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PHOTOPOLYMERIZATION OF POLY(HYDROXYETHYL ACRYLATE) (PHEA): EXPERIMENTAL PARAMETERS-VISCOELASTIC PROPERTIES RELATIONSHIP

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Abstract. The activity of the photoinitiator system, based on triethanolamine (TEOA) and methylene blue (MB), on the photopolymerization of hydroxyethyl acrylate (HEA) monomer under very soft irradiation conditions, was evaluated. A remarkable difference in the polymerization kinetics of a set of PHEA experiments was underlined according to TEOA/MB concentrations, as well as the solutions pH. Indeed, the complex viscosity (η*), storage modulus (*G′*), and loss modulus (*G″*) of the resulting polymers were potentially dependent on these experimental parameters despite comparable values of monomer conversion.

Keywords: photopolymerization, dye, amine, pH, rheological properties.

1. Introduction

In recent years, visible-light-induced polymerization (VLIP) has attracted great interest due to a large number of applications, ranging from photo-resists and coating to new technologies such as stereolithography for 3D printing.[1,2] In view of its widespread use in several industrial fields, VLIP technology has received a great deal of attention because of its advantages over photopolymerization under UV light such as low energy necessity, and the higher penetration of visible light in comparison with UV light.[3,4] Often in practice, the photopolymerization process is required in the presence of a photoinitiator, which absorbs the visible light delivered generally by conventional lamps (Hg or Xenon) or upon sunlight, halogen lamps, and household LED. Indeed, the active centers are generally produced *via* electron transfer followed by a proton transfer from the electron donor (typically an amine) to the photo-excited molecule (generally a dye).[5,6]

It is well known that the excellent candidates for free radical photopolymerization are acrylate and methacrylate monomers, which are rapidly polymerized to give materials with different properties, serving several application fields.[7,8] However, for more sensitive applications such as biomedical and microelectronic devices, it is necessary to evaluate the relationship between the molecular structure that is related to the composition and concentration of the photoinitiator (PI) and the mechanical and rheological properties of the final materials. There are few works dedicated to understanding this relationship, for this purpose the combination of two techniques allowing to follow the chemical and mechanical changes has gained importance.[9,10] In this area, Steeman *et al.* investigate the photopolymerization of acrylate monomers regarding the evolution of acrylic double bond consumption and mechanical properties simultaneously with using Hyphenated rapid real-time dynamic mechanical analysis (RT-DMA) and time-resolved near-infrared spectroscopy (RT-NIRS), experimental results show the dependence of mechanical properties on the conversion percentage.[11] On the other hand, He *et al.* studied the photopolymerization of methacrylic acid in water/ethanol solution and confirmed that the solvent and the light intensity affect the polymerization kinetics and the resulting viscosity.[12,13] Zhang *et al.* studied the effect of initiator concentration on the rheological properties of semi-IPN hydrogel based on konjac glucomannan and methacrylic acid and confirmed their effect on the swelling behavior, as well as, the storage modulus of obtained hydrogels.[14]

These encouraging results showing the correlation between the molecular structure and mechanical-rheological properties have recently garnered the curiosity of several researchers with the aim of predicting the per-

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formance of properties by modifying experimental conditions to better target the desired application.[15,16] To keep up with the evolution of VLIP technology, a short overview of the literature shows that the photoinitiator chemical composition strongly influences the polymerization kinetics,[17] whilst its effect on viscoelastic properties of resulting polymers is not well investigated. On the other hand, and to our knowledge, the effect of pH and the concentration of each photoinitiator constituent on kinetics and viscoelastic properties remains to be discussed.

The purpose of this research is to study the relation of some kinetic parameters, on the one hand, the polymerization efficiency and the flow behavior of the resulting polymers on the other one. Indeed, the study of photopolymerization kinetics of a two-component photoinitiator system (containing a dye and an amine) taking into account its concentration and pH value, allows the fundamental information regarding the effect of each parameter on the photopolymerization process. The Fourier Transform Infrared (FTIR) technique is used to monitor the polymerization by looking at the consumption of the acrylate bond after each irradiation. In the following section, we have focused our attention on the viscoelastic properties of polymers showing a high conversion yield. The photopolymerizable system used in this work is an acrylate-based photopolymer; it consists of three basic components: a sensitizer dye (MB), an amine co-initiator (triethanolamine TEOA), and an acrylate monomer (2-hydroxyethyl acrylate HEA).

