



Photopolymerization of acrylamide with benzophenone/methylated- β -cyclodextrin inclusion complex in the presence of jeffamine based dendrimers as coinitiators in aqueous media

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ARTICLE INFO

Article history:

Received 9 March 2010

Received in revised form 20 April 2010

Accepted 25 April 2010

Available online 31 May 2010

Keywords:

Benzophenone

Water soluble photoinitiator

Cyclodextrin

Dendrimer

Free radical polymerization

ABSTRACT

BP/Me- β -CD inclusion complex was synthesized and used in photoinduced free radical polymerization of acrylamide as a type II photoinitiator in the presence of a dendritic co-initiator. Characterization and photophysical studies of the inclusion complex were determined by ¹H NMR, UV, laser flash photolysis and phosphorescence spectroscopy. According to acrylamide polymerization of the BP/Me- β -CD water soluble photoinitiator, BP/Me- β -CD initiates polymerization of acrylamide effectively with six and twelve armed dendritic co-initiators in aqueous media. The 24 armed dendritic co-initiator was not as efficient as the six and twelve armed dendritic co-initiators with the BP/Me- β -CD inclusion complex, due to the sterical hindrance of the amine groups in the co-initiator.

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1. Introduction

Photoinitiated free radical polymerization has enormous commercial importance, and has gained much attention because of extensive commercial applications. The traditional applications of UV-curable systems are in the industrial areas where temperature sensitive substrates are coated, like wood, paper and plastics, as well as in imaging applications, like electronics and printing plates. Due to the many advantages of UV curing and photoinduced polymerization, a lot of new applications for radiation curable coatings are emerging. Among them are printing applications, like UV-inkjet, label printing, gravure and wide web flexo, adhesives like pressure sensitive adhesives or CD bonding, clear coatings for metallized plastics, exterior coil coating of steel and aluminum, and automotive applications [1–3].

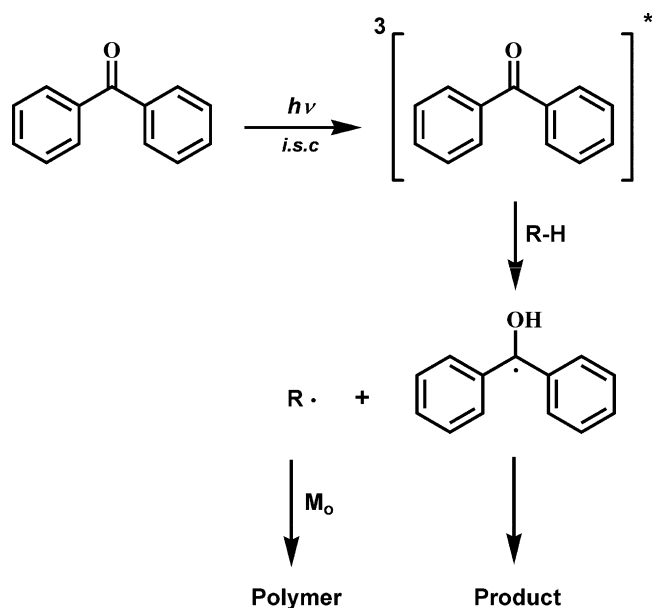
There are two types of photoinitiators in free radical polymerization: an alpha type scission initiator (type I) and a hydrogen abstraction type photoinitiator (type II). Because the initiation is based on a bimolecular reaction, type II photoinitiators are generally slower than type I photoinitiators, which are based on a unimolecular formation of radicals. Benzophenone (BP) is a well-known type II photoinitiator (PI) for the radiation curing of coatings,

printing inks, etc. After triplet state excitation, benzophenone is able to abstract hydrogen from ether, amine, alcohol or thiol functional co-initiators. Thus, reactive centers can be generated on co-initiator molecules to initiate free radical polymerization (see Scheme 1) [4].

