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Ultraviolet-Induced Crosslinking of Poly(vinyl Alcohol) in the Presence of Sensitizers

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Synopsis

Ultraviolet-induced crosslinking of the film of polyvinyl alcohol with different degrees of polymerization was investigated in air at 25°C. in the presence of sodium benzoate as a sensitizer. Crosslinking is always accompanied by photolysis of the sensitizer. In the absence of the sensitizer, no crosslinking occurred. The gel content increased with irradiation time, and tended to a limiting value, depending on the initial sensitizer concentration. The final gel content increased as a function of the initial amount of sodium benzoate. A plot of solubility ($S + S^{1/2}$) against the reciprocal of the concentration of sensitizer converted gives a straight line in each case. The number of crosslinks is directly related to the number of sensitizer molecules destroyed. The crosslinking occurred predominantly, and main-chain scission was negligible. This result is in marked contrast to the effect of ionizing radiation, since the ionizing radiation causes only degradation under the identical conditions. This ultraviolet method was applied successfully to the crosslinking of water-soluble cellulose derivatives, such as methyl cellulose and sodium carboxymethyl cellulose.

Introduction

Many studies have reported on the ultraviolet-induced crosslinking of polymers. Oster et al.[1] found that polyethylene can be easily crosslinked by ultraviolet irradiation when a suitable sensitizer such as benzophenone is incorporated into the polymer. He also reported[2] that ultraviolet light can crosslink polyisobutylene, polypropylene, and poly(methyl methacrylate) in the presence of sensitizers. Recently, Charlesby et al.[3,4] reported a quantitative study of the crosslinking of polyethylene and paraffins by ultraviolet radiation in the presence of benzophenone as sensitizer.

We have found that poly(vinyl alcohol) (PVA) is readily crosslinked by ultraviolet light of 254 mμ wavelength at room temperature both in air and vacuum when a small amount of a sensitizer, such as benzoic acid, is introduced into the polymer prior to irradiation; preliminary studies have already been reported.[5,6] Sensitizers which have been found to be effective are sodium benzoate, benzoic acid, ethyl benzoate, benzamide, benzaldehyde, and monochloroacetic acid. These sensitizers are more or less soluble in water and homogeneously miscible with solid PVA to some extent. The irradiation of PVA in the absence of these sensitizers resulted in

only degradation under the conditions studied. The method of crosslinking PVA by ultraviolet radiation using such sensitizers has not previously been reported as far as we know. The irradiated PVA film in this way is satisfactorily rendered insoluble not only in water, but also in organic solvents in which it is normally soluble, such as dimethyl sulfoxide or ethylenediamine, retaining its original form even after being boiled in these solvents. Furthermore, the irradiated film was not discolored in most cases and its mechanical and thermal properties are considerably improved. A detailed study on the physical properties of the crosslinked PVA film thus obtained will be published elsewhere.[7] The crosslinking occurs through a radical mechanism, since these sensitizers decompose to produce free radicals on irradiation with ultraviolet light (200–300 mμ). This result is in marked contrast to the fact[8] that when PVA in the solid form is subjected to ionizing radiation such as γ-rays, no crosslinking takes place and only degradation occurs at ambient temperature. Therefore, this ultraviolet method has a number of advantages over the ionizing radiation method, particularly for crosslinking of PVA film.

The present paper is concerned with a study of the ultraviolet-induced crosslinking of PVA films with sodium benzoate as a sensitizer which has been done on a more quantitative basis. In addition to this, the crosslinking of water-soluble cellulose derivatives was also carried out in a similar manner.

Experimental

The polymers used consisted of three samples of PVA (samples A, B, and C) whose weight-average degrees of polymerization were 5700, 3300, and 1100, respectively. The weight-average degrees of polymerization were determined viscometrically, by using the relationship:[9]

$$[\eta] = 4.80 \times 10^{-1}\ \mathrm{DP}^{0.64}$$

The molecular weight distribution of these polymers was confirmed to follow a random distribution by column elution fractionation.[10] The polymers were purified by a Soxhlet extraction with methanol before use. The residual acetate group contents of the polymers were less than 0.05 mole-%. Sodium benzoate, which proved to be the most effective sensitizer, was the purest grade commercially available (Tokyo Kasei Co., Ltd. G. R. Grade) and used without further purification.