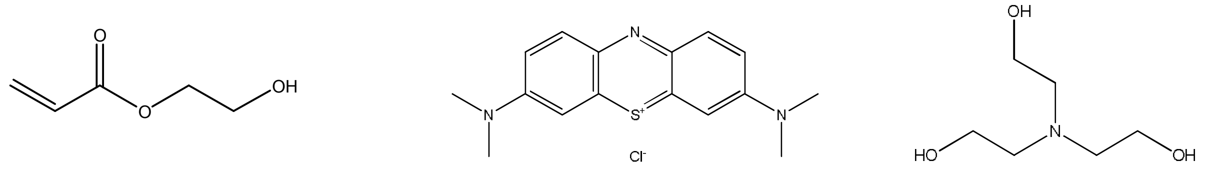
2. Experimental Part

2.1. Reagents and Chemicals

The monomer 2-hydroxyethyl acrylate (HEA) (Aldrich, 98%), methylene blue (MB) (Aldrich, 98%), and triethanolamine (TEOA) (Aldrich, 98%) were used as received, without further purification. The chemical structures of all reagents are illustrated in Fig. 1.

2.2. Photopolymerization of 2-Hydroxyethyl Acrylate HEA

Hydroxyethyl acrylate polymers were synthesized by photopolymerization of 2-hydroxyethyl acrylate monomer, under the following experimental conditions: weight content of MB [10^{-3}-10^{-2} wt. %], weight percent of TEOA [1-7 wt. %], and pH [3-11]. In order to study the effect of these experimental parameters on the monomer conversion, several formulations were conducted at different irradiation times (5, 10, 15, 20, 25, 30, 40, 45, and 50 min). For this, a required amount of HEA monomer, MB and TEOA were stirred for 1 hour, in dark, at 298 K. Then, the solution was deposited on the CaF_2 cell and irradiated at a wavelength $\lambda > 400$ nm, with an intensity of 2 mW/cm^2, under air. All experiments were conducted in triplicate and mean values were considered. The progress of the photopolymerization was evaluated by examining the evolution of the peak at 1635 cm^{-1}, assigned to the elongation vibration of C=C in the HEA monomer. The synthesis conditions were summarized in Table below.



2-Hydroxyethyl acrylate (HEA) Methylene blue (MB) Triethanol amine (TEOA)

Fig. 1. Chemical structures of reagents

Table. Reaction conditions, HEA monomer conversion and polymerization rates after 50 min irradiation

Entry	Series		MB (wt. %)	TEOA (wt. %)	pH	Monomer Conversion (%)	Rp/M_0 (s^{-1})
M1	1	PHEA $_{M0.01T1P7}$	10^{-2}	1	7	72	0.034
M2		PHEA $_{M0.01T3P7}$	10^{-2}	3	7	**89**	**0.045**
M3		PHEA $_{M0.01T5P7}$	10^{-2}	5	7	**80**	**0.04**
M4		PHEA $_{M0.01T7P7}$	10^{-2}	7	7	47	0.018
M5	2	PHEA $_{M0.001T3P7}$	10^{-3}	3	7	58	0.028
M6		PHEA $_{M0.005T3P7}$	$5x10^{-3}$	3	7	**84**	**0.041**
M7		PHEA $_{M0.05T3P7}$	$5x10^{-2}$	3	7	55	0.026
M8	3	PHEA $_{M0.01T3P9}$	10^{-2}	3	9	**90**	**0.048**
M9		PHEA $_{M0.01T3P11}$	10^{-2}	3	11	47	0.025
M10		PHEA $_{M0.01T3P3}$	10^{-2}	3	3	7	0.003

2.3. Instrumentation

FTIR spectra of the mixtures before and after photochemical irradiation were recorded in the absorption mode with TA Instruments infrared spectrophotometer. The analyses were performed in the frequency range of 4000-400 cm^{-1}, at a resolution of 2 cm^{-1}and an accumulation of 32 scans. The rheological behaviors of obtained polymers were examined with a dynamic oscillatory viscometer (Discovery Hybrid HR-2), using parallel plates with a diameter of 40 mm (Peltier plate Steel, 100261) and a gap of 1 mm. Experiments were performed at 298 K with a frequency sweep from 0.1 to 100 rad/s, and 1% strain level.

