Erythrosine/Triethanolamine System to Elaborate Crosslinked Poly(2-hydroxyethylmethacrylate): UV-Photopolymerization and Swelling Studies

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Summary: A system composed of Erythrosine and Triethanolamine was applied as photo-initiator for the UV-photopolymerization of 2-Hydroxyethyl methacrylate together with a crosslinking agent 1,6-Hexanediol diacrylate, in aqueous medium. The analysis of UV-visible and infrared spectra, which were taken at different times during polymerization/crosslinking, makes it possible to obtain useful information on the reaction mechanism. The swelling behavior of these elaborated crosslinked polymer networks in different solvents is examined. It was found that the disappearance of the Erythrosine molecule depends on the nature of the solvent. The theoretical results calculated with the Fick diffusion model show a good correlation with the swelling experiments.

Keywords: Erythrosine; Fick diffusion model; polymerization; swelling kinetics; tertiary amine

Introduction

Among various kinds of polymeric systems, hydrophilic polymers based on 2-Hydroxyethylmethacrylate have been widely studied due to their good chemical reactivity and ability to simulate biological tissues, which leads to many applications.[1–4] Such materials are often prepared via a photopolymerization mechanism. Xanthene dyes[5,6] like Erythrosine, Rose Bengal and Eosin, in the presence of electron donors such as tertiary amines, have been described as efficient photoinitiators for the free radical polymerization of acrylate monomers in aqueous solutions.[7–9] The tertiary amine is used as oxidizing species whereas the dye acts as reducing agent.[10] In particular, M.V. Encinas et al.[11] studied Xanthene dye/amine systems as photoinitiators for radical polymerization. They compared the efficiency of several xanthene dyes as photoinitiators of the polymerization of acrylamide in aqueous solution under visible radiation, since xanthenes dyes are convenient visible photoinitiators due to their high absorption in the wavelength region 500–580 nm. Triethanolamine was used as co-initiator. The authors found that the active radicals are the amine radicals formed from the interaction of the xanthane triplet state with the amine.

The incorporation of a difunctional crosslinking agent provides a polymer network structure with ability to swell in different solvents. Many research groups have reported on the swelling behavior of polymers networks. Bouchaour et al.[12,13] discussed swelling and deswelling of photochemically crosslinked polymer networks made up of poly(n-butylacrylate), allowing to evaluate the polymer-solvent interaction parameter according to the temperature. In a previous paper,[14] we studied the influence of pH on the swelling ratio of acrylic polymer networks and it was found that the influence of pH is inversely proportional to the swelling kinetics.

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In this work, hydrophilic three-dimensional polymer networks were elaborated, made up of poly(2-Hydroxyethylmethacrylate). A photoinitiator system composed of Erythrosine and Triethanolamine was used for UV-light exposure, since Erythrosine also absorbs in the wavelength region 250–300 nm. Application of UV radiation on the mono-functional monomer (2-Hydroxyethylmethacrylate) leads generally to linear polymeric chains. The addition of a small quantity of 1,6-Hexanedioldiacrylate allows to obtain a crosslinked polymer network. UV-visible and infrared spectra were taken at different times during the polymerization/crosslinking process, allowing to obtain useful information on the reaction mechanism. The swelling kinetics of these polymer networks in different solvents were also examined. The theoretical results based on the Fick diffusion model will be presented.

Experimental Part

Materials

The monomer chosen for this study was 2-Hydroxyethylmethacrylate (HEMA), exhibiting a purity of 97% (from Sigma-Aldrich). The cross-linking agent was 1,6-Hexanedioldiacrylate (HDDA), with a purity of 98%, supplied by Cray Valley (France). Erythrosine and Triethanolamine (TEOA) were purchased from Prolabo Paris, Dimethyl Sulfoxide (DMSO) and Methanol from Sigma-Aldrich, and Tetrahydrofuran (THF) from Biochem Chemopharma. All products were used as received.

Sample Preparation

The photocurable formulation was prepared as follows: 95.93wt-% HEMA, 0.5wt-% HDDA, 0.01wt-% erythrosine (powder), 3.05wt-% TEOA, and 0.51wt-% of distilled water. This solution was stirred for 15 minutes, at $T = 20°C$.

