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1-(2-Naphthyl)-2-(1-pyrrolidinyl)ethanone as a Photoinitiator for Methyl Methacrylate Polymerization

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1-(2-Naphthyl)-2-(1-pyrrolidinyl)ethanone (MPY) was synthesized as a photoinitiator for free radical polymerization and the structure was characterized by spectral analysis. MPY has ability to initiate the polymerization of methyl methacrylate (MMA) monomer in air upon irradiation. Absorption and fluorescence properties of this initiator are investigated and the singlet excited-state energy value calculated in dichloromethane. According to the results, MPY acts as a type 2 photoinitiator.
Keywords: Photoinitiator, Photopolymerization, Acetonaphthone

1. Introduction

Polymerization reactions are extensively performed in various commercial areas such as coatings, 3D curing, imaging materials, photoresists, halographic recordings and nanoscale micromechanics [1-6]. The development of the photocuring industry depends on improvement of photoinitiating systems that have the standards required for industrial fabrication. Nowadays, a great amount of photoinitiating systems possessing different criteria, such as selectivity of wavelength and solubility, are applied in industrial processes [7-9].

Photoinitiators produce reactive species like free radicals or ions that are efficient in UV-curing systems. They are responsible for the initiation of polymerization of multifunctional monomers. Photoinitiators are classified as two types: α-cleavable initiators (Type 1) and hydrogen abstraction type photoinitiators (Type 2). Type 1 photoinitiators generate two radicals by performing an α-cleavage process by irradiation [10-13]. Type 2 photoinitiators can be taken into account advantageous compared with Type 1 as in most cases. These initiators produce the initiating radicals by reacting with co-initiators like thiols, amines, ethers and alcohols. Type 1 initiators require high energy for bond cleavage and they need to use high-energy light sources that have short wavelengths [14-17].

The α-hydroxy ketones have been used as photoinitiators for many years. The use of α-amino ketones has gained importance in this field especially for curing of pigmented coatings. When compared to acetophenone type photoinitiators, they have higher molar absorptivities in the 300-400 nm region [18,19]. The effectiveness of these systems was investigated in the presence of sensitizers such as thioxanthones [20].

Recently, two photoinitiators namely 2-(*N*-methyl-*N*-phenylamino) acetonaphthone (MPA) and 2-morpholino acetonaphthone (MPM) respectively, were synthesized and characterized [21,22]. These α-cleavable initiators have absorption characteristics in the UV region, and also they can initiate the polymerization of methyl methacrylate monomer. Photopolymerization kinetics of MPA and MPY were investigated by photo-DSC technique at different light intensities [23]. Furthermore, visible initiators were synthesized using MPA and MPM as starting materials [24,25].

The aim of this study is to synthesize a new photoinitiator, namely 1-(2-naphthyl)-2-(1-pyrrolidinyl)ethanone (MPY) [26] and perform its photochemical and photophysical properties.

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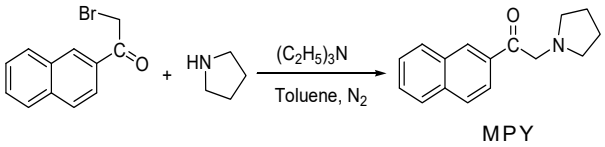
2. Experimental

2.1. Materials

α-Bromo-2'-acetonaphthone, pyrrolidine and trimethylamine were obtained from Aldrich, and used as received. *N,N'*-Dimethylformamide (DMF, Aldrich, 99%), toluene, dichloromethane and *N*-methyldiethanolamine (MDEA, Aldrich, 99%) were supplied from Merck and used as received. Methyl methacrylate (MMA, Alfa Aesar, 99%) was passed through a column of alumina to remove the inhibitor and dried over $CaCl_2$.

2.2. Synthesis of 1-(2-naphthyl)-2-(1-pyrrolidinyl) ethanone (MPY)

2.5 g of α-bromo-2'-acetonaphthone (0.02 mol) was dissolved in 15 mL of dry toluene in a flask. Afterwards, 1.4 mL of triethylamine and 0.85 mL pyrrolidine mixture, was poured in the stirred solution. After putting in, the reaction mixture was stirred for five nights under nitrogen (N_2) atmosphere at room temperature as shown in Scheme 1.



Scheme 1. Synthesis of MPY.

