Journal of Photochemistry and Photobiology A: Chemistry 333 (2017) 63–69

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photocatalysis of viologens for photoinitiated polymerization using carboxylic acid as electron donors

Liangcheng Cao[a,*], Yuechuan Wang[b]

[a] Chongqing Institute of Green and Intelligent Technologies, Chinese Academy of Sciences, Fangzheng Avenue 266, Chongqing 400714, China
[b] College of Polymer Science & Engineering, State Key Laboratory of Polymer Materials, Sichuan University, South section of 1st ring road 24, Chengdu 610065, China

ARTICLE INFO

Article history:
Received 29 June 2016
Received in revised form 25 September 2016
Accepted 12 October 2016
Available online 13 October 2016

Keywords:
Viologen
Photocatalysis
Electron transfer
Photopolymerization

ABSTRACT

Hydroxyl radicals ($^•$**OH**), together with carbon-centered radicals ($^•$**R**), derived from photoinduced electron transfer (**PET**) interactions between viologen and carboxylic acid ion pairs ([**bipy**$^{++}\cdots$**RCOOH**]), were developed to photoinitiate the polymerization of various acrylate monomers in the presence of oxygen. The mechanism of the radicals' formation was established using nanosecond laser flash photolysis and electron spin resonance methods. Carboxylate anion (electron donnor, **D**) gave one electron to viologen (electron acceptor, **A**) via either intermolecule (**D/A**) or intramolecular (**D-A**) **PET**, to yield carboxylate radicals (**RCOO**$^•$) that later underwent decarboxylation, yielding $^•$R radicals which can initiate the photopolymerization of many acrylate monomers. Simultaneously, reduced viologen cation radical (**bipy**$^{+•}$) was oxidized by dissolved $\mathbf{O_2}$ and returned back to **bipy**$^{++}$ dications. $^•$OH radicals emerged from the reaction of **H**$^+$ with the superoxide radicals ($\mathbf{O_2}^{•-}$) that formed during the oxidation of **bipy**$^{+•}$. In this way, viologens were observed to act as photocatalysts in the radical generation process based on their strong electron acceptor, as well as efficient light absorption nature. Photopolymerization performance with **D-A** type viologens, for instance, **bipy**$^{++}$–$\mathbf{(CH_2)_nCOOH}$, extra carboxylic acid was not a requirement.

1. Introduction

Photoinduced electron transfer (PET) interactions between separated molecules (inter-PET) or between two distinct chromophores incorporated in a single molecule (intra-PET) have been found to play a fundamental role in such reactions as organic synthesis, photosynthesis, biological processes, and novel energy sources [1–4]. PET interactions were very often accompanied by bond formation and/or bond cleavage in both reductive and oxidative conditions. A field that has attracted considerable attention is the preparation of dissociative electron transfer photoinitiators for free radical polymerization [5–8]. Such photoinitiators can be tuned by designing and preparing suitable organic molecules consisting of light absorbers (dyes) and electron donors (D). Acridines [9], thiazines [10], azomethine [11], pyrene [12], flourone [13], and cyanine dyes [14,15] have been previously reported as light absorbers, while aliphatic tertiary amines, phenoxyacetic acid, and sulfur-containing amino/carboxylic acids have behaved as electron donors. Radical initiators were formed by bond cleavages following photoinduced electron transfer from electron donors to the singlet or triplet state of the dyes.

