Photodepolymerization of Hydroxypropylmethylcellulose

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Synopsis

The light-induced degradation of aqueous hydroxypropylmethylcellulose (HPMC; D.S. 1.9) solutions has been investigated under a variety of conditions. The HPMC was sensitized to short-wavelength radiation (<500 nm) by the addition of sodium nitrite, the degradation being accompanied by increased acidity and the generation of oxides of nitrogen. Addition of eosin dye increased the sensitivity to visible light (>500 nm), and the effect was considerably more pronounced when strong electron donors were added. Analysis of the shear–viscosity relationship of the solutions, during the degradation, indicated that both chain disentanglement and chain scission occurred but that the primary process was the depolymerization of the cellulose chain. It is proposed that both the dye- and nitrite-induced depolymerizations are a consequence of peroxide attack on the β-glucosidic ether link. The results indicate that, in the case of sodium nitrite addition, the peroxide was generated by the aqueous photolytic decomposition of the nitrite ion. The peroxide formation in the eosin–TEA system was a consequence of leuco-dye production, under the influence of the light, followed by the reduction of traces of dissolved oxygen by this activated dye.

INTRODUCTION

The degradation of cellulose and its derivatives by various agents has been extensively reported.[1] Chain scission in celluloses by microorganisms is a well-known phenomenon; for instance, the enzyme cellulase has been found to degrade cellulose ethers. In these cases, the D.S. (the average number of substituted hydroxy groups per anhydroglucose unit) is a critical factor.[2] This is illustrated by the commercially available methylcelluloses, which have D.S. values of about 1.9 and are much more stable than the ethers of lower D.S. such as hydroxyethylcellulose.

Depolymerization of cellulose ethers by acid hydrolysis is also sensitive to the D.S.;[3] for instance, hydroxypropylmethylcellulose (D.S. 1.9) is reported to be stable from pH 3 to 10 for reasonable periods.[4] Cellulose ethers may also be depolymerized by peroxides, light, and thermo-oxidative attack. However, it has been reported that a major effect of light is to initiate peroxide formation,[5] and recent work has established that thermo-oxidative degradation also proceeds via peroxide formation at ether links.[6]

In this study, we wished to control the photodegradation of a cellulose ether in solution. We therefore selected hydroxypropylmethylcellulose

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(HPMC; D.S. 1.9), which is stable to ambient light and microbiologic attack and is the most stable of all the cellulose ethers to acids. The necessary peroxide ion was generated by photolysis of nitrite ion. We also investigated the dye-influenced degradation of HPMC by visible light.

Further studies of the photodegradation of other water-soluble polymers are in progress.[7] In this paper we report the observations and mechanistic studies conducted on HPMC.

EXPERIMENTAL

High molecular weight hydroxypropylmethylcellulose was obtained from the Dow Chemical Company (Methocel 90HG,50,000). Extrapolating from the viscosity–$\bar{M}_N$ data published for methylcelluloses,[8] we obtained an approximate $\bar{M}_N$ of 160,000. The chemical structure of this material can be represented by
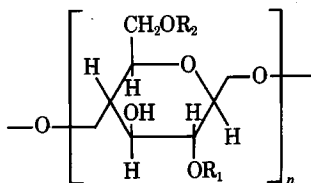
where R_1 and R_2 are substituent groups, either methyl or hydroxypropyl. The total D.S. is in the range 1.7–1.9, with an approximate methoxy D.S. of 1.6 and a hydroxypropyl D.S. of 0.2. The material possessed a small degree of residual incombustible ash residue (<0.1%), which was assumed to consist of various sodium salts. Sodium nitrite, hydrochloric acid (ACS grade), and Eosin B dye (C.1, No. 45400) were obtained from Fisher Scientific Co.

Viscosities were determined on small samples by the Gardner-Holdt method using the time of rise of a standard size bubble in a calibrated tube. The viscosities of large samples were determined using a Brookfield RVF-100 rotational viscometer. Values were taken for all appropriate spindle sizes and averaged. To observe changes in the pseudoplastic behavior as the degradation proceeded, we varied the shear rate on the Brookfield viscometer by varying the spindle speed. Shear rates were calculated from the data using the formula

$$\text{shear rate} = \frac{2\theta R_c{}^2}{R_c{}^2 - R_d{}^2}$$

where R_c is the container diameter, R_d is the spindle diameter, and θ is the angular velocity in radians/sec. This value represents the shear rate at the rim of the rotating spindle and therefore is the maximum shear developed. All viscosity determinations were taken after thermostating the samples at 25°C.

