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Using 2-(N-Methyl-N-Phenylamino) acetonaphthone as photoinitiator for the polymerization of methyl methacrylate

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Summary

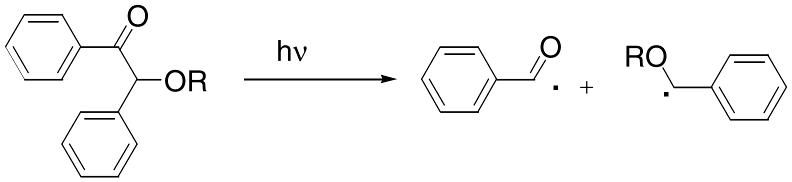
2-(N-Methyl-N-phenylamino) acetonaphthone (MPA) was synthesized as a cleavable photoinitiator and the structure of the photoinitiator was confirmed by spectral and elemental analysis. MPA shows a much higher molar absorptivity than the commercially used acetophenone derivative. The photoinitiation capability of MPA was demonstrated by using methyl methacrylate and a formulation containing multifunctional monomers. Incorporation of the naphthoyl moiety into the polymer was demonstrated by spectroscopic methods.

Introduction

Photoinitiated free radical polymerization reactions are used widely on a commercial scale for a number of different applications, such as the curing of coatings on various materials, adhesives, printing inks and photoresists [1-5]. The growth of the radiation curing industry depends on continuous innovation to support this technology. A wide range of free radical photoinitiating systems, fulfilling requirements for industrial application, e.g. wavelength selectivity, solubility e.t.c. is now available. A large portion of today's relevant research concerns photoinitiators, i.e. the introduction of new initiators or improvement of the solubility of available initiators [1-4]. Photoinitiated radical polymerization may be initiated by both cleavage (Type I) and H-abstraction type (Type II) initiators. The derivatives of benzoin were some of the earliest cleavable initiators to be introduced (Scheme 1) [2].

Because of their vital role in photopolymerization, photoinitiators are the subject of particularly extensive research. Most of this research has focused on Type I photoinitiators, which upon irradiation undergo an α-cleavage process to form two radical species.

A major improvement in this field was made by the introduction of substituted α–aminoketone photoinitiators [5-7]. These compounds have higher molar absorptivities in the 300–400 nm region than the usual acetophenone type photoinitiators and are therefore suitable for the curing of pigmented systems.



Scheme 1. Decomposition of benzoin

In this article, we report the synthesis of 2- N-methyl-aminophenyl-acetonaphthone (MPA) by a new method and the efficiency of MPA as a cleavable photoinitiator for the polymerization of mono and multi-functional acrylates.

Experimental Section

Materials

α-Brom-2'-acetonaphthone, N-methylaniline, and triethylamine were obtained from Aldrich, and used as received. Toluene, dichloromethane, ethanol, methanol, acetonitrile, acetone and chloroform were supplied by Riedel and purified by conventional drying and distillation procedures. Trimethylol propanetriacrylate (TMPTA) and N-methyldiethanolamine (MDEA) were also obtained from Aldrich and used as received. Methyl methacrylate (MMA) was washed with NaOH (5%), dried with Na_2SO_4 and used as monomer after vacuum distillation. 2-Methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one (Irg 907), 2-benzyl-2-dimethyl-amino-1-(4-morpholinophenyl)-butan-1-one (Irg-369) and 1-[4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methyl-propane-1-one (Irg-2959) were obtained from Ciba Specialty Chemicals. Epoxyacrylate (EA) and Tripropyleneglycoldiacrylate (TPGDA) were obtained from Cognis France.