Benzophenone is an oil soluble photoinitiator and the aim of this study was to prepare a water-soluble complex of this initiator. Cyclodextrins (CD) are cyclic oligosaccharides consisting of six (α -CD), seven (β -CD), eight (γ -CD) and nine (δ -CD) units of 1, 4-linked d-glucose units [5]. Therefore, methylated- β -cyclodextrin (Me- β -CD) was employed to synthesize the water soluble BP/Me- β -CD inclusion complex. Water-insoluble molecules become water-soluble upon treatment with aqueous solutions of CDs without any chemical modification of the guest molecule because there are no covalent bonds formed by the host/guest interaction of the CD and the water-insoluble molecule [6,7]. The hydrophobic photoinitiator/ β -CD complex efficiency on photoinitiated free radical polymerization has previously been studied by several research groups [8–12].

Dendrimers are highly branched and have well-defined architectures with a number of special chemical and physical properties [13,14]. Their highly branched and uniform structures can be used in the field of coatings in industry, chemical sensors and drug delivery systems [14]. Poly(propylene imine) dendrimers were recently used as the hydrogen donor for type II photoinitiation of methylmethacrylate monomer in free radical polymerization [15,16].

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Scheme 1. Photoinitiation mechanism of benzophenone as a type II photoinitiator in the presence of a co-initiator.

In this text, the BP/Me- β -CD inclusion complex was prepared and characterized by ^1H NMR, FTIR and UV spectroscopy successfully. This complex was used in the photoinduced free radical polymerization of acrylamide (AAM) in the presence of 6, 12 and 24 armed jeffamine based water soluble dendrimers as co-initiators in water.

2. Experimental

2.1. Materials

Methylated- β -cyclodextrin (Me- β -CD, average $M_n = 1310$, Aldrich) and acrylamide (AAM, 97%, Merck) and methanol (Merck) were used as received. Benzophenone (BP) was purchased from Aldrich and recrystallized from ethanol. Jeffamine based dendrimers were synthesized and characterized according to previous literature [17].

2.2. Complexation of photoinitiator

The host/guest complex of BP/Me- β -CD was prepared with a molar ratio of 1:2. 0.20 g of (1.1 mmol) BP in 20 mL of acetone and 2.82 g of Me- β -CD (2.2 mmol) in 20 mL of water were dissolved separately and then the BP solution was added gradually to the CD solution while stirring. The mixture was heated to 50 °C and stirred under cooling condenser until a clear solution was observed. After the clear solution occurred, the solvent was evaporated, and the solid complex was dried under vacuum.

2.3. Photopolymerization in aqueous media

Typical procedure: first, the photoinitiator (BP/Me- β -CD) and the co-initiator (dendrimeric J-6/12/24) were added to 1 mL (1 M) of acrylamide solution in water. The solution was put into a Pyrex tube and irradiated in a photoreactor equipped with 12 Phillips' lamps emitting at $\lambda = 350$ nm for 60 min in an air atmosphere. Polyacrylamide, formed at the end of irradiation, was precipitated in 10-fold excess methanol and dried in vacuo. Monomer conversions were calculated for all samples gravimetrically.

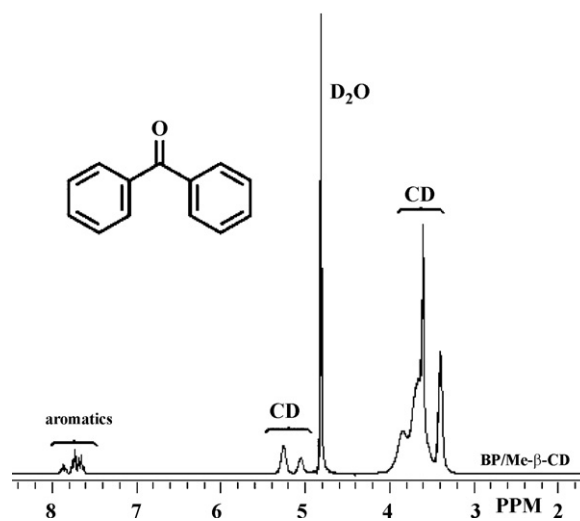


Fig. 1. ^1H NMR spectrum of BP/Me- β -CD in D_2O .

