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The effect of an aminoalcohol on the polymerization of acrylates with type II initiators

Feyza Karasu · Nergis Arsu

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Abstract In this study, the authors report the use of an aliphatic amine and an aromatic aminoalcohol as synergists with various Type II initiators by using Photo-DSC (Photo-differential scanning calorimetry) technique. The photopolymerization of triacrylate and diacrylate was performed under nitrogen atmosphere in the presence of an amine or aminoalcohol with type II initiators, which allowed us to compare the efficiency of the initiating radicals. The oxygen scavenging role of the amine was left out.

Keywords Photopolymerization · Free radical polymerization · Photo-differential scanning calorimetry · Synergist · Type II photoinitiator

Introduction

Photoinitiated radical polymerization may be initiated by both α-cleavage (Type I) and H-abstraction (Type II) initiators [1]. Type II photoinitiators are a second class of photoinitiators and are based on compounds whose triplet excited states are reacted with hydrogen donors thereby producing an initiating radical [1–3]. Benzophenone (BP) and thioxanthone (TX) are well known Type II photoinitiators for the radiation curing of coatings, printing inks, etc., [4–7].

Tertiary amines can fulfil two roles in the curing of UV systems by a free radical route: they can scavenge peroxy intermediates formed by the reaction of oxygen with radical sites or, as the corresponding α-aminoalkyl radicals, they can react with oxygen, thereby reducing the retarding effect of oxygen on the rate of cure [8, 9].

In this study, the aromatic aminoalcohol, Erythro-2-morpholino-1,2-diphenylethanol (AA) and the well known aliphatic amine, *N*-Methyldiethanolamine (MDEA), were used as synergist for the polymerization of acrylates in the presence of various type II initiators (Thioxanthone, isopropylthioxanthone, benzophenone and 5-thianapthasen-12-one).

Photopolymerization was followed by Photo-DSC, and the effect of light intensity on the rate of polymerization was also investigated.

Experimental part

Materials

Thioxanthone (TX; 98%, Aldrich), isopropylthioxanthone (ITX; 97%, Aldrich), benzophenone (BP; 99%, Aldrich) and *N*-methyldiethanolamine (MDEA; 99%, Aldrich) were used as received. 5-thianapthasen-12-one (TX-Np) [10] and Erythro-2-morpholino-1,2-diphenylethanol (AA) [11] were synthesized according to the previously described procedure. Trimethylolpropanetriacrylate (TMPTA) was obtained from Cognis, France and 1,6-hexanediol diacrylate (HDDA) was obtained from ABCR.

Photo-DSC applications

Photo-DSC experiments were taken on a TA DSC 100 instrument and a TA Q PCA photo unit equipped with a high pressure mercury lamp. Prepared formulations were weighed into the aluminum pans and irradiated with the light source of the photo unit at different light intensities.

F. Karasu · N. Arsu (✉)
Department of Art and Science Faculty Chemistry, Yildiz Technical University, 34210 Esenler Topkapi-Istanbul, Turkey
e-mail: narsu@yildiz.edu.tr

Measurements were carried out in isothermal mode at 25 °C and under inert atmosphere (nitrogen flow: 50 mL/min). The polymerization rates and polymerization conversions were calculated.

The reaction heat liberated in the polymerization is directly proportional to the number of acrylates reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (*C*) or the extent of the reaction was determined according to Eq. 1:

$$C = \Delta Ht/\Delta H_0^{\mathrm{theory}} \quad (1)$$

where ΔHt is the reaction heat evolved at time t and $\Delta H_0^{\mathrm{theory}}$ is the theoretical heat for complete conversion. A reaction heat for an acrylate double bond polymerization of $\Delta H_0^{\mathrm{theory}} \leftarrow 86\,\mathrm{kJ/mol}$ was used [12]. The rate of polymerization (*R*p) is directly related to the heat flow (d*H*/d*t*) by Eq. 2:

$$R\mathrm{p}(\mathrm{d}C/\mathrm{d}t)(\mathrm{d}H/\mathrm{d}t)/\Delta H_0^{\mathrm{theory}} \quad (2)$$

Results and discussion

Thioxanthone, isopropylthioxanthone, and benzophenone are well known type II initiators; thioxanthone naphthalene has recently been introduced as a new type II initiator [10]. The UV absorption properties of these initiators are given in Fig. 1.

