

## Photocrosslinking of Low Molar Mass Poly(ethylene glycol)s

Ki-Chul Hong, Jinhwan Kim, and Jin-Young Bae\*

*College of Applied Chemistry, Polymer Technology Institute, Sungkyunkwan University,  
300 Chunchun-dong, Jangsan-gu, Suwon, Kyunggi-do 440-746, Korea*

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**Abstract :** Crosslinked poly(ethylene glycol)s (PEGs) were prepared by ultraviolet irradiation of low molar mass, liquid PEGs in the presence of benzophenone (BP) as a photoinitiator. The networks obtained have been characterized by DSC, IR, and contact angle measurements, and their water absorption and equilibrium swelling have been examined. The percent of gel formed and degree of swelling of the networks in water were dependent on the amount of BP in the reaction mixture, irradiation time and molar mass of PEG. Gel fraction yield exceeded 84%, and equilibrium swelling in water varied from 49 to 244%.

### Introduction

Poly(ethylene oxide)s (PEOs) (and/or PEGs), which have ethylene oxide linkages in the main chain, are water-soluble polymers of considerable industrial significance (e.g., in medicine, pharmacy, cosmetics, textiles, agriculture, and food industry).<sup>1,2</sup> Crosslinked networks derived from them have also been shown to have a number of applications such as: controlled drug release systems, phase transfer catalysts, membranes and many others.<sup>3</sup> For crosslinking of PEO, various methods can be introduced including chemical and radiation processes. PEOs were crosslinked by  $\gamma$ -irradiation<sup>4,5</sup> or by UV irradiation in the presence of BP as a photoinitiator.<sup>6-8</sup> Chemical crosslinking of PEOs was also reported.<sup>9</sup> Relatively safe and cost-effective UV-induced crosslinking provides significant advantages for many applications over other methods. Although BP and its derivatives can efficiently initiate photocrosslinking of PEO (and acrylate end-capped PEGs), the UV initiated crosslinking of low molar mass PEG has not yet been investigated. Thermal, radiation, and photo-reaction mechanism of high molar mass PEO has been well understood, however, there is much less

information about the photoreaction of PEG. Therefore, we decided to develop a novel photocrosslinking process of low molar mass PEG in order to provide a more convenient method for producing a hydrogel based on crosslinked PEGs.

In this study, we report that relatively robust PEG network films can be obtained by UV initiated crosslinking of low molar mass, liquid PEGs. We also investigated the effects of the amount of BP used in the reaction mixture and the length of PEG segments on crosslink density, gel fraction yield, equilibrium swelling, and the thermal properties of the networks.

### Experimental

**Materials.** The PEGs used in this work were PEG200, PEG400, PEG600, PEG1000, PEG2000, PEG3400 and PEG4600 from Aldrich. Benzophenone (BP, purity > 99%) from Aldrich Chem. Co. was used as a photoinitiator. All other reagents were purchased from commercial sources (Aldrich or Fisher Scientific) and used without further purification unless otherwise noted.

**Preparation of PEG Network Films.** The reaction conditions for the photopolymerization of various molecular weight PEGs is shown in Table I, and only a representative example (i.e.,