2.4. Characterization

UV-vis spectra were taken on an Agilent 8453. Phosphorescence spectra were recorded on a Jobin Yvon-Horiba Fluoromax-P. A Nicolet 6700 FT-IR spectrophotometer was used for recording IR spectra. ^1H NMR spectra were recorded on a Bruker 250 instrument with D_2O as the solvent and tetramethylsilane (TMS) as the internal standard. Laser flash photolysis experiments employed the pulses from an Applied Photophysics with YAG laser (355 nm, pulse, 5 ns) and a computer controlled system. An aqueous solution of BP/Me- β -CD complex was prepared with a concentration of BP such that the absorbance was 0.3 at the excitation wavelength (355 nm).

Gel permeation chromatography (GPC) measurements were performed at room temperature with a setup consisting of a pump (HP 1050), a refractive index detector (HP 1047A), and three high resolution Waters columns (AQ3.0, AQ4.0, and AQ5.0). The effective molecular weight ranges were 1000–60,000, 10,000–400,000 and 50,000–4,000,000, respectively.

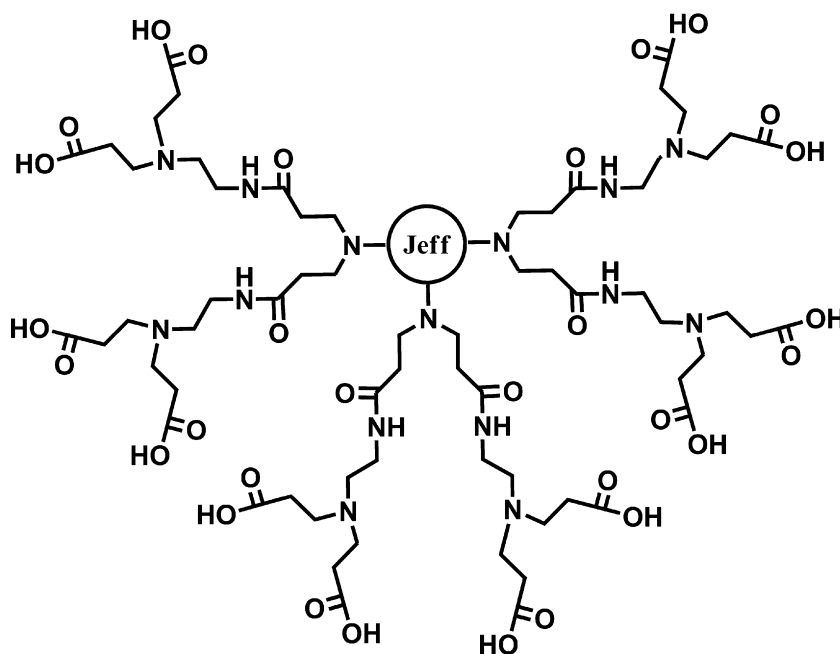
Water was used as eluent at a flow rate of 0.5 mL/min at room temperature. Data analyses were performed with HP Chemstation Software. Calibration with linear polyethylene oxide standards (Polymer Laboratories) was used to estimate the molecular weights.

3. Results and discussion

Three different Jeffamine type dendrimers (J-6, J-12 and J-24, see Scheme 2) were prepared as given in the experimental part and these water soluble dendrimers were employed as co-initiators for the free radical polymerization of acrylamide with the BP/Me- β -CD inclusion complex.

The preparation of this inclusion complex began by dissolving Me- β -CD in water, and then benzophenone was added while stirring the cyclodextrin solution, in the ratio of 2:1. The turbid solution was stirred in 50 °C until a clear solution occurred. After evaporation of water, BP/Me- β -CD inclusion complex was obtained successfully (see Section 2).

