ORIGINAL ARTICLE

CAMPHORQUINONE AS A PHOTOINITIATOR IN THE POLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE IN AQUEOUS SOLUTION: A KINETIC STUDY

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ABSTRACT

The photoinitiated polymerization of 2-hydroxyethyl methacrylate (HEMA) (1–3 M) using camphorquinone (CQ) / triethanolamine (TEOHA) system has been studied in the pH range 6.0–9.0. The kinetics of the reaction has been evaluated during the initial stages causing about 5% HEMA conversion to avoid the effects of any variation in the volume of the solution. The change in the concentration of HEMA during polymerization has been determined by a UV spectrometric method at 208 nm with a precision of ±3%. The apparent first-order rate constants (k_{obs}) for the polymerization of HEMA by CQ in the presence of 0.01 M TEOHA, carried out up to 100 s, range from 3.35–7.78 (1 M), 2.72–6.78 (2 M) and 2.33–5.89$\times10^{-4}$ s^{-1}(3 M). The second-order rate constants for the interaction of TEOHA radicals with HEMA (1–3 M) range from 2.33–7.78$\times10^{-2}$ M^{-1} s^{-1}at pH 6.0–9.0 indicating an increase in the reactivity of TEOHA radicals with an increase in the pH of the solution. There is a linear relation between k_{obs} (1–3 M HEMA) and inverse of solution viscosity suggesting the quenching of CQ excited state with an increase in the viscosity of the medium.

Keywords: Camphorquinone, 2-hydroxyethyl methacrylate, pH effect, polymerization, viscosity effect.

1. INTRODUCTION

Vinyl monomers, particularly 2-hydroxyethyl methacrylate (HEMA), are widely used as components in glass ionomer cements. HEMA undergoes polymerization photoinitiated by compounds absorbing in the blue region (450–495 nm) of visible radiation[1]. Riboflavin (RF) as a photoinitiator in the polymerization of HEMA in association with triethanolamine (TEOHA) has extensively been studied[2-6]. Camphorquinone (1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione) (CQ) as a photoinitiator is a component of light activated composites used as dental restorative materials[7]. CQ has previously been used as a photoinitiator along with TEOHA in the polymerization of HEMA by several workers[8-12]. A study has reported the use of CQ in the photoinitiated polymerization of HEMA in organic solvents[13]. In the present work, we have conducted a kinetic study of the polymerization of HEMA in the presence of CQ/TEOHA system and have evaluated the effects of pH, TEOHA concentration and viscosity of the medium on the rates of the reaction. The chemical structures of HEMA, CQ and TEOHA are shown in Fig. 1.

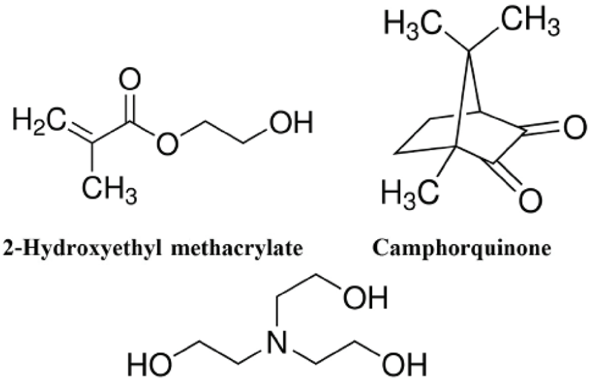

Fig. 1. Chemical structures of HEMA, CQ and TEOHA.

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2. MATERIALS AND METHODS

2.1. Materials

CQ (99%), TEOHA and HEMA were obtained from Sigma-Aldrich Company Ltd. (Dorset, UK). CQ was used as received while TEOHA and HEMA were distilled under reduced pressure before use. Water was purified using a Millipore Milli-Q system. All other chemicals used in the study were of analytical grade.

