

Ultraviolet-Induced Crosslinking of Solid Poly(ethylene oxide)

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ABSTRACT: Poly(ethylene oxide) (PEO) of molecular weight from 200,000 to 2,000,000 was crosslinked by exposure to ultraviolet radiation with a high-pressure 150 W mercury lamp. Photochemical crosslinking of PEO proceeds in the presence of photoinitiators such as benzophenone and acetophenone which act as a hydrogen-abstracting agent. Gel fraction yield exceeds 90%, and the number-average molecular weight between crosslinks determined by equilibrium swelling in chloroform varies from 3,000 to 100,000. The degree of crosslinking can be controlled by changing the irradiation temperature. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2299–2307, 1997

Key words: poly(ethylene oxide); photocrosslinking

INTRODUCTION

Poly(ethylene glycols) and poly(ethylene oxides) (PEOs) are fascinating groups of nonionic water-soluble materials with great industrial significance. Crosslinked polymers derived from them have also been shown to have a number of applications (i.e., wound dressings,¹ controlled-release drug systems,^{2,3} phase transfer catalysts,⁴ semi-permeable membranes,⁵ solid electrolytes for batteries,⁶ and many others). Crosslinked PEO was first obtained as a product of γ -irradiation of degassed dilute aqueous solutions.⁷ Later, methods based on chemical crosslinking were suggested.⁸ Recently it has been shown that PEO can be successfully crosslinked by irradiation with ultraviolet (UV) light with or without benzophenone (BP) as photoinitiator.⁹ In the latter study, only a few and not-well-reproducible data on UV-induced crosslinking of high-molecular-weight PEO ($M_w = 5 \times 10^6$) in the presence of 0.5 mol % BP were

reported. The assumption of these authors that the photocrosslinking is the result of the photolysis of the polyether seems unconvincing.

The ease, relative safety, and low cost of UV-induced crosslinking should provide significant advantages for many applications over other methods. We considered it worthwhile to study the photocrosslinking process of PEO in more detail in order to provide a practical method for producing well-defined networks. The purpose of the present study was to examine the role of different factors, such as type of photoinitiator, its concentration, duration of irradiation and temperature, molecular weight of the polymer, and others, on the efficiency of UV-induced crosslinking of PEO.

EXPERIMENTAL

Materials and Solvents

BP puriss. (Koch Light Laboratories, Ltd.) and acetophenone (AP) (Laborchemie-Apolda; purity > 99%) were used without further purification. Benzoin methyl ether (BME; Aldrich) and benzoin (Bn; Fluka) were recrystallized from ethanol.

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4,4-Bis(dimethylamino)benzophenone (Michlers ketone, MK) was purified by repeated crystallization from ethanol prior to use. Darocur® 1173 [2-hydroxy-2-methyl-1-phenylpropan-1-one], Darocur® 953 [1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one], Darocur® 1116 [1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one], and Darocur® 1664 [mixture containing 2-(1-methylethyl)-9H-thioxanthen-9-one and 2-hydroxy-2-methyl-1-phenylpropan-1-one] (Ciba) were used as received. Methylene chloride, acetonitrile, and chloroform of analytical grade (Fluka) were used as received. Technical-grade methylene chloride from ICI was used for extractions only. Commercial PEOs of various molecular weights (Polyox® 205, Polyox® 1105, Polyox® N-12 K, Polyox® N-60 K, Polyox® COAG, and Polyox® 308; Union Carbide Corp.) were used without further purification.

Sample Preparation

Preparation of PEO Samples by Casting from Solution

PEO (3 g) was added under intensive stirring to a CH₂Cl₂ (100 mL) solution containing the dissolved amount of photoinitiator. The homogeneous, viscous solution was cast onto a glass Petri dish, kept in the dark, and allowed to evaporate in air. The samples were subjected to additional drying for 1 h under vacuum at room temperature prior to irradiation. The thickness of the sample was measured with a micrometer.

Preparation of PEO Samples by Press-Molding

A mixture (1.6 g) of PEO (Polyox® N-12 K) and BP was thoroughly homogenized and spread on a dismountable mold of cylindrical form. The mold was pressed between two heated brass plates at 120°C for 5 min under a pressure of 150 kG/cm². The mold was allowed to cool under pressure to ambient temperature.

