

Photopolymerization of methyl methacrylate using dye-sensitized semiconductor based photocatalyst

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Abstract

Photopolymerization of methyl methacrylate (MMA) was carried out using semiconductor (CdS) as a photocatalyst under visible light exposure. The influences of additives like eosin (dye) and triethylamine on the photochemical properties of semiconductor (CdS) particle and photopolymerization of MMA were studied. A 2–3% conversion was achieved on using only CdS as photocatalyst. On using an electron donor (Et₃N) along with CdS however a conversion of up to 14% was reached. The molecular weight in this case however was low. On carrying with eosin dye along with CdS, up to 22% yield of the polymer was obtained. The polymer so obtained was characterized by GPC. Polydispersity was found to be in the range of 6–6.5 for the polymer obtained by using dye as sensitized semiconductor catalyst and 4–4.5 for the polymer obtained using only dye as catalyst. The free radical polymerization of MMA has been established with EPR spectra.
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1. Introduction

The heterogeneous photocatalysis reaction with various semiconductors TiO₂, ZnO, CdS, ZnS, etc. has been studied extensively over the last decades [1,2]. The effectiveness of these semiconductors as photocatalyst depends upon how well the radiation wavelength used corresponds to the band gap excitation energy of the semiconductor [3,4]. Semiconductors are also used for carrying out many organic reactions. Kalyansundaram and Gratzel [5] reported the applicability of semiconductor particles as photocatalyst for reduction/oxidation of water and for oxidation/reduction of contaminant in water in the presence of sacrificial electron donors/acceptors. The semiconductor particle has also been used as sensitizer for organic photosynthetic processes studied by Kraeutler and Bard [6]. It is also possible to introduce the alternative pathway of Kolbe's reaction for

the formation of acetic acid by applying rutile TiO₂ as photoanode. Semiconductor colloids and Q particle (Q indicates particle showing size quantization effect) has also been used by different research groups [7,8]. Hoffmann et al. [9] showed the rate of photoinitiated polymerization of several vinyl monomers by Q-sized semiconductor particles of CdS, ZnO and TiO₂ increases with increasing particle size.

Surface modification of semiconductor particles is a matter of extensive research nowadays. The prime objective is to increase quantum efficiency through reactions that prolong charge separation and retard the electron–hole recombination after excitation. Metal coating, metal doping, dye sensitization, etc. usually modify the properties of semiconductors. Dye sensitization of semiconductor via chemisorbed or physisorbed is one of the efficient processes to expand the wavelength ranges of absorption and prolong the electron–hole separation [10]. After dye sensitization, the oxidation power is measured by the highest occupied molecular orbital (HOMO) of the dye, which is usually less powerful as an oxidant than the electron hole.

In this communication the photopolymerization of MMA in presence of semiconductor CdS particle with different ad-

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ditives is reported. The effect of dye on semiconductor assisted photopolymerization of MMA has been studied. The stability of dye during exposure to light has also been explored.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) was purified by repeated washing with 4% aq. NaOH solution, and then washed with distilled water to make it free from alkali. The washed monomer was dried over anhydrous BaO for 24 h and distilled under reduced pressure. The middle fraction was used for all experiments. Acetone and petroleum ether were distilled prior to use. High pressure mercury vapour lamp (GE India Ltd. 125 W, radiation intensity 750 W m^{-2}) has been used as a visible light source. A light filter was used to cutoff the UV portion of incident light source. PBN (α -phenyl-*tert*-butyl nitrene) had been used as spin trapper in EPR spectra without further purification. CdS and eosin were also used as such.

2.2. Methods

2.2.1. Photopolymerization

A three-necked flask (250 mL) fitted with a stirrer, a thermometer pocket and a nitrogen inlet was used for the polymerization. A known amount of purified monomer (MMA) was taken in the flask and nitrogen was passed slowly through MMA. CdS and/or triethylamine or dye (1 wt.% of MMA) was added and set up was exposed to the light source with intermittent stirring. The reaction time was varied from 1 to 6 h and temperature was kept in the range of 35–40 °C. The polymer was precipitated by pouring the contents of the reaction vessel slowly in a beaker containing petroleum ether under stirring condition. Then the polymer was filtered and washed thoroughly with acetone to make it free from the unreacted monomer. The purification was carried out by reprecipitation in petroleum ether and finally the product was dried at 60 °C under vacuum. In order to optimize the catalyst concentration, a number of sets of polymerization were carried out using catalyst and additives with different exposure time. In each case, MMA without any additives was polymerized as a standard set for comparison. The yield of the reaction was reported as percentage conversion.