3. Results and Discussion

3.1. Photopolymerization

The photopolymerization of HEA was achieved using visible light irradiation, under air, using TEOA/MB as a photoinitiator system. Several formulations (see Table) were prepared to underline the photopolymerization efficiency of PHEA.

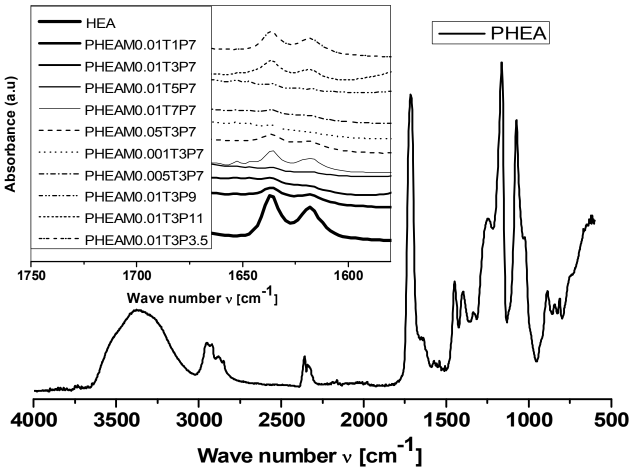


Fig. 2. Typical FTIR spectra of PHEA $_{M0.01T3P7}$ with the magnification of C=C bond for all systems

Fig. 2 depicts the infrared spectra of PHEA $_{M0.01T3P7}$ in the range of 4000-500 cm^{-1} and zooming of the peaks appeared at 1650-1600 cm^{-1}, assigned to C=C of the monomer, for all formulations after 50 min irradiation. In the PHEA spectrum, the large band centered on 3415 cm^{-1} is relied on to the stretching vibrations of hydroxyl function (–OH). The strong absorption peak at 1712 cm^{-1} is assigned to the carbonyl ester group (C=O) of the polymer. The peaks at 1410 cm^{-1} and 927 cm^{-1} are attributed to CH_2 groups and the peaks at 1635 cm^{-1} and 810 cm^{-1} rely on C=C function. It is important to note that, the consumption of acrylic double bond was not totally achieved after 50 min of irradiation, for all formulations. To better understand the effect of each parameter on the monomer conversion, the photopolymerization progress was examined following the evolution of the characteristic peak at 1635 cm^{-1}, at different irradiation times, using FTIR data. The monomer conversion was calculated according to the equation below.

$$Conv = \frac{A_0 - A_t}{A_0} \tag{1}$$

where A_0 and A_t are the initial absorbance and the absorbance value after the irradiation time t, respectively.

The kinetic parameter Rp/M_0 was calculated according to Eq. (2).[18,19]

$$R_P / M_0 = \frac{[(conversion)_{t2} - (conversion)_{t1}]}{(t_2 - t_1)} \tag{2}$$

where Rp and M_0 are the actual rate of polymerization and the initial monomer concentration, respectively. Rp was determined only at the initial stage of photopolymerization, where an almost linear increase in the conversion was observed. The rate of polymerization was obtained from each conversion curve, and this parameter was used to evaluate the impact of the photoinitiator system and solution pH on the photopolymerization efficiency. The obtained polymerization rates are collected in Table.

3.2. Effect of Different Experimental Parameters on HEA Monomer Conversion

In order to highlight the experimental parameters effect on the photopolymerization efficiency, the photoinduced reaction mechanism is firstly illustrated. Fig. 3 highlights the detailed mechanism of the photoinitiation reaction and the chains mechanism growth.