UV Irradiation of PEO Samples

The irradiation was carried out with a TQ 150 Original Hanau high-pressure 150 W mercury lamp provided with a quartz tube and a cooling jacket. The UV lamp, jacketed and water-cooled, was put in a glass vessel equipped with another thermostatted jacket. The PEO sample was fixed on the inner side of the glass wall. To avoid quenching by oxygen, the irradiation was carried out under constant flow of argon or in a dynamic

vacuum of 5×10^{-2} Torr. The highest intensity of the UV lamp was found to be emitted in a 4–5-cm zone around the light source. Larger samples revealed a lower degree of crosslinking outside of this zone. Therefore, 30-by-80-mm rectangular samples for irradiation were cut out of the originally prepared circular ones.

Sample Characterization

Gel Fraction Determination

The irradiated PEO samples were weighed and then extracted with methylene chloride in a Soxhlet extraction apparatus for 24 h. After extraction they were dried to constant weight under vacuum and weighed. The gel fraction (GF) equals (weight of extracted sample divided by initial weight) $\times 100\%$.

Swelling

The equilibrium degree of swelling (ES; weight of swollen sample divided by weight of dry sample) was determined at room temperature. Dry disks from the crosslinked sample were equilibrated in distilled water and chloroform for at least 72 h, removed from the solvent, blotted with filter paper, and weighed. Then they were dried to constant weight under vacuum and weighed again.

Estimation of Crosslink Density

The crosslink density in a polymer network is inversely proportional to the number-average molecular weight between crosslinks (M_c). According to the Flory–Rehner model,¹⁰ M_c can be estimated from the equation

$$\frac{1}{M_c} = \frac{2}{M_n} \frac{[\ln(1 - V_{2S}) + V_{2S} + \chi V_{2S}^2]}{V_1 \rho_2 \left(V_{2S}^{1/3} - \frac{V_{2S}}{2} \right)}$$

where V_{2S} , V_1 , and ρ_2 are the polymer volume fractions in the swollen gels at equilibrium, the molar volume of solvent, and the polymer density, respectively. The Flory–Huggins theory assumes random mixing of solvent and polymer segments. Thus a highly hydrogen-bonding solvent, such as water, is not suitable for measuring M_c by swelling because there are strong, orientation-dependent interactions between water molecules and polymer chains, as well as water-structuring effects. The thermodynamic properties of such systems will deviate from those predicted by the

Flory–Huggins theory. To diminish this deviation we used chloroform because it is a poor hydrogen-bonding solvent as well as a good solvent for PEO. The Flory–Huggins theory defines χ as a residual free-energy function, which permits its separation into enthalpic and entropic contributions:

$$\chi = \chi_H + \chi_S$$

According to the regular solution theory by Hildebrand and colleagues¹¹ and the Bristow and Watson¹² semiempirical equation, the equation for the interaction parameter becomes

$$\chi = \frac{V_1}{RT} (\delta_s - \delta_p)^2 + 0.34$$

The solubility parameter of chloroform is 9.3 (cal/cm³)^{1/2}.¹³ The solubility parameter of PEO is 10.3 (cal/cm³)^{1/2}.¹⁴ The calculated interaction parameter χ for the system CHCl₃-PEO is 0.477.

Differential Scanning Calorimetry (DSC) Measurements

The DSC curves were obtained with a Perkin–Elmer DSC-2 thermal analysis system at a stan-

	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_p \times 10^{-3}$	(RT)	\bar{M}_w / \bar{M}_n
0	1448	336	663	(14.07)	4.3
1	1409	354	514	(14.27)	4.0
2	811	122	547	(14.97)	6.7
3	587	49	61	(15.87)	11.9

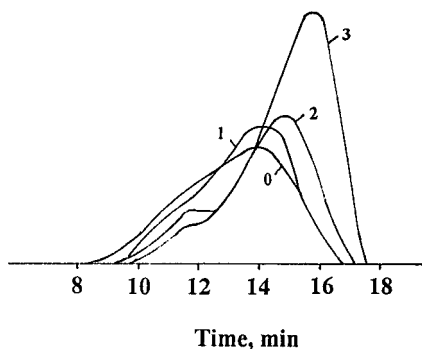


Figure 1 GPC curves of PEO samples containing BP. 0: pure PEO ($M = 1 \times 10^6$); 1: 2 days after preparation; 2: 4 days after preparation; 3: 6 days after preparation.