The structure of the water soluble photoinitiator was confirmed by several spectral analyses. ^1H NMR spectroscopy was used to characterize the water soluble BP/Me- β -CD complex. Because of the good solubility of the BP/Me- β -CD inclusion complex in aqueous medium, the spectrum was easily recorded in D_2O (see Fig. 1). Since benzophenone has no solubility in water or D_2O , the peaks



Scheme 2. Twelve armed Jeffamine based dendrimer.

observed on the ^1H NMR spectrum belonged entirely to the BP/Me- β -CD inclusion complex.

^1H NMR spectroscopy shows that two phenyl groups of benzophenone were complexed with two CD rings. Complexation between BP and two Me- β -CD rings was calculated using the values of the integrals of the characteristic peaks for BP and Me- β -CD (see Fig. 1). The ratio of 1:2 of the BP/Me- β -CD inclusion complex was obtained according to the integral ratio of ^1H NMR signals.

BP/Me- β -CD has an absorption characteristic similar to the parent benzophenone with a maximum at 329 nm in water (Fig. 2). Due to the insolubility of benzophenone in water, the UV spectrum of benzophenone was taken in methanol and the BP/Me- β -CD complex was prepared in water with a similar concentration.

The infra-red spectrum also indicated the formation of the BP/Me- β -CD complex. The characteristic signal for the carbonyl group of BP shifted significantly to higher frequencies from 1649 cm^{-1} to 1659 cm^{-1} due to the effect of complexation between BP and the CD rings [8]. After characterization of the inclusion

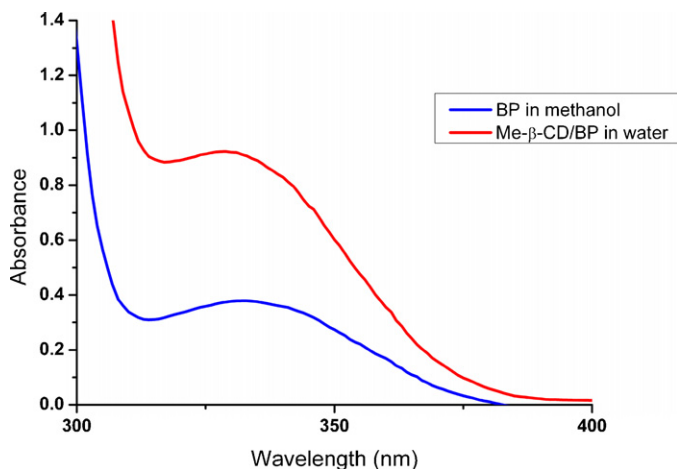


Fig. 2. Absorption spectra of BP/Me- β -CD [6×10^{-3} M] in water and BP [5×10^{-3} M] in methanol.

complex, photolysis, phosphorescence measurements, laser flash photolysis and photopolymerization experiments were performed, respectively.

The photolysis experiments of the BP/Me- β -CD complex in aqueous solution were performed and the decomposition of the inclusion complex was followed by spectral changes in UV spectroscopy. The UV spectra of BP/Me- β -CD complex in aqueous solution in the absence and presence of dendritic co-initiators (J-6/J-12/J-24) were recorded after the solution had been exposed to the light of a UV lamp at several intervals in an air atmosphere. As can be seen in Fig. 3, the photoinitiator in the complex with dendritic co-initiators was rapidly photoreduced under UV irradiation due to the hydrogen abstraction from the co-initiators. The increase in the absorption band at 330 nm might be attributed to the formation of photoreduction (benzophenone ketyl radical) products [18,19]. Photoreduction of BP in Me- β -CD takes less irradiation time in the presence of dendritic co-initiators. The most efficient hydrogen donor was J-24 (see Fig. 3).

BP/Me- β -CD exhibits phosphorescence emission in ethanol at 77 K upon excitation with 330 nm light (see Fig. 3). The (0, 0) emission band occurs at 413 nm, corresponding to approximate triplet energy of ca 289.6 kJ/mol (see Fig. 4).