The resulted solution was filtered and toluene was removed. Finally, the residue was recrystallized from ethanol and yellow product was achieved. m.p: 149 °C. ^{1}H-NMR (500 MHz, DMSO-d_6), δ: 2.25-1.70 (m, 4H, CH_2), 3.20-2.80 (m, 4H, CH_2), 3.35 (s, 2H, CH_2), 8.70-7.45 (m, 7H, aromatic). FTIR (ATR): υ 3055 (C-H), 2956 (C-H), 1671 (C=O), 1337 (C-N) cm^{-1}. UV (CH_2Cl_2): λ_{340nm} (ε=7020 L·mol^{-1}·cm^{-1}).

2.3. Photopolymerization

Proper solutions of MPY initiator and MMA monomer were irradiated in the presence and absence of MDEA by a medium pressure mercury lamp for 30 minutes either in air or in N_2 atmosphere. The formation of poly(methyl methacrylate) (PMMA) is followed by a precipitation in a 10-fold excess of methanol and dried *in vacuo*. Polymerization rates and the conversion percentages were calculated for all samples gravimetrically.

2.4. Analysis

^{1}H NMR spectrum was recorded on a Bruker 500 MHz instrument with DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard. The infrared spectrum was taken on a Nicolet 6700 FT-IR spectrophotometer. Absorption spectrum was measured with an Agilent Technologies 8453 spectrophotometer. Fluorescence spectra were obtained using a Varian Eclipse spectrofluorometer at room temperature by using 1 cm path length quartz cuvettes.

3. Results and discussion

1-(2-Naphthyl)-2-(1-pyrrolidinyl)ethanone (MPY) was synthesized according to procedures given in our previous studies [21,22] and characterization of MPY was approved by UV, ^{1}H NMR and IR spectroscopy techniques.

3.1. Absorption properties of MPY

Figure 1 demonstrates the absorption spectrum of MPY. MPY possesses absorption characteristics similar to MPA and MPM with a maximum at 340 nm (ε=7020 L · mol^{-1} · cm^{-1}). The high molar absorptivity of MPY makes it attractive as a photoinitiator to perform polymerization experiments.

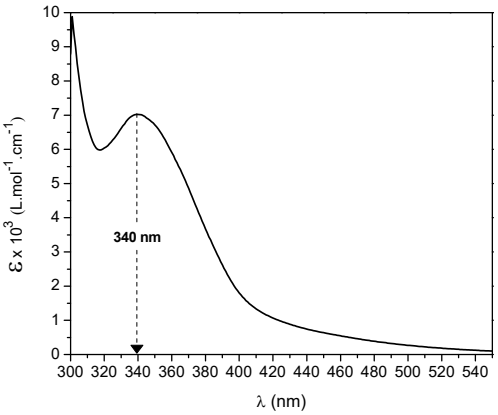


Fig. 1. Absorption spectrum of MPY [2.5 × 10^{-4} M] in CH_2Cl_2.

Selection of a photoinitiator with high initiation efficiency and fast bleaching under UV light is very important. Rapid photolysis of MPY is advantageous for decreasing the residual photoinitiator content and increasing cure speed [27]. The exposure of solution to the UV light generated by a spot-light curing system at intervals of 10 sec. during photolysis, followed by recording the changes to the absorption spectra of MPY in CH_2Cl_2.

As shown in Fig. 2, MPY/CH_2Cl_2 solution was decomposed after 60 sec. upon exposure to UV light in the environment air.

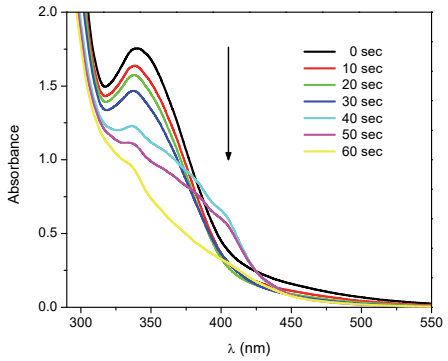


Fig. 2. Photolysis of MPY [2.5 × 10^{-4} M] in CH_2Cl_2. (Light intensity = UVA: 2000 W/m^2, UVB: 300 W/m^2).

3.2. Photopolymerization

MPY was used as a photoinitiator for the polymerization of MMA as a model acrylate in the presence and absence of air. To see the synergistic effect of a tertiary amine, MDEA was added to the formulations. The results are compiled in Table 1.

Table 1. Bulk polymerization of MMA at 25 °C with MPY as a photoinitiator.