The ultraviolet source was a filtered Blak-Ray B100A, 100-W ultraviolet lamp (Ultraviolet Products, Inc., San Gabriel, Cal.). The radiation from this lamp was predominantly 365 nm. Samples in glass jars were below this lamp, while ambient light was excluded. The accelerated degradation tests detailed below were conducted using a Hanovia 7340 1000-W UV lamp (Englehard Hanovia, Inc., Newark, N.J.) fitted with Corning #7910 and #9863 filters. All samples were air cooled continuously to maintain a 30°C ambient temperature.

By means of UV meters (Ultraviolet Products, Inc., San Gabriel, Cal., J221 Longwave and J225 Shortwave), we measured the intensities of the 365-nm and 254-nm radiations seen by the sample in each determination. Intensities were read through the glass sample containers and are listed in the results.

Incandescent lamps were used to irradiate the samples with visible light, these samples being kept in brown bottles which had a 500-nm optical cut-off. Visible intensities were measured with a Gossen Tri-lux ft-candle meter (P. Gossen & Co., G.m.b.H., 8520 Erlangen ℳ, Germany).

RESULTS AND DISCUSSION

HPMC, 1.8% solution with 0.2% sodium nitrite, degraded rapidly when exposed to 365-nm radiation. The solution viscosity decreased from ~34,000 cp to 4,000 cp (Brookfield, 25°C, 10 rpm) in 6 hr and further declined to 24 cp in 60 hr. Control samples of the same composition, also rolled in the same irradiation chamber but protected from the UV, showed no significant degradation in 60 hr. Samples irradiated without sodium nitrite showed only a small viscosity drop. The viscosity-versus-time of irradiation and viscosity-versus-rate of shear data are plotted in Figures 1, 2, and 3; and the data for the control samples, compared with the degradation data, are tabulated in Table I.

The pH values of the solutions were measured at various intervals during the exposure and are tabulated in Figure 4. No significant changes in pH

TABLE I
Effect of Sodium Nitrite on the Viscosity of HPMC Solutions

Sample	Irradiation, μW/cm^2 at 365 nm	Viscosity after irradiation,[a] cps			
		0 hr	6 hr	23 hr	50 hr
HPMC	none	36,000	35,900	35,600	33,800
HPMC	3000	36,000	33,600	32,800	31,600
HPMC NaNO$_2$	none	34,000	32,900	30,600	29,500
HPMC NaNO$_2$	3000	34,000	4,000	52	24

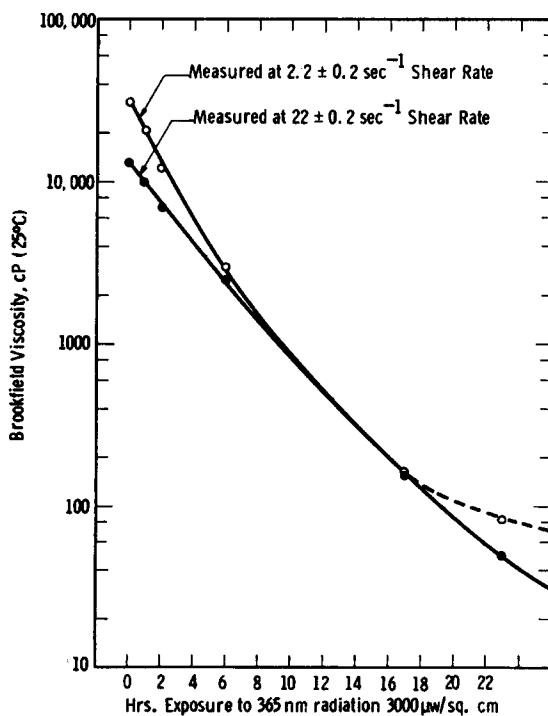[a] Measured at 25°C using a Brookfield RVF-100 at 10 rpm and appropriate spindle sizes.