2.2. Polymerization

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 in the presence of CQ (absorbance of the solution at 468 nm was kept low (0.125) to avoid in homogeneous free radical distribution)[14] and 0.0025–0.010 M TEOHA at pH 6.0–9.0 (adjusted by HCl / NaOH solution) under anaerobic conditions at 25°C. The solution was irradiated using a General Electric 15 W fluorescent lamp (emission in the visible region), fixed horizontally at a distance of 25 cm from the center of the vessel in a radiation chamber.

2.3. Spectral Measurements

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

2.4. Light Intensity Measurement

The intensity of the General Electron 15 W fluorescent lamp was measured using potassium ferrioxalate actinometery[15], as $2.85 \pm 0.26\times10^{16}$ quanta s^{-1}.

2.5. Viscosity Measurements

The measurement of the viscosity of HEMA solutions was carried out using Brookfield RV viscometer (Model DV-II + Pro, Essex, UK).

2.6. Determination of HEMA

The determination of HEMA in freshly prepared and polymerized solutions was performed by adjusting the pH of the solution to 7.0 (0.05 M phosphate buffer) and measurement of the absorbance at the absorption maxima at 208 nm after appropriate dilution[6]. At the dilution of HEMA solutions used for its determinations, CQ has negligible absorption at the analytical wavelength.

3. RESULTS AND DISCUSSION

3.1. Spectral Characteristics of CQ

CQ exhibits an absorption maximum at 468 nm (molar absorptivity, 46 ± 2 M^{-1} cm^{-1}) in aqueous solution[11]. The value of the absorption maximum is similar to that of RF at 445 nm used as a photoinitiator in the polymerization of HEMA in previous studies[2-4,6,13,16]. However, the value of molar absorptivity of CQ at 468 nm is much lower than that of RF at 445 nm (12500 M^{-1} cm^{-1}) [17,18] as a result of $n–\pi^*$ transition[19]. This may affect its reactivity as a photoinitiator compared to that of RF as observed by Ahmad et al.[6]. A low absorbance level of the photoinitiator as in the case of RF (0.125) has been suggested by Alvarez et al.[14] to avoid inhomogeneous free radical distribution. Therefore, a 2.7×10^{-3} M concentration of CQ was used during the polymerization reactions.

The spectra of the aqueous solutions of CQ photolyzed alone at various pH values during irradiation (5 min) do not show any change in absorbance at 468 nm in the visible region (the duration of a HEMA polymerization reaction in the presence of CQ was up to 100 s). This may be due to the use of a low intensity (15 W) irradiation source which does not produce any change in the molecule during the short period of exposure to visible light. It indicates that aqueous solutions of CQ are less sensitive to light compared to RF[6] and would remain stable during the period of polymerization reactions. In oxygen-free solutions CQ is photoreduced to α-hydroxyketones[20].

3.2. Determination of HEMA

The determination of HEMA in 1.0–3.0 M aqueous solutions (pH 6.0–9.0), polymerized in the presence of CQ, has been carried out at 208 nm as in the case of reactions carried out in the presence of RF[6]. The high molar absorptivity (8000 M^{-1} cm^{-1}) of

