

UV Irradiation-Induced Crosslinking of Aqueous Solution of Poly(ethylene oxide) with Benzophenone as Initiator

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ABSTRACT: The development of a water-based polymer system that could be photocrosslinked during the drilling of fragile formations could be of a great interest. In this context, aqueous solutions of poly(ethylene oxide) (PEO) were photocrosslinked by ultraviolet radiation in the presence of benzophenone (BP). The photochemical crosslinking reaction showed a rate constant of $1 \times 10^{12} \text{ L mol}^{-1} \text{ s}^{-1}$, indicating the formation of a complex between the reactants. The crosslinked PEO was fully characterized showing an yield dependency on the irradiation time, concentration of benzophenone, and on the presence of oxygen. During the study of the effect of BP concentration, it was observed that low concentrations and the presence of oxygen favor chain scission, while crosslinking was the dominant effect at higher BP concentrations. The storage modulus (G') value for some of the materials was found to be higher than the loss module (G'') suggesting a predominantly elastic solid-like behavior which was corroborated by the scanning electron microscopy (SEM) results. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2458–2467, 2013

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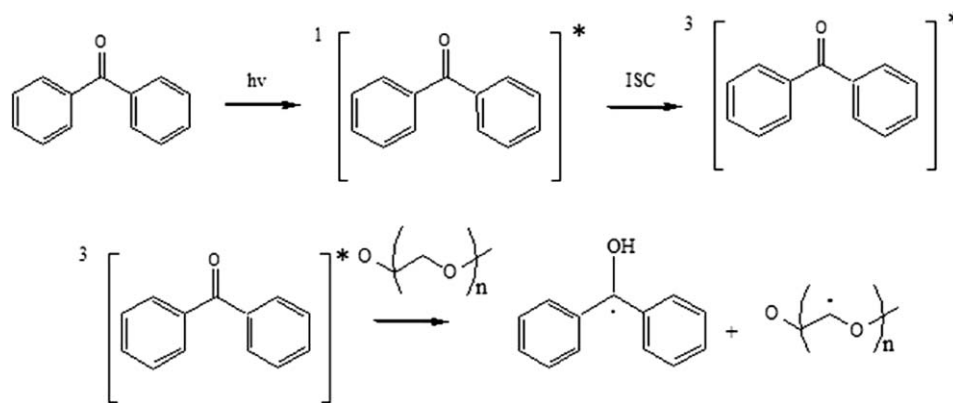
INTRODUCTION

Wellbore instability is one of the most important challenges during drilling through fractured and unstable formations. Stability of boreholes in these scenarios requires a careful consideration of *in situ* stresses, rock strength, pore pressure, wellbore fluid pressure and drilling fluids characteristics.¹ The search for a highly inhibitive and shale strengthening water-based drilling fluid (WBDF) system has been of continuous interest in the drilling fluid industry.² Thus, it would be very interesting to develop systems that would consist of an environment-friendly polymer as shale inhibitor, a fluid-loss control additive and that would also provide strengthening of fragile or fractured rocks during oil well drilling. Several authors have invested in the development of systems that could act in the strengthening of fragile formations. Deolarte et al.³ used an organically crosslinked copolymer of acrylamide and *t*-butyl acrylate system for strengthening a naturally fractured carbonate reservoir. In another work, Romero-Zeron et al.⁴ used highly crosslinked gels of partially hydrolyzed polyacrylamide chromium [(HPAm)/Cr(III)] acetate gel to improve the conformance in naturally fractured formations. Therefore, it would be interesting to develop a water based polymer system that could be UV photocrosslinked during the drilling of fragile formations.

Poly(ethylene oxide) (PEO) is a biocompatible, biodegradable, non-ionic water-soluble polymer of considerable industrial

importance.^{5–7} Crosslinked PEO forms an important class of new materials with a number of applications in fields such as controlled release drug systems, semipermeable membranes, detergents, paints and many others.^{6,8} The crosslinked PEO can be obtained by radiation techniques in a several ways, including irradiation of a solid polymer, of a monomer (in bulk or in solution) or of an aqueous solution of the polymer.⁹ PEO appears to undergo both chain scission and crosslinking reactions when irradiated. Crosslinking involves the loss of a hydrogen from the main chain carbon and chain scission could take place in several different ways. Previous studies of bulk PEO irradiation have shown that degradation (chain scission) predominates over crosslinking. On the other side, irradiation of aqueous solutions takes advantage of the mobility of the polymer chains and increases the probability of free radical crosslinking.¹⁰

Crosslinked PEO has been first obtained as a product of γ irradiation of degassed dilute aqueous solutions.¹¹ Later, methods based on chemical crosslinking through end groups were suggested.¹² Chemical crosslinking was observed for low molecular weight polymers in the reaction between the end groups in PEO and multifunctional crosslinking agents. Crosslinked PEO could be also successfully obtained by irradiation with ultraviolet (UV) light with benzophenone as initiator.^{13,14} Benzophenone (BP) has been widely used as a conventional type II



Scheme 1. Photochemical process followed by BP and PEO according to Doytcheva et al.¹³

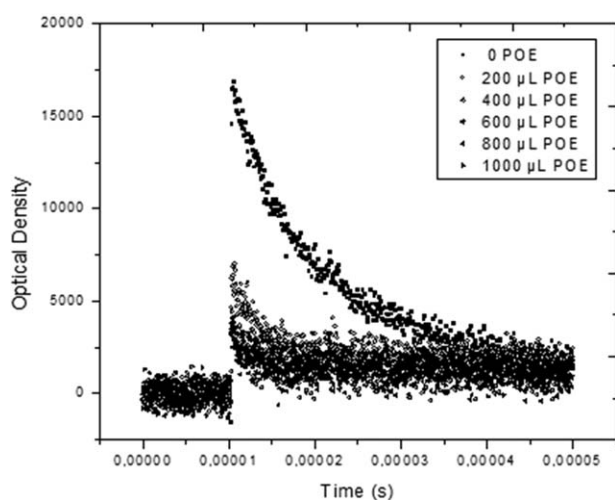


Figure 1. Decay of ³BP by addition of PEO aqueous solutions.

photoinitiator for free radical UV curing systems.¹⁵ However, these processes have been carried out in organic solvents, impairing its use in water based drilling fluids.

Irradiation of polymers in aqueous solution are easier to control and study, and lower numbers of the usually unwanted processes occurs, as, for example, homografting of the monomer on the polymer chain that may lead to branched structures.

