

## RESEARCH ARTICLE

# PHOTOINITIATED POLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE BY SAFRANIN T / TRIETHANOLAMINE IN AQUEOUS SOLUTION: A KINETIC STUDY

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## ABSTRACT

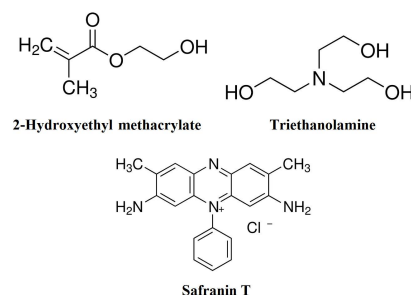
This study involves the polymerization of 2-hydroxyethyl methacrylate (HEMA) (1–3 M), photoinitiated by safranin T (ST) / triethanolamine (TEOHA) system in the pH range 6.0–9.0. The kinetics of the reactions during the initial stages of polymerization (~5% HEMA conversion, within 150 s) has been evaluated to avoid the effects of any volume changes in the solution. The concentration of HEMA in polymerized solutions has been determined spectrometrically at 208 nm with a precision of  $\pm 3\%$ . The apparent first-order rate constants ( $k_{\text{obs}}$ ) for the polymerization of HEMA by ST in the presence of 0.010 M TEOHA range from 2.57–6.08 (1 M), 2.14–5.44 (2 M) and  $1.79\text{--}4.81 \times 10^{-4} \text{ s}^{-1}$  (3 M) at pH 6.0–9.0. The second-order rate constants for the interaction of TEOHA with HEMA (1–3 M) range from  $1.79\text{--}6.08 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at pH 6.0–9.0. This indicates that the reactivity of TEOHA radicals increases with an increase in pH of the solution. The viscosity of HEMA solutions exerts an influence on the rates of polymerization and the values of  $k_{\text{obs}}$  show a linear relation with inverse of solution viscosity. This could be due to the quenching of the ST excited triplet state with an increase in the viscosity of the solution.

**Keywords:** Initiators, irradiation, kinetics, pH, photopolymerization, viscosity.

## 1. INTRODUCTION

The acrylic acid derivative, 2-hydroxyethyl methacrylate (HEMA), has widely been used for dental applications<sup>1-3</sup>. Various types of glass ionomer cements containing HEMA have been developed as light cure restorative materials in dentistry<sup>4</sup>. The photoinitiated polymerization of vinyl polymers has extensively been studied<sup>5</sup> and the kinetics of photopolymerization reactions has been discussed<sup>6-8</sup>. The medium characteristics, ionization behavior of reacting species and efficiency of the photoinitiators are among the major factors that affect the rate of polymerization reactions<sup>9</sup>. The light activated composites for dental restorative purpose contain a photoinitiator that is sensitive to blue light<sup>3</sup>. One of the most studied systems is the polymerization of HEMA, photoinitiated by riboflavin (RF) / triethanolamine (TEOHA), in aqueous and organic solvents<sup>10-15</sup>. Besides this, some work has also been carried out on the polymerization of HEMA in the presence of camphorquinone<sup>15-20</sup> and safranin T

(ST)<sup>21-23</sup> as photoinitiators. The chemical structures of HEMA, ST and TEOHA are shown in Fig. 1. The present work is based on the study of the kinetics of polymerization of HEMA (1–3 M) using ST / TEOHA as a photoinitiator system. The effects of pH, TEOHA concentration and viscosity of the medium on the kinetics of the reaction have been evaluated and the data compared with those of RF as a photoinitiator in this system. The role of ST excited triplet state has been explained through its involvement in the process of polymerization.



**Fig. 1.** Chemical structures of HEMA, TEOHA and ST.

## 2. MATERIALS AND METHODS

ST was obtained from Sigma and used as received. TEOHA (Sigma) and HEMA (Aldrich) were distilled under reduced pressure before use. Water was purified using a Millipore Milli-Q system.

### 2.1. Polymerization

The polymerization of HEMA (monomer/water ratios 1.21:8.79, 2.42:7.58 and 3.63:6.37, v/v, corresponding to 1.0, 2.0 and 3.0 M solution, respectively) was carried out using ST as a photoinitiator (absorbance of the solution at 520 nm was low, 0.125) to avoid inhomogeneous distribution of free radicals<sup>9</sup>, and 0.0025–0.010 M TEOHA as a co-initiator at pH 6.0–9.0 (adjusted by HCl / NaOH solution) under anaerobic conditions at 25°C. The solution was exposed to a General Electric 15 W fluorescent lamp (emission in the visible region). The lamp was fixed horizontally at a distance of 25 cm from the centre of the vessel in a radiation chamber.