Unless otherwise indicated, uniform films, 0.02 mm. thick, were prepared by casting aqueous solutions of the polymer containing different amounts of sodium benzoate on a glass plate or PVC plate and allowing water to evaporate. After being dried completely over phosphorus pentoxide, the films were irradiated in air at 25°C. with a Toshiba 15-w. germicidal-type resonance mercury lamp (emitting mainly at 254 mμ) at a distance of 3 cm. The light intensity was determined to be 6×10^{-9} einsteins/cm.^{2}-sec. at a distance of 3 cm. from the surface of the lamp. The irradiated films were put into boiling water and extracted for about 7 hr.

The gel fraction was determined from the portion insoluble in boiling water.

Commercially available methyl cellulose (30% methoxy) and carboxymethyl cellulose (Na–CMC) as Cellogen (Daiichi Kogyo Seiyaku Co., Ltd.) with 0.65 weight fraction of ether group, both of which are soluble in water, were also used in this study. The film was prepared and irradiated in the same manner as described above. The irradiated films were put into a large excess of water and extracted at 25°C. for one week.

Results and Discussion

Typical plots showing the effect of irradiation on gel formation for several samples containing different amounts of sodium benzoate are shown in Figure 1. After a short period an insoluble fraction appeared. The gel content increased with irradiation time and tended to a limiting value in each case. This final gel content increased with initial amounts of sodium benzoate.

In Figure 2 are shown the spectral changes which occurred when a sensitized film was irradiated. The absorption peak of the sensitizer at 225 mμ was decreased by irradiation, indicating that the sensitizer was photodecomposed. It may be noted that during irradiation a new absorption maximum appeared in the vicinity of 270 mμ which, on further irradiation, was destroyed. After prolonged irradiation, no absorption band appeared in the visible region.

Figure 3 shows the course of photochemical decomposition of sodium benzoate in the film and gel formation. As is seen in Figure 3, the crosslinking essentially accompanies the photolysis of the sensitizer. As the absorption peak at 225 mμ reached the limiting value the gel content varied only very slightly, indicating that sodium benzoate was almost completely decomposed. Extended exposure to ultraviolet light has only a slight effect once all the sensitizer has been destroyed. It is therefore reasonable to relate the final crosslinking density to the initial concentration of sodium benzoate. The correct measure of dose in the present case is not the

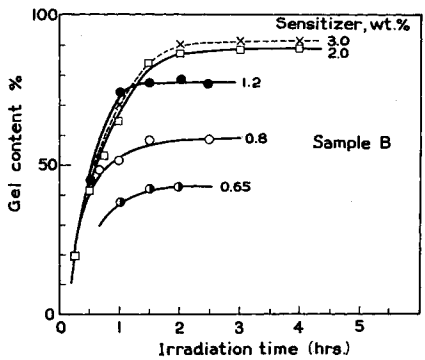

Fig. 1. Plot of gel content vs. irradiation time of PVA films 0.02 mm. thick (sample B) containing various amounts of sodium benzoate.

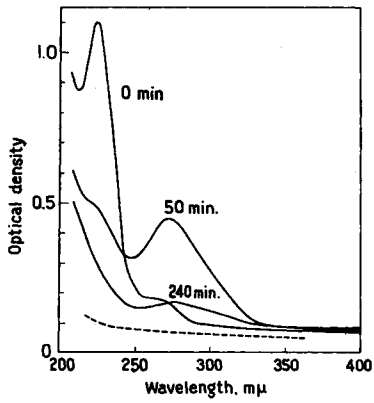

Fig. 2. Spectral changes in sodium benzoate-sensitized PVA film (sample A, 0.02 mm. thick). Initial sensitizer concentration 0.75 wt.-%. Broken curve is for unsensitized PVA.

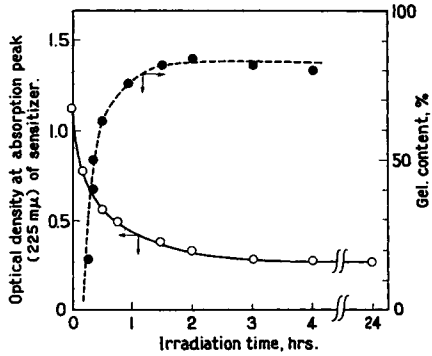

Fig. 3. Relationship between photodecomposition of sodium benzoate in the film and gel formation for PVA sample A film, 0.02 mm. thick and containing 0.75 wt.-% sodium benzoate as sensitizer.

total amount of ultraviolet light absorbed, but change in sensitizer concentration.

In Figure 4 is illustrated the effect of increasing the sodium benzoate concentration for three different samples. The irradiation was carried out until the gel content tended to the limiting value. The irradiation times were sufficient to convert all the sensitizer. For the samples having higher molecular weights, the gel content increased more rapidly and reached nearly 100%. The minimum concentration of sodium benzoate required to produce gel increased with decreasing degree of polymerization.