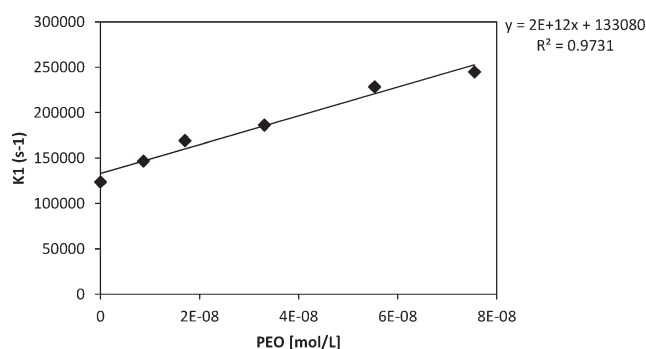


Figure 2. Life times of ³BP* as a function of PEO concentration.

Therefore the hydrogels formed in that way present no need for further purification.

To the best of our knowledge there is no work reported in the literature describing PEO UV photocrosslinking in the presence of benzophenone in water. Higher safety and lower costs are the significant advantages of processes involving UV irradiation of aqueous solutions compared to the ones involving UV irradiation of organic solvents solutions. Benzophenone was selected because of its high hydrogen abstraction efficiency.

The aim of this work was to study the photocrosslinking of PEO in water in the presence of benzophenone aiming at its future use in the development of a new process of shale reactivity inhibition and fragile rocks strengthening during oil well drilling.

EXPERIMENTAL

Materials

All reagents were of the purest grade commercially available and were used without further purification. Poly(ethylene oxide) was obtained from Sigma-Aldrich Chemistry with an average molecular weight of 1,000,000. Benzophenone, methanol, ethanol,

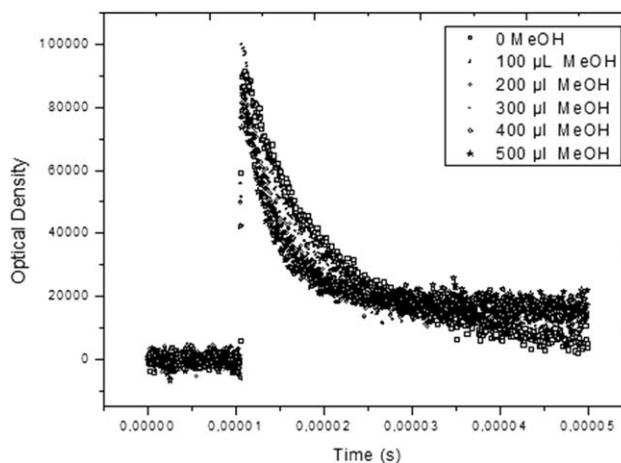
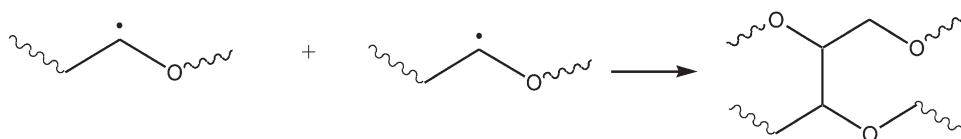
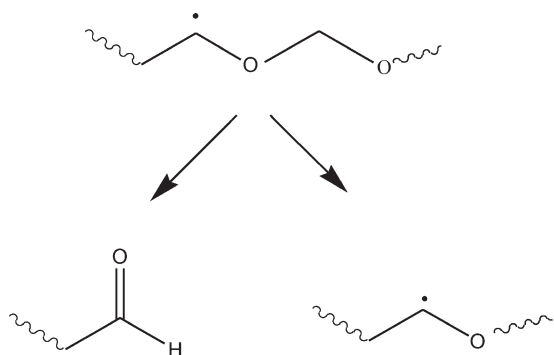


Figure 3. Effect of methanol on optical density of ³BP.



Scheme 2. Formation of crosslinkages in PEO (Doytcheva et al.¹³).



Scheme 3. Chain scission of the PEO radical (Hassouna et al.⁵).

and acetonitrile were obtained from Vetec Química Fina Ltda (Rio de Janeiro, Brazil).

Laser Flash Photolysis Study

The reaction between the triplet excited state of benzophenone ($^3BP^*$) and PEO was carried out by laser flash photolysis using a Nd: YAG laser 355 nm laser as excitation source and by following the BP triplet absorption at 520 nm. Nd: YAG laser provides 355 nm pulses with a duration of 4 to 6 ns and a maximum energy of 40 mJ per pulse was used as the pump light source.

A benzophenone aqueous solution (5.0×10^{-3} mol/L) was prepared by dissolving it in 1.0 mL methanol followed by the addition of 99.0 mL of water. A PEO aqueous solution (1.0×10^{-6} mol/L) was prepared and samples were deaired with N_2 for at least 15 min before photolysis. The reaction of $^3BP^*$ with PEO was carried out by adding 200 μ L of the PEO aqueous solution to the BP solutions. The methanol reactivity toward triplet BP was

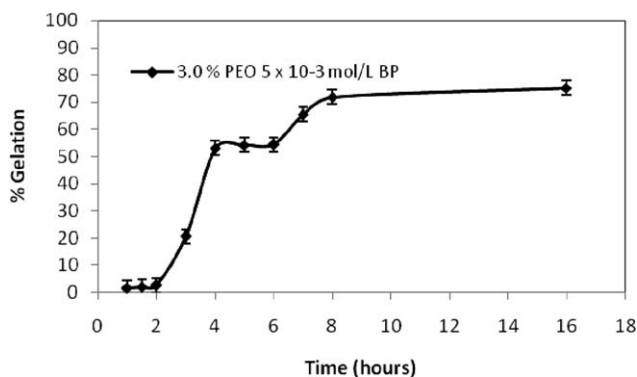


Figure 4. Dependency of % gelation with irradiation time.

evaluated separately by adding pure methanol to a BP solution in acetonitrile and following the same photolysis procedure.

Preparation of Hydrogels

The solutions were prepared by dissolving benzophenone (1.0×10^{-4} to 5.0×10^{-3} mol/L) in 2.0 mL of ethanol, followed by the addition of 198 mL of distilled water and PEO at 3.0% (3.0×10^{-5} mol/L). The resulting solution was heated for 4 h at 60°C before the irradiation process.

The irradiation of PEO aqueous solutions was carried out in the presence and absence of oxygen at room temperature. Nitrogen gas was passed through the solutions for 15 min to remove the dissolved oxygen. The aqueous solution of PEO was irradiated in a pyrex reactor equipped with one medium-pressure mercury lamp and cooled by water circulation. The time of irradiation varied from 0.5 to 16.0 h.