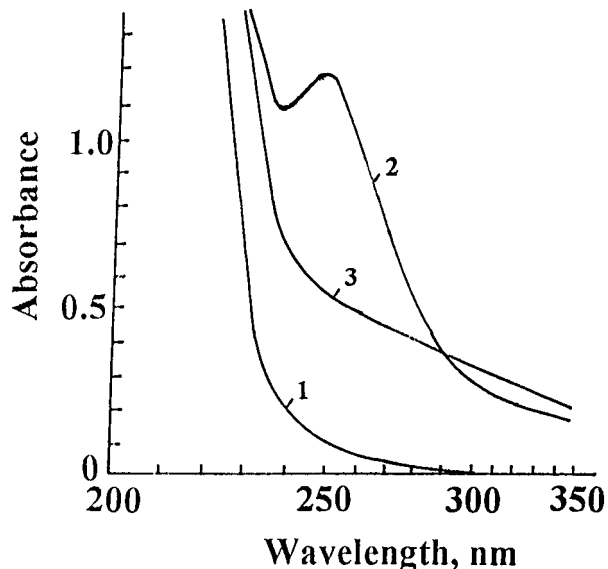


Figure 2 UV spectra of photocrosslinked PEO in acetonitrile. [BP]/[–EO–] = 1×10^{-2} . 1: pure solvent; 2: prior to extraction; 3: after extraction.

standard heating and cooling rate of 10°C min⁻¹. Samples of about 12 mg were run in an argon atmosphere over a temperature range of –60°C to 120°C. Indium ($T_m = 156.6^\circ\text{C}$) was used for temperature calibration.

Gel Permeation Chromatography (GPC) Measurements

M_w , M_n , and M_w/M_n values of Polyox samples were determined with a Waters gel permeation chromatograph equipped with a differential refractometer R-401, UV detector M-440, and one column with Ultrahydrogel 2000. Water/acetone (80 : 20) was used as eluent at a flow rate of 0.7 mL/min at ambient temperature.

UV/visible absorption spectra were recorded on a Specord UV/VIS Carl Zeiss Jena spectrometer. Optical micrographs were taken using a Reichert-Zetopan polarizing microscope.

RESULTS AND DISCUSSION

The samples for UV irradiation in the form of films were prepared from methylene chloride solutions of PEO. Methylene chloride was the solvent of choice because of its volatility and solubility properties. The duration of irradiation was usually 40 min, the initial 10 min being necessary for reaching the standard emission of the UV lamp.

Table I Effect of the Type of Photoinitiator on Crosslinking Efficiency

Photoinitiator	Thickness (μm)	Gel Fraction (%)	Equilibrium Swelling		
			H ₂ O	CHCl ₃	M_c in CHCl ₃
BP	160	90.3	4.1	5.3	8,000
	170	92.3	3.7	3.9	3,500
	190	92.1	4.0	5.4	8,000
	200	91.7	4.4	5.3	8,000
Bn	210	90.0	4.7	7.2	17,000
	250	90.3	4.9	6.9	15,000
	250	90.5	5.4	8.3	23,000
AP	240	75.3	11.8	21.5	110,000
	250	74.8	12.7	22.2	113,000
MK	230	3.7	—	—	—
	250	5.8	—	—	—
BME	250	77.0	10.3	13.6	60,500
	250	80.4	10.2	12.7	54,000
Darocur [®] 1173	210	88.0	7.0	11.8	48,000
Darocur [®] 953	290	68.3	13.8	36.1	157,000
Darocur [®] 1116	250	65.0	25.0	27.5	135,000
Darocur [®] 1664	230	74.5	12.7	13.8	60,500

UV irradiation under a flow of argon at $[\text{PI}]/[-\text{EO}-] = 5 \times 10^{-3}$. Samples from Polyox N-12 K, $M_v = 1 \times 10^6$, $M_n = 4.0 \times 10^5$. Irradiation time = 40 min. BP, benzophenone; Bn, benzoin; AP, acetophenone; MK, Michler's ketone; BME, benzoin methyl ether; PI, photoinitiator.

The thickness of the film samples varied between 200 and 250 μm .