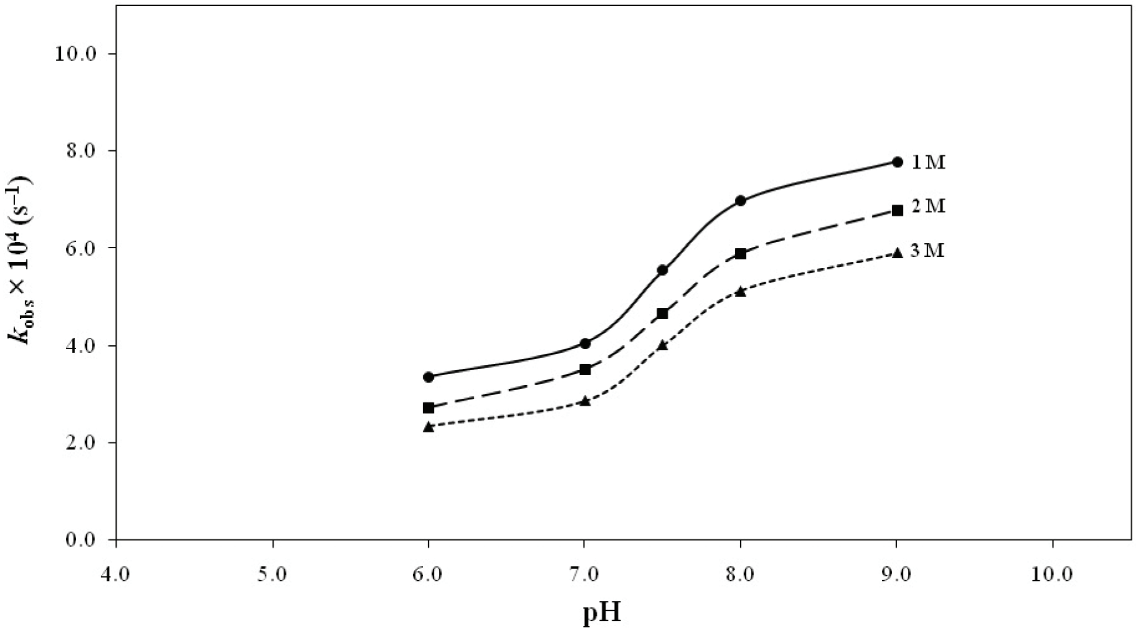

Fig. 2. k_{obs}–pH profiles for the polymerization of HEMA (1–3 M) in the presence of CQ and 0.010 M TEOHA.

HEMA at this wavelength results from π–π* transition. The validity of Beer's Law has been confirmed in the concentration range of 0.1–1.0×10^{-4} M solutions of HEMA. The RSD of the method is within ±3%. This method has previously been used for the study of the polymerization of HEMA in the presence of RF in aqueous and organic solvents[6,13].

3.3. Kinetics of Polymerization

The polymerization of HEMA in the presence of different photoinitiators takes place by an apparent first–order kinetics[6,13,24]. This has been studied in the presence of CQ during the initial stages of the reaction (within 5% conversion) to obtain an approximate measure of the kinetics of the system without involving any secondary reactions. It has been found that the polymerization of HEMA follows an apparent first-order kinetics during the irradiation period (up to ~100 s), and at low conversion is homogenous as the polymer remains soluble in the monomer-rich aqueous solutions[21]. Above this concentration level the polymerization reaction is complicated by secondary reactions resulting in volume changes and nonlinear behavior[9]. The kinetics of polymerization of HEMA solutions (1.0–3.0 M) has been studied as a function of pH (6.0–9.0), TEOHA concentration (0.0025–0.01 M) and viscosity of the medium, and the results are discussed in the following sections.

3.4. Effect of pH

The polymerization of HEMA using CQ as a photoinitiator has been carried out in the pH range 6.0–9.0 and the values of apparent first-order rate constants (k_{obs}) for these reactions have been determined. The k_{obs}–pH profiles for the reactions of 1, 2 and 3 M HEMA solutions in the presence of CQ and 0.01 M TEOHA are shown in Fig. 2. The values of k_{obs} gradually increase with pH showing a relatively fast increase in the pH range 7–8. This is probably due to the deprotonation of TEOHA (pK_a 7.82)[22] and consequently the ease in electron transfer from TEOHA to the excited triplet state of CQ to facilitate the polymerization of HEMA as observed by Orellana et al.[3] in the case of RF. The relatively slow rate in the pH range 8–9 may be due to the lower susceptibility of neutral TEOHA to form free radicals involved in the polymerization of HEMA. An increase in the rate, with pH, is attributed to the presence of a labile proton on the hydroxyl group of HEMA[9]. A decrease in the rate of polymerization with an increase in HEMA concentration (1.0–3.0 M) could be due to viscosity effect. Solvents effects on the polymerization of HEMA have been observed[13,23,24].