Gelation %

In order to verify the gelation percentage of the materials, samples were dried after irradiation, weighted (W_0) and then soaked in distilled water for several days, until reaching a constant weight, the equilibrium swelling (W_S), in order to remove the soluble and unreacted species.¹⁶ The gels were then dried again in air to obtain the dried weight (W_E). The % gelation was calculated by the eq. (1):

$$\% \text{ Gelation} = W_E / W_0 \times 100 \quad (1)$$

where W_0 is the weight of the dried gel after irradiation, and W_E is the weight of the dried sample after extraction of the soluble and unreacted species.

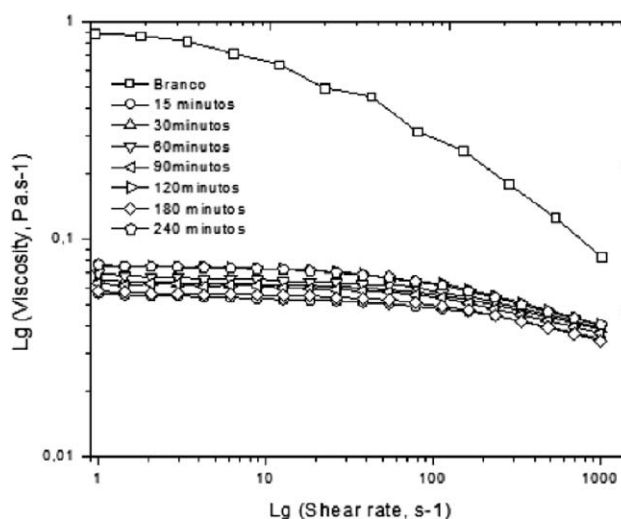
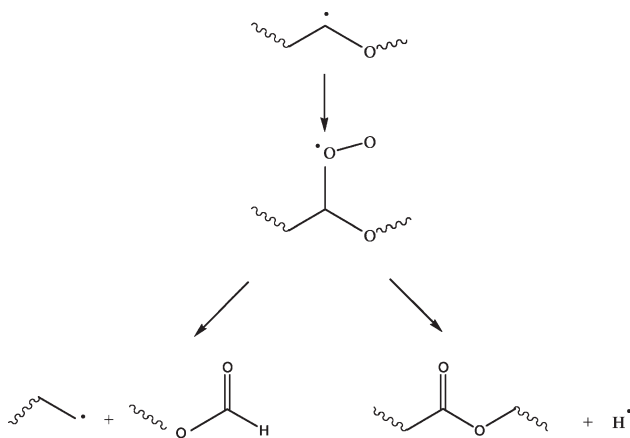


Figure 5. Viscosity of the irradiated solutions as a function of the shear rate.



Scheme 4. Photooxidation process of PEO radical (Deolarte et al.³).

Rheological Measurements

The rheological behavior of the irradiated samples was characterized with a Haake RS1 rheometer. For samples with low viscosity, the tests were performed in the rotational mode with a double gap DG43Ti sensor, shear rates ranging from 1 to 1000 s⁻¹ and at a temperature of 25°C, controlled by a Haake

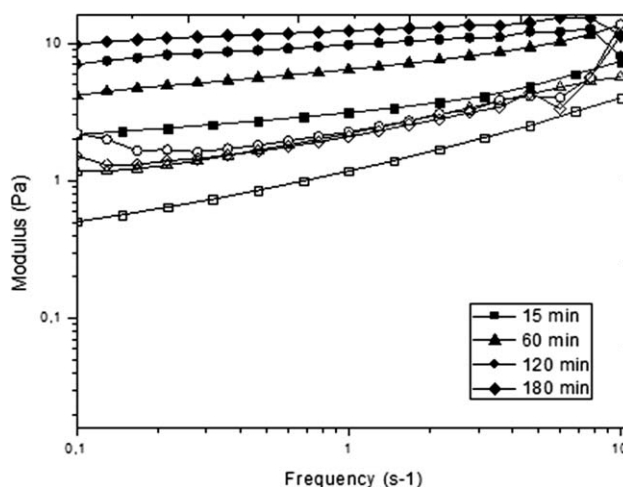


Figure 6. Hydrogels storage modulus G' (solid color) and loss modulus G'' (hollow) as a function of frequency.

thermostatic bath. For this type of analysis 11.5 mL of solution was used. For the hydrogel samples, the analysis were carried out in the oscillatory mode with a cone-plate HC60/1 sensor,

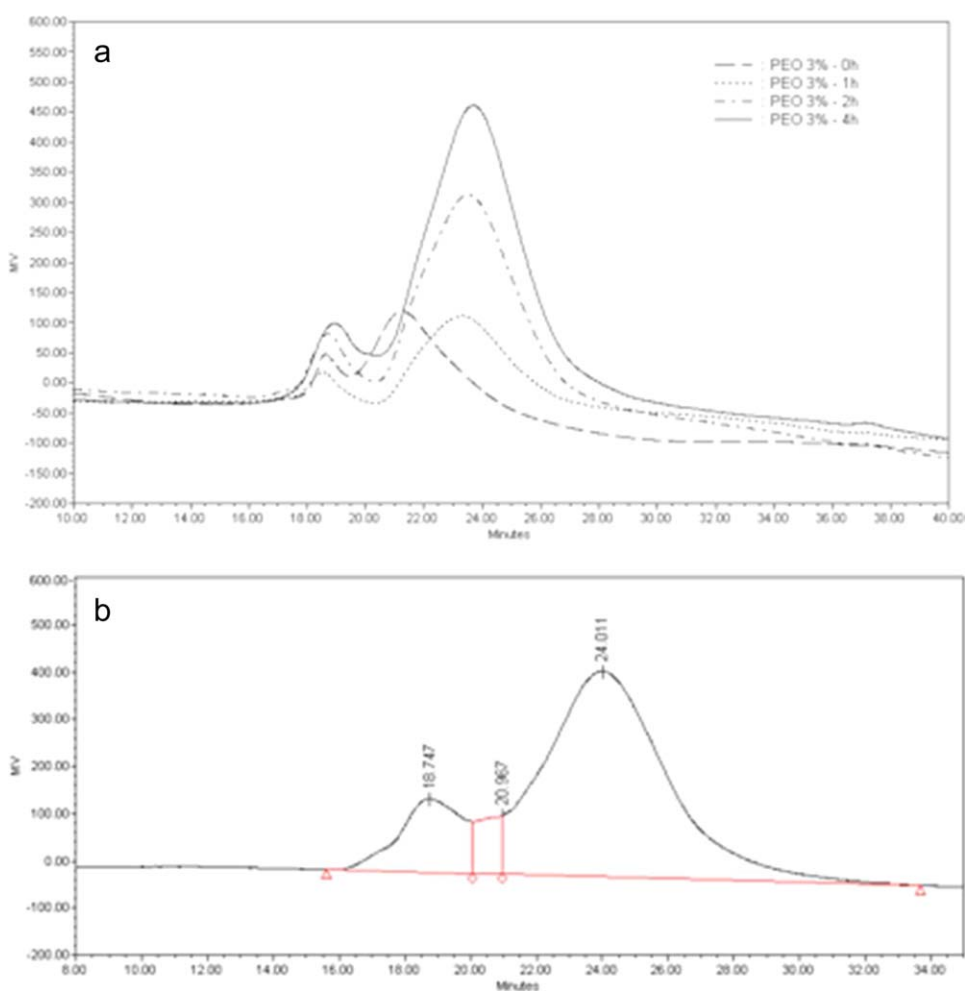


Figure 7. (a) Chromatogram of PEO solutions with low concentrations of BP after different period and (b) after 16 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