Viologens (1,1′-disubstituted 4,4′-bipyridinium salts) were widely accepted as strong electron acceptors (A) as well as efficient light absorbers in the ultraviolet region below 300 nm. Given the importance of viologens in the applications of electrochromic [16–21], photo-chromic devices [16,22,23], molecule redox gate [24–28], photocatalyzed reduction of water to hydrogen [29–31], and self-assembly [32–36], the authors became interested in the pioneering work of Ledwith and Zisk, who reported the **PET** interaction between bipyridylium dications (**bipy**$^{++}$) and carboxylate anions (**RCOO**$^-$) [37–39]. In this study, for the first time, photoinitiation behavior of viologens was found for the free radical polymerization of acrylate monomers, including acrylic acid, acrylamide, β-hydroxyethyl methacrylate (**HEMA**), 4-acryloylmorpholine (**AcMo**), and N-isopropylacrylamide (**NIPAAm**). Yagci and coworkers have reported that radical cations and alkoxy radicals, formed by the N-—O bond cleavage of N-alkoxy pyridinium salts, can photoinitiate the polymerization of epoxides and vinyl ethers but in a different way than cationic polymerization [40–44]. In the **PET** interactions between **bipy**$^{++}$ and **RCOO**$^-$, viologens were found

* Corresponding author.
E-mail address: caolc@cigit.ac.cn (L. Cao).

http://dx.doi.org/10.1016/j.jphotochem.2016.10.019
1010-6030/

to undergo a reversible redox process as: **bipy^{++}** $\leftrightarrow$ **bipy$^{+\bullet}$**. In the meantime, carbon-centered radicals (**$^{\bullet}$R**) were formed after decarboxylation, and hydroxyl radicals (**OH$^{\bullet}$**) were also observed in the **PET** interactions in the presence of oxygen. **Bipy^{++}** initially oxidized the **RCOO^{-}** to produce a carboxylate radical (**RCOO$^{\bullet}$**) and later reduced the dissolved oxygen to provide a superoxide radical (**$O_2^{\bullet-}$**). **R$^{\bullet}$,** together with **OH$^{\bullet}$**, were confirmed as radical initiators for photoinitiated polymerization by laser flash photolysis and electron spin resonance studies.

2. Experimental

2.1. Synthesis

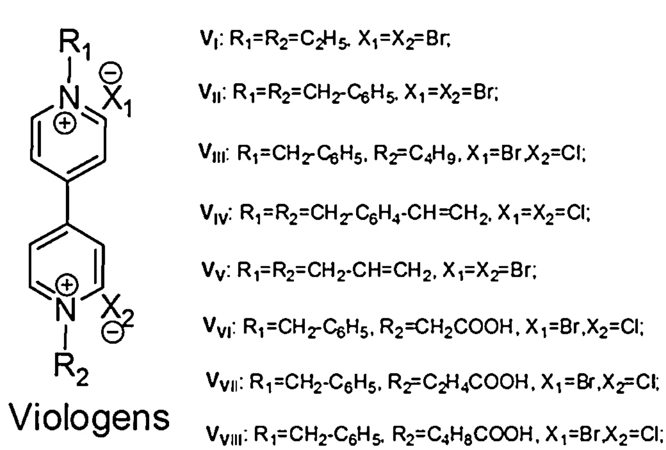
Viologens I–VIII were synthesized and fully characterized (see Supporting information for detail). Chemical structures of viologens were listed in Scheme 1.

2.2. Photopolymerization

Typical procedures: viologens and carboxylic acid (equal molar ratio) mixtures (0.3–1.0 wt%) were added to monomers (e.g., acrylamide, β-hydroxyethyl methacrylate, 4-acryloylmorpholine, and N-isopropylacrylamide) under stirring to form a homogenous phase, a trace amount of distilled water (1 wt%) was added to dissolve the viologens. However, carboxylic acid was not added for monomers that carrying carboxylic groups (e.g., acrylic acid, methacrylic acid). The mixture was then poured into a quartz mold ($15 \times 15 \times 1\ mm^3$), covered with a polyethylene terephthalate film, and irradiated under a high-pressure mercury lamp (400w, maximum intensity: $100\ mW\,cm^{-2}$) for 5 min. After this, polymer was peeled off from the mold and purified for measurement. All the polymerizations using different viologens, carboxylic acids, monomers, and irradiation densities were performed under identical experimental conditions unless otherwise stated.