In the presence of TEOA, the MB molecule, which is absorbed in the visible range, follows an excitation once irradiated and forms a semi-reduced radical after extraction of an electron from the TEOA molecule to that of MB. The MB molecule is then photoreduced by extraction of hydrogen from the TEOA, to produce TEOA radicals which will initiate the polymerization.[20] Interestingly, these findings were drawn from an experimental study of the phototransformation of MB in the absence and presence of TEOA, in our previous work.[21] It is also worth noting that the irradiated MB molecules possess a singlet excited state (1MB*), and triplet excited states (3MB*) with a longer lifetime.[22,23] Both excited states can interact with TEOA molecules to generate TEOA radicals. Thus, the interaction between the excited states of the dye (MB*) and the amine (TEOA) can strongly affect the photoinitiation step efficiency. So, this interaction must be sufficient to produce efficient radicals able to initiate the photopolymerization reaction.

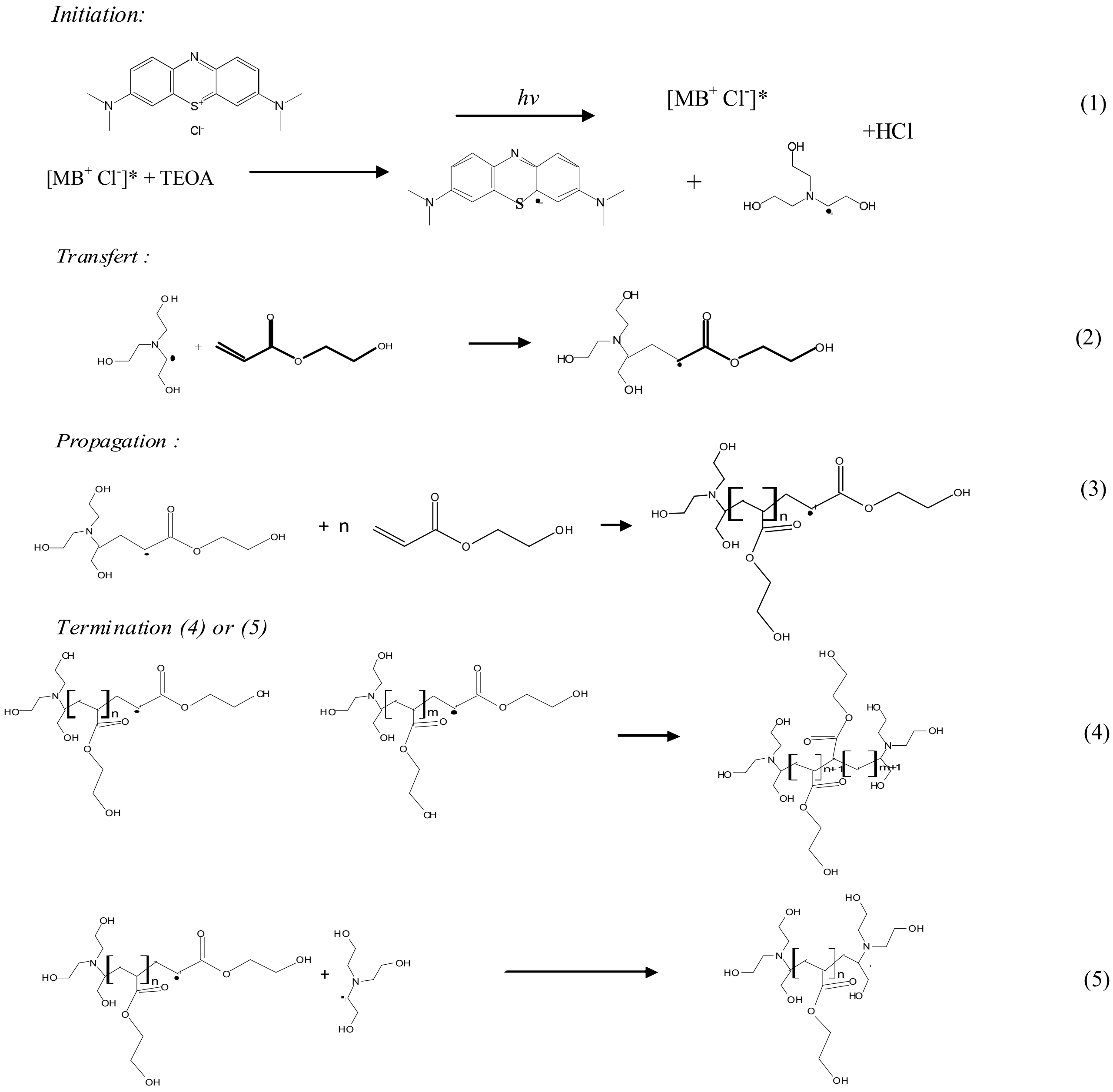


Fig. 3. Illustration of the photo-initiator system formation and radical polymerization of HEA