### 2.2. Spectral Measurements

All spectral measurements on fresh and polymerized solutions of HEMA were carried out on a Shimadzu UV–1601 recording spectrophotometer using quartz cells of 10-mm path length.

### 2.3. Measurement of Light Intensity

Potassium ferrioxalate actinometry<sup>24</sup> was used to measure the intensity of the 15 W fluorescent lamp and a value of  $2.85 \pm 0.26 \times 10^{16}$  quanta s<sup>-1</sup> was obtained.

### 2.4. Determination of HEMA

The concentration of HEMA in the fresh and polymerized solutions was determined by adjusting the pH of the solution to 7.0 (0.05 M phosphate buffer) and measurement of absorbance at 208 nm after appropriate dilution<sup>14</sup>. ST has negligible absorption at 208 nm in the diluted solution and, therefore, does not interfere with the HEMA determination.

### 2.5. Measurement of Viscosity

The viscosity of HEMA solutions was measured using a Brookfield RV viscometer (Model DV–II + Pro, Essex, UK).

## 3. RESULTS AND DISCUSSION

### 3.1. Spectral Characteristics of ST

ST absorbs at 520 nm (molar absorptivity,  $2900 \text{ M}^{-1} \text{ cm}^{-1}$ ) in aqueous solution<sup>25</sup>. It has a lower energy of the excited state compared to that of riboflavin (RF) (445 nm, molar absorptivity,  $12500 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>26</sup>, and camphorquinone (CQ) (468 nm)<sup>19</sup>. Both RF<sup>10-12,14,15</sup> and CQ<sup>15,17-20</sup> have been used as photoinitiators in the polymerization of HEMA in aqueous and organic solvents. A  $4.3 \times 10^{-5} \text{ M}$  concentration of ST has been used to keep its absorbance around 0.125 in HEMA solutions to maintain homogenous distribution of free radicals as suggested by Alvarez et al.<sup>9</sup>. Similar ST solutions (pH 6.0–9.0), on irradiation for a period up to 5 min, did not show any absorbance change at the maximum (520 nm) indicating that ST concentration remains constant in the solution and the photoinitiator is stable to light during irradiation (up to 150 s) in the polymerization reactions.

### 3.2. Determination of HEMA Solutions

A spectrometric method has been used for the assay of HEMA at 208 nm in polymerized solutions. The method has previously been used for the study of the polymerization of HEMA in the presence of RF in aqueous and organic solvents<sup>14,15</sup>. HEMA has a molar absorptivity of  $8000 \text{ M}^{-1} \text{ cm}^{-1}$  at 208 nm and the method is very sensitive for the assay of HEMA. The calibration curve is linear in the concentration range of  $0.1\text{--}1.0 \times 10^{-4} \text{ M}$  HEMA and the method has a precision of  $\pm 3\%$ .

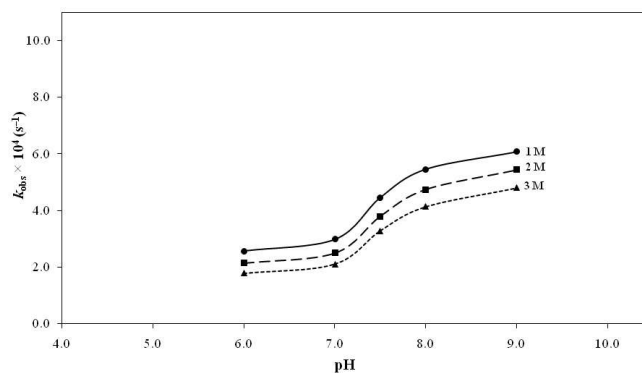
### 3.3. Kinetics of Polymerization

The kinetics of polymerization of HEMA solutions (1–3 M), photoinitiated by ST/TEOHA system, has been studied only in the initial stages of the reaction (~5% HEMA conversion, 100–150 s) at pH 6.0–9.0 to avoid any variations in the volume of the solutions. HEMA undergoes polymerization by an apparent first-order kinetics as observed in the case of RF and CQ<sup>14,15</sup>. Beyond this level the first-order plots are nonlinear suggesting the involvement of secondary reactions or a change in the mode of the reaction. The values of the rate constants are affected by the pH and viscosity of the medium as well as the TEOHA concentration. These values are lower

than these obtained in the presence of RF<sup>14</sup> suggesting the ST has a lower efficiency as a photoinitiator compared to that of RF.