\*e-mail : jinbae@yurim.skku.ac.kr

**Table I. Characteristics of PEG Networks**

| Entry | Sample           | Gel Fraction (%) | Contact Angle (degree) | $T_g$ (°C) |
|-------|------------------|------------------|------------------------|------------|
| 1     | unreacted        | -                | 12.0                   | 17         |
| 2     | PEG200/1 wt% BP  | -                | 13.0                   | -          |
| 3     | PEG200/3 wt% BP  | 20               | 15.4                   | 27         |
| 4     | PEG200/5 wt% BP  | 45               | 16.3                   | 28         |
| 5     | PEG200/10 wt% BP | 53               | 18.5                   | -          |
| 6     | PEG200/15 wt% BP | 74               | 19.5                   | 37         |
| 7     | PEG200/20 wt% BP | 80               | 22.5                   | -          |
| 8     | PEG200/25 wt% BP | 84               | 26.5                   | 31         |
| 9     | PEG400/5 wt% BP  | 35               | 19.3                   | -          |
| 10    | PEG600/5 wt% BP  | 24               | 21.5                   | -          |
| 11    | PEG1000/5 wt% BP | 22               | 22.0                   | -          |
| 12    | PEG2000/5 wt% BP | 20               | 23.5                   | -          |
| 13    | PEG3400/5 wt% BP | 16               | 25.0                   | -          |
| 14    | PEG4600/5 wt% BP | 13               | 27.5                   | -          |

PEG200) is given here. PEG200 (1 g) was added under stirring to a methanol (3 mL) solution containing BP (0.05 g). The solution was cast onto a glass plate or a 25 × 25 mm rectangular aluminum foil, and the solvent was allowed to evaporate in air prior to irradiation. The irradiation was carried out with a KIIC-1019 high pressure 400 W mercury lamp (Joil Illumination Company) at 12~13 cm distance from the light source. The duration of irradiation was ~13 h. The thickness of the network film obtained was measured with a micrometer and varied between 100 and 120 μm.

**Sample Characterization.** The thermal characterization of the prepared sample was carried out by Differential Scanning Calorimeter (DSC) with a heating rate of 10°C/min on a DSC TA 2910 instrument. Samples of 7~8 mg were run in a nitrogen atmosphere over a temperature range of -90 to 130°C. Indium ( $T_m = 156.6^\circ\text{C}$ ) was used for temperature calibration. Thermal stability of the sample was monitored by a TGA TA 2910 instrument. IR spectra of the sample were recorded on a Unicam Mattson 5000 FT-IR spectrometer.

**Gel Fraction Determination:** The irradiated PEG samples were weighed and then extracted with distilled water for 24 h. After extraction they were dried under vacuum and weighed. The gel fraction was simply calculated by ratio of initial weight polymer to weight of extracted polymer.

**Measurements of Water Absorbency:** The equilibrium degree of swelling (ES) was determined at room temperature. Dry samples were equilibrated in distilled water for at least 180 h, then removed from the solvent, blotted with filter paper, and weighed. ES was simply calculated by ratio of initial weight polymer to weight of extracted polymer.

**Contact Angle Measurements:** The irradiated PEG samples on the glass plate were dried under vacuum for 24 h before measurements. Contact angle of the samples was measured using a Contact Anglemeter (Goniometer Type, G-1). The data reported in Table I represent average value of 2 repeats.

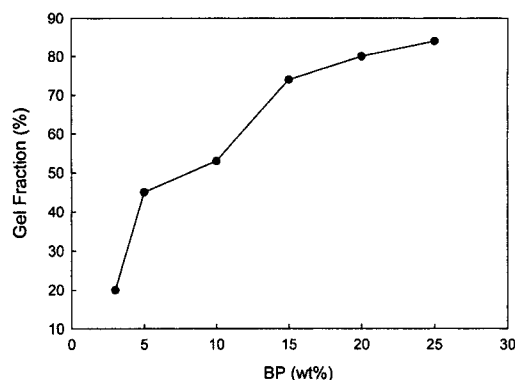
## Results and Discussion

Photocrosslinking of PEGs was carried out in the presence of BP as a photoinitiator. BP was the initiator of choice because of its high hydrogen abstraction property. The ratio between PEG and BP was varied in the range of 1:0.01 to 1:0.25 weight PEG per weight BP. The thickness of the prepared network films was varied between 100 and 120 μm. It was found that PEG undergoes a crosslinking process when irradiated for relatively long periods of time (~13 h) with short wavelength UV light to form a dimensionally stable network film. The degree of crosslinking could be

