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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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### The Role of Amines in the Camphorquinone Photoinitiated Polymerization of Multifunctional Monomer

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**To cite this Article** Jakubiak, J. , Wrzyszczyński, A. , Linden, L. Å and Rabek, J. F.(2007) 'The Role of Amines in the Camphorquinone Photoinitiated Polymerization of Multifunctional Monomer', *Journal of Macromolecular Science, Part A*, 44: 2, 239 – 242

**To link to this Article:** DOI: 10.1080/10601320601031440

**URL:** <http://dx.doi.org/10.1080/10601320601031440>

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## NOTE

# The Role of Amines in the Camphorquinone Photoinitiated Polymerization of Multifunctional Monomer

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Received and accepted August, 2006

The influence of the camphorquinone (CQ) concentration and thirteen amines on the rate of polymerization of trimethyleneglycol dimethacrylate (TEGDMA) was investigated. As shown, the rate of polymerization of TEGDMA increases with the increasing of the camphorquinone concentration. However, over  $6 \times 10^{-2}$  M it deviation from the linearity is observed. Some of the amines decrease the rate of polymerization and some of them increase the rate. The acceleration effect on CQ photoinitiated polymerization of TEGDMA is caused by amines radicals formed by the direct hydrogen atom abstraction from amines by triplet  $^3\text{CQ}^*$ , rather than by the electron–proton transfer reaction.

**Keywords:** initiators; kinetics (polym); photochemistry; amines

## 1 Introduction

In past years many papers have been devoted to investigating the mechanism of camphorquinone (CQ)-amine (AH) photoinitiated polymerization of multifunctional monomers (1–13). The hydrogen abstraction reaction of triplet  $^3\text{CQ}^*$  with amines proceeds much faster compared to reactions with pure monomers. Because the amines have a much lower oxidation potential compared with other hydrogen donors, it was assumed to mean that the CQ-amine system reaction was facilitated by the electron-proton transfer (3,12). Amine derived radicals act as a polymerization initiator, whereas camphorquinone/ketyl radicals are ineffective initiators of acrylate/methacrylate polymerization. On the other side, many tertiary amines are used as effective inhibitors of polymerization. In this case, amine radicals may terminate initiation radicals and/or growing propagation radicals. Many tertiary amines also have the ability to ameliorate the effect of oxygen upon free radical polymerization

processes which leads to poor surface cure. For amines to act as a coinitiator, a feature of great importance is the ease with which the exciplex, hydrogen transfer from the amine to the carbonyl group occurs. However, proton transfer can be inefficient due to the fact that the amine may quench the excited state of CQ, thereby decreasing the efficiency of the polymerization process. In the polymerizing medium, the rates of reaction can only be at the maximum of the diffusion controlled rate limit unless there is association between CQ and amines prior to CQ excitation. The diffusion controlled limit is directly related to the viscosity of the medium and this has an important consequence for the polymerization rate, since that bimolecular reaction occurs so the viscosity increases.

Though the basic mechanism for the electron-proton photo-reduction of CQ by amines has been established (3,12), many significant questions remain unsolved. It is not known why high polymerization rates are observed, even if  $\Delta G^\circ$  for the electron-proton transfer is higher than zero. If electron transfer does not occur from an amine, can the amine radical formation be a result of direct hydrogen atom abstraction by the triplet  $^3\text{CQ}^*$ ? In this communication we will address these questions by the examining the triethyleneglycol dimethacrylate (TEGDMA) polymerization using CQ and 13 different aromatic amines (AH1-1AH13).

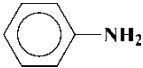
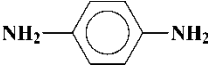
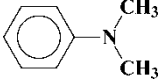
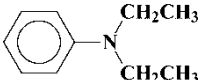
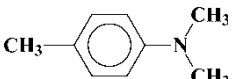
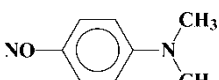
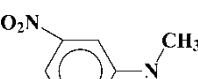
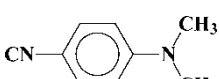
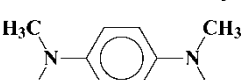
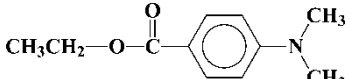
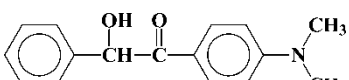
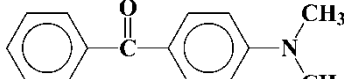
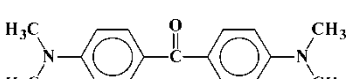
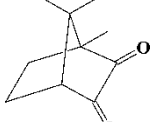
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## 2 Experimental

