4-methyl-4-[2-(naphthalene)-2-oxoethyl] morpholin-4-ium iodide as a water soluble photoinitiator

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Abstract: Quaternary ammonium salt namely 4-methyl-4-[2-(naphthalen-2-yl)-2-oxoethyl] morpholin-4-ium iodide (WSMPM) was synthesized and characterized. High molar absorptivity at 347 nm (1910 L · mol^{-1} · cm^{-1}) and good solubility in distilled water (10^{-2} M) allows WSMPM to be used as an effective photoinitiator also in water-soluble systems. Photopolymerization of acrylamide monomer with WSMPM (10^{-3} M) and a tertiary amine (N-methyldiethanolamine), resulted in 84.4% monomer to polymer conversion. Based on laser photolysis and electron spin resonance, a photoinitiator mechanism was proposed.

Keywords: photopolymerization, water-soluble photoinitiators, quaternary ammonium salt.

Jodek 4-metylo-4-[2-(naftalen-2-ylo)-2-oksoetylo]morfolin-4-iowy jako rozpuszczalny w wodzie fotoinicjator

Abstrakt: Otrzymano i scharakteryzowano czwartorzędową sól amoniową – jodek 4-metylo-4-[2-(naftalen-2-ylo)-2-oksoetylo]morfolin-4-iowy (WSMPM). Związek charakteryzuje się dużą wartością molowego współczynnika absorpcji promieniowania o długości fali 347 nm (1910 L · mol^{-1} · cm^{-1}) oraz dobrą rozpuszczalnością w wodzie, co pozwala na jego zastosowanie jako efektywnego fotoinicjatora, także w układach wodnych. W przypadku fotopolimeryzacji akryloamidu w obecności WSMPM i trzeciorzędowej aminy (N-metylodietanoloaminą) uzyskano ponad 84-proc. konwersję monomeru do polimeru. Na podstawie fotolizy laserowej i elektronowego rezonansu spinowego zaproponowano mechanizm fotoinicjacji.

Słowa kluczowe: fotopolimeryzacja, fotoinicjatory rozpuszczalne w wodzie, czwartorzędowe sole amoniowe.

Photoinitiated free radical polymerization has gained significant importance in commercial applications in recent years [1-4]. Examples are imaging applications, 3D curing, photomasks, printing plates, electronics, holographic recordings, and nanoscale micromechanics [5-7]. The development of the photocuring industry depends on the design of suitable photoinitiator systems (PIs). Currently, photoinitiators with the appropriate wavelength and resolution are preferred in industrial production. PIs are responsible for the generation of reactive species, such as free radicals or ions, and initiate polymerization reactions of multifunctional monomers and oligomers. They can be divided into type I photoinitiators (α-cleavage), type II (H abstraction) and single-component type II photoinitiators [8-10]. Type I photoinitiators generate initiating radicals via bond cleavage processes by light absorption. Type II initiators are ketone components that undergo photo excitation processes and interact with compounds called co-initiators [11–13]. α-Aminoacetophenone and acetonaphthone derivatives are α-cleavable photoinitiators that have been synthesized in recent years. 2-(N-methyl-N-phenylamino)acetonaphthone (MPA), morpholino acetonaphthone (MPM) and pyrrolidine acetonaphthone (MPY) are synthesized by our group [14–18].

Applications of water-soluble photoinitiator started in the 1980s, especially water-based ink systems have been developed. For this purpose, water-soluble hydrophilic photoinitiators have been designed [19–22]. It is a significant task to transform the conventional photoinitiator to water-soluble type. To achieve this property, substituents can be added to the structure such as non-ionic ethers, polyether's, sulfonates, thiosulfates, carboxylic acids and quaternate ammonium salts (QAS) [23, 24]. QAS are prepared by the alkylation reaction of tertiary amines with a halocarbon. QAS are widely used especially in medicine and industry. Paints, cleaning agents, emulsifiers, surfactants, moisturizers, and antistatic agents are exemplary uses [25, 26]. QAS, especially those with long chains are highly active against microbial membranes. For this reason, photoinitiators in

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the quaternate ammonium salt structure have been synthesized in UV curing industry [27–30].

In this article, a quaternary ammonium salt namely 4-methyl-4-[2-(naphthalen-2-yl)-2-oxoethyl] morpholin-4-ium iodide (WSMPM) was synthesized and characterized as a water-soluble photoinitiator for the photopolymerization of acrylamide monomer.