In the scope of this study, Erythro-2-morpholino-1,2-diphenylethanol (AA) was synthesized as indicated in the literature [11] and used as a synergist with Type II photoinitiators. The obtained results were compared with the well-known aliphatic synergist namely, *N*-methyldiethanolamine (MDEA) (Chart 1).

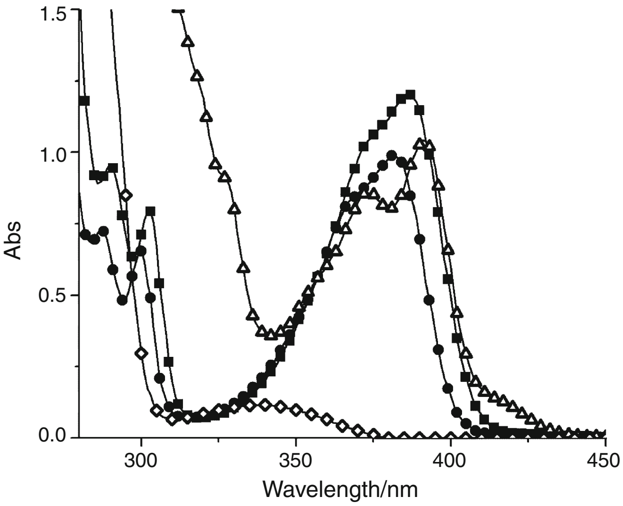


Fig. 1 UV-absorption spectra of ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*) and BP (*diamond*) in CH_2Cl_2.([ITX], [TX] and [TX-Np] = 0.15 mM; [BP] = 0.6 mM)

Erythro-2-morpholino-1,2-diphenylethanol (AA)

N-methyldiethanolamine (MDEA)

Chart 1 Structures of synergists

Formulations were prepared with TMPTA and HDDA as the tri- and diacrylates, respectively, in the presence of the initiators and co-initiator. Photopolymerization of the formulations was followed by photo-DSC. Here, the synergistic effects of the aliphatic amine and the aromatic aminoalcohol were investigated as well as the effects of various type II initiators. To study the effects of the amine synergists on photopolymerization of TMPTA or HDDA, samples containing 1 wt% of Type II photoinitiators and 5 wt% of MDEA or AA as synergist were polymerized at different light intensities (15, 30, 60 $\mathrm{mW/cm^2}$) under nitrogen atmosphere and the isothermal photo-DSC results recorded as heat flow versus time. The reaction heat liberated in the polymerization was directly proportional to the number of vinyl groups which reacted in the system.

The photo-DSC profiles of TMPTA for Type II initiators with MDEA with a light intensity of 15 $\mathrm{W/m^2}$ are shown in Fig. 2. The same experiments were performed with AA instead of MDEA and the results obtained for the rate of polymerization and conversion percentages are given in Fig. 3. The initiating efficiency of radicals produced by AA and MDEA were found to be different for the same initiators. The most efficient initiator was TX-Np with MDEA followed by ITX, TX, and BP. In fact when MDEA was