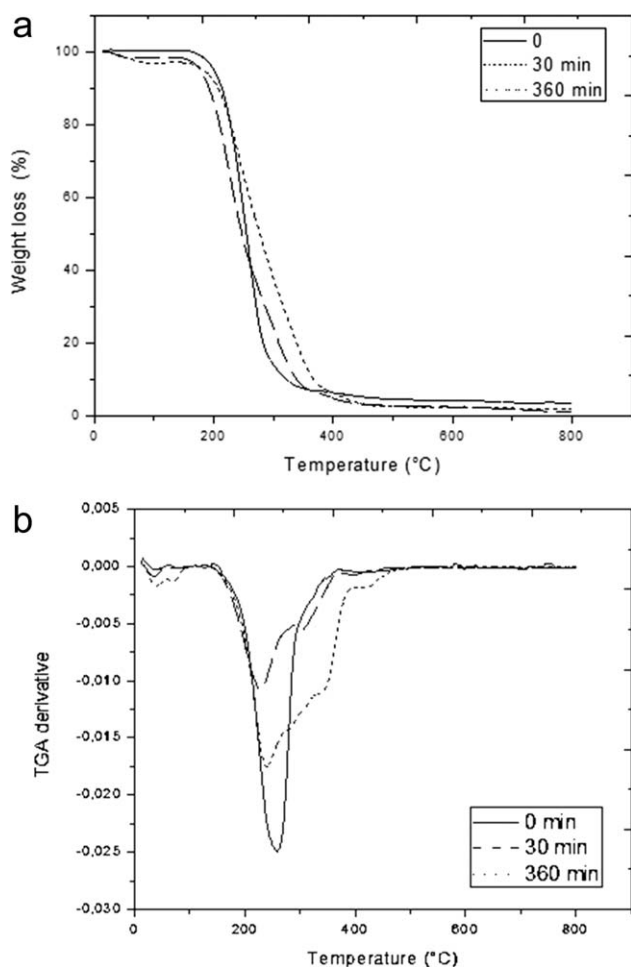


Figure 8. (a) Weight loss results for samples before and after irradiation, as a function of temperature and (b) derivative of the TGA curves for the irradiated and non-irradiated samples as a function of temperature.

range from 1 Pas, fixed voltage and frequency range between 0.1 and 10 Hz.

Gel Permeation Chromatography

The GPC analysis were performed with a Waters system composed by a detector (Model: Refractive Index Detector 2410), a pump (Model 515), a temperature controller, a column oven, and degasser. A poly sep-GFC-P column was used with a solution of nitrate/nitrite as the mobile phase. The volume of solution injected was 200 μL and the analyses were performed at 40°C at a rate of 1 mL/min.

Thermogravimetric Analysis

For de TGA analyses 15 mg of the material were used in a capsule of alumina, subjected to a heating rate of 10°C/min in a SHIMATZU instrument, model 52-TGA, under a N_2 flow of 20 mL/min until the temperature of 800°C.

Scanning Electron Microscopy

The pore size of the hydrogels formed were analyzed by scanning electron microscopy. PEO and PEO irradiated with benzophenone samples were dried and coated with gold by the sputtering technique. The equipment used was a Scanning Electron Microscope—JSM—6460 LV. The studies were performed

with secondary electron signal in a high vacuum and a filament voltage of 20 kV.

RESULTS AND DISCUSSION

The irradiated samples showed different results depending on the irradiation time and the benzophenone concentration employed.

Reaction of Benzophenone $^3\text{BP}^*$ with PEO

According to the literature, the photochemical process followed by BP is well understood.¹³ After the photon absorption, BP undergoes several photophysical processes like, rise to the n,π^* singlet state, followed by intersystem crossing to triplet state (T^1). The benzophenone T^1 can abstract BP to form the PEO radical, as shown in Scheme 1.

The decay of $^3\text{BP}^*$ was followed by its absorption at 520 nm. The observed reduction of the $^3\text{BP}^*$ optical density by increasing the POE concentration (Figure 1) indicates the occurrence of the $^3\text{BP}^*$ quenching.

The $^3\text{BP}^*$ quenching rate (k_q) by PEO was obtained from a plot of its decay constant values *versus* the concentration of PEO ([POE]) as shown in Figure 2:

$$K_1 = k_0 + k_q [\text{PEO}] \quad (2)$$

where k_0 is the rate constant for the decay of $^3\text{BP}^*$ in the absence of PEO.

The value of the quenching rate for the $^3\text{BP}^*$ ($2 \times 10^{12} \text{ mol L}^{-1} \text{ s}^{-1}$) is higher than the diffusion limit in solvents, thus suggesting the formation of a complex between PEO and benzophenone in the S_0 state, so the reaction takes place with both reactants in close contact.

Pulse radiolysis studies on the decay of macroradicals derived from poly(ethylene oxide) in aqueous solution have shown that the rate constant of the reaction of hydrated electrons with PEO is lower than $5 \times 10^6 \text{ mol L}^{-1} \text{ s}^{-1}$.¹⁷

Reaction of Benzophenone Triplets with Methanol

From Figures 1 and 3 it is clear that methanol quenches $^3\text{BP}^*$ less efficiently than PEO. The quench rate (k_q) by methanol, $5 \times 10^7 \text{ mol L}^{-1} \text{ s}^{-1}$ is about 5 orders of magnitude lower than that by PEO, which indicates that the rate for hydrogen abstraction from methanol by $^3\text{BP}^*$ has no influence on the reaction of PEO photocrosslinking.

Gelation %

When the polymer solution is irradiated in the presence of BP, PEO radicals are produced as a result of an indirect effect of radiation. These radicals disappeared either through the formation of crosslinkages (Scheme 2) or by intramolecular linking or else by chain scission (Scheme 3).