Instruments

GPC analyses of the polymers were performed with a set-up consisting of a pump (Waters) and four ultrastryragel columns of different porosities. THF was used as the eluent (flow rate 1 ml x min^{-1}) and the detection was carried out with the aid of a differential refractometer. The number of average molecular weights was determined by using polystyrene standards. ^{1}HNMR spectra were recorded on a Bruker 250 instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standart. UV-Vis spectra were taken on a Philips PU 8700 UV-Vis spectrophotometer. The IR spectra were recorded on an ATI Unicam Mattson 1000 FT/IR-3 spectrophotometer on a KBr disc. The mass spectrum of the photoinitiator in acetonitrile after photolysis was taken by the VG-Zab Spect –FAB (Fast Atom Bombardment). The light intensities of our various light sources were determined by using a potassiumferrioxalate actinometer solution [8]. The photolyzing light was generated by a medium pressure mercury lamp (Flexicure UV system) and was conducted through a flexible fiber optic for the photolysis of MPA. K_2CrO_4 [$5x10^{-4}$M] in water a solution was chosen as a band pass filter (365nm). The light intensities are respectively; I^a : $7.12x10^{16}$ photon x s^{-1}; I^b: $4.37x10^{16}$ photon x s^{-1}; I^c: $4.24x10^{16}$ photon x s^{-1}

^{a}:Medium pressure mercury light (400W); ^{b}: Flexi-cure ; ^{c}:Flexi-cure with filter solution.

Synthesis of 2(N-methyl-N-phenylamino) acetonaphthone

α-Brom-2'-acetonaphthone (1.5 g; 6.0 mmol) was dissolved in 10 ml of dry toluene in a two-necked round-bottomed flask. A mixture of triethylamine (0.9 ml; 6.5 mol), and N-methylaniline (0.7 ml; 6.5 mol) in toluene, was slowly added to the stirred solution. After the addition, the reaction mixture was left overnight for stirring at room temperature under nitrogen atmosphere. The solution was filtered and toluene was removed by using a rotary-evaporator. The residue was recrystallized from ethanol. m.p: 110^0C. ^{1}H NMR (250 MHz) in $CDCl_3$: δ 8.51 – 6.69 (m,12H, aromatic), 4.91 (m,2H,CH_2), 3.13 (s, 3H,CH_3) ppm IR (KBr) : ν 3055, 2902, 2305, 1702, 1600, 1523, 1370, 1217, 936, 834, 757 cm^{-1}. Calculated for $C_{19}H_{17}ON$: C 82.9, H 6.18. Found: C 83.37, 6.18 H. UV (acetonitrile) λmax 342.4 nm (ε = 1897.6 l x mol^{-1} x cm^{-1})

Photopolymerization

Appropriate solutions of monomer and the initiator (MPA) were irradiated in the presence and absence of N-methyldiethanolamine by a medium-pressure mercury lamp for 10 and 15 minutes in either an air or a N_2 atmosphere. Polymer were obtained after precipitation in methanol and drying in vacuo. The conversion % and polymerization rates were calculated gravimetrically for all samples.

Results and Discussion

Photoinitiated radical polymerization may be initiated by both cleavage (Type I) and H-abstraction type (Type II) initiators. The majority of Type I initiators are aromatic carbonyl compunds containing suitable substituents which facilitate direct photofragmentation. 2-(N-methyl-N-phenylamino)acetonaphthone (MPA) was synthesized and characterized by elemental and spectral analysis. The absorption spectra of the initiator have two maxima at 329 (ε=1828 l x mol^{-1} x cm^{-1}) nm and at 342 nm (ε= 1824 l x mol^{-1} x cm^{-1}), but similar molar absorptivity (see Figure 1). Extinction coefficients of some of the commercial initiators are similar or much lower than MPA at 340nm.

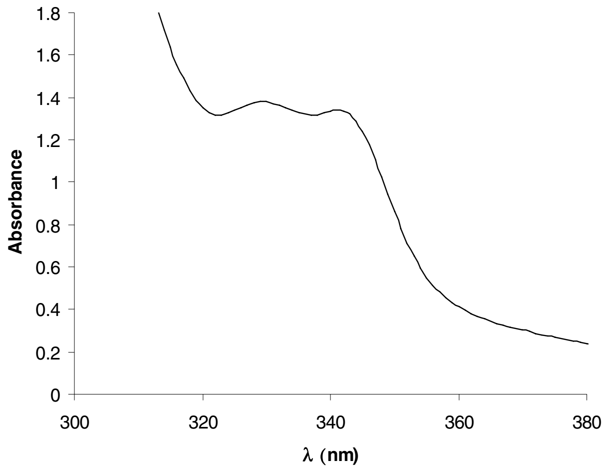


Figure 1. Absorption spectra of MPA [7.5x10^{-4} M] in CH_2Cl_2.