For the study of the swelling behavior of the polymer network, the photocurable formulation was cast into a Teflon mold. After 30 minutes of UV-irradiation (Philips TL08 source, $\lambda = 365nm$ with intensity $I_0 = 0.6mW/cm^2$) under air atmosphere at room temperature ($T = 20°C$), the polymer networks were obtained in pellet form which was washed in distilled water before starting the swelling experiments.

Real-Time Infrared Spectroscopy

Uniform samples were prepared by casting the photocurable formulation between a NaCl plate and a Polyethyleneterephthalate (PET) film, possessing a thickness of 0.013mm. The samples, which were analyzed by infrared spectroscopy (Perkin Elmer 2000 FTIR model, transmission mode, spectral resolution $4cm^{-1}$), were simultaneously exposed to the UV light source mentioned above, at $T = 20°C$. The distance sample-UV source was 6.7cm. The spectrophotometer was provided with a Fourier transformed algorithm.[15] The following equation was used to calculate the conversion of acrylic double bonds:

$$Conv.(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 represents the initial absorbance and A_t is the absorbance value at irradiation time t.

Ultraviolet/Visible Spectroscopy

The absorption spectra of all solutions were obtained from a Varian Cary 100 UV-visible double-beam spectrophotometer, equipped with a Peltier accessory for precise temperature control ($\pm 0.1°C$). The measurements were made using standard Hellma quartz cells (100-QS) of 10 mm thickness.

Swelling Measurements

The swelling kinetics of the polymer network in different solvents were evaluated. Pre-weighed dried samples were immersed in an appropriate solvent at room temperature to reach the equilibrium state. At fixed time intervals, the samples were weighted after removing the excess solvent by filter paper.[16] The swelling ratio can thus be calculated by the following

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equation:

$$Swelling\,ratio\,(\%) = \left(\frac{W_s - W_d}{W_d}\right) \times 100 \quad (2)$$

where W_d represents the weight of the dried sample, and W_s is the weight of the swollen sample at different swelling times.

Results and Discussion

Photopolymerization Studies

The absorption spectrum of Erythrosine in water is shown in Figure 1. It should be noted that there is an important absorption around 527nm due to the chromophore of the dye. The UV-photopolymerization of the formulation consisting of the system (Erythrosine/TEOA and HEMA), in the presence of a crosslinking agent (HDDA), was studied by means of a UV-Visible spectrophotometer. Figure 2 presents the decrease of the absorption peak of the Erythrosine molecule at 527nm with irradiation time.

The photo-induced electron transfer from the dye to the amine leads to the formation of a radical produced from the carbonyl compound (ketyl type radical), and another radical derived from the

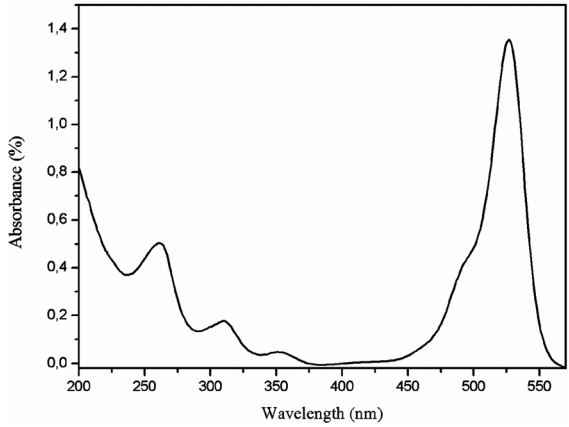

Figure 1.
UV-visible absorption spectra of Erythrosine dye in water (0.16 mg/mL), at $T = 20^{\circ}C$.