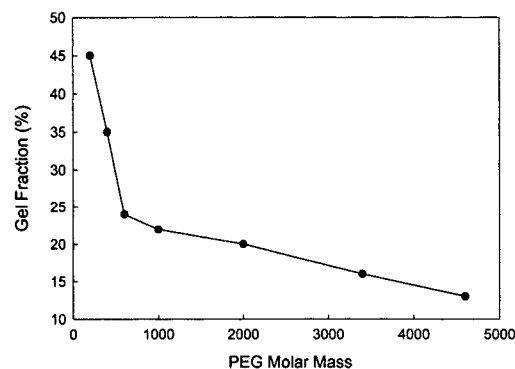
controlled by tuning the irradiation time. But, a completely insoluble network was obtained when irradiated for 24 h. Extending the irradiation time over 13 h did not provide greater amounts of gel fraction.

Network films of PEG were characterized by DSC measurement and the corresponding data of the network are presented in Table I. No endothermic peak appears in a temperature range from  $-100$  to  $120^{\circ}\text{C}$ . DSC traces showed glass transition temperatures ( $T_g$ ) that increased regularly with the percentage of BP in the solution. It should be pointed out that the irradiation of PEG only without BP added results in a totally unaffected polymer that does not change solubility. From these DSC data it appears that the crosslinked PEG is an amorphous polymer. In particular, the second scan of PEG200 networks shows a  $T_g$  at  $17\sim 31^{\circ}\text{C}$ . In the first scan of most samples, broad endothermic peak, which is most likely due to evaporation of residual water, was observed. The disappearance of a  $T_g$  for higher amount of BP is probably due to the inhibition of polymer segmental motions by the completely cross-linked structure of the polymer. From the typical TGA analysis of PEG network system, the material seems to be stable up to  $200^{\circ}\text{C}$  under nitrogen.

The crosslinked networks were also characterized after irradiation by first determining the percentage of gel formed during the UV light exposure and successively measuring their swelling characteristics. Gel fraction was measured gravimetrically first by weighing irradiated samples of PEGs, successively by immersing them in water and methanol, respectively to extract un-crosslinked part (soluble fraction) of the film, and eventually by weighing the dry extracted film (Table I). In order to investigate whether the crosslink density depends on the amount of BP used, several samples of different composition were crosslinked under identical irradiation conditions. The data shown in Table I and Figure 1 indicate that increasing the amount of BP in the reaction mixture gives a higher value for gel fraction and degree of crosslinking. PEG200/25 wt% BP system gave the highest gel fraction yield of 84% (entry 8). This is probably due to the increased



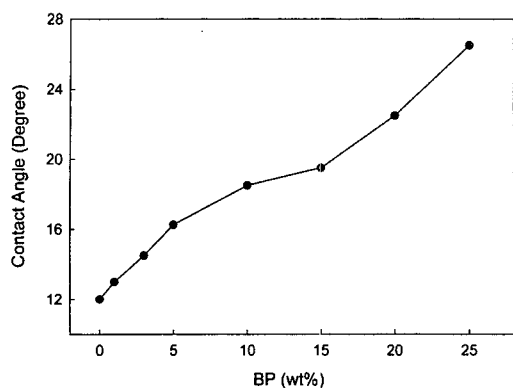
**Figure 1.** Dependence of the gel fraction on the BP content of the PEG200 network.



**Figure 2.** PEG/5 wt% BP networks as a function of PEG molar mass.

amount of active PEG macroradicals formed with increasing BP content.