Figure 4 shows the % gelation curves as a function of the irradiation time for PEO crosslinking in the presence of oxygen. The amount of hydrogel increases with time, up to 4 h of irradiation, when it levels off (Figure 4), showing a first small plateau. Apparently, at this stage, the photoinitiator molecules would have reached all the nearby reactive sites, bringing the photocrosslinking

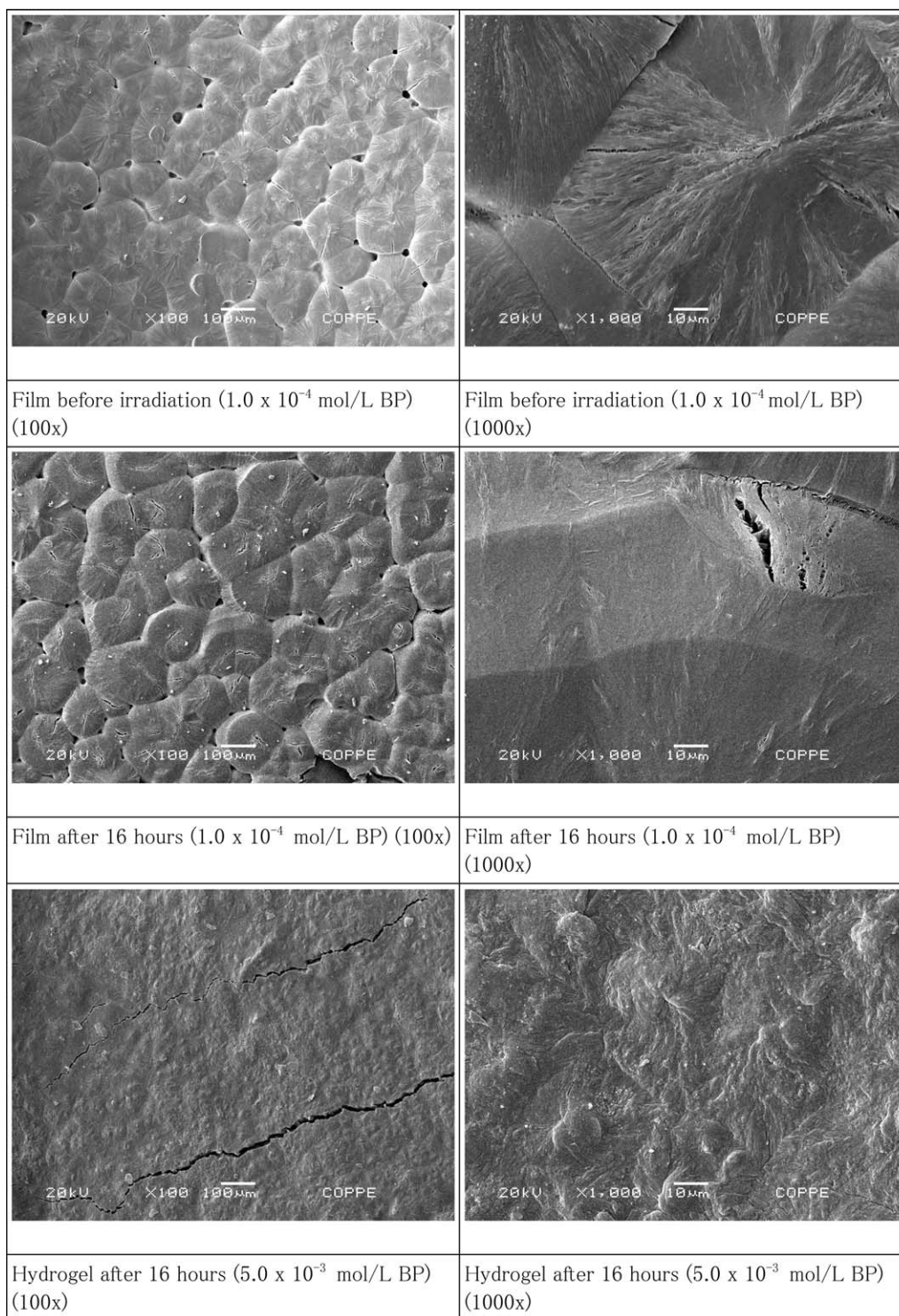


Figure 9. Micrographs of films and hydrogels obtained using different concentrations of benzophenone.

process to an end. However, with time (2 h) the initiator molecules were able to diffuse and start again the photocrosslinking. Within the range of concentration considered in this work, higher percentages of gelation were obtained with solutions of higher BP concentrations. Lopérgolo et al.¹⁶ noted that the % gelation for hydrogels of poly(*N*-vinyl-2-pyrrolidone) (PVP) is dependent on

the irradiation time. The author also observed that the % gelation increases to a maximum and then it levels up.

Rheological Measurements

Rheological measurements provide a quantitative characterization of the viscoelastic properties of the hydrogels through the