Run[a]	MPY (mol·L^{-1})	MDEA (mol·L^{-1})	Conv.[c] (%)	R_p × 10^4 (mol·mL^{-1}·min^{-1})
1	5 × 10^{-3}	-	-	-
2	5 × 10^{-3}	-	0.2[b]	6
3	5 × 10^{-3}	0.34	1.1	33
4	5 × 10^{-3}	0.34	3.0[b]	85
5	1 × 10^{-2}	-	-	-
6	1 × 10^{-2}	-	0.4[b]	12
7	1 × 10^{-2}	0.34	1.9	59
8	1 × 10^{-2}	0.34	3.3[b]	103
9	2 × 10^{-2}	-	-	-
10	2 × 10^{-2}	-	0.3[b]	9
11	2 × 10^{-2}	0.34	2.1	65
12	2 × 10^{-2}	0.34	3.1[b]	96

[a] [MMA] = 9.35 mol·L^{-1}. [b] Under N_2 atmosphere.
[c] $t_{irr.}$= 30 min in 400 W mercury lamp,
(Light intensity= UVA: 48 W/m^2, UVB: 2 W/m^2).

To determine the optimum value of photoinitiator concentration, different initiator concentrations were used. As it can be seen in Table 1, no polymer was formed in air atmosphere for all concentrations. When samples were irradiated under N_2 atmosphere, it was observed that conversion of monomer to polymer was very low (0.3% for 2 × 10^{-2} M). This indicates that the photoinitiator could not undergo α-cleavage and produce active radicals. When the polymerizations are carried out under both air and N_2 atmosphere, in the presence of N-methyl diethanolamine (MDEA), a significant increase was observed in the conversion percentages (2.1% for 2 × 10^{-2} M). This shows that amine inhibits retardant effect of oxygen and acts as a co-initiator to form radicals which initiate polymerization. It is also observed that the rate of polymerization (R_p) values increased with increasing photoinitiator concentration, and optimum photoinitiator concentration was determined as 2 × 10^{-2} M.

3.3. Fluorescence studies

Fluorescence study of MPY was performed in dichloromethane and nearly mirror-image-like relation was observed between excitation and emission (Fig. 3).

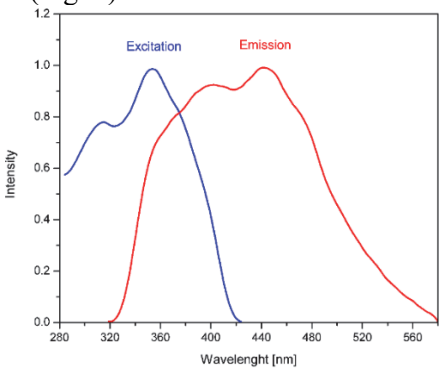


Fig. 3. Normalized fluorescence excitation and emission of CH_2Cl_2 solution of MPY (λ_{ex} = 300 nm) at room temperature.

The shape of the excitation spectrum is almost same as the absorption spectrum of MPY. The singlet excited-state energy value of MPY was calculated in dichloromethane from the intersection of the excitation-emission spectra as 319 kJ/mol.

3.4. Photoinitiation mechanism

The proposed photoinitiation mechanism of MPY according to the polymerization results is shown in Fig. 4. Polymerization results of methyl meth-

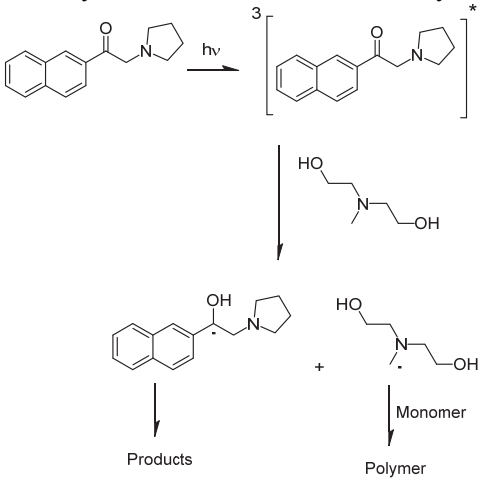


Fig. 4. Proposed photoinitiation mechanism of MPY.

acrylate in the presence of MPY showed no formation of polymer in the air environment without a co-initiator. This demonstrates that after irradiation MPY abstracts hydrogen from amine and α-amino alkyl radicals initiate the polymerization process.

4. Conclusion

1-(2-Naphthyl)-2-(1-pyrrolidinyl)ethanone (MPY) was synthesized and characterized as a new photoinitiator. MPY has a large absorption band and a high molar absorption coefficient in the UV-Vis region at a maximum of 340 nm. Photolysis in a short period of 60 sec. in the air environment allows MPY to be used as a photoinitiator. According to the proposed initiation mechanism, MPY acts like type 2 photoinitiator. Laser flash photolysis technique will be used to clarify the photoinitiation mechanism [28].