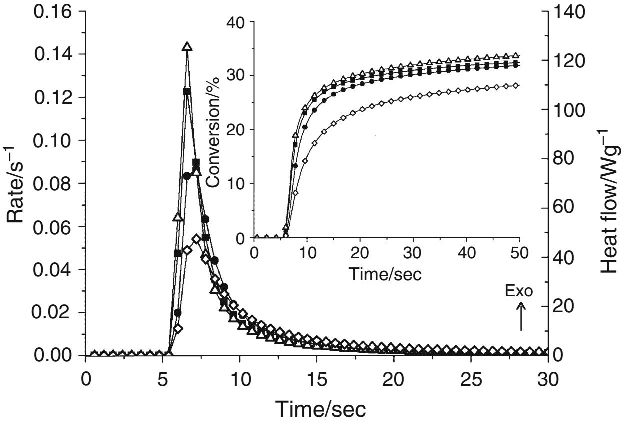


Fig. 2 Rate and conversion values (*inset*) of TMPTA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of NMDEA (Light Intensity: 15 $\mathrm{mW/cm^2}$)

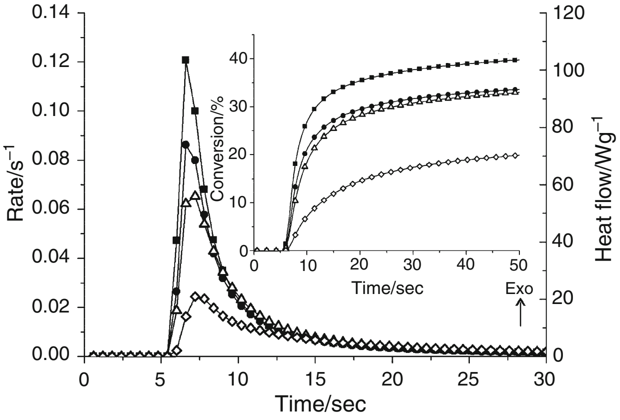


Fig. 3 Rate and conversion values (*inset*) of TMPTA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of AA (Light Intensity: 15 mW/cm^2)

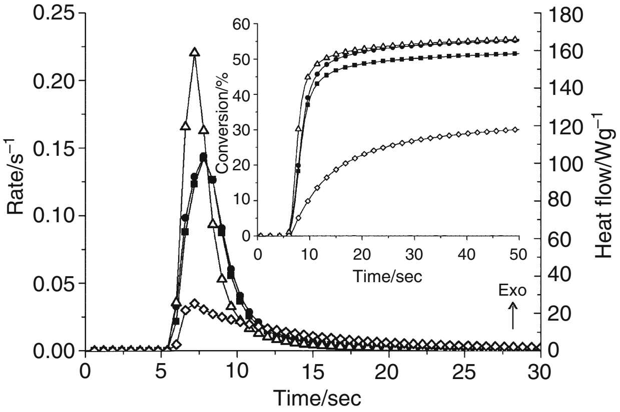


Fig. 4 Rate and conversion values (*inset*) of HDDA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of MDEA (Light Intensity: 15 mW/cm^2)

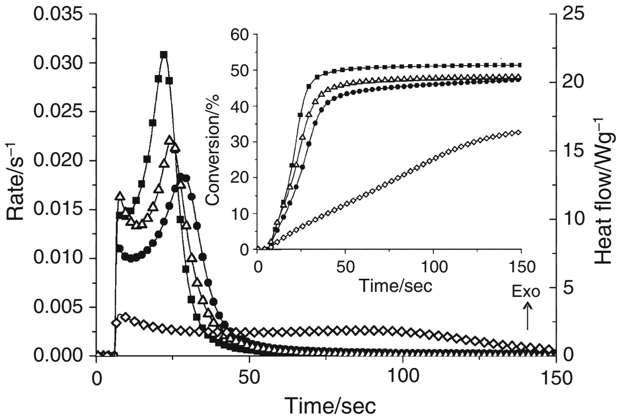


Fig. 5 Rate and conversion values (*inset*) of HDDA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of AA (Light Intensity: 15 mW/cm^2)