The molar mass dependence of the efficiency of UV-irradiated crosslinking of PEG is shown in Table I and Figure 2. It has been reported that with regard to PEO network percent of gel formed usually increases with larger molar mass of PEO.<sup>10</sup> However, in our experiments, the gel fraction yield falls with the increase of molar mass of PEG. The amount of the insoluble PEG/5 wt% BP mixture upon irradiation decreases going from 45% for PEG of 200 Da to 13% for PEG of 4600 Da (Table I, entries 4 and 14). It is likely that the proximity of hydroxy groups between PEG components in the sample is a very important factor for crosslinking reactions upon irradiation. We suggest that efficient photochemical reactions between the two PEG chains in the sample are not possible

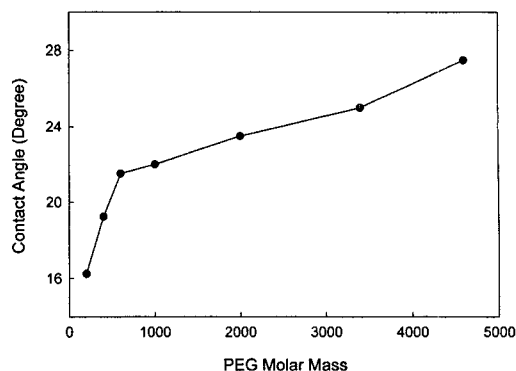


**Figure 3.** Contact angles of PEG200 networks as a function of BP content.

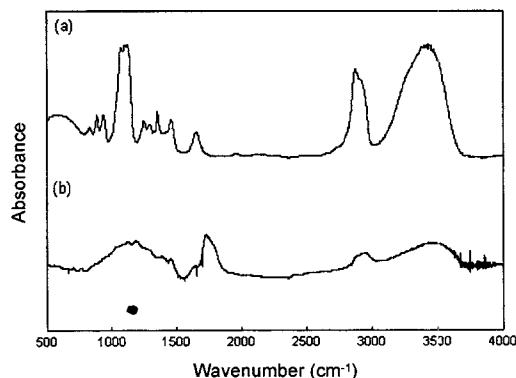
if the two partners of relatively high molar mass in the mixture are physically segregated in the different domains. Lower molar mass PEG favoured better crosslinking, since the greater mobility of the polymer segments provides a increased number of mutual contacts. On the other hand, higher molar mass PEG chains are entangled to render the active macroradical formation difficult.

Contact angle measurements of the network films were carried out for surface analysis of the prepared samples. Table I and Figure 3 show contact angle values of PEG200 networks that increased with the percentage of BP in the solution, that is, the hydrophobicity of PEG200 network increases as the crosslink density increases. This result implies that in addition to the recombination reaction of two macroradicals producing carbon-carbon bonds between PEG main chains, the hydroxy units of PEG are also consumed during UV irradiation, possibly due to the onset of hydrogen abstraction reactions both from ethylene oxide group and hydroxy group of PEG to form highly reactive ethylene oxide radical and O ( & H·) radicals. Figure 4 shows contact angle values of PEG/5 wt% BP samples that increased with the molar mass of PEG. This result is most probably due to the increasing concentration of the hydrophobic part in the networks.

IR spectroscopy provides more information on the changes that occur upon irradiation. The characteristic band of the hydroxy group of PEG appears at 3500  $\text{cm}^{-1}$ . The band decreases with increasing irradiation times. This confirms that the



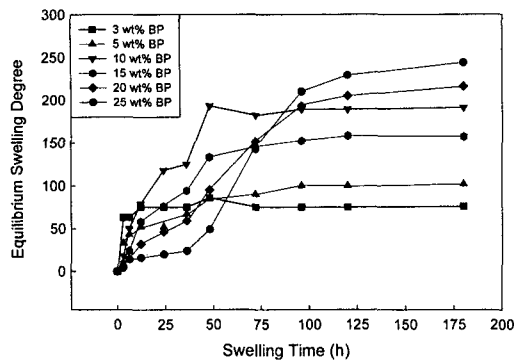
**Figure 4.** Contact angles of PEG/5 wt% BP networks as a function of PEG molar mass.