The polymerization reaction of HEA follows a radical chain mechanism. The general mechanism of this photoinitiated reaction is presented in Fig. 3 with an initiation step (1), a transfer step (2), a propagation step (3), and finally a termination step (4) and (5). The termination can be done by the recombination of the growing radical polymer with a photoinitiator radical (4) or with another radical polymer chain (5).[24] Other reactions, which are not shown in Fig. 3, can occur, *e.g.*, chain transfers, recombination of primary radicals, and disproportionation reactions.

3.2.1. Effect of TEOA Concentration

In order to underline the amine concentration effect on the HEA conversion and the polymerization rate, several combinations of MB/TEOA were examined (see Table). As mentioned above, the TEOA is a good electron donor and is highly efficient in initiating the system when combined with MB electron acceptors.

It should be noted that the experiments were performed in an air atmosphere; therefore, the presence of the amine is important not only for the radical formation but also for the reduction of oxygen molecules able to inhibit the action of amine radicals.[25]

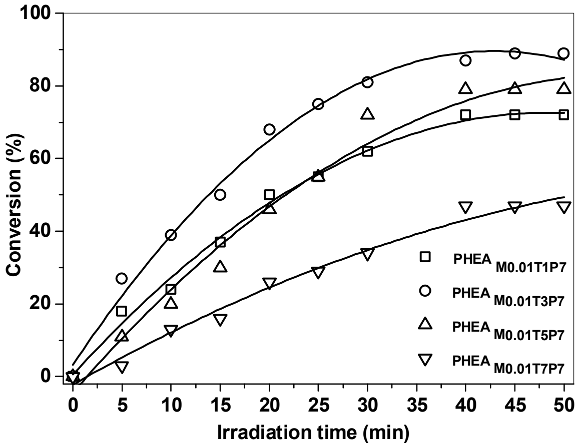


Fig. 4. Conversion evolution of HEA versus irradiation time obtained by varying TEAO concentration

Fig. 4 shows the evolution of HEA conversion as a function of irradiation time, knowing that the concentration of MB is kept constant and the concentration of TEOA was varied.

Careful examination of Fig. 4 reveals that the increase of TEOA concentration results in an increase of the HEA conversion until reaching a maximum of monomer conversion (89%) at 3 wt. % of TEOA.

This increase is attributed to the increase of amine radical quantum yield, acting as a co-initiator and oxygen consumer.

The same trend was observed for *Rp* values shown in the table where the photopolymerization rate increases with increasing TEOA concentration. The increase in polymerization rate is expected because the rate is usually proportional to the initiator concentration, so an increase in TEOA concentration would normally be required to achieve a similar result.[26]

Further amine addition slightly decreases the conversion and *Rp* values. Indeed, exceeding 5 wt. % value of amine concentration, the monomer conversion shows a pronounced decrease and achieves 47%, at 7 wt. % of TEOA. This result can be relied on the quenching of both singlet and triplet excited states of MB molecules by the excess of TEOA radicals leading to a decrease in the polymerization efficiency.[25,27] Notably, these results confirm that further polymerization in the presence of radicals generated by the BM/TEOA photoinitiator system requires an appropriate concentration of TEOA as the co-initiator.

3.2.2. Effect of MB Concentration

The effect of MB concentration on HEA photopolymerization was examined in the presence of a fixed concentration of TEOA (3 wt. %).