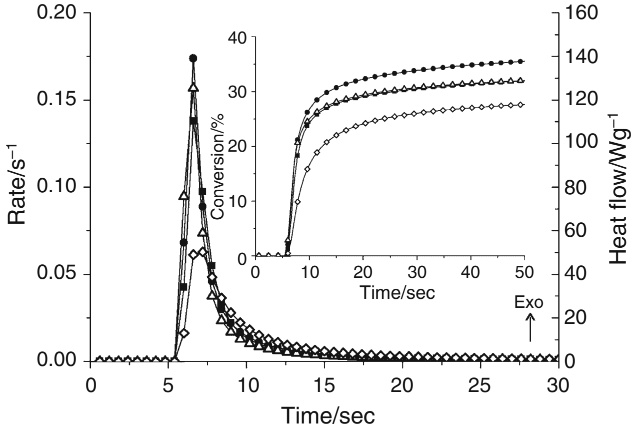


Fig. 6 Rate and conversion values (*inset*) of TMPTA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of MDEA (Light Intensity: 30 mW/cm^2)

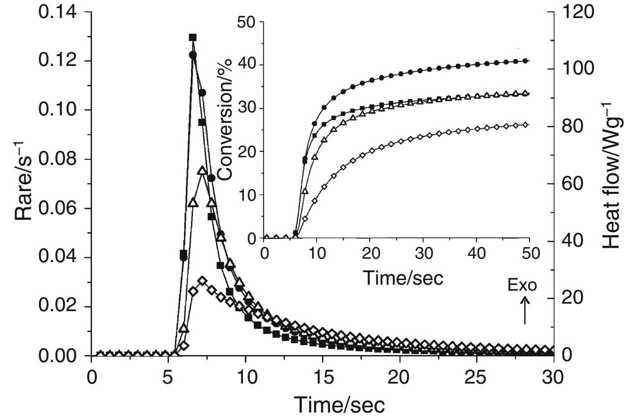


Fig. 7 Rate and conversion values (*inset*) of TMPTA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of AA (Light Intensity: 30 mW/cm^2)

omitted and AA was added to the formulation, the following trend was observed: instead of TX-Np, the most efficient initiator was found to be ITX followed by TX, TX-Np, and BP. The highest conversion percentage value of 39.80 was obtained for ITX with AA (Fig. 3), and 33.70 for TX-Np with MDEA (Fig. 2).

Owing to the fast initial polymerization of TMPTA, HDDA was employed as another monomer to see the effect of the synergists more clearly. At the same light intensity, photopolymerization results of HDDA with Type II initiators in the presence of synergists are given in Figs. 4 and 5.

When HDDA was employed instead of TMPTA, the final conversion values increased for all formulations. The order of efficiency of the photoinitiator in the presence of MDEA was found to be TX-Np = TX > ITX > BP (Fig. 4). When AA was added to the formulation, ITX was again found to be the most efficient photoinitiator (Fig. 5),

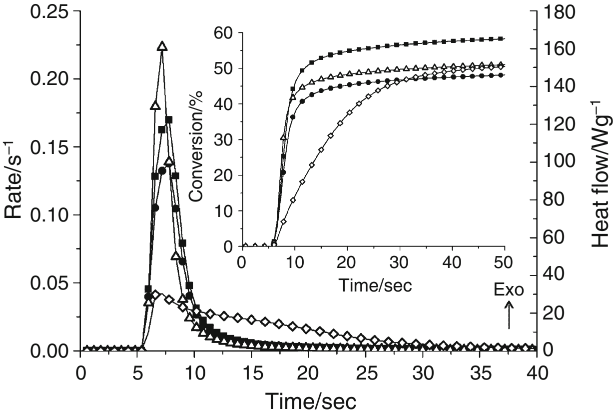


Fig. 8 Rate and conversion values (*inset*) of HDDA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of MDEA (Light Intensity: 30 mW/cm^2)