3.5. Effect of TEOHA

TEOHA is an essential component of the photoinitiation process in the polymerization of HEMA[2-4]. It acts as a co-initiator with CQ to induce the reaction by radical mechanism. In order to study the interaction of TEOHA with CQ to form radicals and subsequently with HEMA to undergo polymerization, reactions have been carried out at 0.0025–0.010 M TEOHA concentrations. The second-order rate constants (k') for the interaction of TEOHA at pH 6.0–9.0 are reported in Table 1. The values of k' increase with pH due to greater reactivity of TEOHA radicals in the polymerization of HEMA in the alkaline region. However, the values of k_2 decrease with an increase in the concentration of HEMA due to viscosity effect as discussed in the next section.

Table 1. Second-order rate constants (k') for the interaction of TEOHA (0.01 M) with HEMA (1–3 M) at pH 6.0–9.0 in the presence of CQ

pH	$k' \times 10^2$ M^{-1} 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	3.35	0.987	2.72	0.989	2.33	0.989
7.0	4.04	0.989	3.51	0.989	2.86	0.990
7.5	5.54	0.993	4.65	0.988	4.01	0.987
8.0	6.97	0.994	5.89	0.992	5.12	0.989
9.0	7.78	0.995	6.78	0.990	5.89	0.990

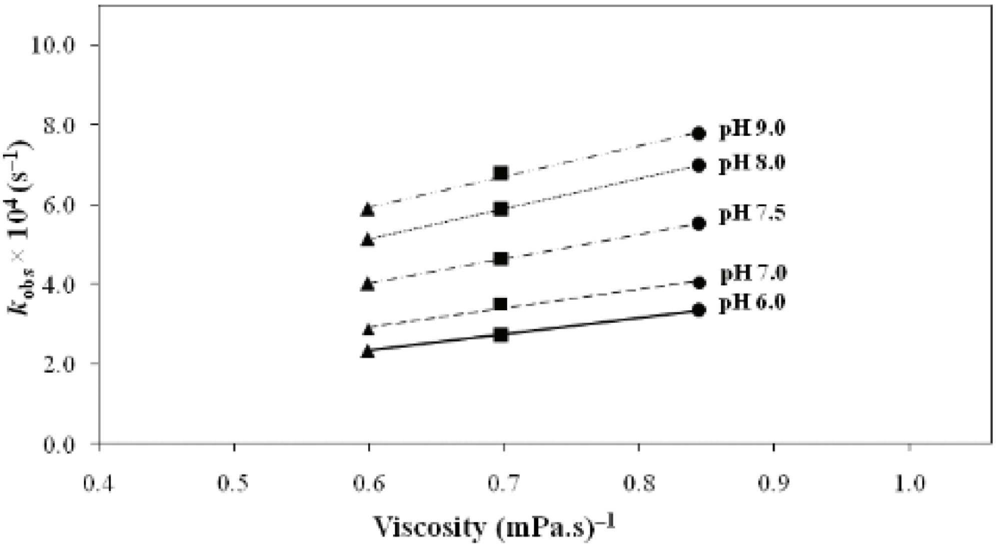

Fig. 3. Plots of k_{obs} for the polymerization of HEMA (1–3 M) in the presence of CQ and 0.010 TEOHA versus inverse of solution viscosity. HEMA (●) 1.0 M, (■) 2.0 M, (▲) 3.0 M

3.6. Effect of Viscosity

Viscosity plays an important role in controlling the rate of chemical reactions since the solute diffusion processes are viscosity dependent[25]. A plot of k_{obs} versus inverse of the viscosity of HEMA solutions (Fig. 3) has been found to be linear and the rates in this relationship increase with pH as observed in the case of HEMA polymerization in the presence of RF[6]. The increase in the viscosity of the medium would cause quenching of the excited singlet and triplet states of CQ and thus would lead to a decrease in the rate of interaction of CQ and TEOHA to form the radical ion pair and subsequently free radicals ($CQH^\bullet$ and $TEOHA^\bullet$) to induce polymerization. Therefore, the yield of polymerization would decrease with an increase in HEMA concentration. Similar effects of viscosity on the photochemical reactions of flavins[26,27] and fluoroquinolones[28,29] have been reported.