Laser flash photolysis of a highly diluted solution of the BP/Me- β -CD inclusion complex affords a readily detectable transient absorption spectrum in water, which decayed in a first-order kinetic with a lifetime of 560 ns at 530 nm (see Fig. 5). The maximum absorption was at 530 nm, which is similar to the triplet-triplet absorption of BP and BP derivatives [19,20]. Transient absorption at 340 nm belonged to the benzophenone ketyl radical formed by hydrogen abstraction of the excited carbonyl group from the Me- β -CD. Benzophenone ketyl radicals are known to have absorption around 300 nm. The triplet life time (τ) of BP in Me- β -CD is in agreement with the value reported for BP in β -CD [19].

Photopolymerization of acrylamide with J-6, J-12 and J-24 as co-initiators was performed. A control experiment in the absence of co-initiators under identical experimental conditions was also performed. The conversions of monomer (acrylamide) into polymer

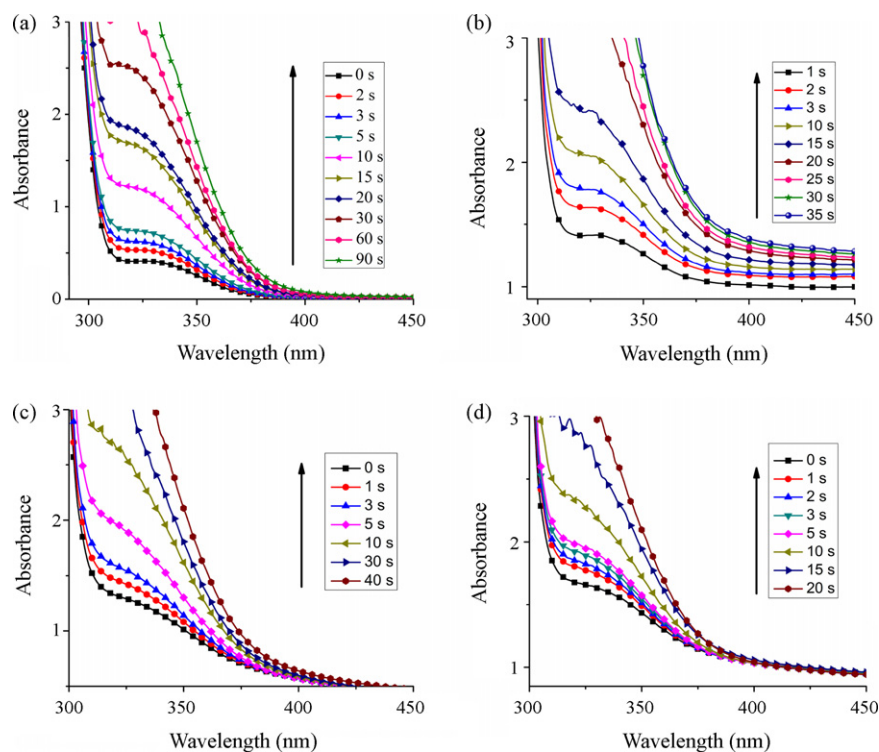


Fig. 3. UV spectra of (a) BP/Me- β -CD, (b) BP/Me- β -CD/J-6, (c) BP/Me- β -CD/J-12 and (d) BP/Me- β -CD/J-24 in air saturated aqueous solutions after irradiation.

were determined gravimetrically and it was found that polymerization did not occur in an air atmosphere with BP/Me- β -CD inclusion complex without adding a co-initiator (see Table 1, Run 1).