Camphorquinone (CQ) (bornanedione, 1,7,7-trimethylbicyclo [2.2.1]heptane-2,3-dione) (Aldrich), was recrystallized twice

from cyclohexane. Amines (AH) presented in Table 1 (Aldrich, Fluka, Kodak) and trimethyleneglycol dimethacrylate (MH) (TEGDMA) (Fluka) were used as received. Acetonitrile (ACN) (Aldrich) was spectroscopically pure. CQ and

**Table 1.** List of amines (AH) used, and values of relative acceleration polymerization ( $R_{REL} R_p^{max}$ ) rates, and double bond conversions ( $p^{max}$ , (%)) after 10 min irradiation)

| AH | Amines                                   | Chemical structure   | $R_p^{max}(AH)/R_p^{max}(CQ)$<br>(dimension-less) | $p^{max}$ (%)<br>at 600 s |
|----|--|--|---|---------------------------|
| 1  | Aniline                                  |     | —   | —                         |
| 2  | 1,4-Phenylenediamine                     |    | —   | —                         |
| 3  | N,N-Dimethylaniline                      |     | 2.5   | 65                        |
| 4  | N,N-Diethylaniline                       |     | 2.3   | 60                        |
| 5  | N,N-Dimethyl-p-toluidine                 |    | 2.3   | 55                        |
| 6  | N,N-Dimethyl-4-nitrosoaniline            |   | 1.5   | 60                        |
| 7  | N,N-Dimethyl-3-nitroaniline              |   | 1.7   | 60                        |
| 8  | 4-Dimethylaminobenzonitrile              |  | 10.8  | 68                        |
| 9  | N,N,N',N'-Tetramethyl-p-phenylenediamine |  | 2.9   | 60                        |
| 10 | Ethyl- 4-diaminobenzoate                 |  | 2.3   | 58                        |
| 11 | 4-Dimethylaminobenzoine                  |  | 1.5   | 62                        |
| 12 | 4-Dimethylaminobenzophenone              |  | 4.6   | 70                        |
| 13 | 4,4'-Bis-(dimethylamino)benzophenone     |  | 5.1   | 70                        |
| CQ | Camphorquinone                           |   | 1.0   | 38                        |

AH concentrations used in experiments were  $10^{-2}$  and  $10^{-4}$  M, respectively.

Photoinitiated polymerization of TEGDMA was carried out under nitrogen using a Philips 500 W lamp (type PF 318 E/49), which produced visible radiation above 400 nm with a total light intensity of  $60 \text{ mW cm}^{-2}$ . Rates of polymerization were measured using a Perkin-Elmer 2DSC, which was arranged for photocalorimetric data. The DSC rate of polymerization ( $R_p^{\text{max}}$ ) profiles are shown elsewhere (3, 12).

Cyclic voltametry was performed with an Electrochemical Cypress System (Model C1-1090), with Ag-AgCl electrodes in a solution of 0.1 M tetrabutylammonium perchlorate (supporting electrolyte) in anhydrous ACN.

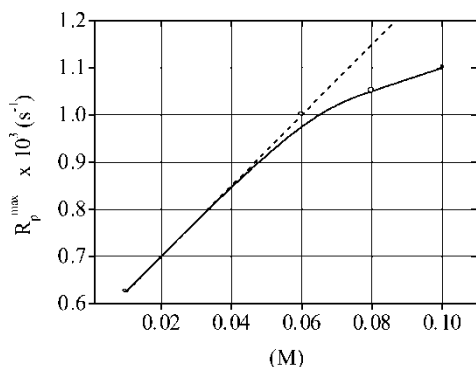
The detailed experiment procedures, measurements and photoisothermal polymerization have been published in our previous publications (5).

### 3 Results and Discussion

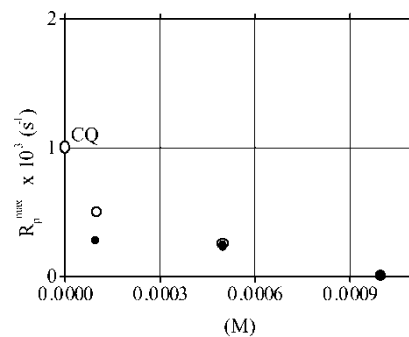
The rate of polymerization ( $R_p^{\text{max}}$ ) of TEGDMA increases with the increasing of CQ concentration (Figure 1). However, over  $6 \times 10^{-2}$  M, deviation from the linearity is observed.

These results indicate the triplet  $^3\text{CQ}^*$  directly abstracts hydrogen atom from the monomer molecule. The monomer radical reacts with other monomer molecules causing a propagation reaction. Increasing the CQ concentration can cause two possible reactions such as concentration quenching of the triplet  $^3\text{CQ}^*$  by CQ molecules and/or termination reactions by a high concentration of formed radicals.