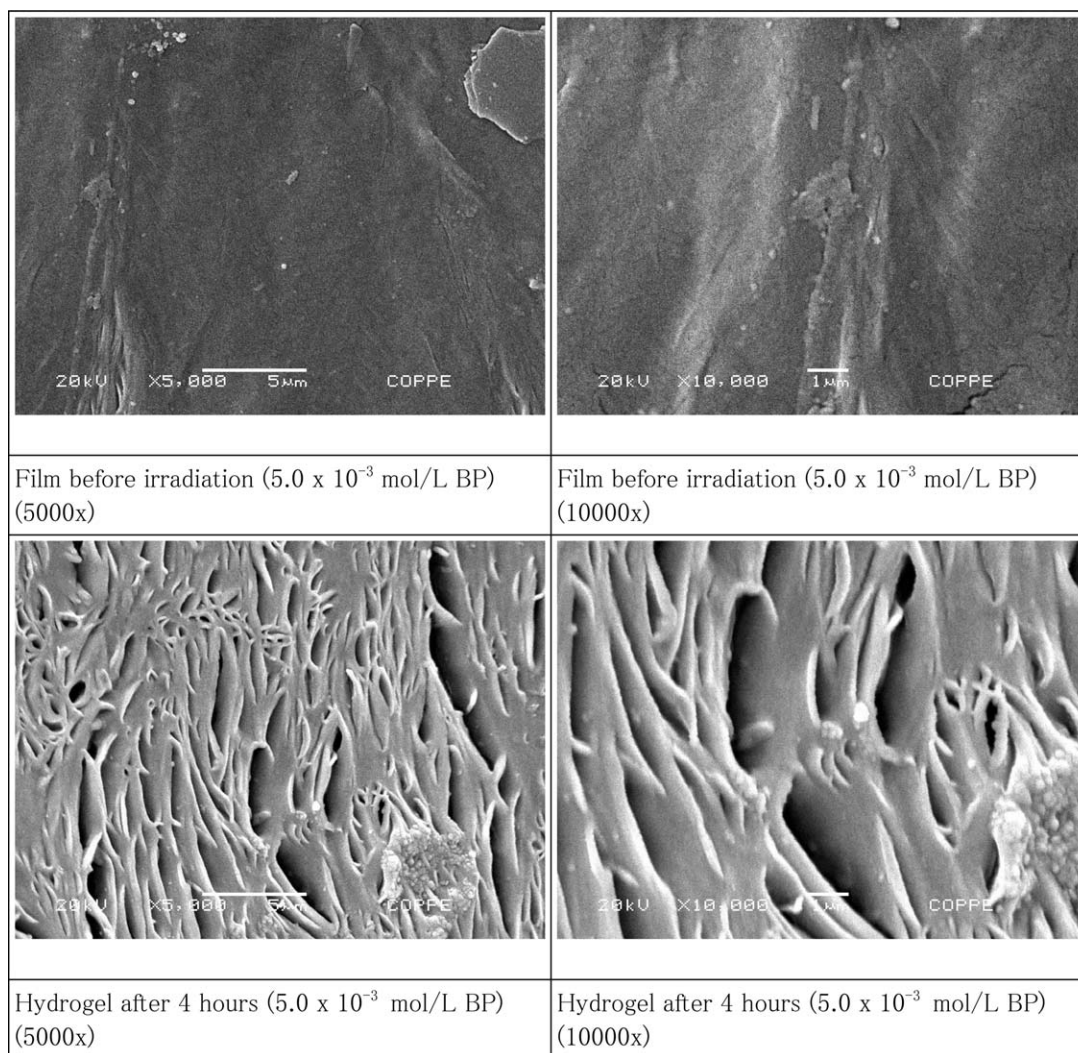


Figure 10. Micrographs of films and hydrogels obtained from 5.0×10^{-3} mol/L of benzophenone.

values of the viscosity, the storage modulus (G') and the loss modulus (G'') of the materials.

The samples which after irradiation remained as liquid solutions were analyzed in order to verify the rotational change in viscosity. The hydrogel samples were analyzed in order to determine the G' and G'' dependency on the frequency of rotation.

Figure 5 shows the variation of the solutions viscosity as a function of the shear rate. The viscosity of the samples drastically decreases after irradiation. However, very small differences were observed with increasing the irradiation time. The experiments were performed in the presence of oxygen and that may interfere in the process of photocrosslinking process. In the study made by Rabek et al. it was observed that the UV degradation of pure PEO causes a decrease in viscosity¹⁸ due to the chains size decrease.

The trapped oxygen would form radical species, originating different transient species and reducing the efficiency of the photocrosslinking process. The PEO has been shown as a polymer sensitive to photo-oxidation. The photosensitivity of polyethers

induced by UV radiation has been shown as a result p of the carbon atoms in α -position to the oxygen atom.⁵

In the process of photo-oxidation, once the PEO radicals are formed, they may react with oxygen to form peroxy radicals which could be stabilized by β -scission leading to the formation of formate and ester groups (Scheme 4).

Figure 6 shows the variation of G' and G'' as a function of frequency for the hydrogels formed with different periods of irradiation. The G' values, for all hydrogels, are higher than the G'' ones over the entire frequency region, suggesting a predominantly elastic solid-like behavior.¹⁹ The G' values increase substantially with increasing the irradiation time while the G'' values increase only slightly. This behavior may be related to the increase in the amount of crosslinking sites in the obtained hydrogels which improves the hydrogels elasticity.

Gel Permeation Chromatography

The changes of molar weights for the systems obtained with low concentrations of benzophenone (1.0×10^{-4} mol/L) were studied by size exclusion chromatography [Figure 7(a)].