The data in Figure 4 can be treated according to the theory of Charlesby and Pinner.[11] When we plotted $S + S^{1/2}$, where S is the final sol fraction, given from Figure 4, against the reciprocal of concentration of initial sodium benzoate as proposed by Charlesby et al.,[3,4] linear plots were obtained for three different samples. The results are shown in Figure 5, in which each straight line passes very close to the origin. It is of great interest that

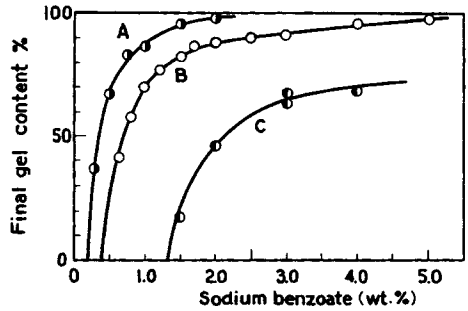

Fig. 4. Final gel content as a function of initial sodium benzoate concentration in PVA after about 4 hr. irradiation: (*A*) DP = 5700; (*B*) DP = 3300; (*C*) DP = 1100.

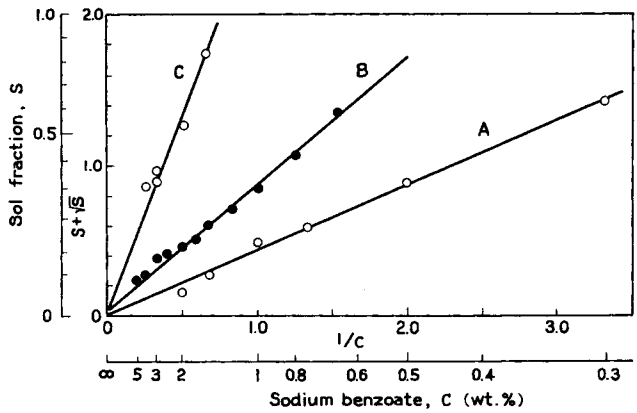

Fig. 5. Relationship between sol fraction and initial concentration of sodium benzoate in various PVA samples: (*A*) DP = 5700; (*B*) DP = 3300; (*C*) DP = 1100.

the chain scission is negligible and predominantly crosslinking occurs. As is seen in Figure 6, it was found that the critical concentration of sodium benzoate to produce gel was inversely proportional to the initial weight-average molecular weight.

The gel films showing the final gel content at each concentration of sodium benzoate were allowed to swell in water at 30°C. after boiling. Figure 7 shows the weight swelling ratio as a function of the initial concentration of sodium benzoate, plotted on a logarithmic scale. The plot gives a nearly straight line of slope of −0.6. This result is in good agreement with the equation derived by Charlesby[12] for the radiation-induced crosslinking, since in our ultraviolet crosslinking the concentration of the sensitizer converted corresponds to the radiation dose.

On the basis of the theory[13] that gel occurs when there is, on the average, one crosslinked unit per weight-average molecule, we estimated from the data in Figure 6 that one crosslink was formed for approximately four molecules of sodium benzoate converted.

The present ultraviolet method was applied successfully for the crosslinking of water-soluble cellulose derivatives. Typical results on the gel

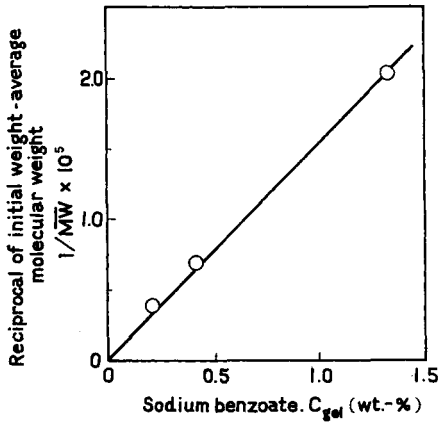

Fig. 6. Critical sensitizer concentration for incipient gelation.

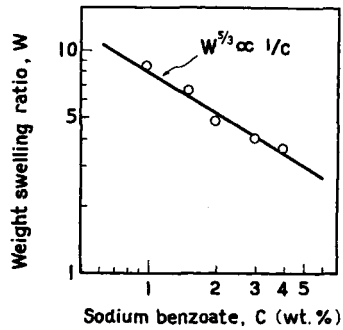

Fig. 7. Relationship between weight swelling ratio and initial sodium benzoate concentration of PVA sample B.

formation of the irradiated films of methyl cellulose and Na-CMC are presented in Figure 8. The results are almost the same as observed for PVA. The films irradiated in the absence of the sensitizer were completely soluble in water. When the sensitized films were irradiated with ionizing radiation, such as γ-rays, no crosslinking was observed.