The stability of PEO samples containing photoinitiator was checked by GPC analysis of films prepared from PEO with $M = 1 \times 10^6$ and 5×10^{-3} mol/mol BP. The GPC chromatograms presented in Figure 1 indicate that this PEO mixture underwent a rapid degradation in the course of a week. Two days after preparation of the films the decrease in molecular weight was still insignificant, but by the fourth day a considerable degradation was observed. For this reason, precautions were taken to avoid the undesired structural deterioration of the PEO–initiator samples: they were irradiated immediately after preparation or stored in the dark.

The first set of UV-irradiation experiments was conducted under vacuum. A dynamic vacuum of 5×10^{-2} Torr was found to be sufficient for oxygen removal and efficient crosslinking. Later UV-irradiation experiments were conducted in an inert atmosphere (under argon) for convenience. Most of the crosslinking experiments were carried out in the presence of BP as a photoinitiator. In order to remove BP and the photoproducts arising from it, as well as to remove the soluble (sol) fraction after irradiation, the samples were subjected to extraction for 24 h with CH₂Cl₂. Extending the

extraction time over 24 h did not afford greater amounts of sol fraction.

UV spectra of films swollen in acetonitrile before and after extraction with CH₂Cl₂ were taken in order to determine whether covalently bonded BP is present in the crosslinked polymer (Fig. 2). After extraction of the irradiated sample, no absorption band at 254 nm for the π, π^* electronic

Table II Crosslinking of PEO Film Samples Exposed to UV Irradiation from One Side Only or From Both Sides

Irradiation Conditions	Gel Fraction (%)	Equilibrium Swelling	
		H ₂ O	CHCl ₃
I and II irradiation— one side exposed to UV	92.0	5.0	6.9
I irradiation— one side and II irradiation— opposite side exposed to UV	93.9	4.9	8.2

UV irradiation under a flow of argon at $[\text{BP}]/[-\text{EO}-] = 5 \times 10^{-3}$. Samples from Polyox N-12 K, $M_v = 1 \times 10^6$, $M_n = 4.0 \times 10^5$. Irradiation time = 40 min; thickness: 250 μm .

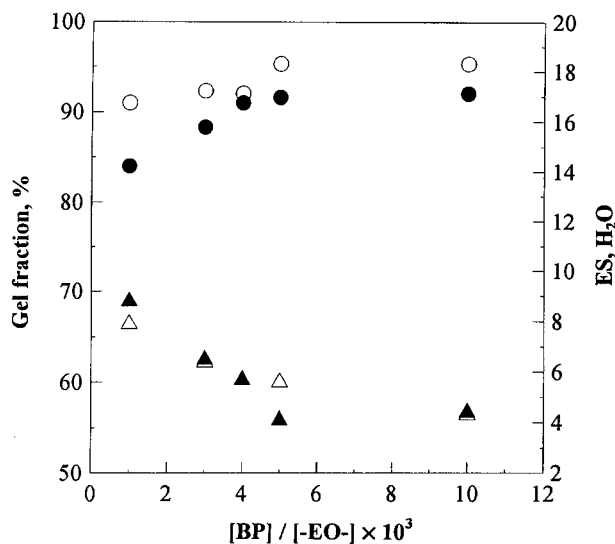
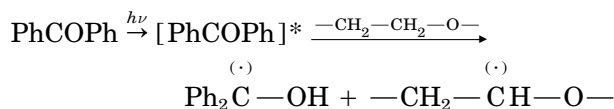


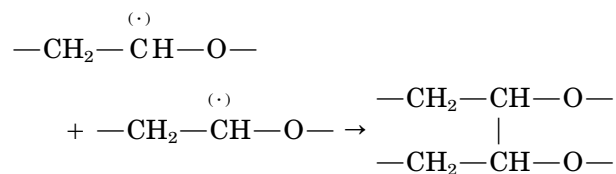
Figure 3 Effect of BP concentration on crosslinking efficiency. Samples from Polyox N-12 K, $M_v = 1 \times 10^6$, $M_n = 4.0 \times 10^5$. Irradiation time = 40 min. GF, %: (○) in vac, (●) in argon; ES, H₂O: (△) in vac, (▲) in argon.

transition of an aromatic moiety was observed, implying the absence of BP or its photoproducts.