### 3.4. Effect of pH

The effect of pH and solvent on the polymerization of HEMA in the presence of RF / TEOHA has been reported<sup>14,15</sup>. This work is based on the polymerization reactions conducted in the pH range 6.0–9.0 in the presence of ST / TEOHA system and the apparent first-order rate constants ( $k_{\text{obs}}$ ) have been determined. The values of  $k_{\text{obs}}$  in the presence of 0.010 M TEOHA range from 2.57–6.08 (1 M), 2.14–5.44 (2 M) and  $1.79\text{--}5.81 \times 10^{-4} \text{ s}^{-1}$  (3 M) at pH 6.0–9.0. The plots of  $k_{\text{obs}}$  for the polymerization of HEMA (1–3 M) in the presence of ST versus pH of the medium (Fig. 2) are similar to those obtained from the reactions in the presence of RF<sup>14</sup>. The rate constants for the reactions increase with an increase in pH showing greater increase in the pH range 7–8 due to a change in the ionized state of TEOHA molecule ( $\text{p}K_{\text{a}} 7.82$ )<sup>27</sup> to facilitate electron transfer from TEOHA to ST excited triplet state. The values of  $k_{\text{obs}}$  for the reactions in the presence of ST are about 3/4th of those determined in the presence of RF indicating a lower reactivity of ST as a photoinitiator in this reaction. The highest rate of polymerization of HEMA at pH 9.0 is in accordance with the observation of Valdebenito and Encinas<sup>28</sup>.



**Fig. 2.**  $k_{\text{obs}}$ –pH profiles for the polymerization of HEMA (1–3 M) in the presence of ST and TEOHA.

### 3.5. Effect of TEOHA

The apparent first-order rate constants ( $k_{\text{obs}}$ ) for the polymerization of HEMA in the presence of a fixed concentration of ST and variable concentrations of TEOHA (0.0025–0.010 M) at pH 6.0–9.0 have been determined. The values of  $k_{\text{obs}}$  at different TEOHA concentrations are lower than those obtained in the presence of RF due to lower efficiency of ST as a photoinitiator. This would suggest a lower rate of formation and interactions of TEOHA radicals with HEMA in the presence of ST. The second-order rate constants for the interaction of TEOHA and HEMA are reported in Table 1. The values are about 1/4 times lower than those obtained in the presence of RF. This is probably due to a lower energy of the absorption wavelength of ST (520 nm) compared to that of RF (445 nm). The  $k_{\text{obs}}$  for the polymerization

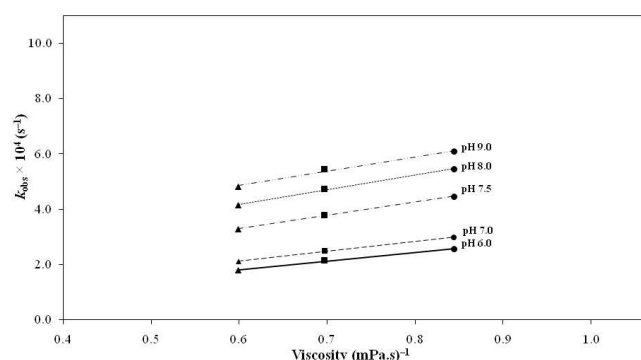
**Table 1.** Second-order rate constants ( $k'$ ) for the interaction of TEOHA (0.0100 M) with HEMA (1–3 M) at pH 6.0–9.0 in the presence of ST.

pH	$k' \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$					
	Monomer: water ratio (1.21:8.79)	Correlation coefficient	Monomer: water ratio (2.42:7.58)	Correlation coefficient	Monomer: water ratio (3.63:6.37)	Correlation coefficient
6.0	2.57	0.991	2.14	0.991	1.79	0.990
7.0	2.98	0.993	2.50	0.990	2.10	0.990
7.5	4.45	0.991	3.79	0.990	3.28	0.990
8.0	5.45	0.990	4.73	0.991	4.14	0.991
9.0	6.08	0.990	5.44	0.994	4.81	0.991

of HEMA are affected by the pH and viscosity of the medium and are a function of TEOHA concentrations used in these reactions. It has been reported that the rate of polymerization of HEMA is maximum in the presence of 0.010 M TEOHA<sup>11</sup> which is the highest concentration used in this work.