3.7. Mechanism of HEMA Polymerization

The mechanism of polymerization of HEMA using CQ as a photoinitiator is similar to that suggested previously for the reaction in the presence of RF[2-4, 6] and later discussed by Jakubiak et al.[9]. It has been suggested that the CQ / TEOHA photoinitiated polymerization of HEMA occurs through electron / proton transfer as in the case of RF / TEOHA system. It involves the interaction of excited triplet state of CQ with TEOHA to form a radical ion-pair $^3[CQ^{\bullet-} + Am^{\bullet+}]$ by electron transfer followed by H abstraction to yield free radicals of $CQH^\bullet$ and $TEOHA^\bullet$.The TEOHA free radicals attach to C=C bond of the HEMA monomer to initiate polymerization[9] (Fig. 4). The efficiency of the polymerization process depends on the efficiency of the quenching of the excited triplet state of CQ by TEOHA and the formation of free radicals to initiate polymerization. The pH, viscosity and TEOHA concentration also play a role in the efficiency of the polymerization processes involved in dental resins and composites[30].

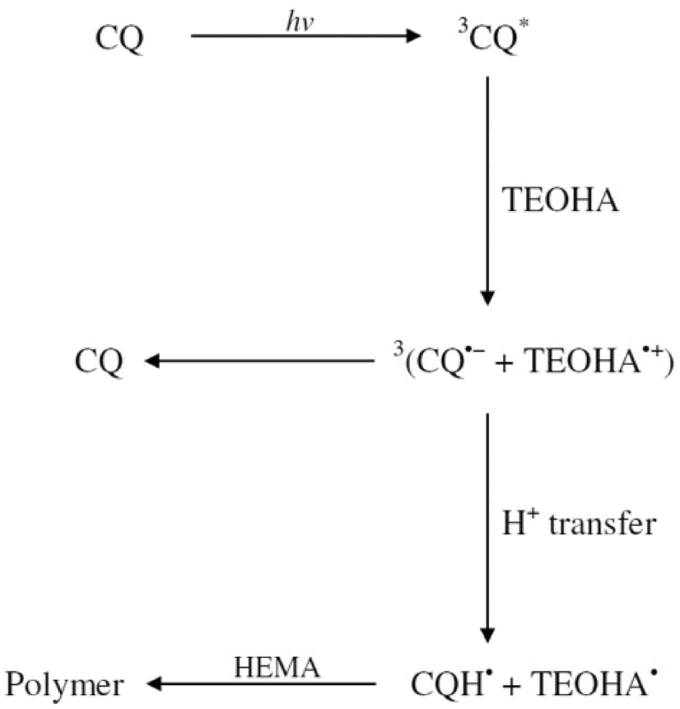

Fig. 4. Scheme of polymerization of HEMA in the presence of CQ and TEOHA.

4. CONCLUSION

The present study involves the evaluation of the kinetics of HEMA (1–3 M) polymerization using CQ / TEOHA system as photoinitiator in the pH range 6.0–9.0. The reactions have been studied only in the initial stages of HEMA conversion (~5%) to avoid any changes in the volume of the medium. The increase in the values of first–order rate constants with an increase in pH appears to be due to the higher reactivity of the CQ excited triplet state in the alkaline medium and is dependent upon TEOHA concentration. The decrease in the rate constants with an increase in the viscosity of the medium (1–3 M HEMA) could be explained on the basis of quenching of the CQ excited states due to the diffusion controlled processes. The CQ / TEOHA photoinitiated polymerization of HEMA occurs through electron / proton transfer to $CQH^{\bullet}$ and $TEOHA^{\bullet}$ free radicals. These radicals attach to C=C bond of the HEMA monomer to initiate its polymerization. HEMA polymerization has important implications in dental resins and composites.

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