Photochemical crosslinking results from hydrogen atom abstraction from the macromolecule of PEO. BP was chosen because of its high hydrogen-abstraction efficiency. The photochemical processes which it undergoes are presently well understood. On photon absorption, BP undergoes several photophysical processes, affording an n, π^* triplet state which then proceeds to reduction of BP and PEO radical formation¹⁵:



Photocrosslinking occurs mainly by recombination reaction of two macroradicals producing carbon-carbon bonds between the main chains:



BP is a good hydrogen-abstracting agent because of several of its characteristics: (a) high intersystem crossing efficiency ($k_{T1-S1} = 10^{10} \text{ s}^{-1}$); (b) high triplet energy (69 kcal/mol); and (c) long triplet lifetime ($k_{T1-S0} = 10^4 \text{ s}^{-1}$).¹⁶ The absorp-

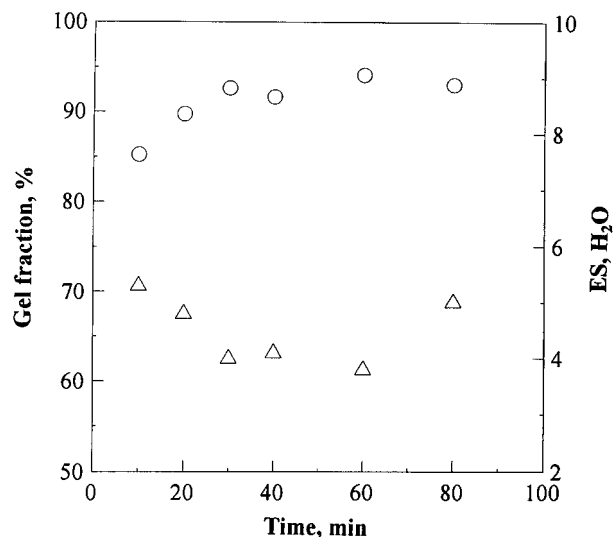


Figure 4 Effect of irradiation time on crosslinking efficiency. UV irradiation under a flow of argon at $[\text{BP}]/[-\text{EO}-] = 5 \times 10^{-3}$. Samples from Polyox N-12 K, $M_v = 1 \times 10^6$, $M_n = 4.0 \times 10^5$. (○) GF, %; (△) ES, H₂O.

tion maxima of BP are $\lambda_{\text{max}1} = 254 \text{ nm}$, $\epsilon = 1.8 \times 10^4$, and $\lambda_{\text{max}2} = 313 \text{ nm}$, $\epsilon = 140$.¹⁷ In this region of the spectrum there is no absorption of PEO.

The efficiency of BP in initiating the crosslinking of PEO was compared with the following available photoinitiators: MK, AP, BME, and Bn. Also, some commercial photoinitiators for radiation-curing of polymers were examined (Table I). UV crosslinking with MK failed although it was well-

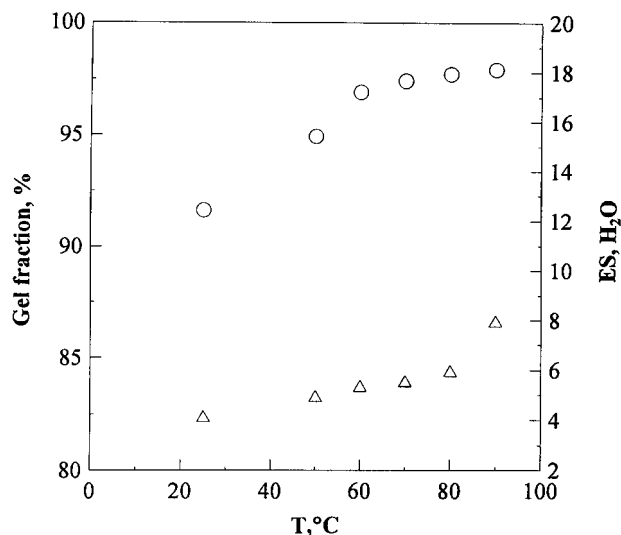


Figure 5 Effect of irradiation temperature on crosslinking efficiency. UV irradiation under a flow of argon at $[\text{BP}]/[-\text{EO}-] = 5 \times 10^{-3}$. Samples from Polyox N-12 K, $M_v = 1 \times 10^6$, $M_n = 4.0 \times 10^5$. Irradiation time: 40 min. (○) GF, %; (△) ES, H₂O.

purified prior to use. BME and AP provide an appreciable degree of crosslinking but less than that of BP. With the exception of Darocur® 1173, the commercial photocuring agents showed much lower hydrogen-abstracting capacity as compared with BP, Bn, and AP. The results confirm that BP

and Bn are the best choices as photoinitiators for the UV-induced crosslinking of PEO.