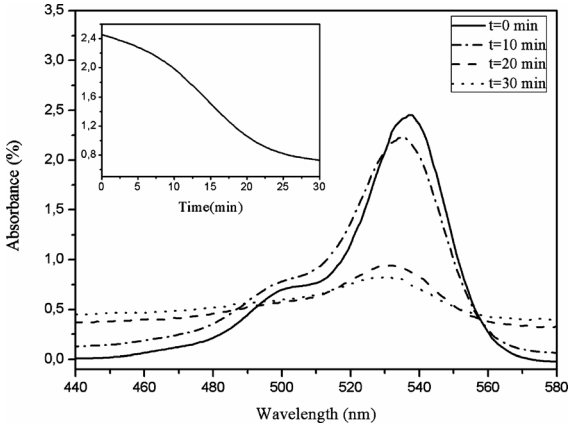

Figure 2.
Spectral changes of Erythrosine in the mixture composed of 95.93wt-% HEMA, 0.5wt-% HDDA, 0.01wt-% Erythrosine, 3.05 wt-% TEOA, and 0.51wt-% of distilled water. Irradiation was performed at $\lambda = 365$nm under air atmosphere at $T = 20^{\circ}C$. The inset shows the decrease of the absorbance at 527nm as a function of reaction time.

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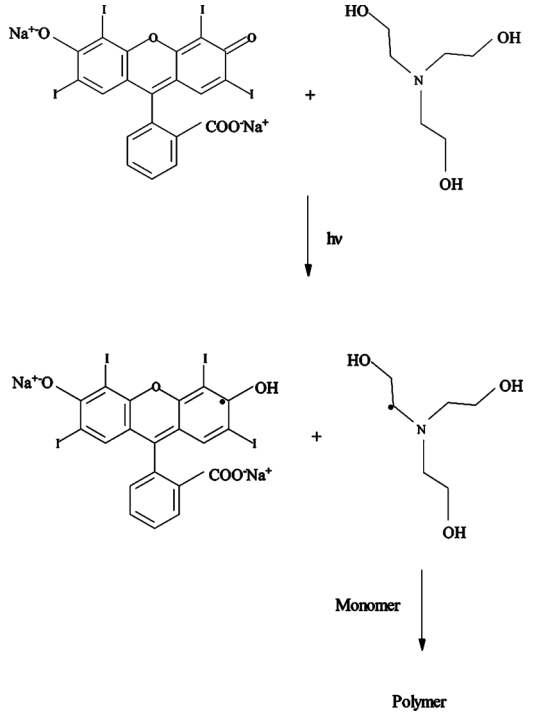

Figure 3.
Reaction scheme of the photoinitiated radical polymerization by Erythrosine.

hydrogen donor. Figure 3 represents the corresponding reaction scheme. The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are generally not reactive toward vinyl monomers due to their sterical hindrance, but they can act as terminating agents of the growing macromolecular chains. TEOA, besides its ability for hydrogen donation, can react with oxygen, thereby influencing the effect of oxygen on the polymerization.

Figure 4 represents the polymerization kinetics of the same mixture as discussed

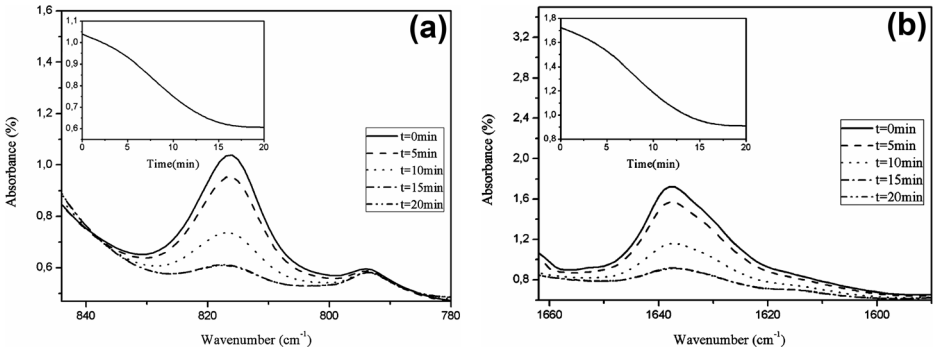

Figure 4.
Infrared spectra changes of the C=C double bond absorptions for: a) 816 cm^{-1}, b) 1637 cm^{-1}. Sample composition: 95.93wt-% HEMA, 0.5wt-% HDDA, 0.01wt-% Erythrosine, 3.05wt-% TEOA, and 0.51wt-% of distilled water. Irradiation was performed at $\lambda = 365$ nm under air atmosphere at $T = 20^{\circ}C$. The insets represent the absorbance at the corresponding peak maxima, as a function of reaction time.