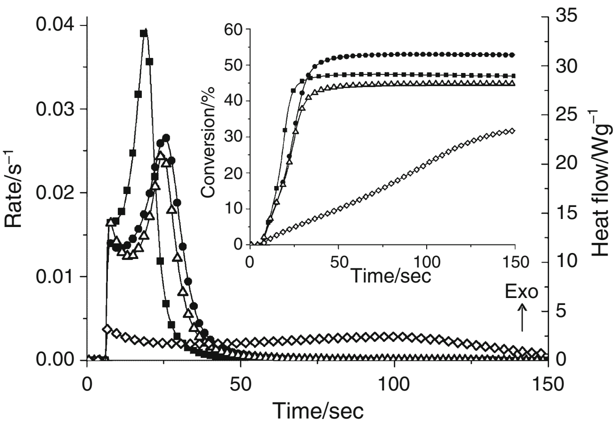


Fig. 9 Rate and conversion values (*inset*) of HDDA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of AA (Light Intensity: 30 mW/cm^2)

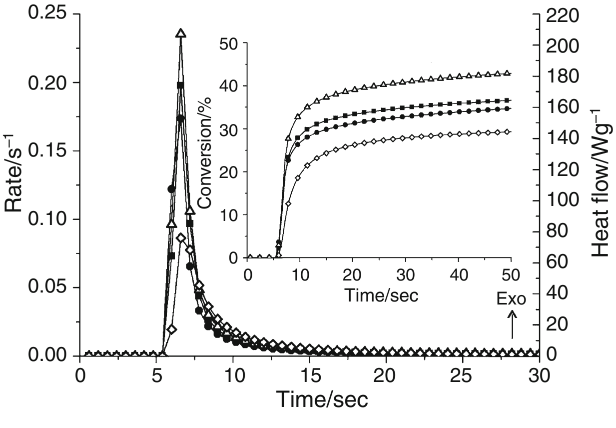


Fig. 10 Rate and conversion values (*inset*) of TMPTA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of MDEA (Light Intensity: 60 mW/cm^2)

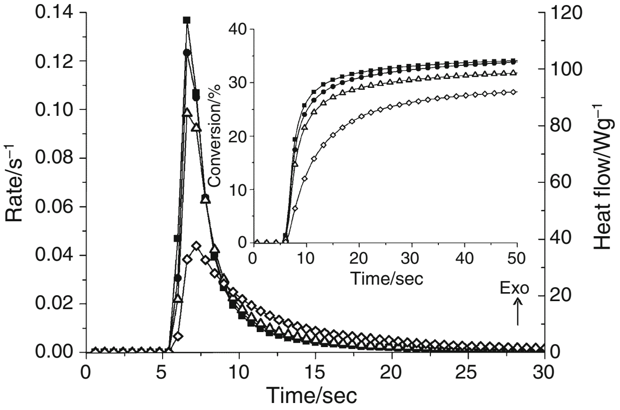


Fig. 11 Rate and conversion values (*inset*) of TMPTA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of AA (Light Intensity: 60 mW/cm^2)

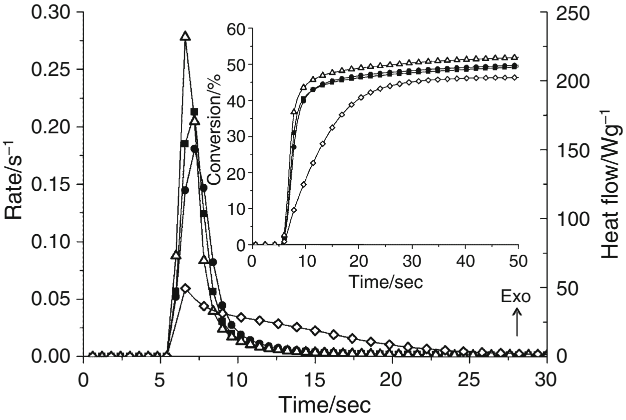


Fig. 12 Rate and conversion values (*inset*) of HDDA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of MDEA (Light Intensity: 60 mW/cm^2)