EXPERIMENTAL PART

Materials

α-Bromo-2'-acetonaphthone (99%), N-methyl diethanolamine (MDEA, 99%), N,N' dimethyl formamide (DMF, 99%), methanol (99.8%), morpholine (99%), methyl iodide (99%), acrylamide monomer (98%) and triethylamine (99.5%) were supplied from Sigma-Aldrich and used without purification. Toluene (99%), ethyl alcohol (98%), and diethyl ether (99.7%) were obtained from Merck, and dimethyl sulfoxide (DMSO, 99.5%) was delivered by Fluka and used as received.

Methods

Visible UV absorption spectra were obtained using an Agilent Technologies 8453 spectrophotometer. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer. 1H-NMR spectra were recorded on a Bruker Biospin AG 500 MHz instrument with a solvent, CDCl$_3$, and an internal standard, tetramethylsilane (TMS). Photobleaching test was performed using a Hamamatsu LC8 spotlight device consisting of a fiber optic cable with a quartz-coated tip and a mercury-xenon lamp. Fluorescence spectra were determined using a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature.

Synthesis of morpholino acetonaphthone (MPM)

1.5 grams of *α*-bromo-2'-acetonaphthone (0.02 mol) was dissolved in 12 mL of dry toluene. A mixture of 0.9 ml of triethylamine and 0.7 ml of morpholine was added to the solution. The solution was stirred at room temperature under inert atmosphere for 24 hours. The precipitate formed was filtered and toluene was removed using a rotary-evaporator. The residue was crystallized from ethyl alcohol, and the yellow crystals formed were dried and characterized [16].
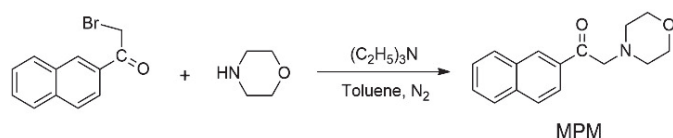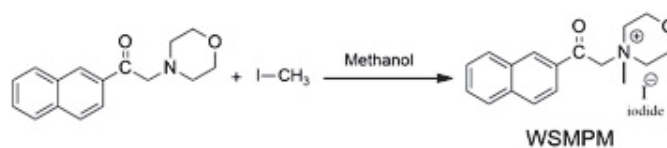

Scheme 1. Synthesis of MPM

^{1}H-NMR (250 MHz, CDCl$_3$) δ: 2.66-2.69 (m, 4H), 3.70-3.89 (m, 4H), 3.97 (s, 2H), 8.65-7.24 (m, 7H, aromatic) ppm.

FTIR (ATR): υ 3053 (aromatic C-H stretch.), 2962 (aliphatic C-H stretch.), 1681 (C=O stretch.), 1625 (aromatic C=C stretch.), 1348 (C-N stretch.) cm^{-1}.
UV (CH$_3$CN): λ $_{342\,nm}$ (ε = 1897 L · mol^{-1} · cm^{-1}).

Synthesis of 4-methyl-4-[2-(naphthalen-2-yl)-2-oxoethyl] morpholin-4-ium iodide (WS-MPM)

Morpholino acetonaphthone (0.5 g; 0.0019 mol) was dissolved in 4 ml of dry methanol in a two-necked round-bottomed flask. Excess of the methyl iodide (1 ml) was added to the stirred solution. After the addition, the reaction mixture was refluxed for 24 hours. The solution was isolated by recrystallization from methanol-ether mixture. Yellow 4-methyl-4-[2-(naphthalen-2-yl)-2-oxoethyl]morpholin-4-ium iodide crystals are dried and characterized.

Scheme 2. Synthesis of WSMPM

^{1}H-NMR (CDCl$_3$, 500 MHz), δ: 3.71 (s, 3H, CH$_3$), 3.98-4.06 (m, 6H, 2xNCH$_2$ and OCH$_2$), 4.24-4.29 (m, 2H, OCH$_2$), 5.97 (s, 2H, CH$_2$), 7.50 (ddd, 1H, J = 7.5 Hz, aromatic), 7.58 (ddd, 1H, J = 7.5 Hz, aromatic), 7.77 (d, 1H, J = 8.5 Hz, aromatic), 7.82 (d, 1H, J = 8.5 Hz, aromatic), 7.93 (dd, 1H, J = 1.5 Hz, 8.5 Hz, aromatic), 8.12 (d, 1H, J = 8.0 Hz, aromatic), 9.00 (s, 1H, aromatic).
FTIR (ATR): υ 3053 (aromatic C-H stretch.), 2962 (aliphatic C-H stretch.), 1681 (C=O stretch.), 1624 (aromatic C=C stretch.), 1350 (C-N stretch.) cm^{-1}.
UV (H$_2$O): λ $_{347\,nm}$ (ε = 1910 L · mol^{-1} · cm^{-1}).