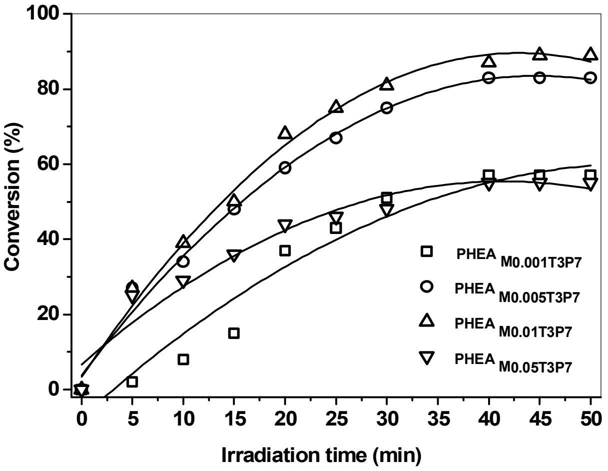


Fig. 5. Conversion evolution of HEA versus irradiation time obtained by varying MB concentration

Fig. 5 depicts the evolution of conversion percentage versus irradiation time by changing the concentration of MB. The experimental results shown in Fig. 5 reveal that the photoinitiating systems with 0.01 wt. % of MB displayed better polymerization reactivity. This concentration of MB may be optimal to produce sufficient amine radicals for HEA photopolymerization. Furthermore, the table's eighth column, which displays the polymerization rate for each system, shows that MB concentration has a significant effect on the kinetic pathway for active center generation and chain growth.

However, some increase of the MB particles in the system resulted in a gradual decrease in polymerization rate and the HEA conversion. This result may be explained by the quenching of the ground state in presence of a great number of MB molecules. In other words, the increase of MB concentration favors the interaction between excited and non-excited dye molecules, leading to some decrease of the interaction MB-TEOA and so, the decrease of the Rp and HEA conversion.[28,29]

3.2.3. Effect of Solution pH

A series of experiments were carried out with changing pH of photoreactive solutions to investigate the effect of solution pH on photopolymerization efficiency.

Fig. 6 depicts the final acrylate conversion with different pH and at optimized MB and TEOA concentrations (at 0.01 wt. % and 3 wt. % respectively). The polymerization rates were also calculated based on the slope of the conversion versus time at the early stage of polymerization and recorded in Table.

Fig. 6 demonstrates that at high acid or basic environment, the polymerization efficiency decreases considerably. The data in the table also show that the system with a pH value of 9 had a higher polymerization rate than the other three systems studied.

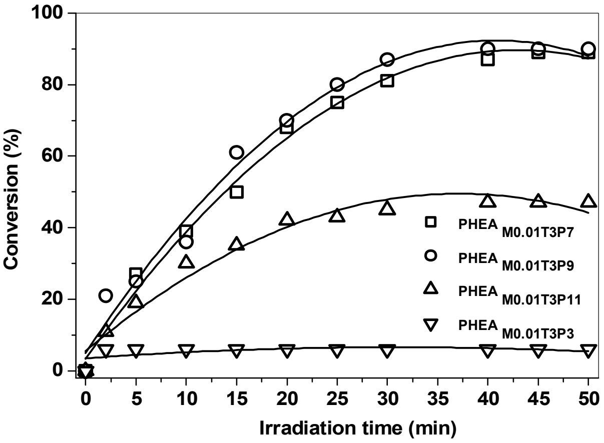


Fig. 6. Conversion evolution of HEA versus irradiation time obtained by varying pH solution

In an aqueous solution, the triplet state of MB molecules can be readily observed by flash photolysis methods;[30] the lifetimes are typically in the microsecond regime and depend noticeably on pH solution. In our case, the maximum monomer conversion obtained at pH=7 and pH=9, respectively can be explained by the lifetimes of the triplet state which is strongly dependent on pH. It has been reported that the triplet state of MB has a longer lifetime than its ground state at higher pH.[31,32]

As expected, these triplet states are efficiently quenched by amines molecules at pH=7 and pH=9 to produce efficiently radicals able to initiate the HEA photopolymerization.

As pH rises from 3 to 7, the monomer conversion increases, this increase can be explained by the increased quantum yield of dye reduction at lower acidity. This is an agreement with the results indicating that dye reduction is more favorable in a lower acidic environment, as compared to a higher acidic one.[33] This is probably related to the triplet state lifetime as shown in other work indicating that the lifetime of the MB triplet state in a strongly acidic environment is 4.5 μs,[34] whereas that of the MB in a neutral environment is much longer: 90 μs.[35]

This explains the high polymerization efficiency obtained in a neutral environment (pH=7) compared to the acid one (pH=3).