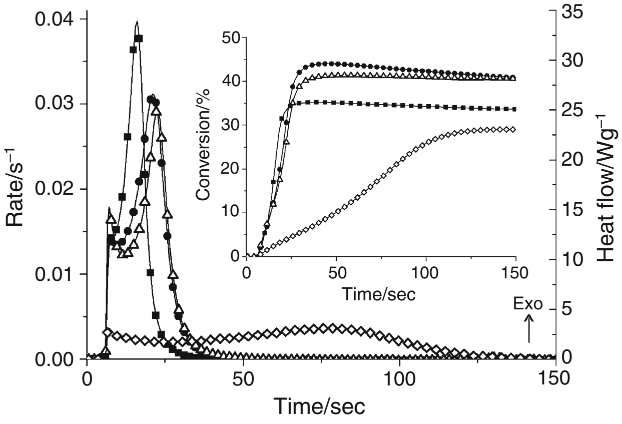


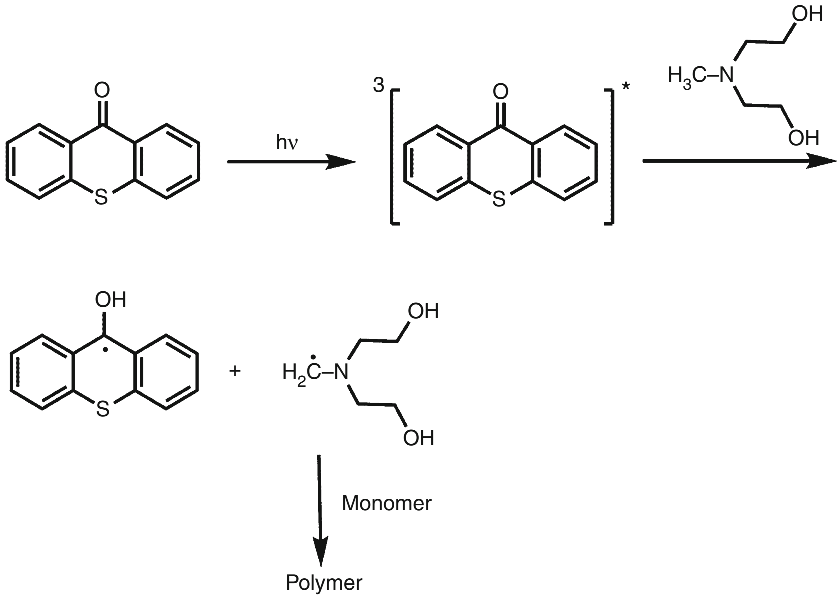
Fig. 13 Rate and conversion values (*inset*) of HDDA polymerization with 4 PI's (ITX (*filled square*), TX (*filled circle*), TX-Np (*triangle*), BP (*diamond*)) in the presence of AA (Light Intensity: 60 mW/cm^2)

similar with TMPTA result. The highest final conversion percentage values were found to be % 51.40 for ITX with AA (Fig. 5), and % 55.57 for TX-Np with MDEA (Fig. 4).