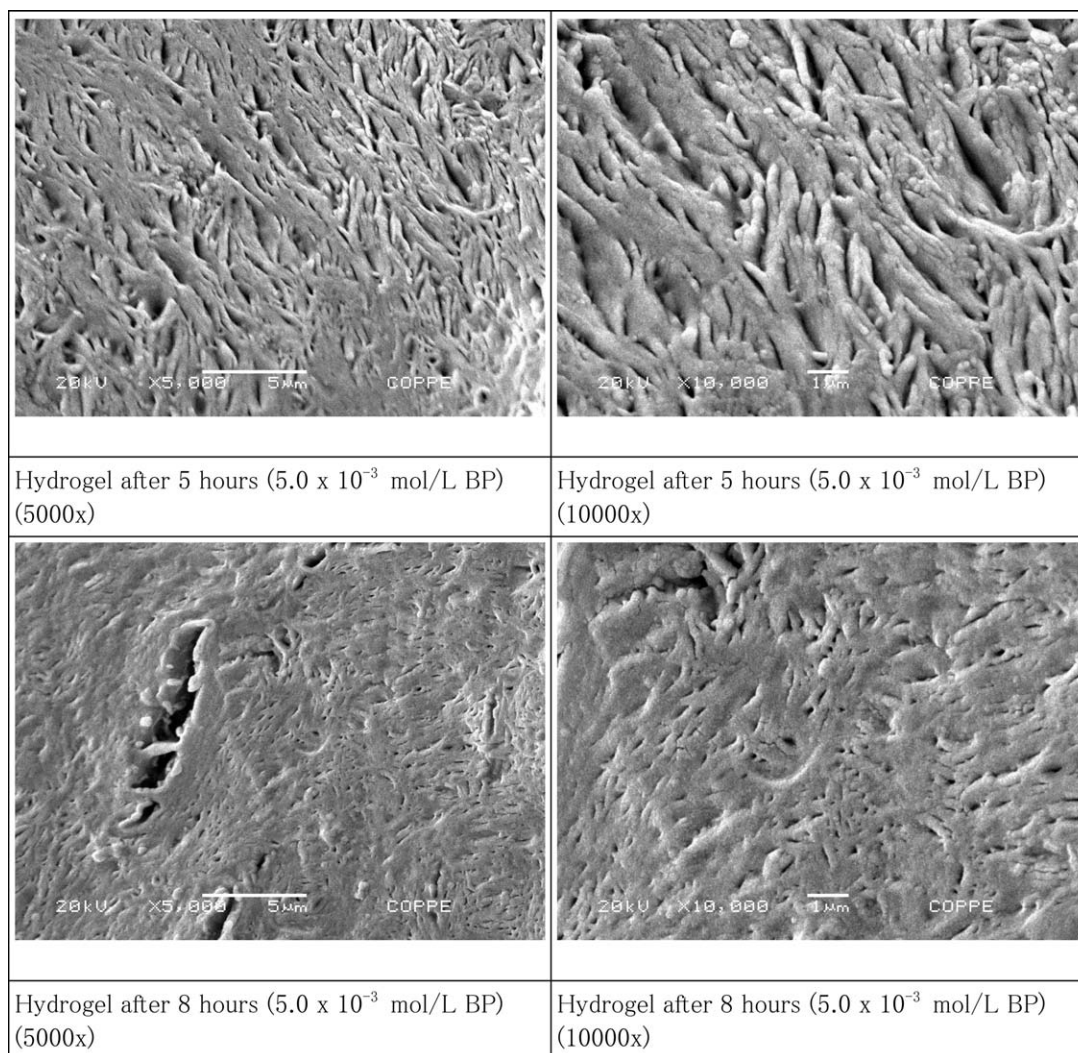


Figure 10. (Continued)

After irradiation, the chromatogram presents a slight displacement of the molecular weight peak distribution to lower weights, suggesting the beginning of the degradation process, which reduces the molecular weight of the system, as noted by Kaczmarek et al.²⁰ Also noticeable is the presence of a new peak in the chromatogram, not observed for non-irradiated PEO, after 16 h of irradiation [Figure 7(b)]. The new peak and the slight displacement of the molar mass distribution to lower weights may be related to the formation of new species resulting from the degradation processes mentioned above.

Thermogravimetric Analysis

The analyses were performed with dried samples from the irradiation process. Figure 8(a) shows the weight loss results for samples before and after irradiation, as a function of temperature and Figure 8(b) shows the results of the derivative of the TGA curves for the irradiated and non-irradiated samples as a function of temperature.

The thermograms show that the degradation of irradiated samples begins slightly earlier i. e., around 175°C after 30 min irradiation

versus 185°C before and that their maximal weight loss occurs also earlier (clearer on Derivative curves) but their degradation kinetics are slower so that they better resist to higher temperatures. For the hydrogels obtained after 30 and 360 min of irradiation the final weight loss occurs at higher temperatures (around 400°C) than the non-irradiated—0 min (360°C), suggesting a higher thermal stability for the hydrogels as noted by Pourjavadi et al.²¹

It was observed in Figure 8(b) that the sample formed by BP and PEO without irradiation shows two temperature peaks of maximum speed of weight loss, while the hydrogels obtained after 30 and 360 min of irradiation show five and seven peaks, respectively. Considering the studied region of weight loss no significant changes were observed. Differences in peak temperatures are probably related to the formation of different degrees of crosslinking.

Scanning Electron Microscopy

The pore structure of the hydrogels was analyzed by scanning electron microscopy. For the materials submitted to this analysis, three parameters were varied: the concentration of

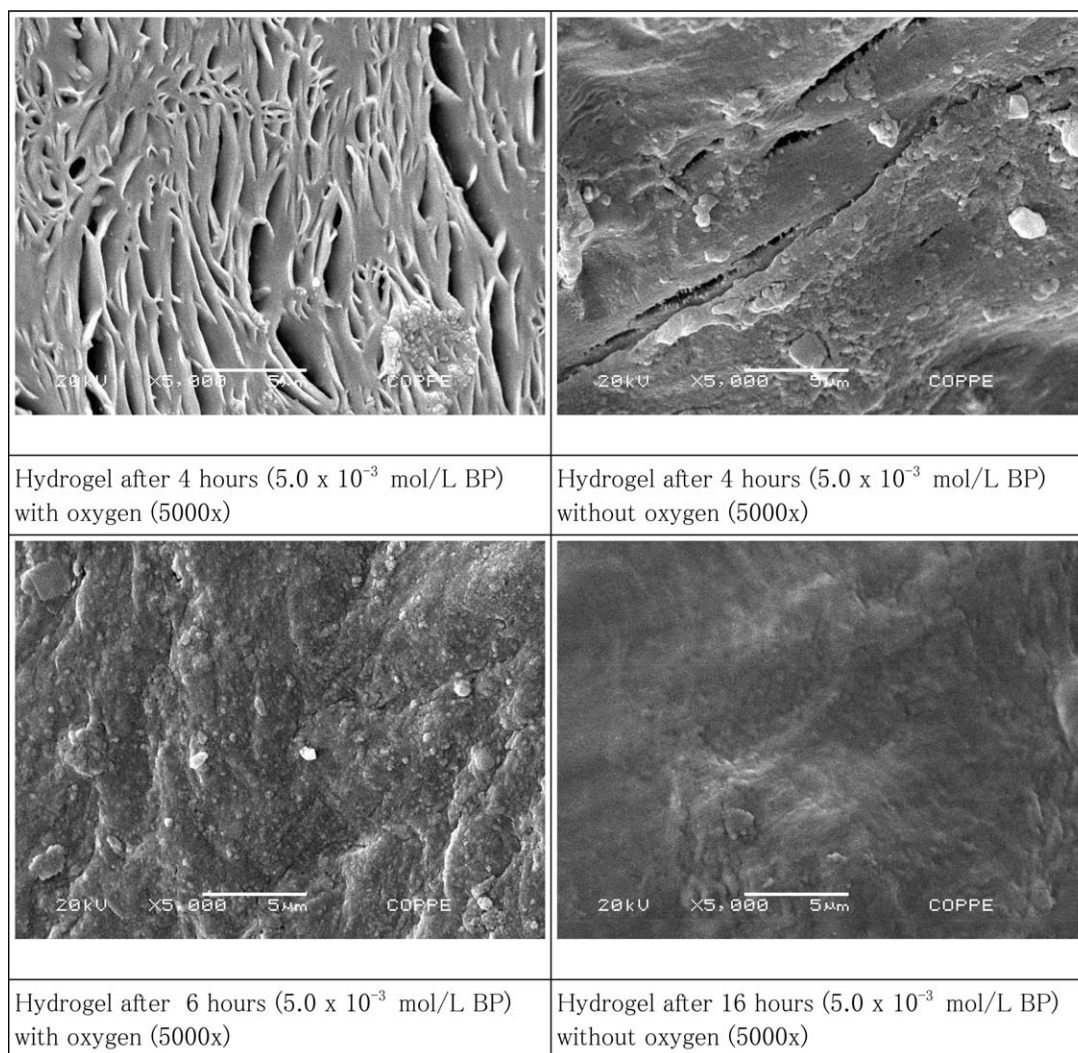


Figure 11. Micrographs of the hydrogels obtained from 5.0×10^{-3} mol/L of benzophenone in the presence and absence of oxygen.

benzophenone, irradiation time, and the presence of oxygen during the irradiation process.