Fig. 1. Photolytic degradation of hydroxypropylmethylcellulose (1.8%) solution
in the presence of sodium nitrite (0.2%).

occurred in the absence of the nitrite.   The nitrite–HPMC solution under
irradiation, however, became increasingly acidic.   Similar behavior was
observed on irradiating a solution of sodium nitrite alone.

The first problem was to establish that a true photochemical depoly-
merization occurs, i.e., the photochemical process causes chain scission,
since there are a number of other conceivable processes that would have the
same effect upon the viscosity of the aqueous solutions.

The most likely alternative would be that the viscosity changes are due
entirely to decreased chain entanglements.   The high molecular weight
cellulose ethers have extensively entangled chains in solution, which is the
reason for the high viscosities observed at low solution concentrations.
Since the pseudoplasticity of these solutions is a consequence of this chain
entanglement, the viscosity–shear relationship can be used to demonstrate
any changes in the degree of entanglement.

To investigate this, we measured the viscosity–shear characteristics for
the degraded samples (Figs. 2 and 3) and compared them to lower molecular
weight samples of HPMC supplied by the Dow Chemical Company.
These lower molecular weight materials are made by controlled air oxidation
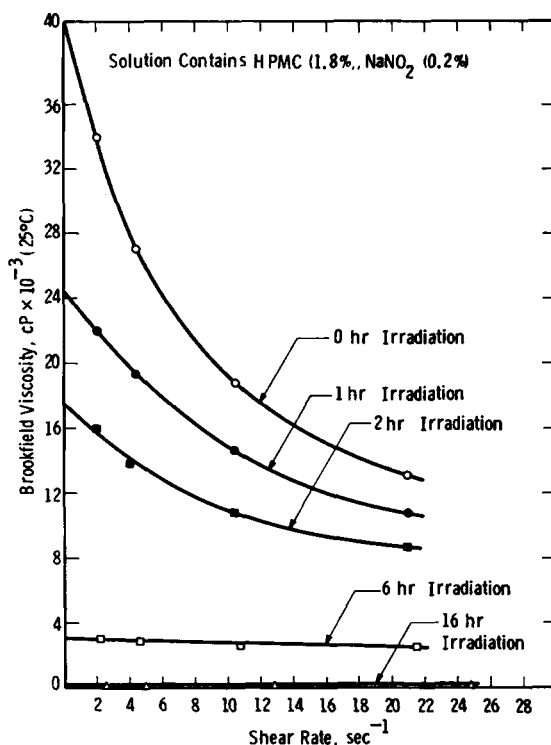of the alkali cellulose.[9]

Fig. 2. Effect of shear rate on the viscosity of HPMC–nitrite solution.

The exposed solution was initially pseudoplastic; but, after 6 hr of exposure, it became Newtonian at least for the shear rates under consideration. Further exposure, beyond 16 hr, apparently imparted dilatent properties to the solution. This is emphasized in Figure 3 where the ordinate is expanded. It can be seen that the shear properties of successive fractions of decreasing molecular weight material compare directly to those of the degrading HPMC.

The data, therefore, indicate that the photochemical degradation is principally a chain scission process similar in eventual result to that occurring in the air oxidation of alkali cellulose. This process appears to occur even up to 60 hr of exposure. However, any chain disentangling, which accounts for the shape of the curves up to 2 hr of exposure, becomes negligible after 6 hr of exposure when the solution shows Newtonian behavior. The apparent dilatent properties, obtained after extended exposure, were considered to be due to turbulent flow at the viscometer spindle.