For (pH > or =11), a proton dissociation is expected from the methylamino groups of MB in an alkaline environment with the formation of the deprotonated forms of MB,[36] which causes decay of MB in a high alkaline environment leading to the polymerization deactivation.[37]

In conclusion, the photoinitiator composition, as well as, the solution pH were determining factors to define the resultant HEA monomer conversion and hence the formation of the PHEA hydrogel with desired properties. Based on the applications fields of this hydrogel, it's important to examine the obtained viscoelastic properties.

3.3. Viscoelastic Properties

In order to highlight the effect of the studied experimental factors (photoinitiator, pH) on the adhesive properties of the resulting polymers, viscoelastic characterizations were carried out for the systems recorded important monomer conversion values: (PHEA $_{\mathrm{M0.01T3P7}}$, PHEA $_{\mathrm{M0.01T5P7}}$, PHEA $_{\mathrm{M0.005T3P7}}$, PHEA $_{\mathrm{M0.01T3P9}}$).

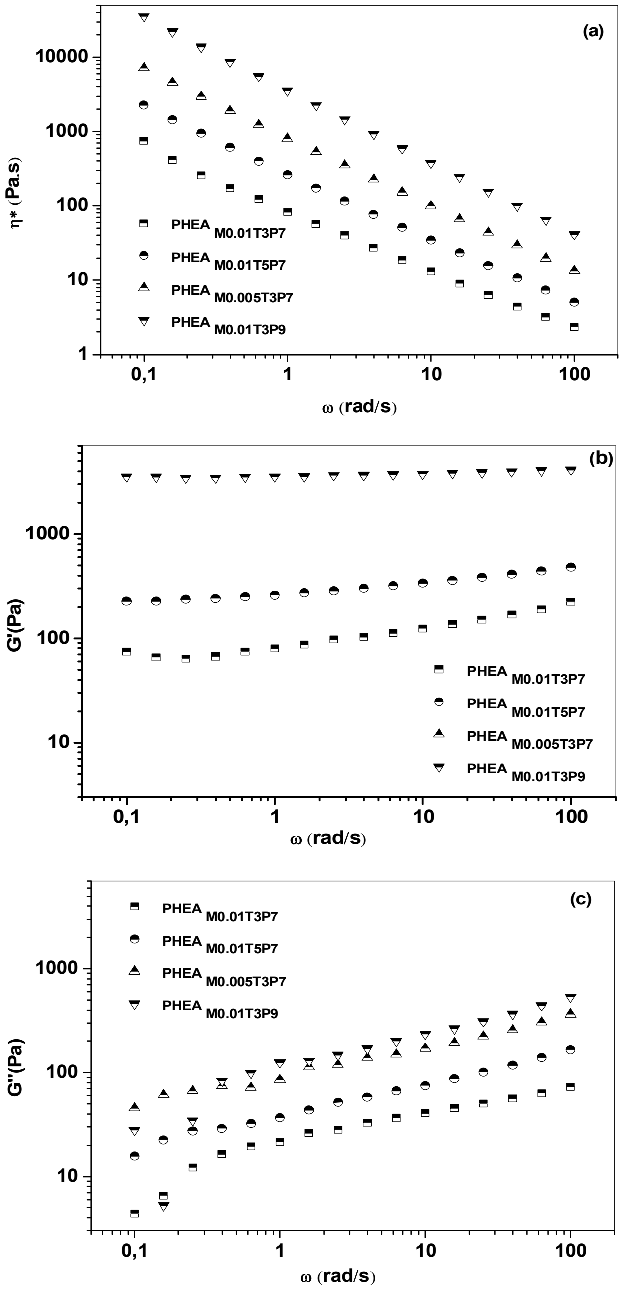


Fig. 7. Complex viscosity (a), storage modulus *G′* (b), and loss modulus *G″* (c) versus angular frequency for different HEA polymers, recorded at 25°C

The complex viscosity (η*), storage modulus (*G′*), and loss modulus (*G″*) as a function of angular frequency were illustrated in Fig. 7a-c, respectively.