MPA was used as photoinitiator for the polymerization of methyl methacrylate and it was demonstrated that polymerization occurs both in the presence and absence of oxygen. The results obtained from the polymerization were compiled in Table 1.

Table 1. Bulk Polymerization of methyl methacrylate in the presence of MPA in air and nitrogen atmospheres

Run [a]	Photoinitiator (mol l^{-1})	Additive (mol l^{-1})	Time (min)	Conversion (%)	Mn [b] (g mol^{-1})
1	MPA ($1x10^{-2}$)	-	15	9.8	47.0
2	MPA ($2x10^{-2}$)	-	15	11.2	43.5
3	MPA ($4x10^{-2}$)	-	15	8.2	38.5
4	MPA ($2x10^{-2}$)	MDEA (0.34)	15	21.4	36.0
5	MPA ($2x10^{-2}$)	-	15	13.5 [c]	37.0

[a] [MMA] = 9.36 mol x L^{-1}

[b] Determined by GPC using polystyrene standarts

[c] Carried out under nitrogen

As it can be seen in Table 1, MMA reached an 11% conversion for the $2x10^{-2}$ M concentration of MPA during 15 minutes of irradiation. Polymerization experiments in the presence of a tertiary amine such as N-methyldiethanol amine (MDEA) as co synergist were also achieved and the conversion percentage of acrylate was doubled. Type I initiator systems avoid the use of large amounts of amines in the system. This is particularly important for curing applications, since the formulation containing high amine concentrations show a plasticizing effect. In addition, the amines act as chain transfer agents, which leads to the formation of polymers with a lower molecular weight and consequently to a reduction in the apparent degree of cure [10,11]. In our study, MDEA plays a dual action in polymerization besides hydrogen donation, MDEA reacts with oxygen and thereby reduces the retarding effect of oxygen on the polymerization of MMA even for the Type I initiators (see Table 1). The optimal photoinitiator concentration is another very important parameter for curing. Thus, we studied the effect of the photoinitiator concentration on the polymerization rate. In accord with the results obtained from polymerization experiments, the cure rate and the degree of polymerization increased with increasing photoinitiator concentration at first and after passing through a maximum or optimum concentration (2 x 10^{-2} M). It is known that this effect is largely dependent on the absorbance characteristics of the photoinitiator and that of the UV curable formulation. The absorbance of UV light appears to generate higher concentration of free radicals near the surface of the film at higher photoinitiator concentrations. Table 1 shows, that the increase in the MPA concentration helped to increase conversion and then the further increase of the concentration of the photoinitiator led to a decrease in the conversion percentage. High concentrations of photoinitiator may lead to an absorption of light in the upper region of the film which decreases the rate of polymerization due to radical termination. Also if the light does not penetrate the whole of the film or solution, radical production will not occur in all of the polymerizable material [13-16].

The same polymerization experiments were carried out for the comparison of MPA with other commercially available cleavable photoinitiators like Irg 907, Irg 369 and

Irg 2959. These initiators are very well known radicalic initiators and when they are cleaved, they initiate the polymerization of acrylates and methacrylates [5].
When we compare the results obtained from the polymerization of MMA in the presence of MPA and commercially avalaible photoinitiators (see Table 1 and Table 2), we see, that MPA initiates the polymerization of MMA as efficiently as other cleavable initiators do.

Table 2. Bulk polymerization of MMA in the presence of various initiators in air atmosphere.