Figure 9 shows micrographs of films and hydrogels obtained using different concentrations of benzophenone, before and after 16 hours of irradiation.

PEO is a polymer with a crystalline structure and it can be observed from Figure 9 that the film formed from the solution of 1.0×10^{-4} mol/L BP presents crystallites, confirming this fact.²² The film obtained from 1.0×10^{-4} mol/L of benzophenone after 16 h of irradiation also shows crystallites, indicating that in these conditions the structure of the film formed after irradiation is very similar to the one of the non-irradiated film. However, increasing the concentration to 5×10^{-3} mol/L BP the crystallites disappear, indicating the formation of crosslinking, since the formation of this type of linkage reduces the degree of crystallinity of the systems.²³

Figure 10 shows micrographs of films and hydrogels obtained from 5.0×10^{-3} mol/L of benzophenone with different irradiation times. It is possible to note the presence of micropores in a micrometer scale. It is also observed that increasing the periods

of irradiation time causes decrease in the number and size of micropores, suggesting that the degree of crosslinking increases with the irradiation time.

Figure 11 shows micrographs of the hydrogels obtained from 5.0×10^{-3} mol/L of benzophenone after 4.0 and 16.0 h of irradiation in the presence and absence of oxygen. On one side, the micropores are observed in the hydrogel obtained with 5.0×10^{-3} mol/L benzophenone with oxygen after 4 h of irradiation whereas these micropores were not observed in the hydrogel obtained in the absence of oxygen after 4 h of irradiation. On the other side, in hydrogels obtained after 16 h of irradiation, both in the presence and absence of oxygen, the micropores were not observed. It is suggested that the increase of irradiation time and the absence of oxygen, increase the degree of crosslinking in such a way that the micropores formed would be too small to be observed by SEM microscopy.

CONCLUSION

PEO-based hydrogels were produced by UV irradiation induced crosslinking of their respective aqueous solution. The

photochemical reaction showed a constant rate of 1×10^{12} L mol⁻¹ s⁻¹, indicating the formation of a complex pair between reactants. The crosslinked PEO was fully characterized by rheological measurements, GPC and SEM. The results showed that the formation of hydrogel depends on the irradiation time, concentration of benzophenone and the presence of oxygen. Within the range of BP concentration studied, it was observed that the chain scission process is favored at low BP concentrations and in the presence of oxygen, although the dominant effect is still crosslinking at higher BP concentrations. The G' value was found to be higher than the G'' suggesting a predominantly elastic solid-like behavior and the SEM results showed the formation of micropores in the hydrogels formed. The results have also shown that there is a potential in the use of UV irradiation of water based systems for shale inhibition and strengthening through hydrogen formation.

REFERENCES

1. Soroush, H.; Sampaio, J. H. B. Paper SPE 101802 Presented at the 2006 SPE Annual Technical Conference and Exhibition, San Antonio, TX, September 24–27, **2006**.
2. Rosa, R. C. R. S.; Rosa, A. L. A.; Farias, S. B.; Garcia, M. H.; Coelho, A. S. Paper SPE 94523 Presented at the SPE Latin American and Caribbean Petroleum Engineering Conference; 2005; p 20–23.
3. Deolarte, C.; Vasquez, J.; Soriano, E.; Santillan, A. Paper SPE 112411 Presented at the 2008 SPE Internatinal Symposium and Exhibition on Formation Damage Control, Lafayette; **2008**; p 13–15.
4. Romero-Zeron, L.; Manolo, F.; Kantzas, A. *Reservoir Evaluation Eng.* **2008**, 439.
5. Hassouna, F.; Morlat-Thérias, S.; Mailhot, G.; Gardette, J. L. *Polym. Degrad. Stab.* **2007**, 92, 2042.
6. Hassouna, F.; Mailhot, G.; Morlat-Thérias, S.; Gardette, J. L. *J. Photochem. Photobiol A* **2008**, 195, 167.
7. Morlat, S.; Gardette, J. L. *Polymer* **2001**, 42, 6072.
8. Stringer, J. L.; Peppas, N. A. *J. Controlled Release.* **1996**, 42, 196.
9. Rosiak, J. M.; Ulanski, P. *Radiat. Phys. Chem.* **1999**, 55, 139.
10. Grollman, U.; Schnabel, W. *Makromol. Chem.* **1980**, 181, 1215.
11. Tsanov, T.; Vassilev, K.; Stamenova, R.; Tsvetano, C. H. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, 33, 2623.
12. Gnanou, J.; Hild, G.; Rempp, P. *Macromolecules* **1984**, 17, 945.
13. Doytcheva, M.; Stamenova, R.; Zvetkov, V.; Tsvetanov, C. H. *Polymer* **1998**, 39, 6715.
14. Doytcheva, M.; Doytcheva, D.; Stamenova, R.; Orahovats, A.; Tsvetanov, C. H.; Leder, J. *J. Appl. Polym. Sci.* **1997**, 12, 2299.
15. Cheng, L.; Shi, W. *Progr. Org. Coat.* **2011**, 71, 355.
16. Lopérgolo, L. C.; Lugão, A. B.; Catalani, L. H. *Polymer* **2003**, 44, 6217.
17. Ulanski, P.; Zainuddin Rosiak, J. M. *Radiat. Phys. Chem.* **1995**, 46, 913.
18. Rabek, J. F.; Linden, L. A.; Kaczmarek, H.; Qu, B. J.; Shi, W. *F. Polym. Degrad. Stab.* **1992**, 37, 33.
19. Malinowska, R. J.; Cvetkovska, M.; Kuzmanova, S.; Tsvetanov, C.; Winkelhausen, E. *Macedonian J. Chem. Chem. Eng.* **2010**, 29, 169.
20. Kaczmarek, H.; Kaminska, A.; Kowalonek, J.; Szalla, A. *J. Photochem. Photobiol. A* **1999**, 128, 121.
21. Pourjavadi, A.; Soleyman, R.; Barajee, G. R. *Starch* **2008**, 60, 467.
22. Winkelhausen, E.; Malinowska, R. J.; Kuzmanova, S.; Cvetkovska, M.; Tsvetanov, C. *World J Microbiol Biotechnol.* **2008**, 24, 2035.
23. Mano, E. B.; Mendes, L. C. *Introdução a Polímeros*; Editora Edgard Blucher, **1999**; 54.