**Figure 5.** IR spectra of PEG networks: (a) uncured PEG200 and (b) PEG200/5 wt% BP.

hydroxy groups are consumed during illumination, which may indicate that the hydroxy group takes part in the network formation by hydrogen abstraction (not only from the  $\text{CH}_2$  groups but also from the hydroxy group) to form a new, not well-defined, O-C bond. Moreover, the reaction of the ketyl radicals with O· radical species present in the system also may lead to the consumption of the hydroxy groups that are responsible for the increase of contact angles with increasing the amount of BP in the solution. However, the presence of remaining hydroxy groups on the crosslinked PEG networks is detected by the IR spectra of the crosslinked films (Figure 5).

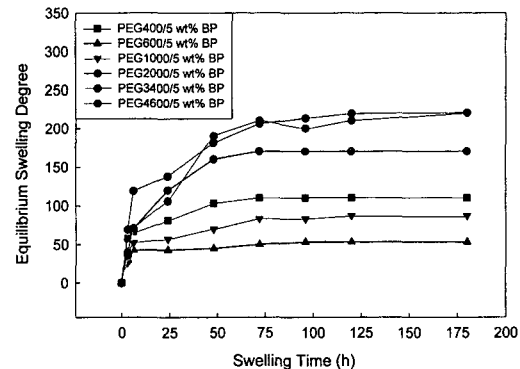
The crosslinked PEG networks were found to very efficiently swell when immersed in water. The BP content and the molar mass of PEG dependence on equilibrium swelling were examined.



**Figure 6.** Equilibrium swelling degree of PEG200 networks as a function of swelling time with different BP content.

Figure 6 shows the equilibrium swelling degree of PEG200 networks in water as a function of swelling time and BP content. All samples except PEG200/3 wt% BP and PEG200/5 wt% BP reached an equilibrium state by swelling within 100 to 120 h, and the degree of swelling increased with the higher BP content. Particularly, after 180 h of equilibrium swelling PEG200/25 wt% BP system gave the highest ES value of 244%. It has been generally accepted that increased number of crosslinks between PEO chains (as obtained by using high amount of chromophore) is able to decrease the swelling ratio of the irradiated PEO.<sup>10</sup> This decreasing tendency results from the increasing degree of crosslinking reaction as BP content increases and the expected denser network structure. However, in our experiments the opposite trend was observed. This strongly suggests that when the network contains lower BP content (i.e., lower crosslink density), the unreacted soluble fraction of the network was washed away during soaking procedure resulting in low equilibrium swelling. On the contrary, an increase of BP in the reaction system brings about the increase in the crosslink density, which is accompanied by a increase in the swelling capability.

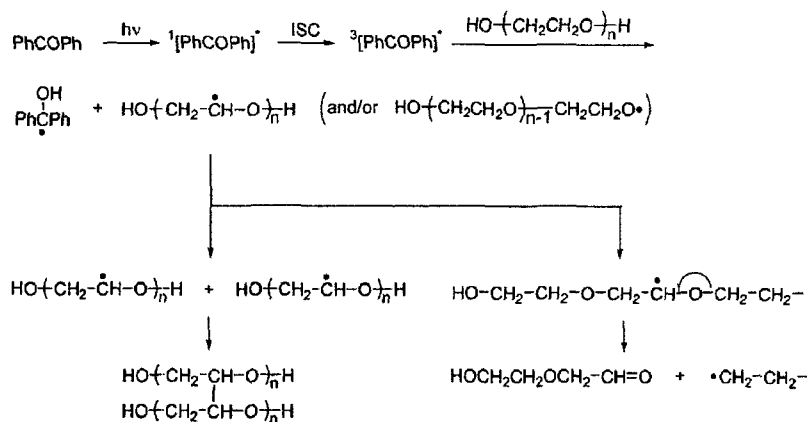
A general attempt to improve the wet strength of the hydrogels is the introduction of a hydrophobic component; however, this reduces the hydrophilicity and usually results in a drop in the equilibrium water content. However, in our case, this trend was not observed. Figure 7 shows the