Run	Photoinitiator (mol l^{-1})	Time (min)	Conversion (%)
1	Irg 907 ($1x10^{-2}$)	15	10.85
2	Irg 2959 ($1x10^{-2}$)	15	11.83
3	Irg 369 ($1x10^{-2}$)	15	8.85

[a] [MMA] = 9.36 mol x L^{-1}

The efficiency of the initiator MPA in the photocuring formulations containing multifunctional monomer (EA) and a diluent (TPGDA) was also studied. The disappearance of double bonds during the photocuring of the formulations was followed by Fourier's transform real-time infrared spectroscopy (RT-FTIR). By monitoring changes in the characteristic monomer IR absorption bands, it allows the direct monitoring of the fast polymerization process continuously [12-13]. In Figure 2, kinetic profiles referring to the polymerization of the mixture epoxyacrylate (75%) (EA) and tripropyleneglycoldiacrylate (25%) (TPGDA) under polychromatic light are shown. The curves were obtained by monitoring the absorption decrease of the band at 810 cm^{-1}. The shape of the curves indicates the existence of two polymerization

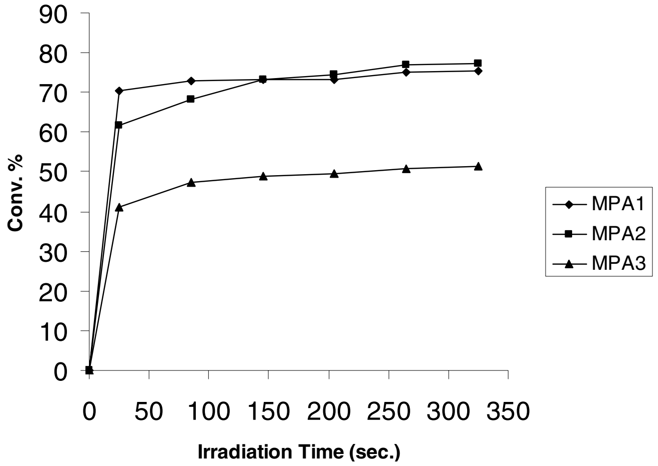


Figure 2. Kinetic profiles demonstrating the photopolymerization of epoxyacrylate/tripropyleneglycoldiacrylate mixture (3/1, v/v) containing photoinitiators with polychromatic light in air atmosphere. Photoinitiator: (MPA1) MPA (1 %), (MPA2) MPA (2 %) and (MPA3) MPA (1 % + 10% NMDEA).

phases , a rapid first phase followed by a slow phase . We have observed, that the low concentration of MPA lead to a high conversion value more rapidly but a higher concentration of MPA (2% w/w) lead to a slightly higher conv. % than in the case of a lower concentration of MPA at prolonged irradiation times.

Although most commercial Type I photoinitiators have very short lived triplet states but inhibition of oxygen is, neverthless observed even Type I photoinitiators. Therefore adding of tertiary amines are invaluable in reducing the concentration of oxygen with film thereby enabling the polymerization process to take place efficiently. A curve for the polymerization with the MPA/MDEA system indicates lowest conversion percentage values, both for the initiation period or prolonged irradiation times. It is clear that MPA photoinitiator avoids the use of large amounts of amines. This is particularly important for curing applications since formulations containing amine cause a decrease either in the hardness of the cured films or in lower conversion % values obtained by IR due to the plasticising effects of the amines [2].

The photolysis experiments of MPA in acetonitrile were performed and the decomposition of MPA was followed by spectral changes by UV spectroscopy. Representative results for the decomposition of the initiator are shown in Figure 3.