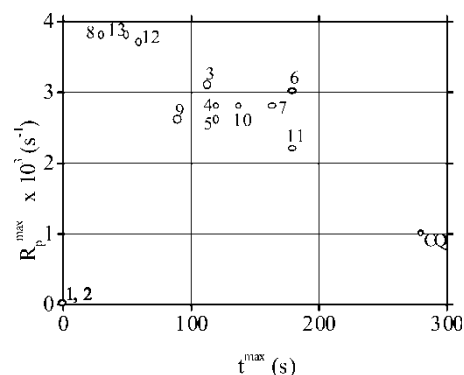
The addition of different amines to the  $^3\text{CQ}^*$  polymerizing mixture causes two different observed reactions. Amines AH1 and AH2 rapidly decrease the rate of polymerization ( $R_p^{\text{max}}$ ), with the increasing concentrations up to  $1 \times 10^{-3}$  M (Figure 2), whereas amines AH3-AH13 accelerate rate of polymerization (Figure 3). The high efficiency of ISC for CQ ( $\Phi_{\text{ISC}} = 1$ ) and the short time of the excited singlet state  $^1\text{CQ}^*$  demands that if reactions occur between  $^3\text{CQ}^*$  and amines, the amine concentration must be used at a  $10^{-3}$  M minimum. At a lower amine concentration



**Fig. 1.** Initial rates of polymerization of TEGDMA ( $R_p^{\text{max}}$ ) in the presence of different amounts of CQ.

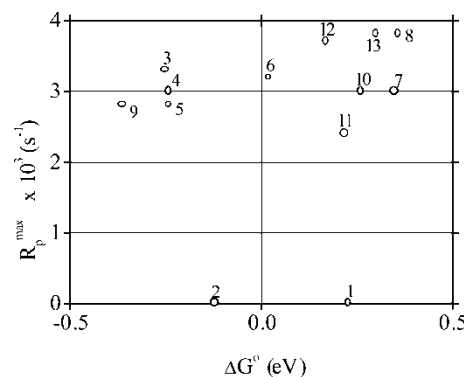


**Fig. 2.** Initial rates of polymerization of TEGDMA ( $R_p^{\text{max}}$ ) in the presence of CQ ( $6 \times 10^{-2}$  M) and different amounts of amines: (o) AH1 and (□) AH2.



**Fig. 3.** Initial rates of polymerization of TEGDMA ( $R_p^{\text{max}}$ ) in the presence of CQ ( $6 \times 10^{-2}$  M) and different amounts of amines AH1-AH13 ( $6 \times 10^{-3}$  M) at the  $t^{\text{max}}$  (s).

( $1 \times 10^{-4}$  M), no acceleration reaction has been observed. The highest rates of polymerization ( $R_p^{\text{max}}$ ), have been observed for amines AH8, AH12, and AH13 (Figure 3), regardless,  $\Delta G^{\circ} > 0$ , (Figure 4) indicates that the electron-proton reaction does not occur. Similar amine behavior ( $R_p^{\text{max}}$ ), was observed for amines AH6, AH7, AH10, and



**Fig. 4.** Initial rates of polymerization of TEGDMA ( $R_p^{\text{max}}$ ) in the presence of CQ ( $6 \times 10^{-2}$  M) and different amounts of amines AH1-AH13 ( $6 \times 10^{-3}$  M) as a function of the free energy change ( $\Delta G^{\circ}$ ) (eV).

AH11.  $\Delta G^\circ < 0$ , (Figure 4) only for amines AH3, AH4, AH5 and AH9. These results indicate that amine radicals which accelerate the initiation of TEGDMA polymerization are formed by direct hydrogen atom abstraction in the reaction with triplet  $^3\text{CQ}^*$  and in this case, reaction electron-proton transfer (3,12) is negligible.

As a propagation reaction occurs, viscosity increases due to increasing the numbers of crosslinks between macromolecules. The accessibility of initiating amine radicals to the double bonds pendant groups in the 3D crosslinked net becomes limited. Therefore, at the end of polymerization, the shielded pendant double bonds (30–40%) remain nearly unreacted, and the double bond conversion does not exceed 70% (Table 1). It is clearly seen, that, although polymerization rates of the TEGDMA, in the presence of amines (Figure 3) are quite rapid, the polymerization does not proceed to completion.

#### 4 Conclusions

The aim of the present work was to show that the amine acceleration effect on the CQ photoinitiated polymerization of TEGDMA is caused by amine radicals formed by the direct hydrogen atom abstraction from amines by triplet  $^3\text{CQ}^*$  (Figure 3), rather than by the electron-proton transfer reaction. The results obtained show also that triplet  $^3\text{CQ}^*$  can abstract hydrogen-atom from the monomer molecule and initiate directly polymerization of TEGDMA.

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