### 3.6. Effect of Viscosity

The photochemical reactions involving radical ion pair or free radicals are generally affected by the viscosity of the medium<sup>29</sup>, as observed in the case of the polymerization of HEMA carried out in 1–3 M solutions. In a similar manner the rate constants for the polymerization reactions in the presence of ST have been found to decrease with an increase in the viscosity of the solutions. A gradual decrease in the values of  $k_{\text{obs}}$  for the reactions performed in 1–3 M HEMA solutions has been observed (Fig. 3). This could probably be due to the quenching of ST excited triplet state in the viscous medium and changes in the diffusional processes of the species involved. This would result in a relatively low rate of interaction of the excited triplet state of ST and consequently a low rate of polymerization compared to that of RF<sup>14</sup>. These observations indicate that it may be necessary to take into consideration the effect of viscosity on the rate of polymerization reactions and ultimately the yield of the polymer.

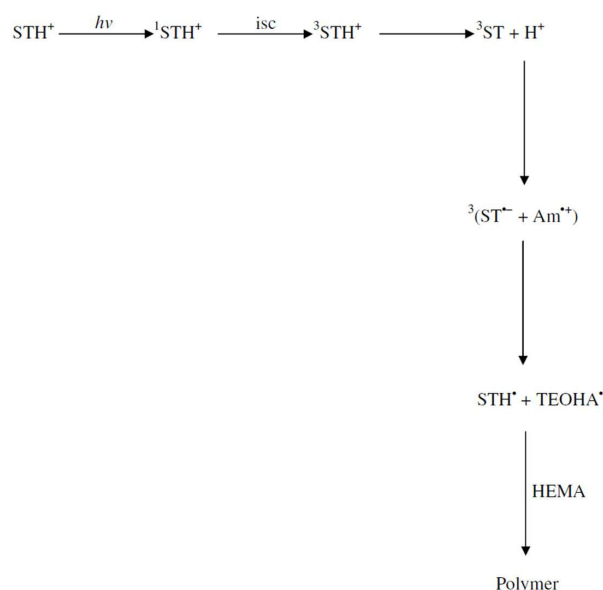


**Fig. 3.** Plots of  $k_{\text{obs}}$  for the polymerization of HEMA (1–3 M) versus inverse of the viscosity of solution. HEMA concentration: (●) 1.0M, (■) 2.0M, (▲) 3.0M.

### 3.7. Mechanism of HEMA Polymerization

The kinetic behavior of the polymerization reactions of HEMA using RF and ST as photoinitiators is

similar with respect to pH, viscosity and TEOHA concentration, suggesting a similarity in the mechanism of these reactions. However, the changes in the rates of polymerization in the presence of different photoinitiators are largely due to variations in the reactivity of individual photoinitiators and the extent of their participation in the polymerization process<sup>15</sup>. The primary reaction in the polymerization process involves the formation of the photoinitiators (e.g. ST) and TEOHA free radicals and subsequently the interaction of TEOHA radicals with HEMA to undergo polymerization as suggested by Orellana et al.<sup>11</sup> and presented in detail by Ahmad et al.<sup>14</sup>. A similar mechanism of the polymerization of HEMA in the presence of ST has been suggested by Encinas et al.<sup>22</sup>. It is based only on the formation of amine radicals and no further reactions to proceed to the polymerization of HEMA. It has now been modified to include the steps suggested by Orellana et al.<sup>11</sup> and is presented in Fig. 4. The protonated ST ( $\text{STH}^+$ ) is promoted to the excited singlet state and then is converted by intersystem crossing (isc) to the protonated excited triplet state [ $^3\text{STH}^+$ ]. In a basic medium [ $^3\text{STH}^+$ ] undergoes deprotonation and on reaction with TEOHA,  $\text{STH}^\bullet$  and  $\text{TEOHA}^\bullet$  free radicals are formed. The  $\text{TEOHA}^\bullet$  free radicals interact with HEMA to initiate the polymerization process.



**Fig. 4.** Scheme for the mechanism of polymerization of HEMA in the presence of ST and TEOHA.

#### 4. CONCLUSION

A study of the polymerization of HEMA solutions (1–3 M), photoinitiated by ST/TEOHA system has been conducted in the pH range 6.0–9.0. The polymerization of HEMA in the initial stages of the reaction (~5% conversion) follows first-order kinetics. The values of rate constants for the reactions increase with an increase in pH as a result of the higher reactivity of ST excited triplet state in the alkaline medium. The rates of the reaction are also dependent on TEOHA concentration and increase with an increase in its concentration. There is a prominent effect of viscosity on the rate of polymerization and the rates decrease with an increase in the viscosity of HEMA solution (i.e. 1–3 M). This is probably due to gradual quenching of the ST excited states on an increase in the viscosity of the medium.

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