2.2.2. Intensity of light source

The intensity of light source was recorded with a thermoelectric pyranometer with respect to distance between reaction vessel and light source.

2.2.3. Fluorescence spectra

The reaction mixture containing monomer and dye was exposed with light source for 2–4 h. Then fluorescence spectra were recorded with a SpexFluoromax-3 Spectrofluorimeter.

2.2.4. EPR measurements

Electron paramagnetic resonance (EPR) signals recorded in the initial stage of polymerization on a Bruker EMX spectrometer operating in the X-band, utilizing a 100 kHz field modulation and a microwave power of 1 mW. The EPR spectrometer was coupled to a computer for data acquisition and instrument control. Monomer, additives (CdS, Et₃N, dye) and PBN spin trapper were incorporated into a sample tube of 3 mm outer diameter and the mixtures were purged with nitrogen gas. The sample tube was irradiated with 125 W high pressure mercury vapour lamp for 30 min and EPR spectra were recorded to detect the different radicals generated in the reaction mixture.

2.2.5. GPC analysis

GPC was performed using GPC (Water, USA Model 515) solvent delivery system at a flow rate of 1 mL/min through a set of three ultrastylegel columns. Analysis was done at controlled temperature at 45 °C using HPLC grade tetrahydrofuran as eluent. Sample concentration and volume of polymer injected were 0.2% (w/v) and 50 μL , respectively.

3. Results and discussion

3.1. Effect of semiconductor based photocatalyst (SCP) and dye on polymerization of methyl methacrylate

The results of photochemical conversion of the monomer (MMA) with or without additives are reported in Table 1. It is found that MMA without additives is not polymerized. In presence of semiconductor particles (CdS) it shows low conversion (2.43%). A higher conversion (14.27%) has been achieved when CdS was used with electron donor like triethylamine. This is possibly due to the easy formation of radical through the oxidation of triethylamine by the hole generated in CdS. Triethylamine without CdS can also initiate the polymerization by the formation of free radicals. In presence of light, triethylamine can generate free radicals for subsequent polymerization [10,11]. Similarly dye without CdS could also initiate the photopolymerization [12,13]. It is found that the conversion increase with exposure time (Tables 2 and 3) and 12.23% conversion has been reached by 6 h exposure in presence of dye as photocatalyst (Table 2). A

Table 1
Photopolymerization of MMA using different additives

Set no.	Mixture	Yield (g)	Percentage conversion ^a (%)
1	MMA	Nil	Nil
2	MMA + CdS	0.023	2.43
3	MMA + CdS + Et ₃ N	0.134	14.27
4	MMA + eosin	0.115	12.23
5	MMA + CdS + eosin	0.213	22.73

MMA = 1 mL, CdS = 0.01 g, triethylamine = 0.02 mL, eosin = 0.01 g. Exposure time = 6h, temperature = 35 °C.

^a Data reported from the average of three samples.

Table 2
Effect of exposure time on polymerization of MMA with dye as photocatalyst

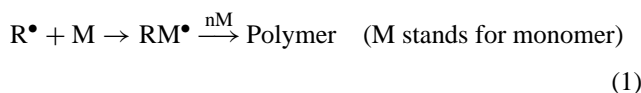
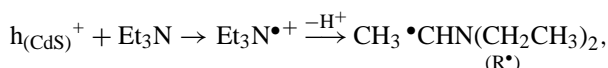
Set no.	Mixture	Exposure time (h)	Yield (g)	Percentage conversion ^a (%)
1	MMA + eosin	1	0.009	1.03
2	MMA + eosin	2	0.018	2.01
3	MMA + eosin	3	0.051	5.42
4	MMA + eosin	4	0.079	8.47
5	MMA + eosin	5	0.092	9.82
6	MMA + eosin	6	0.115	12.23

MMA = 1 mL, eosin = 0.01 g, temperature = 35 °C.

^a Data reported from the average of three samples.

conversion of 22.73% has been noted when polymerization was performed with dye-sensitized semiconductor photocatalyst (Table 3).