In attributing the chain scission directly to photochemical activity, we ignore the possibility that uncontrolled secondary factors might be causing the degradation. It is conceivable that the illumination could accelerate microbiologic degradation of the cellulose ether. However, the irradiated
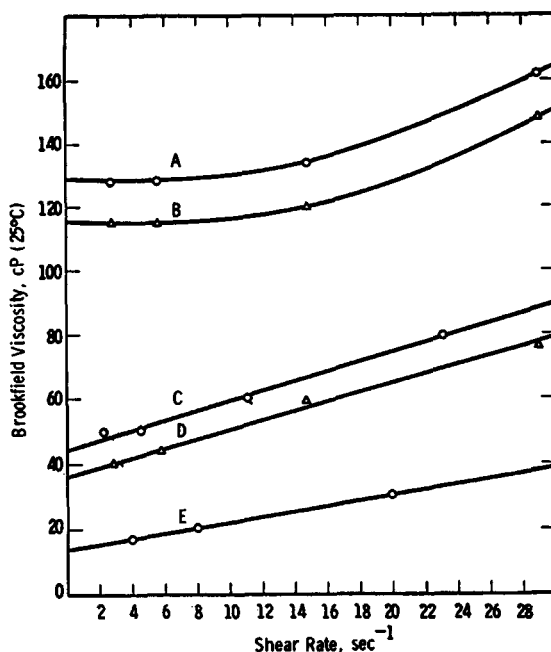
Fig. 3. Effect of shear rate on the viscosity of HPMC–nitrite solutions; correlation with data for air-oxidized HPMC: (A, C, E) HPMC–nitrite solution after 16.5, 23, 60 hr of irradiation; (B, D) air-oxidized low molecular weight HPMC, Dow Methocel 90HG100 and 65HG50, respectively. All samples at same concentration.

sample without nitrite did not degrade; since nitrites have actually been used to prevent microbiologic growth, this mode of degradation is therefore unlikely.

An interesting alternative is that the combined action of the light and the nitrite causes dehydration of the water sheath around the cellulose ether molecule in solution. It is well established that the solution of these high molecular weight cellulose ethers is easily disturbed.[10] Since no obvious precipitation occurred in the solution upon irradiation, and as we were able to induce this precipitation easily in degraded solutions by raising the temperature above the reversible gel temperature of the ether (90°C), we concluded that this mechanism was also unlikely.

The next problem was to determine whether the degradation is a consequence of the particular properties of the nitrite or whether it is an indirect acid hydrolysis caused by the pH changes occurring. Firstly, we can rule out simple acid hydrolysis since these materials are reportedly[4] stable between pH 3 and 10 in the absence of light, nitrite, etc. The changes we are concerned with are between pH 4 and 7. However, the possibility of photolytically catalyzed acid hydrolysis cannot be so easily eliminated.

To test this possibility, we acidified a HPMC solution with dilute HCl (pH 4) and subjected it to accelerated degradation. Also included in this
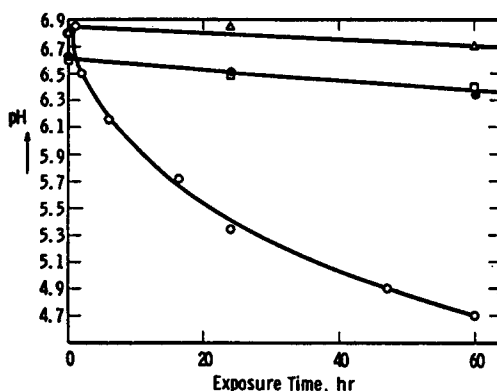
Fig. 4. Changes in pH in irradiated HPMC–nitrite solutions and controls: (●) HPMC–irradiated; 365 nm, 5000μWatts/sq cm; (□) HPMC; no irradiation; (O) HPMC–NaNO₂, irradiated; 365 nm, 5000μWatts/sq cm; (△) HPMC–NaNO₂, no irradiation.

test were untreated HPMC and a sample with 0.1% sodium nitrite. The results are shown in Table II. Under these conditions some degradation occurred in all samples, but the loss of viscosity of the sample containing nitrite was complete, whereas the other samples were considerably less affected. We concluded that acidification was a factor that increased the photoinstability; however, this factor alone cannot explain the rapid nitrite–HPMC degradation, which therefore must be directly associated with the nitrite ion. The degraded nitrite–HPMC solution turned a light-brown color, and the characteristic smell of oxides of nitrogen could be detected. Solutions of sodium nitrite alone also exhibited these photolytic decomposition properties.