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above, obtained by FTIR analysis. Changes could be observed in the intensities of the stretching frequencies of the C=C double bond by exposing the sample to UV light. Conversion rates of 88% and 82% were obtained corresponding to the bands at: a) 816cm^{-1} and b) 1637cm^{-1}, respectively. Only trace amounts of remaining monomers and oligomers were observed at an irradiation time of 20 min.

Swelling Studies

Figure 5 shows the swelling kinetics of the poly(HEMA)/0.5wt-% HDDA system in DMSO, Methanol and THF, at $T = 20°C$. In each case, the swelling of polymer networks presents two steps: first, one observes a rapid increase of the swelling ratio caused by the rapid diffusion of solvent into the polymer networks. The second step is characterized by a constant level of the swelling ratios which were obtained after approximately 16 hours of immersion of the sample in the solvent, indicating that the system reached an equilibrium state: The number of solvent molecules diffusing into and out of these networks is identical. For DMSO a more important swelling effect was recorded, compared to that for Methanol and THF. Indeed, a swelling ratio of about 120% and 41% was reached after 50 hours of immersion in Methanol and THF, respectively, whereas a plateau value of approximately 440% was found for DMSO. It can be concluded that the swelling ratio at equilibrium varies with the chemical nature of the solvent. DMSO can be considered as good solvent, Methanol as an intermediate solvent, and THF as a bad solvent.

Table 1.
Parameters k_1, n, k_2 and A for poly(HEMA)/0.5wt-% HDDA, in different solvents.

Component	k_1	n	k_2	A
Dimethyl Sulfoxide	0.1125	0.2743	0.0022	0.7896
Methanol	0.3778	0.123	0.003	0.4752
Tetrahydrofuran	0.6028	0.0539	0.0008	0.2752

Theoretical Analysis of the Experimental Swelling Results

The swelling kinetics can be rationalized by using the Fick diffusion model. Calculations of the swelling curves were carried out by using the following equation[17]

$$\left(\frac{M_t}{M_f}\right) = k_1 \times t^n \tag{3}$$

where M_t is the mass of solvent absorbed at time t, M_f is the mass of solvent absorbed at equilibrium, k_1 is a characteristic constant of the network, and n is a characteristic exponent describing the mode of the transport mechanism. The constants n and k_1 were calculated from the slopes and intercepts of ln (M_t/M_f) versus ln(t),

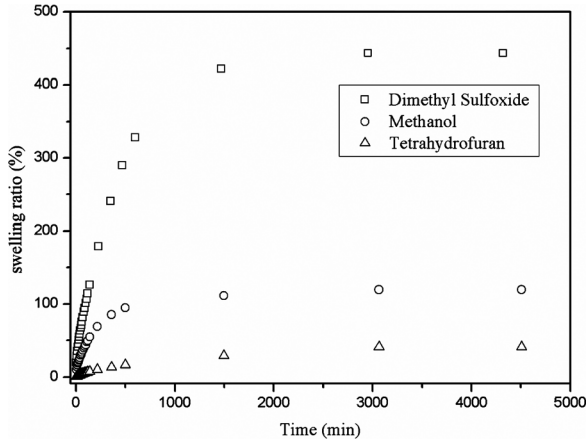

Figure 5.
Swelling kinetics of poly(HEMA)/0.5wt-% HDDA in different solvents at $T = 20°C$.