To investigate whether the crosslink density varies throughout the thickness of the samples, two identical films were crosslinked as follows: the first was irradiated twice with the same side

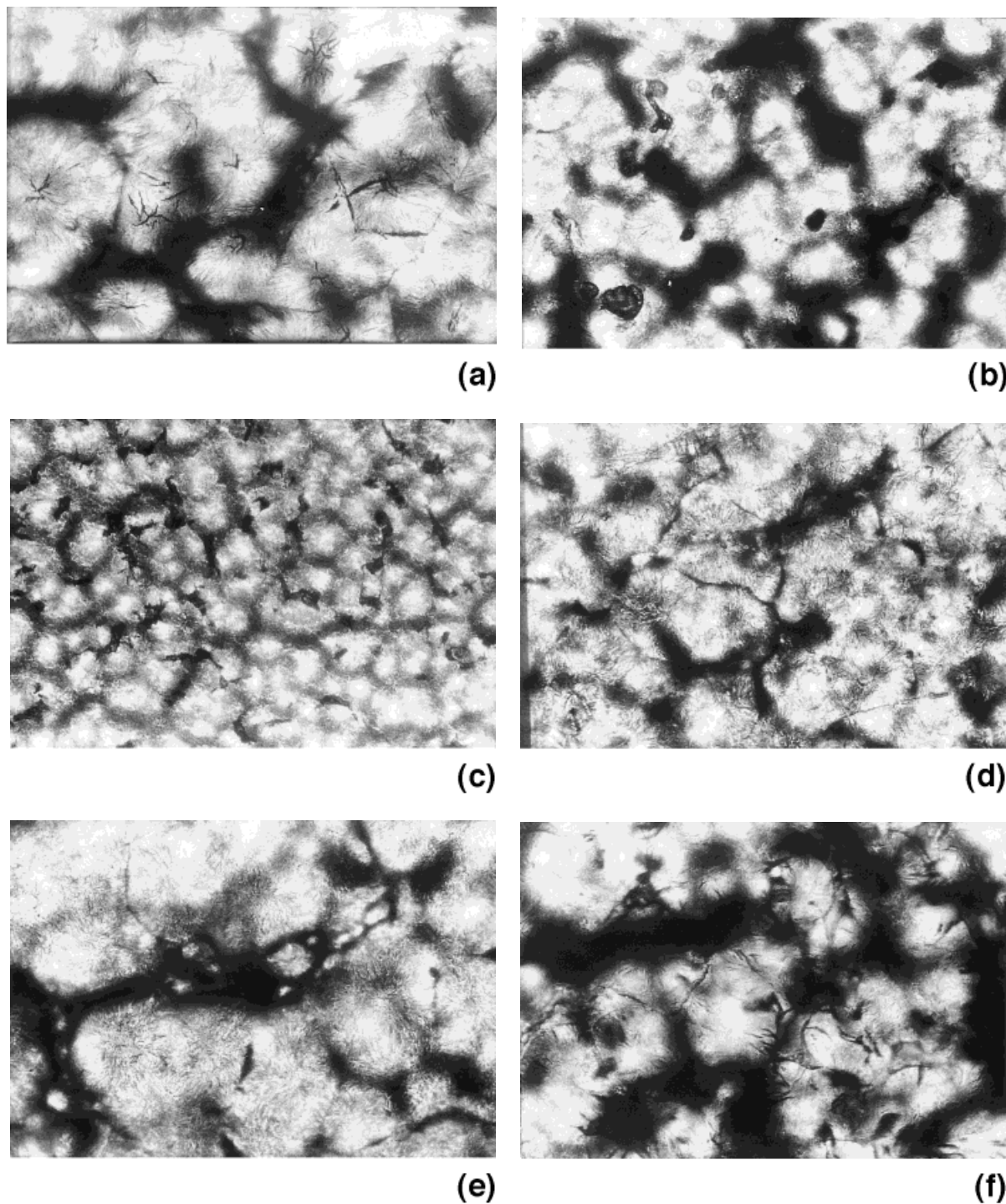


Figure 6 Photomicrographs ($\times 32$) of UV-crosslinked PEO morphology as a function of temperature. (a) 25°C; (b) 50°C; (c) 60°C; (d) 70°C; (e) 80°C; (f) 90°C.