To establish if visible light also initiated degradation, samples of HPMC (1%) with sodium nitrite (0.1%) and without nitrite were placed in brown

TABLE II
Effect of Sodium Nitrite and Hydrochloric Acid on the Viscosity of HPMC Solutions

| | | Viscosity,[a] sec | |
| | | --- | --- |
Sample	Irradiation, μW/cm² at 254 nm	Initial	After 16 hr of Irradiation
HPMC	3000	23	15
HPMC + HCl[b]	3000	23	10
HPMC + NaNO₂[c]	3000	23	<1
HPMC	0	23	23
HPMC + HCl[b]	0	23	23
HPMC + NaNO₂[c]	0	23	23

[a] Viscosity was measured by the time of rise of a standard air bubble in a Gardner-Holdt tube at 25°C.
[b] 1% HPMC solution, HCl acidification to pH 4.
[c] 1% HPMC solution, 0.1% NaNO₂.

glass bottles which had an optical cut-off at 500 nm. These bottles were illuminated with an incandescent lamp. This procedure eliminated all ultraviolet radiation. The results are shown in Table III. No significant viscosity drop was observed. The reaction must then be principally sensitive to blue and ultraviolet light; this follows from Draper's law, since the solution was essentially transparent to visible light.

Much recent work on photopolymerization and photocrosslinking has shown that addition of dyes can accelerate photochemical reactions by significantly increasing the range of sensitivity.[11]

Oster has worked extensively in this field and has used the dye eosin for a number of systems.[12] We added eosin to HPMC solutions, with and without nitrite, and exposed them to a broad spectrum of visible light, extending to 300 nm. The results are presented in Table III. The small amount of

TABLE III
Effect of Dye, Reducing Agent, and Sodium Nitrite
on the Visocisty of HPMC Solutions Exposed to Light >300 nm

| | | Viscosity,[b] sec | |
| | | After irradiation[c] | |
Sample[a]	Initial	24 hr	48 hr
HPMC	23	23	20
HPMC + eosin	23	23	20
HPMC + eosin + TEA	23	4	1.5
HPMC + NaNO$_2$	23	17	10
HPMC + NaNO$_2$ + eosin	23	15	7
HPMC + NaNO$_2$ + eosin + TEA	23	6	2.5

[a] The following concentrations were used in the solutions: 1% HPMC, 0.1% NaNO$_2$, 0.001% eosin B, 0.025% TEA.

[b] Viscosity determined by the time of rise of a standard air bubble in a Gardner-Holdt tube.

[c] The irradiation source consisted of incandescent and CW fluorescent lamps giving a total of 3000 ft-candles.

degradation of the HPMC alone was not increased by the addition of the dye. The addition of sodium nitrite had a much greater degrading effect, and this was enhanced by the presence of eosin. All the degradations observed must have been a consequence of the small amount of UV above 300 nm given by the fluorescent tubes used. Repeating the tests with sample tubes that absorbed all radiation below 500 nm resulted in no degradation (Table IV).

Strong electron donors have been found to enhance the sensitivity of dye-initiated photochemical reactions.[13] Accordingly, the addition of triethanolamine (TEA) to a HPMC–eosin solution resulted in a dramatic decrease in the viscosity. The large decrease in viscosity occurred both in the presence and absence of nitrite. The same result was found using both visible radiation down to 300 nm and only that above 500 nm.

Effect of Dye, Reducing Agent, and Sodium Nitrite on the Viscosity of HPMC
Solutions Exposed to Light >500 nm

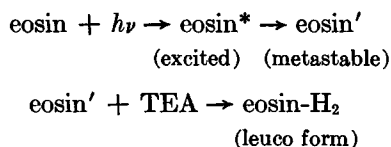| | | Viscosity,[b] sec | |
| | | | After irradiation[c] | |
Sample[a]	Initial	60 hr	120 hr
HPMC	23	23	22
HPMC + NaNO$_2$	23	23	22
HPMC + Eosin + TEA	23	10	4
HPMC + Eosin + TEA + NaNO$_2$	23	9	3

[a] The following concentrations were used in the solutions: 1% HPMC, 0.1% NaNO$_2$ 0.001% eosin B, 0.025% TEA.

[b] Viscosity determined by time of rise of standard air bubble in Gardner-Holdt tube, 25°C.