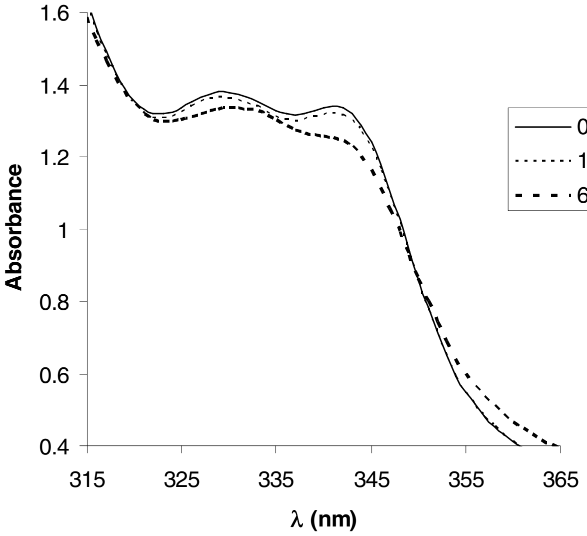
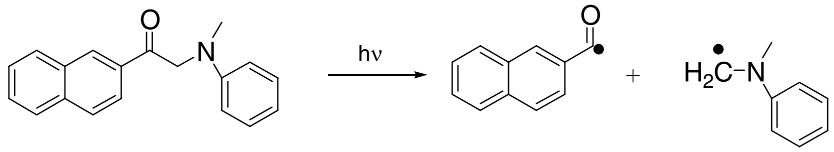


Figure 3. UV Spectral changes of MPA on irradiation at λ > 300 nm under air atmosphere in CH_3CN (800sec).

Type I initiators such as MPA, undergo α-cleavage to produce radicals. As the reaction proceeds, the photoinitiator is consumed and the absorption spectra change [9]. The UV spectra of the MPA/acetonitrile solution were recorded after the solution had been exposed to the light of the UV lamp for subsequent intervals of 50 and 100 seconds each. Additionally, the photochemical cleavage of MPA was determined by product analysis.

The MPA [$1x10^{-2}$ M] / acetonitrile solution was irradiated for 60 min by using the merry-go-round system [Io: $6.74x10^{16}$ foton.s^{-1}]. The Mass spectrum of the solution was obtained after irradiation. From the evaluation of the mass spectrum, the recombination product of naphtoyl radical was determined (309 Daltons of masses in FAB-MS) with a higher percentage besides other products and the photodecomposition of MPA was predicted as shown in Scheme 2.



Scheme 2. Decomposition of 2-(N-Methyl-N-phenylamino) acetonaphthone

One of the consequences of the above mechanism is that naphtoyl moiety should be incorporated into the polymer chain. Indeed, the uv-vis spectra of the resulting polymethylmethacrylate (PMMA) purified by several reprecipitations, present an absorption with a maximum at 340nm similar to that of the lower molecular weight precursor, MPA (Figure 4).

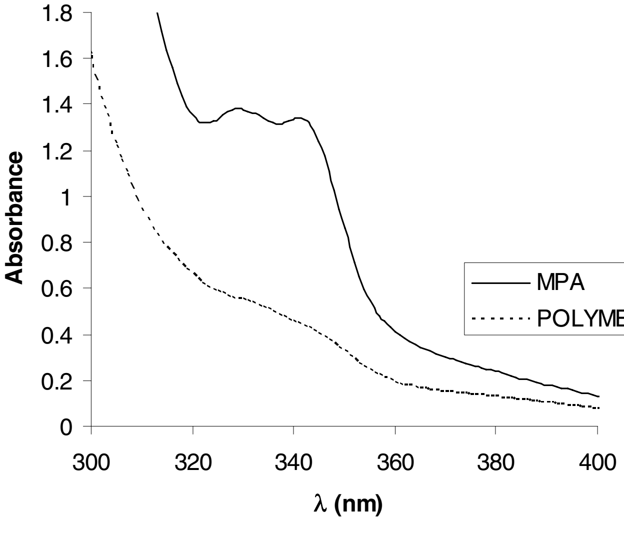


Figure 4. Absorption spectra of MPA and poly(methyl methacrylate) obtained by photoinitiated polymerization by using MPA in tetrahydrofuran.

In conclusion, the results show that MPA is capable of initiating free radical polymerization of methyl methacrylate in air atmosphere upon irradiation. In addition, MPA is an efficient photoinitiator for photocuring of epoxy acrylate and TPGDA monomer system . All these results indicate that MPA initiates the polymerization of acrylates according to the Norrish Type I reaction.

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