A}_{max} (nm)	λ^{Fl}_{max} (nm)	$\Delta\nu^{a}$ (cm^{-1})	$E_{red}{}^{b}$ (V)	$E_{ox}{}^{c}$ (V)	E^{S}_{00} (eV)	ΔG_{el} (eV)
Fc-phCl	294.8	336.6	4212.4	−1.257	0.459	3.89	−1.512
Fc-Naph	294.2	336.4	4264	−1.131	−0.388	3.89	−1.638
Fc-(N-Et)CZ	294.2	336.4	4264	−1.621	−1.212 0.459 1.263	3.88	−1.138

[a] $\Delta\nu$ is Stoke's shifts.
[b] E_{red} is the reduction potential of Fc.
[c] E_{ox} is the oxidation potential of Fc.



Scheme 2. Mechanism of photoinitiating radicals photopolymerization by Fc/NMP.

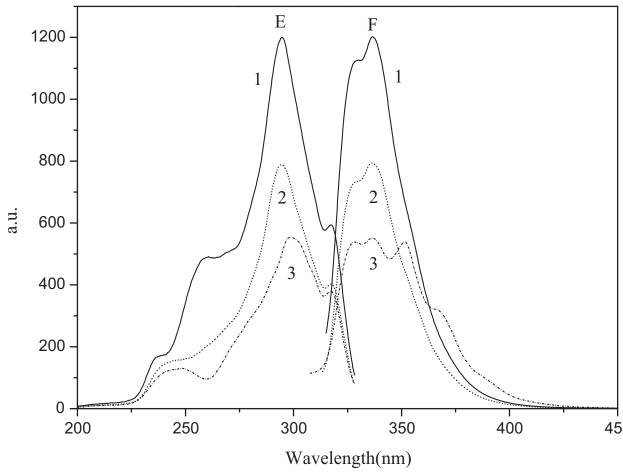


Fig. 5. The fluorescence spectra of the Fcs in dichloromethane. E: the excitation spectra of the Fcs; F: the emission spectra of the Fcs. 1: Fc-PC; 2: Fc-NP; 3: Fc-CZ. The concentration of photoinitiator is 10^{-4} M.

and Fc-CZ/NMP systems indicate that the electron transfer processes for the studied photoredox pairs are thermodynamically allowed.

The electrochemical behaviors of Fcs in the presence of NMP were studied by the CV method. The CV curves of the Fcs added to NMP exhibited new oxidation and reduction peaks compared with those in the absence of NMP. This confirms that a new compound exists. Fig. 6 indicates that this compound is probably the ground state complex produced by the combination of Fc-PC with NMP.

3.4. *Proposed mechanism of photoinitiating radicals by Fc/NMP*

As mentioned in Section 1, the mechanism of the Fc/hydroperoxide or Fc/dye photoinitiator system for free radical photoinitiation was proposed by Fouassier. Fc was demonstrated to play a very important role in these systems. Fc reacts with hydroperoxide or excited dye to generate efficient intermediates by electron transfer, a reaction that was also studied in this paper. Based on the results of this study, a mechanism for initiating radicals by Fc/NMP is proposed in Scheme 2.

Scheme 2 shows that the Fc first generates a ground state complex with NMP before irradiation. This ground state complex will absorb a photon to reach its excited state in the presence of light and

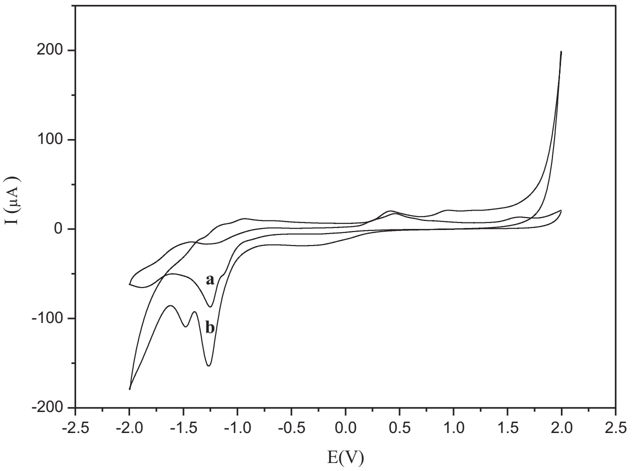


Fig. 6. Cyclic voltammogram curves of 8.3×10^{-3} M Fc-PC. (a) Without NMP; (b) 1.0 M NMP. Scan rate: 0.1 V/s.

finally generate α-aminoalkyl radicals ($B^\bullet$ or $C^\bullet$) by photoinduced electron transfer (PET) process. The α-aminoalkyl radical initiates free radical polymerization of the acrylate monomer (AH to $A^\bullet$). $Fc^\bullet$ is also an active intermediate [1] in that it has an unpaired electron on the arene ligand that may dimerize or react with the radicals produced by the acrylate monomer that has been already initiated ($R^\bullet$) to generate FcR. It may also partly abstract a hydrogen atom from the acrylate monomer to generate FcH and $A^\bullet$, leading to the formation of more potential radicals to promote free radical polymerization of the acrylate monomer.

4. Conclusions

NIR spectroscopy results indicate that this new bimolecular photoinitiator system consisting of an Fc and NMP exhibits good initiation ability and high efficiency for the free radical polymerization of acrylate monomer under visible light. The mechanism for the electron transfer reaction between the Fc and NMP was studied by photochemical and electrochemical studies. Further investigations will be undertaken to utilize the potential of this new bimolecular photoinitiator system in the field of visible light-induced free radical polymerization.

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