Photoinitiated polymerization

A solution containing 1 · 10^{-3} M of WSMPM in H$_2$O (1 mL) was added into 1 M of acrylamide (AA) monomer. The mixture was placed in a Pyrex tube (internal diameter = 9 mm) and then irradiated in a photoreactor consisting of 8-watt UVA (254 nm) and UVC (365 nm) lamps in an air atmosphere. After the irradiation, the resulting polyacrylamide was precipitated in an excess of methyl alcohol and dried in vacuo (yield=38.86%, Table 1). Other photopolymerization processes were performed with and without N-methyl diethanolamine as co-initiator. Photoinitiated polymerizations were also conducted with different initiator concentrations (Table 1). On the other hand, same solutions were flushed with dry nitrogen upon removal from a Pyrex tube for the experiments performed with nitrogen. Conversion percentages and polymerization rates were determined gravimetrically and calculated according to Equations (1) and (2).

$$\mathrm{Conv.}\,(\%) = \frac{w}{m} \cdot 100 \qquad (1)$$

where: w – weight of polymer (g), m – weight of monomer (g).

$$R_p = \frac{w \cdot 10000}{M \cdot V \cdot t} \qquad (2)$$

where: M – molar mass of monomer (g), w – weight of polymer (g), V – volume of solution (ml), t – polymerization time (min).

RESULTS AND DISCUSSION

Absorption properties of WSMPM

4-methyl-4-(2-(naphthalen-2-yl)-2-oxoethyl) morpholin-4-ium iodide (WSMPM) was synthesized by using MPM photoinitiator as a starting material and characterization of WSMPM was approved by UV, ^{1}H-NMR, and IR spectroscopy techniques. Synthesis reactions of MPM and WSMPM are shown in Scheme 1 and 2. Figure 1 indicates absorption spectra of WSMPM in distilled water, DMSO and DMF. WSMPM is characterized by good solubility in water at a concentration of $8.6 \cdot 10^{-4}$ M and a wide absorption band in the UV-vis range with high molar absorption ($\varepsilon = 1910$ mol·mL^{-1}·min^{-1}) at a wavelength of 347 nm.

Samples are prepared in distilled water, DMSO and DMF at equal concentrations. Like other acetonaphthone type initiators, $\pi{\rightarrow}\pi^*$ transitions are observed at wavelength about 305 nm and $n{\rightarrow}\pi^*$ transitions are around 350 nm. It is also seen that the increase in solvent polarity has a hyperchromic effect ($OD_{H2O}>OD_{DMSO}>OD_{DMF}$) [16, 17].

Additionally, when the absorption spectrum of the substance is examined in DMF, it is seen that the molar absorptivity of WSMPM is slightly shifted to visible region compared to MPM (Fig. 2).

Photo-bleaching of WSMPM

Designing a photoinitiator with high initiation efficiency and fast photo-bleaching is a significant task [31, 32]. Rapid photolysis of WSMPM has high advantageous to reduce the residual photoinitiator content and to increase curing speed. The exposure of solution to the UV light generated by a spot-light curing system at intervals of 15 minutes during photolysis, followed by recording the changes to the absorption spectra of WSMPM in H$_2$O at a concentration of 5×10^{-4} M. Light intensity of spot-light curing system is measured as UVA = 24.1 mW/cm^2. The absorption peak of the initiator decreased in 30 minutes and increased after 60 minutes due to the hydrogen bonds formed between initiator and water. Formation of the new absorption band at wavelength of 338 nm was observed at 60 min of irradiation time of the WSMPM/H$_2$O solution (Fig. 3).

Photoinitiated polymerization of WSMPM

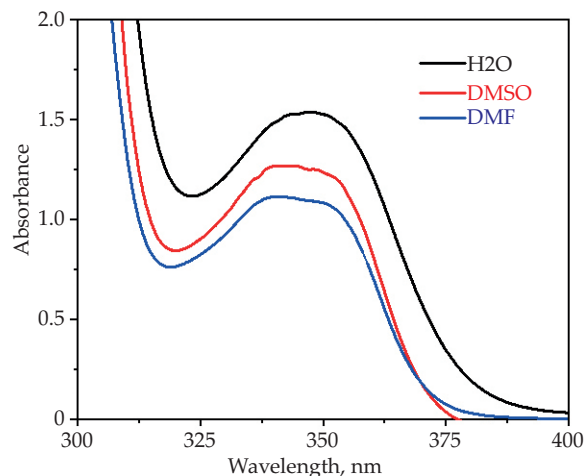Polymerization of acrylamide monomer (AAm) was performed with WSMPM with and without amine and