**Figure 7.** Equilibrium swelling degree of PEG networks as a function of swelling time with different PEG molar mass.

equilibrium degree of swelling of PEG networks in water as a function of molar mass of PEG. The degree of swelling increased with increasing molar mass of PEG. It was thought that ES increased because crosslinking density decreased with increasing molar mass of PEG. However, hydrophilicity of a slightly crosslinked PEG network increased. The increase of ES values when increasing the molar mass of PEG in water is probably caused by the higher percent of less crosslinked fraction in the sample. From the gel fraction measurements, the networks of high molar mass PEG seem to contain a loosely crosslinked structure, while lower molar mass PEG provides a densely crosslinked amorphous fraction. These results imply that since the water absorption capacity is closely associated with the microstructure of the network, crosslinked polymers obtained from higher molar mass PEG have lower crosslink density and are more sensitive to plasticization by water.

The photochemical process of UV-induced crosslinking of PEG is most likely to be similar to that of PEO.<sup>11,12</sup> Based on the above studies of IR & contact angle measurement, a similar mechanism in the photoinitiated crosslinking of PEG can be proposed in Scheme I. When the photoinitiator, BP, absorbs a photon, it is excited to the singlet state and then rapidly relaxes to the more stable triplet state through intersystem crossing (ISC). This can abstract hydrogen from the PEG chains to give the formation of ethylene oxide



**Scheme I.** A proposed mechanism of BP photoinitiated crosslinking of PEG.

radicals in both PEG components proceeding to the reduction of BP and PEG chain radical formation. The two polymer radical chains combine with each other to produce carbon-carbon bonds between the main chains. However, a hydrogen abstraction from hydroxyl groups during the UV-induced crosslinking of PEG also can not be excluded.

## Conclusion

In this paper, novel PEG networks were obtained by UV irradiation of low molar mass PEGs containing BP initiator. The microstructure, water absorption and equilibrium swelling of the networks are strongly affected by the BP content and the molar mass of PEG. The percent gel formed increases with increasing the amount of BP found in the sample. The degree of crosslinking of the irradiated PEG/BP mixtures is the factor dominating the swelling capability of these materials, especially when higher molar mass PEGs are irradiated.

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## References

- (1) J. D. Andrade, *Hydrogels for Medical and Related*

*Application*, ACS Symposium Series 31, American Chemical Society, Washington D. C., 1996.

- (2) D. A. Allen, *Modern Superabsorbent Polymer Technology*, F. L. Buchholz and A. T. Graham, Eds., John Wiley & Sons, New York, 1998.
- (3) S. W. Shalaby, C. L. McCormick, and G. B. Butler, *Water-soluble Polymers*, ACS Symposium Series 467, Washington, 1991.
- (4) T. Tsanov, K. Vassilev, R. Stamenova, and Ch. Tsvetanov, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 2623 (1995).
- (5) P. A. King and N. Y. Warwick, U.S. Pat. 3,264,202 (1966).
- (6) S. E. Sloop, M. M. Lerner, T. S. Stephenes, A. L. Tipton, D. G. Paull, and J. D. Stenger-Smith, *J. Appl. Polym. Sci.*, **53**, 1563 (1994).
- (7) M. Doytcheva, D. Dotcheva, R. Stamenova, A. Orahovats, C. Tsvetanov, and J. Leder, *J. Appl. Polym. Sci.*, **64**, 2299 (1997).
- (8) M. Doytcheva, R. Stamenova, V. Zvetkov, and Ch. B. Tsvetanov, *Polymer*, **39**, 26 (1998).
- (9) J. Gnanon, G. Hild, and P. Rempp, *Macromolecules*, **17**, 945 (1984).
- (10) F. Minto, M. Gleria, A. Pegoretti, and L. Fambri, *Macromolecules*, **33**, 1173 (2000).
- (11) N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cumming Co., Inc., Menlo Park, CA, 1978.
- (12) J. F. Rabek, *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*, John Wiley & Sons, New York, 1987.