For comparison, polymerization with a linear amine, namely triethylamine was also included (Runs 2 and 3). As can be clearly seen from the results in Table 1 dendritic co-initiators, regardless of the generation number, exhibit higher initiation efficiency than the linear amine in polymerization under the same experimental conditions. The inhibiting effect of oxygen on the rate of polymerization was observed (Run 1). The highest conversion was achieved at a concentration level of co-initiators of 1 mM. Increasing the

local amine concentration accelerated the hydrogen abstraction between the excited state of BP photoinitiator and dendrimers to generate a larger number of radicals, which resulted in the higher conversion of AAm polymerization. The decrease in the molecular weights of the resulting polymers by increasing the generation numbers also confirmed this, with the exception of the J-24 dendritic co-initiator. Increasing the amine concentration helped to increase the conversions. The 24 armed jeffamine based co-initiator was not found to be as efficient as the J-6 and J-12 armed co-initiators for hydrogen donation. This was also confirmed by an increase in the molecular weight of the polymers, for formulations containing 24 armed jeffamine as the co-initiator, after an increase

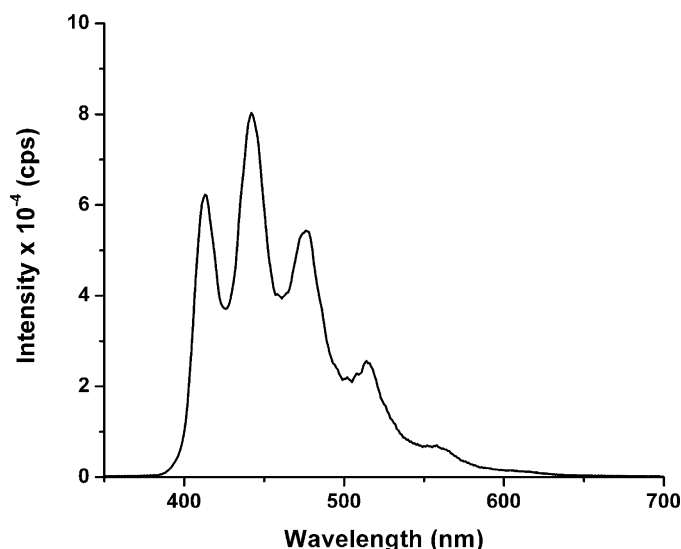


Fig. 4. Phosphorescence spectrum of BP/Me- β -CD in ethanol at 77 K.

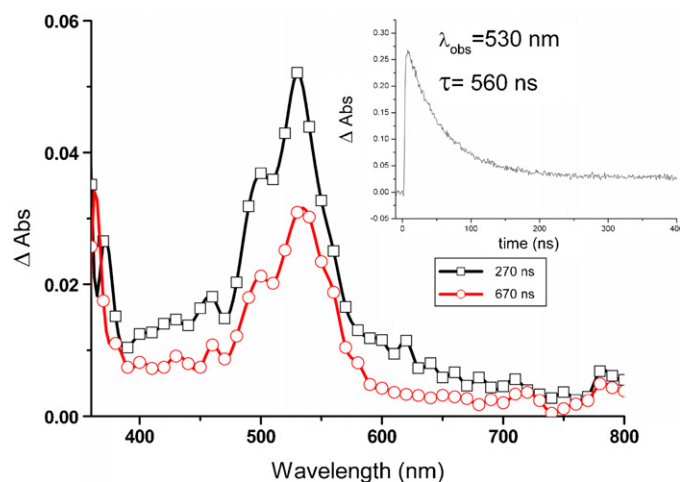
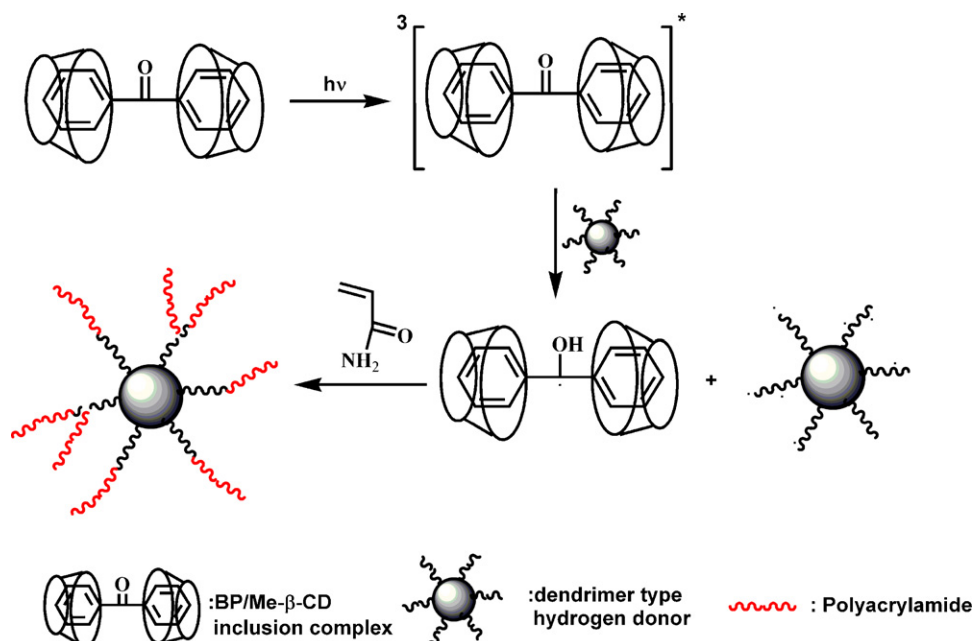