The triethylamine in presence of semiconductor can generate stable monomer free radical via following mechanism:



In reaction (1) triethylamine is oxidized by reaction with positive hole in the valence band of semiconductor and subsequently it produces stable free radical on deprotonation. This free radical subsequently generates the monomer free radical, which ultimately leads to polymer product.

The paramagnetic species generation in this case is better understood by EPR spectra of initial stage of polymerization of MMA in presence of Et₃N and CdS. The EPR spectra were recorded using PBN as a spin trapper to observe the generation of free radicals. The EPR spectra for this system represented in Fig. 1 (curve c). The EPR spectrum shows signals for two different types of radical-spin trap adducts [possibly one for free radical initiator (R[•]) and other for monomer or polymer radical (RM[•])]. The intensity of EPR signals is low possibly due to lower amount of paramagnetic species generated in the system.

Table 3
Effect of exposure time on polymerization of MMA using dye-sensitized semiconductor photocatalyst

Set no.	Mixture	Exposure time (h)	Yield (g)	Percentage conversion ^a (%)
1	MMA + CdS + eosin	1	0.013	1.35
2	MMA + CdS + eosin	2	0.023	2.44
3	MMA + CdS + eosin	3	0.053	5.63
4	MMA + CdS + eosin	4	0.089	9.46
5	MMA + CdS + eosin	5	0.170	18.08
6	MMA + CdS + eosin	6	0.214	22.73

MMA = 1 mL, CdS = 0.01 g, eosin = 0.01 g, temperature = 35 °C.

^a Data reported from the average of three samples.

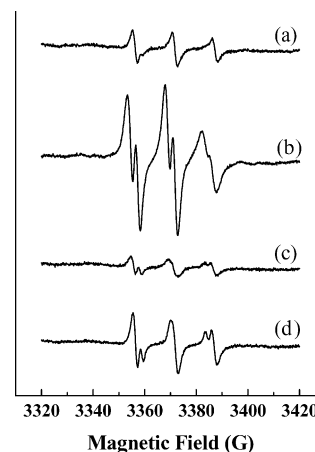
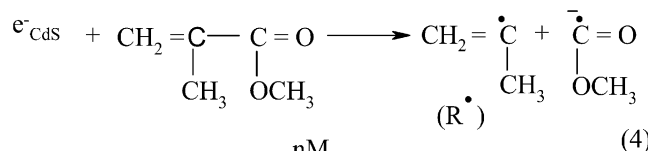
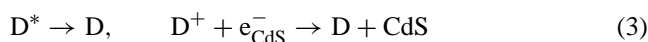


Fig. 1. EPR spectrum of paramagnetic species observed at 25 °C after 30 min of exposure on different systems (after 6 scans): (a) MMA–CdS–PBN, (b) MMA–CdS–dye–PBN, (c) MMA–CdS–Et₃N–PBN, (d) MMA–dye–PBN.

Dye-sensitized semiconductor photocatalyst can initiate photopolymerization and the possible reaction mechanism can be represented as follows:



The photochemical excited dye (D^{*}) injects the electron [10] to the conduction band of the semiconductor according to reaction (2), subsequently competing with the deactivation reaction (3). The resulting charge separated system undergoes a relaxation and a recombination process with typical time constant in the range from 10 fs up to 500 μs [11]. Further electron in conduction band of semiconductor may transfer it to the monomer and subsequently generates free radical (4), which is again confirmed by EPR signal represented as curve b in Fig. 1. The intensity of EPR signal is high enough and reveals the higher concentration of paramagnetic species in the system during the initial stage of polymerization. MMA–CdS system (curve a in Fig. 1) shows only one type of free radical-spin trap product. The non-existence of second set indicates the absence of monomer radical in the spectra. This is probably due to short time (30 min in all the cases) exposure, which is not sufficient to generate monomer free radical. The same system (MMA–CdS) showed two sets of EPR signal when the system was irradiated for slightly longer period of time (45 min) shown in Fig. 2. Although EPR spectra with different exposure time were recorded. It was found that beyond 30 min exposure spectra were similar in nature and provides no special information (except spectra in Fig. 2). After 1 h exposure the solution became very vis-