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References

1. K. Dietliker, *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints*, Vol. III, SITA Technology Ltd., London, (1991).
2. B. F. Howell, A. De Raaff, and T. Marino, *Photopolymerization. Fundamentals and Applications*, A. B. Scranton, C. N. Bowman, and R. W. Pfeiffer, Eds., American Chemical Society, Washington, DC, Chapter 16, 219–232 (1997).
3. D. C. Neckers and W. Jager, *Photoinitiation for Polymerization: UV& EB at the Millenium* Wiley, New York, Vol. 7 (1999).
4. R. S. Davidson, *Exploring the Science. Technology and Applications of U.V. and E.B. Curing,* SITA Technology Ltd., London, (1999).
5. J. P. Fouassier, *Photoinitiating Systems*, Elsevier Appl. Sci., Amsterdam, *Vol. II* (1993).
6. M. Aydin, G. Temel, D. K. Balta, and N. Arsu, *Polym. Bull*., **72** (2015) 309.
7. S. P. Pappas, *UV Curing: Science and Technology*, Technology Marketing Corp., Norwalk, CT, (1978).
8. J. P. Fouassier, *Photoinitiation, Photopolymerization, Photocuring: Fundamentals and Applications*; Hanser Publishers, Munich, (1995).
9. J. Qiu and J. Wei, *J. Appl. Polym. Sci*., **131** (2014) 40659.
10. J. Lalevee, X. Allonas, S. Jradi, and J. P. Fouassier, *Macromolecules*, **39** (2006) 1872.
11. W. Sluggett, P. F. McGarry, I. V. Koptyug, and N. J. Turro, *J. Am. Chem. Soc.,* **118** (1996) 7367.
12. R. S. Davidson, *Advances in Physical Chemistry*, D. Bethel and V. Gold, Eds., Academic Press, London, (1983).
13. K. Dietliker, *A Compliation of Photoinitiators Commercially Available for UV Today*, SITA Technology Ltd., London, (2002).
14. S. Dadashi-Silab, C. Aydogan, and Y. Yagci, *Polym. Chem*., **6** (2015) 6595.
15. J. Kreutzer and Y. Yagci, *J. Polym. Sci. Part A: Polym. Chem.,* **55** (2017) 3475.
16. P. Gauss, M. Griesser, M. Maarkovic, A. Ovsianikov, G. Gescheidt, P. Knaack, and R. Liska, *Macromolecules*, **52** (2019) 2814.
17. R. Liska, *J. Polym. Sci. Part A: Polym. Chem.*, **42** (2004) 2285.
18. S. Jockusch and N. J. Turro, *J. Am. Chem. Soc*., **121** (1999) 3921.
19. C. S. Colley, D. C. Grills, N. A. Besley, S. Jockusch, P. Matousek, A. W. Parker, M. Towrie, N. J. Turro, P. M. W. Grill, and M. W. George, *J. Am. Chem. Soc*., **124** (2002) 14952.
20. G. Rist, A. Borer, K. Dietliker, V. Desobry, J. P. Fouassier, and D. Ruhlmann, *Macromolecules*, **25** (1992) 4182.
21. S. Keskin and N. Arsu, *Polym. Bull.,* **57** (2006) 643.
22. S. Keskin and N. Arsu, *Prog. Org. Coat*., **57** (2006) 348.
23. S. Keskin Dogruyol, *J. Photopolym. Sci. Technol*., **30** (2017) 651.
24. S. Keskin Dogruyol, Z. Dogruyol, and N. Arsu, *J. Polym. Sci. Part A: Polym. Chem.,* **49** (2011) 4037.
25. S. Keskin Dogruyol, Z. Dogruyol, and N. Arsu, *J. Luminescence*, **138** (2013) 98.
26. U. Çalıs, S. Dalkara, M. Ertan, and R. Sunal, *Arch. Pharm. (Weinheim)*, **321** (1988) 841.
27. S. Mutlu, K. Watanabe, S. Takahara, and N. Arsu, *J. Polym. Sci. Part A: Polym. Chem.,* **56** (2018) 1878.
28. N. Karaca, N. Ocal, N. Arsu, and S. Jockusch, *J. Photochem. Photobiol. A: Chem*., **331** (2016) 22.