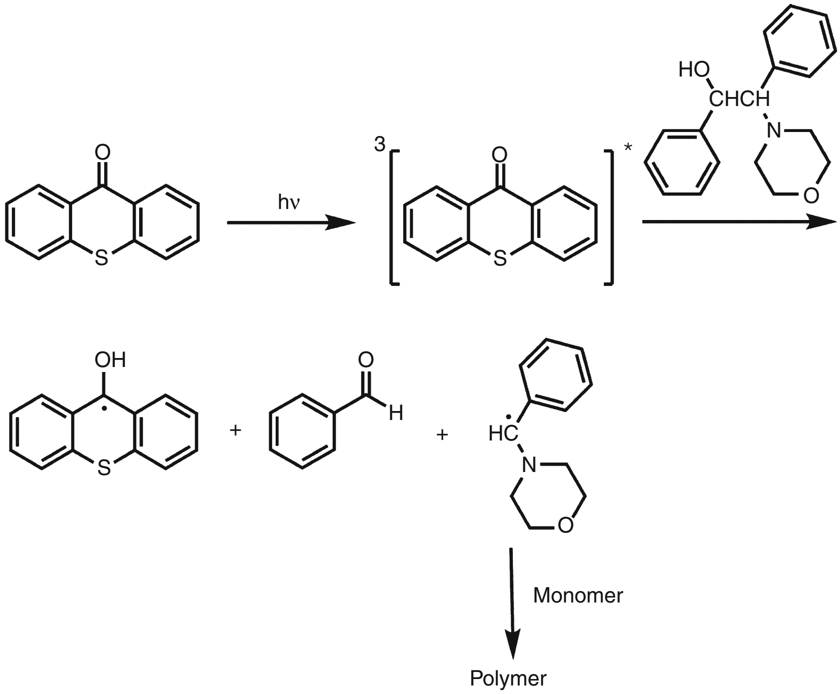
UV light intensity is one of the most important factors that affect the reaction kinetics of the photopolymerizable formulations [13, 14]. Therefore, light intensity was increased to 30 mW/cm^2 and used for irradiation of the formulations. The rate of polymerization of TMPTA increased and the conversion percentage was changed by increasing the light intensity. The order of efficiency of photoinitiator changed as TX > TX-Np = ITX > BP when MDEA was present in the formulation (Fig. 6). When AA was used instead of MDEA, conversion percentages slightly increased for TX-Np, ITX, and TX, the order of efficiency of the initiators were found as same as MDEA results (Figs. 6 and 7).

From Figs. 8 and 9, it can be seen that an increase in the light intensity up to 30 W/m^2, generally enhanced the rate of polymerization of HDDA. But increasing the rate of polymerization does not always lead to an increase in the

Scheme 2 Photoinitiation mechanism of TX in the presence of MDEA



Scheme 3 Photoinitiation mechanism of TX in the presence of AA



monomer conversion. Increased light intensity provides more energy for initiation, leading to more formed primary radicals in the solution or on the surface. The excessive radicals formed on the surface of the coating create a filter effect, which limits the penetration of UV light into the samples, and the final conversion values decrease [14–19]. In HDDA case this was seen for TX-Np and TX with MDEA and for ITX and TX with AA (from 15 to 30 W/cm^2, see Figs. 4, 5, and 8, 9).

A further increase in the light intensity up to 60 W/m^2 helped a little to increase the final conversion of TMPTA with TX-Np, ITX and BP in the presence of MDEA but the conversion percentage values for TX-Np and TX with AA were lowered (from 30 to 60 mW/cm^2; Figs. 10 and 11). In the case of HDDA, it was clearer for both synergists; the conversion percentage values dropped, possibly because of the filter effect of the radicals (from 30 to 60 mW/cm^2; Figs. 12 and 13). Of all the formulations, BP was the least efficient initiator in the presence of both synergists.

Since aminoalcohols and tertiary amines have two roles in the polymerization process: first, to scavenge the oxygen and second, to act as synergist, nitrogen atmosphere was deliberately employed to eliminate the role of oxygen in order to see the synergistic effect of the amine and aminoalcohol.

According to the type II initiating mechanism, the aminoalcohol or amine will react over the triplet state of the thioxanthone or benzophenone to generate a α-aminoalkyl radical which will initiate polymerization of acrylates and methacrylates (see Schemes 2 and 3).

If one considers the C–H bonds attached to the nitrogen atom as being responsible for the radical formation, MDEA has more potential compared to AA. However, it is likely that the difference in reactivity of the C–H bonds plays a role [20, 21]. As an aromatic aminoalcohol, AA may have some UV absorption properties which may explain the low reactivity of AA as a synergist compared with MDEA.

Conclusions

In conclusions, an aromatic aminoalcohol and an aliphatic tertiary amine were used as synergists with various Type II initiators for polymerization of TMPTA and HDDA. Photopolymerization reactions under nitrogen atmosphere were followed by Photo-DSC using different light intensities to determine the optimum conditions. Overall conversion percentage values for nearly all initiators were found to be slightly higher when MDEA was used instead of AA.

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