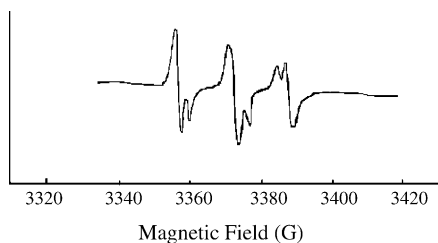
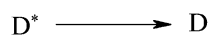
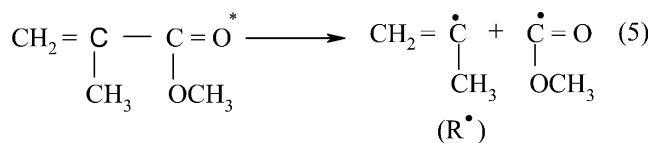
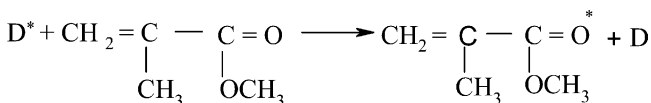


Fig. 2. EPR spectrum of paramagnetic species observed at 25 °C after 45 min of exposure on MMA–CdS–PBN system (after 6 scans).

cous and solidified and EPR spectra were not well resolved. Therefore we have reported only one set of spectra of 30 min of exposure.

When dye (D) is used as photocatalyst in visible light, it forms the electronically excited state (D^*) by absorption of light. Later it transfers its energy to the acceptor (monomer) and the resulting excited state acceptor (monomer) dissociates into free radical (R^\bullet) by intramolecular bond cleavage (5) [14]:



The generation of paramagnetic species may be supported by EPR spectra as curve d in Fig. 1. Here again two sets of EPR spectra reveals two different paramagnetic species generated during the initial polymerization of MMA–dye system, one of which initial radical (R^\bullet) spin trap adduct and another for monomer radical-spin trapper. The low intensity spectrum indicates the lower concentration of initiating radical, which readily decomposes to monomer free radical and subsequently, leads the polymer product.

The fluorescence spectra were recorded at different interval of exposure with visible light (Fig. 3). In case of dye–monomer, the fluorescence maximum was observed around 550 nm [15]. This is an excited singlet to ground state transition for the dye, which is characteristic transition for the dye [16,17]. The intensity of the fluorescence maxima showed that the fluorescence maxima for dye exposed to 6 h visible light was higher than the fluorescence maxima for the dye exposed to 2 h visible light, which in turn was higher than the dye, which was not exposed to visible light at all. This is possibly due to dyes were involved various photochemical reaction i.e. excited dye molecules were trapped by the free

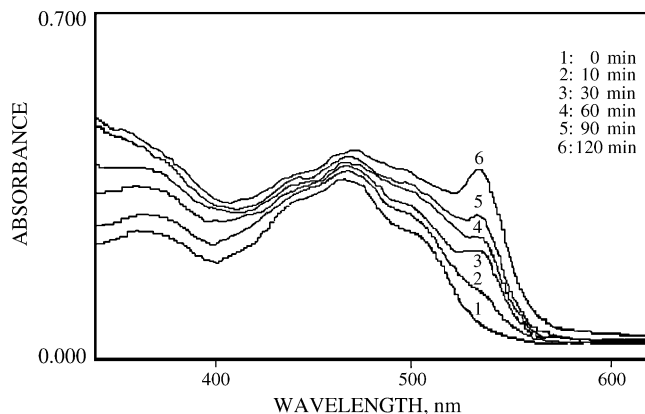


Fig. 3. Fluorescence emission spectrum of dye (eosin) and monomer (MMA). 0.001 g dye in 1 mL MMA.

radical generated in the systems during initial exposure [18]. As exposure time proceeds, dye became free and behaves like original dye (with no exposure). The fluorescence emission spectrum clearly shows the active participation of dye in the photopolymerization of MMA–dye system.

3.2. Stability of dye in presence of semiconductor particles

The stability of dye exposed to visible light during photopolymerization was studied in presence of monomer and CdS. The MMA–dye and MMA–CdS–dye systems were irradiated for different time intervals and absorption spectra were recorded with Hitachi UV-Visible Spectrometer (Model 2001). In case of dye–MMA system, a new peak was observed after 30 min of exposure with light (Fig. 4, curve 3). This is possibly due to the generation of new species from dye, indicating instability of dye. However dye in MMA–dye–CdS system is quite stable. There is no change of trend in absorption curve (Fig. 5). Although polymerization was going smoothly in both the cases. It indicates that dye is quite stable in MMA–CdS–dye system.