2.3. Real time infrared spectroscopy (RTIR) measurements

The kinetic profiles of the UV-induced polymerizations were studied by real time FT-IR. RTIR spectra, experimental apparatus and procedures have been described in detail elsewhere [45]. The double bond conversion (DC) of the mixtures was monitored by using near IR spectroscopy with a resolution of $4\ cm^{-1}$. The absorbance change of the =C—H peak area from 6148 to $6206\ cm^{-1}$ was correlated to the extent of polymerization [46].



Scheme 1. Schematic illustrate the molecular structures of Viologens I–VIII.

After baseline correction, DC and rate of polymerization (R_p) could be calculated by measuring the peak area at each time of the reaction and determined according to Eq. (1) and (2).

$$DC\% = \frac{A_0 - A_t}{A_0} \times 100\% \tag{1}$$

$$R_P = [\mathbf{M}]_0 \frac{\mathbf{d[DC]}}{\mathbf{dt}} \tag{2}$$

DC is the degree of double bond conversion at time t, A_0 is the initial peak area before irradiation, and A_t is the peak area of the double bonds at t. The rate of photo-polymerization is calculated by the differential of the conversion of double bonds versus irradiation time. During irradiation, the decrease of the =C—H absorption peak area accurately reflected the extend of polymerization, at the same time, the R_p could be calculated by the time derivative of the DC, whereas $[M]_0$ is the initial monomer content.

2.4. Nanosecond laser flash photolysis (LFP) measurements

Nanosecond LFP experiments and data collection were performed using apparatus that have been described in detail elsewhere [47]. Radius of the laser beam cross section was 4 mm. The LFP samples were transferred to a $10 \times 10\ mm^2$ quartz cell and excited at 266 nm with pulse durations of 5–6 ns. 8.0×10^{-4} M phenylacetic acid together with 8.0×10^{-5} M V_I in MeCN/H_2O (equal volume ratio) solutions were employed as D/A type photoinitiator for an intermolecular electron transfer interaction study; while 8.3×10^{-5} M V_{VIII} in distilled water was used as D-A type photoinitiator for an intramolecular electron transfer interaction study.

2.5. Electron spin resonance (ESR) measurements

ESR measurements were recorded with a JEOL ES-USH500 spectrometer, operating at X-band frequencies of 100 kHz. In situ photolysis was carried out in the cavity of the ESR spectrometer by an ultra-high voltage mercury lamp (Type USH-500SC), using irradiation wavelengths between 260 and 350 nm. The ESR sample tube was made of quartz with diameter of 2.0 mm 5,5′-Dimethyl-1-pyrroline-N-oxide (DMPO) was used as spin trapping agents.

3. Results and discussion

3.1. Photopolymerization of acrylic acid

Our preliminary motivations focused on studying the charge and energy-transfer of viologens during the photochemical redox processes. Viologens I–VIII gave the same maximum UV absorption bands at $\lambda_{max} = 260$ nm (Fig. 1a). Initial success was obtained upon exposing acrylic acid to UV irradiation ($15\ mW\,cm^{-2}$) for 5 min, with **V_I** (0.3 wt.%) in distilled water (1 wt.%) as photosensitizer. These conditions resulted in a conversion of 83.1%, a maximal rate of polymerization of $1.9\ min^{-1}$, and poly(acrylic acid) with a high average molecular weight $(\overline{Mw} = 1.5 \times 10^6, \overline{Mw}/\overline{Mn} = 2.8)$ (Fig. 1b and Fig. s1).The molecular structure of poly(acrylic acid) was also confirmed with **NMR** (Fig. s2). Subsequent experiments revealed that **$V_{II-VIII}$** could also photoinitiate the polymerization of acrylic acid and led to ≥75% conversions of the starting monomers within 5 min (Table 1). These experiments were also successfully applied to other carboxylated acrylate monomers, for example, methacrylic acid. Compared to the classic photoinitiators, Darocur 1173 and Irgacure 907, viologens exhibited notably equal photoinitiation efficiency (Fig. s3).