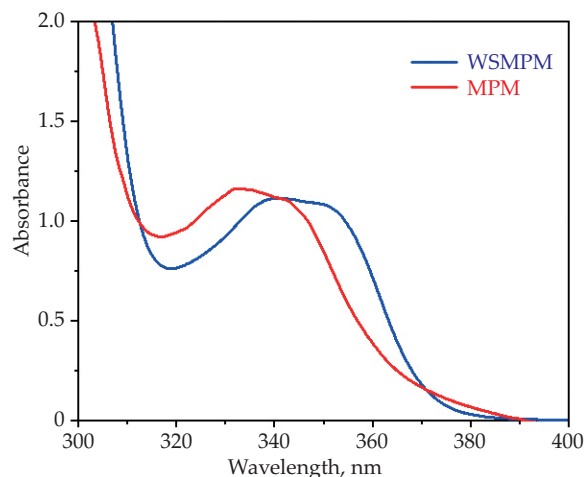**Fig. 1. Absorption spectra of WSMPM in H$_2$O, DMSO and DMF**

Fig. 2. Absorption spectra of MPM and WSMPM in DMF

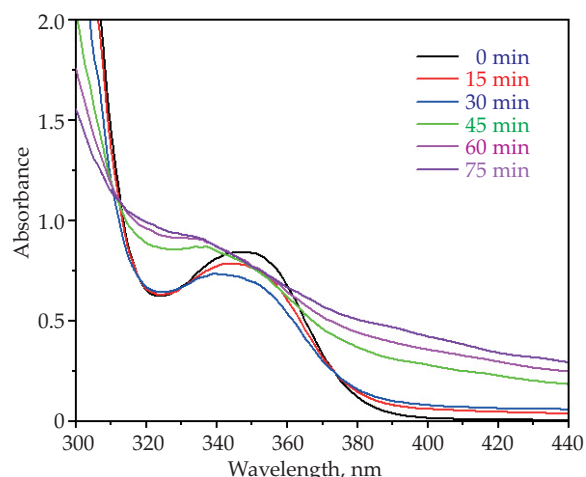**Fig. 3. Photo-bleaching of WSMPM in H$_2$O**

nitrogen or air atmosphere to investigate the initiation efficiency of the generated radicals. Conversion percentages of monomer to polymer and rate of polymerization values are calculated and the results are indicated in Table 1.

T a b l e 1. Bulk polymerization of AAm at 25°C with WSMPM as a photoinitiator

Run[a]	PI mol · L^{-1}	MDEA mol · L^{-1}	Conv.[c] %	$Rp \cdot 10^5$ mol · mL^{-1} · min^{-1}
1	$1 \cdot 10^{-3}$	–	–	–
2	$1 \cdot 10^{-3}$	–	38.9[b]	10.6
3	$1 \cdot 10^{-3}$	0.03	54.3	14.9
4	$1 \cdot 10^{-3}$	0.03	84.4[b]	23.1
5	$1 \cdot 10^{-2}$	–	–	–
6	$1 \cdot 10^{-2}$	–	–[b]	–
7	$1 \cdot 10^{-2}$	0.03	39.6	10.8
8	$1 \cdot 10^{-2}$	0.03	67.9[b]	18.6

a) [AAm] = 1 mol · L^{-1}; b) Under N_2 atmosphere; c) $t_{irr.}$= 60 min in photo reactor. Light intensity UVA: 24.8 W/m^2.

The emission spectra of the UVA (254 nm) and UVC (365 nm) lamps in the photoreactor used in the photopolymerization study are compatible with the absorption spectrum of the photoinitiator used. Thus, this situation has a positive effect on polymerization conversion percentages (Table 1). Different initiator concentrations were used to determine the optimum photoinitiator value. No polymer formation was observed in the air atmosphere regardless of the initiator concentration. However, polymer formation was obtained under the N_2 atmosphere (1×10^{-3}; conv~38.9 %) at low initiator concentrations. Oxygen quenching and synergistic abilities of N-methyl diethanolamine (MDEA) were examined in air and inert atmosphere as shown in Table 1 [33]. Formulations consisting of MDEA resulted in higher conversion values of monomer to polymer in inert atmosphere. 10^{-3} M of WSMPM led to 84.4 % conversion with AAm in the presence of MDEA under nitrogen atmosphere.
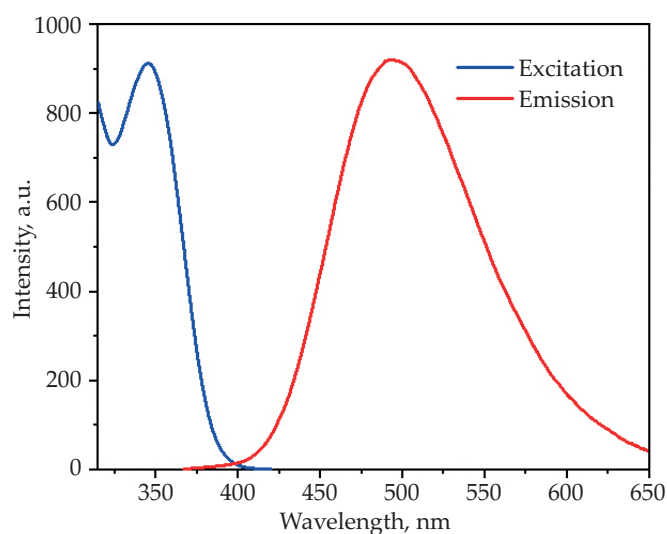