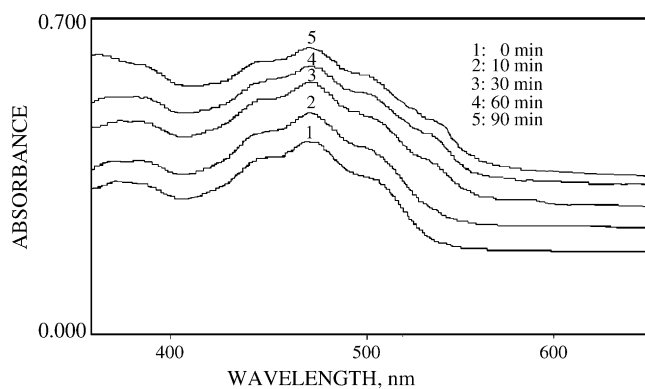


Fig. 4. Changes in the absorption spectrum of eosin (dye)–monomer (MMA) solution with time of illumination: initial dye concentration, 0.06 g in 10 mL monomer.

Table 4
Molecular weight of different PMMA by GPC

Sample particulars	Percentage conversion	\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_{z+1}	Polydispersity
PMMA (eosin as catalyst)	12.23	26010	126050	602240	1735100	4.69
PMMA (eosin and CdS as catalyst)	22.74	61860	386580	1462320	3258700	6.25

MMA = 1 mL, CdS = 0.01 g, eosin = 0.01 g, temperature = 35 °C.

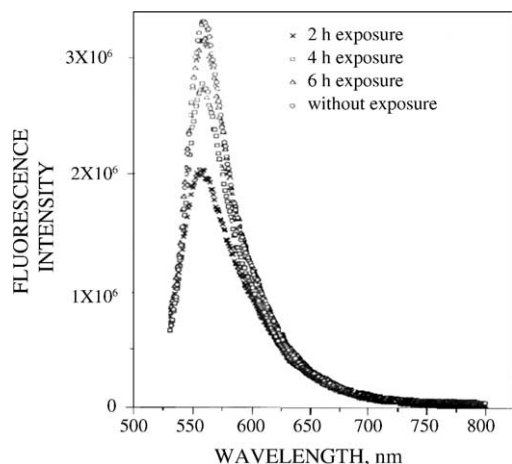


Fig. 5. Changes in the absorption spectrum of eosin (dye)–monomer (MMA) and CdS solution with time of illumination: initial dye concentration, 0.06 g in 10 mL monomer and amount of CdS, 0.01 g.

3.3. Effect of variation of exposure time on percentage conversion

Table 2 shows that percentage conversion increases with exposure time for MMA–dye system. The maximum percentage conversion achieved is 12.23 after 6 h of exposure. A similar trend is observed with MMA–CdS–dye system (Table 3). The maximum conversion of 22.75% is achieved after 6 h exposure with MMA–CdS–dye. This shows efficient catalytic effect of CdS–dye system for photopolymerization of MMA.

3.4. Nature of polymer and molecular weight

The GPC results are given in Table 4. The GPC result shows higher polydispersity for CdS–dye system than the eosin only. MMA–CdS–dye produces higher average molecular weight than MMA–dye system. There is a remarkable difference in molecular weight of PMMA but the explanation is yet to be established.

4. Conclusion

The semiconductor based photocatalyst in combination with a suitable dye has been shown to be a promising initiator for the polymerization of MMA. In the photopolymerization of MMA, CdS–dye system produces the highest conversion and higher molecular weight of polymer than dye (eosin) system. It has been observed that the semiconductor based photopolymerization of MMA proceeds through the free radical

mechanism. The generation of initiating radical in different systems follows different pathway but ultimately initiating radical combines with the monomer to start the chain reaction. EPR spectra clearly show two sets of signals for initial radicals and monomeric radicals. Fluorescence spectra show active participation of dye in initial polymerization. This type of semiconductor with different additives can be used as an efficient catalyst for photopolymerization of vinyl monomer. The reasons behind the producing higher molecular weight of PMMA with CdS–dye system are being studied.

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