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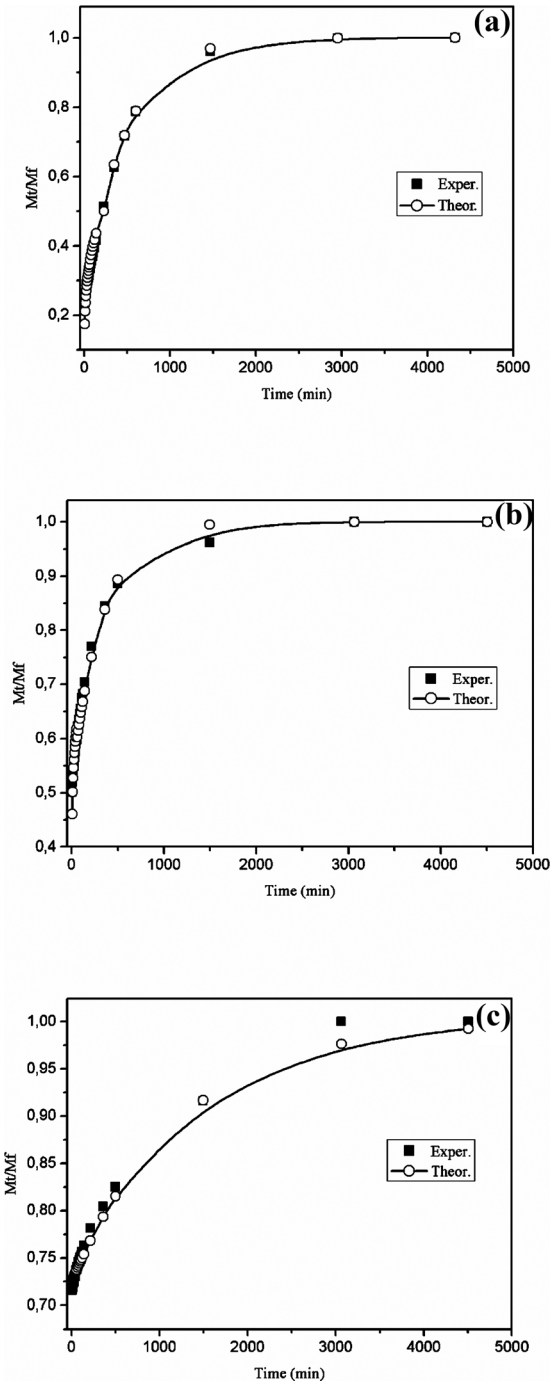

Figure 6.
Experimental and theoretical swelling curves of the poly(HEMA)/0.5wt-% HDDA system in: a) DMSO, b) Methanol, c) THF.

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and the corresponding values are gathered in Table 1.

Previously discussed models fail to give an accurate analysis for $(M_t/M_f) > 0.60$. To obtain a better description, the hypothesis was made that for long swelling periods, the sorption of solvent was mainly dominated by the relaxation of the polymer network and that the sorption process of the polymer by relaxation was of first order. Therefore, the Berens-Hopfenberg[18] differential equation for relaxation processes could be written as follows:

$$\left(\frac{dM_t}{dt}\right) = k_2(M_f - M_t) \quad (4)$$

where k_2 is the relaxation rate constant. The integration of this equation leads to:

$$\left(\frac{M_t}{M_f}\right) = 1 - A\exp(-k_2 t) \quad (5)$$

where A is a constant. In this study, the constants A and k_2 were calculated from the slopes and intercepts of the plots of $\ln(1\text{-}(M_t/M_f))$ versus time t at times beyond those corresponding to $(M_t/M_f) = 0.60$. The results are given in Table 1.

Figure 6 shows the superposition of the theoretical curves obtained with the Fick model using experimental data for the swollen poly(HEMA)/0.5wt-% HDDA system. A good correlation between theory and experimental data was observed for all three cases DMSO, Methanol, and THF.

Conclusion

The system composed of Erythrosine and TEOA was used as an efficient photoinitiator to elaborate crosslinked polymer networks. The kinetic study of the polymerization/ crosslinking reactions and the swelling behavior enable to conclude that the Erythrosine molecule has a significant impact on these processes.

The poly(HEMA)/0.5wt.-% HDDA network can be easily swollen in DMSO yielding high swelling ratios, so that this solvent can be considered as a relatively good solvent, while Methanol and THF can be considered as intermediate and bad solvents, respectively. The theoretical results obtained within the Fick diffusion model reveal a good agreement with the experimental data of all systems studied.

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