exposed to the UV light source; the second was also irradiated twice, exposing first one surface of the film and then the opposite side. The data shown in Table II indicate that the two methods of irradiation produce similar crosslinking efficiency. However, a small difference in structure was indicated by film behavior during the swelling measurement. When the disk prepared by single-side irradiation was soaked in water, it rolled up rapidly; whereas the disk obtained by irradiation on both sides retained its form in water and remained flat. This observation indicates that PEO films are not completely homogeneous through their thickness in crosslink density.

The effects of such different factors as BP concentration and time and temperature of irradiation on the crosslinking efficiency was followed on the samples prepared from PEO of $M = 1 \times 10^6$.

Photoinitiator-free PEO (Polyox[®], $M = 1 \times 10^6$) samples showed about 30% gel fraction after irradiation. Samples prepared from PEO synthesized in our laboratory containing no additives or photoinitiators gave no gel fraction on UV irradiation. Evidently, the additives in the Polyox[®] exhibit a small degree of photoactivity.

BP concentration was varied in the range of 1×10^{-3} to 1×10^{-2} moles BP per mole of ethylene oxide ($-EO-$) units, which corresponds to 0.4 to 4.0 wt %. Figure 3 shows the change of gel fraction and the equilibrium degree of swelling in water as a function of BP concentration. The gel fraction levels off at a maximum value of 91 to 95% at BP

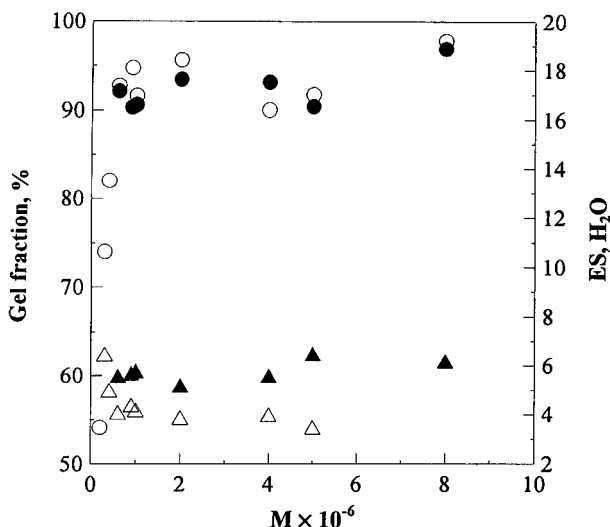


Figure 7 Effect of PEO molecular weight on crosslinking efficiency. UV irradiation in a flow of argon at $[BP]/[-EO-] = 5 \times 10^{-3}$. Irradiation time = 40 min. GF, %: (○) cast samples; (●) press-molded samples; ES, H₂O: (△) cast samples; (▲) press-molded samples.

Table III UV Crosslinking of Low-Molecular-Weight PEO

Irradiation Temperature (°C)	Gel Fraction (%)	Equilibrium Swelling	
		H ₂ O	CHCl ₃
25	57.9	—	—
50	76.4	7.5	12.8
60	86.7	7.8	14.1
70	89.5	8.6	16.0

UV irradiation under a flow of argon at $[BP]/[-EO-] = 5 \times 10^{-3}$. Samples from Polyox N-80, $M_v = 200,000$. Irradiation time = 40 min; thickness: 200–250 μm .

concentration of 4 to 5×10^{-3} mol/mol (1.5–2 wt %). The same trend is observed in the degree of crosslinking. All subsequent crosslinking experiments were therefore conducted with a BP concentration of 5×10^{-3} mol/mol. As seen from Figure 3, the crosslinking efficiency obtained by UV irradiation of PEO in a dynamic vacuum or under constant flow of argon does not differ.

The influence of the irradiation duration on crosslinking efficiency is shown in Figure 4. It can be seen that irradiation times above 20 min are sufficient to achieve more than 90% gel fraction yield. Maximal crosslink density is observed in the interval of 30–60 min irradiation. At an irradiation time of 80 min, an increase in equilibrium swelling and decrease in crosslinking density is observed at constant GF yield. This is most likely due to the competitive process of polymer chain scission at extended irradiation times. The optimal irradiation duration in the employed experimental conditions is thus between 30 and 40 min.