Fig. 4. Fluorescence excitation and emission spectra of WSMPM in H_2O
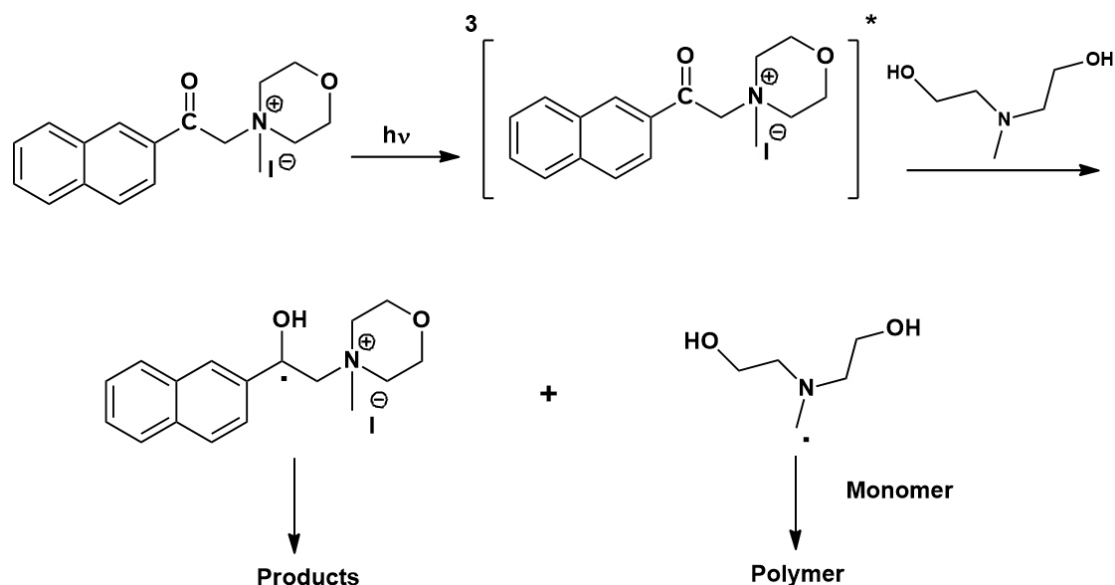

Fig. 5. Proposed photoinitiation mechanism of WSMPM

Fluorescence study

The solution of WSMPM in distilled water was excited at 347 nm and the emission graph was obtained at a maximum wavelength of 494 nm. A mirror-like image relation was observed between excitation and emission of WSMPM solution (Fig.4).

Proposed photoinitiation mechanism

Possible photoinitiation mechanism of WSMPM is indicated in Figure 5. WSMPM becomes excited triplet when irradiated with UV-vis. light. In this case, it is reduced to the ketol radical because of electron and proton extraction from the co-initiator NMDEA. The α-amino alkyl radicals formed to initiate the polymerization reaction in the presence of acrylamide monomer.

CONCLUSIONS

The quaternary ammonium salt, 4-methyl-4-[2-(naphthalen-2-yl)-2-oxoethyl]morpholin-4-ium iodide, was synthesized using a type I photoinitiator (MPM) and used to polymerize acrylamide monomer. Compared to the MPM, the absorption spectrum of the WSMPM has shifted to the visible region, and the molar absorption value is higher. Photopolymerization of the AA monomer led to 84% conversion under nitrogen with a tertiary amine. Thanks to its high molar absorption and good solubility in water, WSMPM can be used as an effective type II photoinitiator in water-based systems. Moreover, the mechanism of the WSMPM photoinitiator can be clarified by electron spin resonance (ESR) technique and laser flash photolysis.

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