[c] The irradiation source was incandescent lamps giving 3000 ft-candles. The samples were in bottles which transmitted 20% of light >500 nm, and nothing <500 nm.

It appears, therefore, that the effect of the eosin–TEA combination is to accelerate the degradation of HPMC independently of any nitrite-induced reaction. The slight accelerating effect of eosin alone on the HPMC–nitrite reaction could be the result of the nitrite ion acting as an electron donor to the dye.

The results indicate that the action of the dye follows the reaction path proposed by Kosar:[11]

$$\text{eosin} + h\nu \rightarrow \text{eosin*} \rightarrow \text{eosin}'$$
$$\text{(excited)} \quad \text{(metastable)}$$

$$\text{eosin}' + \text{TEA} \rightarrow \text{eosin-H}_2$$
$$\text{(leuco form)}$$

The reduced eosin then produces hydroxy and peroxy radicals from traces of dissolved oxygen, both of which can initiate chain scission:

$$\text{eosin-H}_2 + O_2 + H_2O \rightarrow OH\cdot + H_2O_2 + \text{eosin-H}\cdot$$
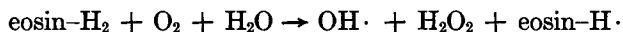
Assuming similar reaction paths proposed for other celluloses,[1] we can suppose that peroxide formation occurs at the ether linkage in the cellulose chain and is followed by propagation of a chain resulting in celluloseoxy free radicals. These eventually rearrange, with cleavage of the ether linkage and consequent D.P. reduction. The β-glucosidic ether links that join the anhydroglucose units in the cellulose chain are known to be the most labile positions, especially under acidic conditions; ether cleavage may also occur at the side chains.

The influence of dyes on the stability of cellulose fibers has been studied extensively. Other authors have observed peroxide formation in dyed fabric decomposition,[14] and the question of leuco dye formation as a stage in this process has been discussed.[15] It seems that this is likely in the case

of eosin; the rate of decomposition of HPMC–eosin without TEA was not accelerated, indicating that electron donation to give the leuco dye is needed for activity. Further evidence is that the eosin–TEA solutions became colorless during exposure. The leuco form is colorless.

The enhanced rate of degradation with nitrite but without TEA probably reflects the ability of the nitrite ion in the presence of water to produce the leuco eosin:

$$eosin' + NO_2^- + H_2O \rightarrow eosin\text{–}H_2 + NO_3^-$$

The nitrite–HPMC degradation in the absence of eosin could proceed in a number of ways. No definitive mechanism can be presented from our data, but some conclusions can be reached:

It is unlikely that the action of nitrite ion proceeds via nitration of the HPMC. Strong nitric acid would be needed, and, although it is possible that the photolytic decomposition of sodium nitrite does yield nitric acid and oxides of nitrogen, the concentrations we are concerned with are far below the 30% needed for HNO_3/N_2O_4 nitration.[16] Any nitration of the cellulose would, however, result in a product very unstable to UV.

A more likely explanation is that the photodecomposing nitrite initiates a radical photo-oxidation process similar to that detailed above. A possible reaction path is:

$$NO_2^- + H_2O + O_2 \rightarrow NO_3^- + H_2O_2$$
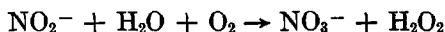
The nitrate ion is then photoreduced to give oxides of nitrogen and further peroxide:

$$2H_2O + 2NO_3^- \rightarrow N_2O_4 + 2H_2O_2 + 2e$$

The peroxide then proceeds to oxidize the ether linkages in the HPMC in a manner similar to the path detailed above.

The mechanism above explains why the pH of the photodecomposing solution decreases. Essentially, it is a consequence of the much greater pK_a for nitric acid over that of nitrous acid (6.0×10^{-6}). The acidity of the solution then enhances the lability of the β-glucosidic ether link. The mechanism is further substantiated by work[17] on the oxidative degradation of cellulose nitrate where nitric acid and oxides of nitrogen were found to have a catalytic effect on the reaction.

IR spectra of HPMC films, before and after nitrite-induced degradation, showed clear indication of the formation of an absorption band at 6.3 μ. This would correspond to carbonyl group formation, which is a likely consequence of photo-oxidation at the ether links.

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