The temperature dependence of UV-initiated crosslinking was examined in the range from 25 to 90°C (Fig. 5). Above 50°C the PEO samples changed their appearance, due to the fusing processes, but kept their form and size. An increase in gel fraction yield and particularly in equilibrium degree of swelling occurred with the rise in temperature. The gel fraction increased over the range of 30–60°C and then remained almost constant at 97–98%. There was a linear dependence of the equilibrium swelling in water on irradiation temperature up to 80°C. The M_c showed a similar trend to GF, although with greater data scattering. These data may reflect a greater degree of chain scission at elevated temperature.

The change in the crystal structure of the crosslinked PEO with temperature was followed by microscopic observation (Fig. 6). Increasing the tem-

Table IV Calorimetric Data for PEO Prior To and After UV Irradiation

Sample	T_m (°C)			DSC—Degree of Crystallinity, X		
	Prior to Irradiation	After Irradiation	After Extraction	Prior to Irradiation	After Irradiation	After Extraction
PEO	68.3	67.9	—	0.76	0.77	—
PEO + BP	62.7	61.8 ^a	59.7	0.80	0.66	0.65
PEO + BP	64.6	65.2 ^b	64.4	0.79	0.64	0.63

UV irradiation under a flow of argon at $[BP]/[-EO-] = 5 \times 10^{-3}$. Samples from Polyox N-12 K, $M_v = 1 \times 10^6$. Irradiation time = 40 min.

^a $M_c = 40,000$.

^b $M_c = 12,000$.

perature to 60°C caused an increase in the amorphous fraction and formation of smaller crystal structures. A further increase in the amorphous fraction and noticeable growth in the size of the crystals was observed above 60°C. The greater interjunction molecular weight, M_c , permits formation of larger crystals. It seems that the irradiation temperature is a reliable factor for control of the network density in the UV crosslinking of PEO.

The effect of the molecular weight of PEO on UV crosslinking efficiency is shown in Figure 7. Varying M_v s from 200,000 to 8,000,000 exerts an appreciable influence on the gel fraction formation: the best yield is obtained from PEO with M_v from 900,000 to 2,000,000 and with M_v of 8,000,000. The curve of GF versus M_v is built from two sets of results: one obtained from samples cast from solutions, and the other from press-molded samples of 300–400- μ m thickness. The good agreement between the two sets of results shows that samples prepared by dry mixing and pressing under heat can be effectively crosslinked by UV irradiation.

The PEO samples with M_v of 200,000 were so weakly crosslinked at 25°C that it was impossible to measure the equilibrium degree of swelling. Attempts were made to find conditions for better crosslinking by changing the BP concentration, irradiation time, and irradiation temperature. Irradiation at temperatures above 50°C favored better crosslinking (Table III) because partial crystal melting at these temperatures leads to a larger amorphous phase where crosslinking takes place. Also, the greater mobility of the polymer segments provides an increased number of mutual contacts. It is, therefore, possible to control the degree of crosslinking by varying the irradiation temperature.

The change in the degree of crystallinity after

UV-induced crosslinking was followed by DSC (Table IV). The mole fraction of the crystalline phase was estimated as the ratio between the experimentally determined enthalpy of melting (ΔH_m) and enthalpy of melting of a 100% crystalline polymer ($\Delta H_{m^0} = 8,276$ J/mol¹⁸). The PEO samples containing the photoinitiator showed a greater crystallinity than the polymer itself. BP favors heterogeneous nucleation and the rate of crystallization rises. This results in formation of a more defective crystalline lattice; T_m is lower. After irradiation the degree of crystallinity is much lower and the well-reproducible endo peaks from the melting of samples of a different thermal prehistory indicate stable network formation.

CONCLUSIONS

PEO films prepared from an organic solvent solution or by dry blending and press-molding can be efficiently crosslinked by UV irradiation in the presence of a hydrogen-abstracting photoinitiator. BP was found to be the most efficient photoinitiator, among several examined, and its optimal concentration is 4 to 5×10^{-3} mol/mol $-EO-$ units. Increasing the irradiation temperature resulted in an increased gel fraction yield and reduced crosslink density. It is therefore possible to control the network density by varying the irradiation temperature.

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