As shown in Fig. 7a, the complex viscosity η* decreased drastically by increasing the angular frequency and follows a typical non-Newtonian pseudoplastic behavior whatever the studied system. However, the initial experimental factors such as MB/TEOA concentration and pH may be affecting significantly the resultant complex viscosity of the PHEA. This result can be caused by the number of radicals formed in the initiation step of polymerization which define the chains length of the synthesized product, as reported by Zhang *et al.*[16] and Chaudhuri *et al.*[17] In our case, we can suggest that the radicals initiators formed in the case of PHEA $_{M0.01T3P7}$, are more important than those of PHEA $_{M0.01T5P7}$ because some TEOA molecules were interacted with MB singlet state and deactivated the formation of radical initiators. Therefore, the chains formed in the case of PHEA $_{M0.01T5P7}$ are longer and the entanglement greater, leading to an increase in the polymer viscosity. On the other hand, at the constant value of TEOA (3 wt. %), and at PH=7, the concentration of MB impacts significantly the resultant viscoelastic properties of PHEA polymers. Indeed, the conversion values of PHEA $_{M0.005T3P7}$ (84%) and PHEA $_{M0.01T3P7}$ (89%) are comparable but the radicals formed in the case of PHEA $_{M0.005T3P7}$ system are fewer than those of the PHEA$_{M0.01T3P7}$, implying a more important entanglement, which enhances the viscoelastic properties of the material. Interestingly, by increasing the pH value from 7 to 9, the complex viscosity of the hydrogel is increased, meaning that the polymer obtained from PHEA $_{M0.01T3P9}$ mixture has a higher resistance to flow.

As is evident from Fig. 7b and Fig. 7c, the storage modulus *G′* and loss modulus *G″* values increased by increasing frequency. This suggested that all mixtures were pseudoplastic fluids with a shear-thinning behavior. It is noted that *G′* exceeds *G″* by more than an order of magnitude for all the studied systems, which is a typical characteristic of a cross-linked gel system, showing the formation of strong links between chains, provided by hydrogen bonds of the OH groups of PHEA. Furthermore, *G″* was more strongly dependent on frequency than *G′*, indicating a solid-like rheological property of obtained polymers.[38]

It is also obvious from Fig. 7b and Fig. 7c that the *G′* and *G″* show an incremental trend as the number of formed radicals decreases. The phenomenon indicates that the balance between MB and TEOA concentration affects the molecular structure of polymer mainly by affecting the chain length of resulting PHEA. This result is consistent with the findings reported by Geever *et al.*,[39] showing that changing the concentration of the photoinitiator and the molecular weight of the macromolecular monomer results in different mechanical and rheological properties of the hydrogels.

4. Conclusions

Hydroxyethyle acrylate polymers were prepared *via* photopolymerization of the monomer using different contents of photoinitiator TEOA/MB, at different pH of the solution, under soft conditions (visible light source, low light intensity, air atmosphere). The conversion degree and the kinetic parameter R_p/M_0 of HEA were discussed according to the experimental factors. The HEA polymers that have shown significant monomer conversion were selected to examine their viscoelastic properties. A remarkable difference in the complex viscosity, storage modulus, and loss modulus of all systems was recorded and relied on the predefined experimental conditions (TEOA, MB concentrations, pH). Overall, this study reveals that HEA polymers are potential candidates for different application fields. Indeed, their viscoelastic properties can be predefined inadequacy with the predicted application, based on the photoinitiator composition, as well as, the solution pH.

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ФОТОПОЛІМЕРИЗАЦІЯ ПОЛІГІДРОКСІЕТИЛАКРИЛАТУ (ПГЕА): ЗВ'ЯЗОК ЕКСПЕРИМЕНТАЛЬНИХ ПАРАМЕТРІВ І В'ЯЗКОПРУЖНИХ ВЛАСТИВОСТЕЙ

Анотація. *Оцінено активність фотоініціювальної системи на основі триетаноламіну (ТЕОА) і метиленового синього (МС) у фотополімеризації мономеру гідроксіетилакрилату (ГЕА) в умовах дуже м'якого опромінення. Виявлено помітну різницю в кінетиці полімеризації для серії експериментів ПГЕА залежно від концентрацій ТЕОА/МС, а також рН розчинів. Дійсно, комплексна в'язкість (η*), модуль зберігання (G') і модуль втрат (G") отриманих полімерів потенційно залежали від цих експериментальних параметрів, незважаючи на співрозмірні значення конверсії мономеру.*

Ключові слова: *фотополімеризація, барвник, амін, рН, реологічні властивості.*