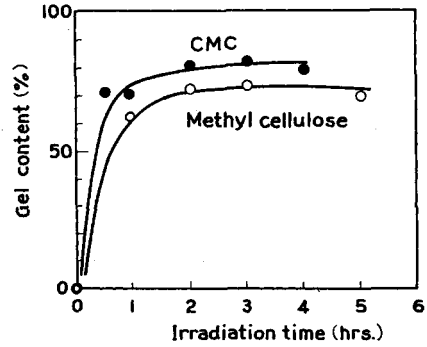

Fig. 8. Gel formation of irradiated films of Na-CMC and methyl cellulose. Films 0.02 mm. thick, containing 3 wt.-% sodium benzoate.

The mechanism of this crosslinking is not completely elucidated at the present stage of the investigation. However, it is probable that a free radical arising from the photolysis of sodium benzoate would abstract a tertiary hydrogen atom from the polymer chain to yield a polymeric radical, which can form a crosslink by combination with another such radical. From the spectral changes in Figure 2, it may be suggested that, on irradiation, sodium benzoate is initially converted to an intermediate with an absorption maximum at a somewhat longer wavelength, which is further decomposed to a radical sufficiently reactive to abstract a hydrogen atom from the polymer. There is spectral evidence to indicate that small amounts of the sensitizer fragments are incorporated into the polymer chains. It has been observed that the formation of carbonyl groups in the polymer chains occurred simultaneously to some extent during irradiation.

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Résumé

Le pontage, induit par irradiation au moyen de lumière ultraviolette, d'un film d'alcool polyvinilique de différents degrés de polymérisation a été effectué à l'air à 25°C, en présence de benzoate de sodium comme sensibilisateur. En absence du sensibilisateur, aucun pontage ne se manifeste. La teneur en gel augmente avec le temps d'irradiation et tend vers une valeur limite, qui dépend de la concentration initiale en sensibilisateur. La teneur finale en gel augmente en fonction de la quantité initiale en benzoate de sodium. Il existe un rapport linéaire, dans chaque cas, entre la solubilité ($S + S^{1/2}$) et l'inverse de la concentration en sensibilisateur consommé. Le nombre de ponts est directement proportionnel à la quantité de molécules de sensibilisateur décomposées. Le pontage est le phénomène prédominant et la scission de la chaîne principale est négligeable. Le résultat est en contraste net avec l'effet de la radiation ionisante, car l'irradiation ionisante produit uniquement la dégradation sous les mêmes conditions. Cette méthode par rayonnement ultraviolet a été appliquée avec succès pour le pontage de dérivés de la cellulose, solubles dans l'eau, tel que la méthyl cellulose et la carboxyméthyl cellulose sodique.

Zusammenfassung

Durch Ultraviolettbestrahlung induzierte Vernetzung von Polyvinylalkoholfilmen mit verschiedenem Polymerisationsgrad wurde in Luft bei 25°C in Gegenwart von Natriumbenzoat als Sensibilisator untersucht. Die Vernetzung wird immer von einer Photolyse des Sensibilisators begleitet. In Abwesenheit des Sensibilisators trat keine Vernetzung auf. Der Gelgehalt nahm mit der Bestrahlungsdauer zu und strebte zu einem von der Ausgangskonzentration des Sensibilisators abhängigen Grenzwert. Der Endgehalt an Gel nahm als Funktion des Ausgangsmenge an Natriumbenzoat zu. Das Diagramm der Löslichkeit ($S + S^{1/2}$) gegen den Reziprokwert der Konzentration des umgesetzten Sensibilisators liefert in edem Fall eine Gerade. Die Zahl der Vernetzungsstellen steht in Direkter Beziehung zur Zahl der zerstörten Sensibilisatormoleküle. Es trat verwiegend Vernetzung auf und die Hauptkettenspaltung konnte vernachlässigt werden. Dieses Ergebnis steht im Gegensatz zum Einfluss ionisieren der Strahlung, da die ionisierende Strahlung unter identischen Bedingungen lediglich zum Abbau führt. Die ultraviolette Bestrahlungsmethode wurde erfolgreich auf die Vernetzung wasserlöslicher Zellulosederivate, wie Methylzellulose und Natriumkarboxymethylzellulose, angewendet.

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