Fig. 5. Transient optical absorption spectrum recorded at 270 and 670 ns following laser excitation (355 nm, 5 ns) in argon saturated aqueous solution of BP/Me- β -CD complex. Inset: triplet decay at 530 nm.



Scheme 3. Free radical photopolymerization mechanism of BP/Me- β -CD inclusion complex with dendrimeric co-initiator in the presence of acrylamide monomer in aqueous media.

in the amine concentration. Although efficient photobleaching was observed when J-24 was added to the inclusion complex formulation, the hydrogen donor efficiency of the J-24 dendritic co-initiator was found to be very poor (see Table 1) probably due to the steric effect.

The possible mechanism for the BP/Me- β -CD involves hydrogen abstraction by the carbonyl group of the BP/Me- β -CD inclusion complex from the dendritic co-initiators and the resulting radicals on the dendritic co-initiators are able to initiate the free radical polymerization of AAm (see Scheme 3).

In conclusion, BP/Me- β -CD water soluble photoinitiator was readily prepared in a conventional complexation procedure, and fully characterized by ^1H NMR, UV and FTIR. Laser flash photolysis and phosphorescence studies show that BP/Me- β -CD complex is similar to the parent benzophenone compound after the complexation reaction. However, this inclusion complex is able to efficiently initiate polymerization of acrylamide in aqueous media in the presence of various dendritic co-initiators possessing hydrogen donating amine groups.

Table 1

Photoinitiated free radical polymerization of acrylamide^a with BP/Me- β -CD^b photoinitiator and 6, 12 and 24 armed jeffamine based dendritic co-initiators in water under an air atmosphere.

Run	Co-initiator	[Col] ($\times 10^{-5}$ mol L ⁻¹)	Conversion (%)	Mn (g mol ⁻¹)	M _w /M _n
1	–	–	0	–	–
2	TEA	100	<1	–	–
3	TEA	10	0	–	–
4	J-6	100	100	41,400	1.32
5	J-6	10	80	44,170	1.39
6	J-6	1	40	51,000	1.22
7	J-12	100	96	37,150	2.30
8	J-12	10	78	28,500	2.52
9	J-12	1	48	13,000	3.11
10	J-24	100	80	92,000	1.17
11	J-24	10	47	80,000	1.14
12	J-24	1	38	36,500	1.86

^a [AAm] = 1 M.

^b [BP/Me- β -CD] = 1×10^{-3} M.

Acknowledgements

The authors would like to thank TUBITAK, DPT and Yildiz Technical University Research Foundation for their financial support.

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