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Ultrasonic Degradation of Hydroxypropyl Cellulose Solutions in Water, Ethanol, and Tetrahydrofuran

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ABSTRACT

Ultrasonic degradations of hydroxypropyl cellulose (HPC) have been carried out in water, ethanol, and tetrahydrofuran (THF) solutions. In the HPC-water system, cavitation intensity did not increase linearly with ultrasound intensity because of a lower threshold of ultrasonic intensity below which cavitation does not occur. At 27°C the rate of degradation in the three solvents followed the order water > ethanol > THF which is not in line with their characteristic impedance values. The rate of degradation for 20 kHz, 70 W ultrasound intensity was found to increase with a decrease in solution volumes, concentration of HPC, and temperature. Increased rate of degradation at lower temperatures supports the concept based on sonoluminescence experiments that it is the cavitation in a polymer solution that is responsible for ultrasonic degradations and the dissolved polymer molecules do not act as cavitation nuclei. Increased surface tension and density of the solvent are thought to be responsible for improved cavitation at low temperatures. Infrared spectroscopy and x-ray analysis of HPC subjected to ultrasonic treatments remained unchanged, suggesting that there were no chemical or structural (e.g., degree of order) changes on irradiation. The decreases in molecular weights on irradiation arise due to random chain scission whereas similar decreases in Huggins coefficients can be attributed to physical changes (decrease in molecular weight or branching) in the degraded HPC samples.

INTRODUCTION

Ultrasonic treatments of cellulose and cellulose derivatives have received considerable attention in recent years [1-17]. Schmid and Beuttenmuller [1] found that the rate of degradation was concentration dependent and decreased with increasing temperature. They further reported that the density of the solvents had little or no effect since the data obtained with carbon tetrachloride-toluene mixtures were similar to that with mixtures of cyclohexane-carbon tetrachloride. Prudhomme and Grabar [2] observed that the time required for degradation is inversely proportional to sound intensity and proportional to solution concentration, but the final degree of polymerization was found to be independent of these factors. Sobue and Ishikawa [3, 5] reported that as the concentration of the solution was decreased, the ultrasonic degradation increased. Akiya et al. [4] noted a decrease in viscosity of methyl cellulose and cotton cellulose when the intensity of ultrasonic waves was increased. Weissler [6] studied the ultrasonic degradation of hydroxyethyl cellulose dissolved in ordinary water and in degassed water, and he concluded "that in the latter case there was no visible cavitation during irradiation and depolymerization did not occur." Thomas and Alexander [9, 10] studied the ultrasonic degradation of cellulose nitrate in ethyl acetate at two different radio frequency powers, 50 and 120 W, and concluded that the rate of degradation was independent of power as long as cavitation was present. Mahalingham and Aldinger [11] observed that the shear degradation of methyl cellulose is preceded by an induction period during which there is an increase in the viscosity attributable to chain entanglement. The subsequent degradation was indicated by the reduction in viscosity due to chain scission. Sato and Nalepa [12] studied the ultrasonic degradation of hydroxyethyl cellulose and hydroxypropyl cellulose and pointed out that although the intrinsic viscosity $[\eta]$ decreased with increasing irradiation time, the Huggins coefficient k_H was not changed and remained constant at 0.6.

Polcin et al. [13] reported structural changes in cellulose fibers under the influence of ultrasonic degradation. Safonova and Klenkova [14] observed that when solutions of cellulose nitrate in butyl acetate were subjected to ultrasound, the rheological properties changed only for those solutions for which the state of the solution was that of a molecular dispersion. At concentrations characteristic of a micelle dispersion, the degree of destruction depended on the molecular weight of the polymer, while at very low concentrations the molecular weight had little effect. Dolgin et al. [15, 16] have carried out intensive research on the effect of mechanical beating of cellulose fibers in water on their crystallinity as well as on the effect of ultrasonic treatment on wood cellulose and on the reactivity of pulp in the viscose process. Laine et al. [17] have reviewed the applications of ultrasound in pulp and paper technology. These authors have pointed out that forest products industry processes in which ultrasonics show promise include barking, wood impregnation, chip penetration, chemical pulping, pulp bleaching, stock preparation, paper drying, laminating, lignin isolation and degradation, cellulose grafting and regeneration, and wood chemical modification.

Most, if not all, of these studies related to ultrasonic treatments of cellulose derivatives have been carried out in aqueous solutions for fixed intensities and at fixed temperatures. Thus for a better understanding of the role of ultrasound in cellulose and polymer modifications (e.g., block copolymers), it was thought necessary to explore the effects of various other parameters, e.g., intensity, temperature, and solvents, on ultrasonic degradations.

Hydroxypropyl cellulose solutions in water, ethanol, and tetrahydrofuran were subjected to ultrasound. The results of these studies are presented in this report.

EXPERIMENTAL

Materials

Hydroxypropyl cellulose (HPC) samples with average molecular weights, $\overline{M}_w$ of 1.0×10^6, 3.0×10^5, 1.0×10^5, and 6.0×10^4, were obtained from Scientific Polymer Products and were used as received. Solvents tetrahydrofuran (THF) (Fisher Certified) and ethanol (Aldrich Chemical Co.) were also used as received.

Degradation Procedure

Ultrasonic degradations of HPC solutions were carried out in batch reactors [(a) 10 cm long, 2.5 cm diameter, volume 50 mL, (b) 10 cm long, 5 cm diameter, 200 mL capacity]. These were equipped with water jackets to maintain a 2°C temperature within measured with a Ni-Cr alloy probe and a Comark digital thermometer. Tubing connections above and below permit filling and emptying without breaking the atmospheric seal. It also allows processing or purging with an inert atmosphere. The sealed reactors [stainless steel (50 mL capacity) and aluminum (200 mL)] screw onto a threaded nodal point on 1.25 cm diameter disruptor horn (Heat Systems Model 375-A with nominal frequency of 20 kHz) where attachment produces no damping. Ultrasonic intensity input was adjusted using the calibration curves of meter reading, power control setting, and power output in watts provided by the manufacturer.

Viscosity Calculations

Calculation of the intrinsic viscosity of HPC samples before as well as after degradation was carried out by making use of the flow time measurement data obtained with Ubbelohde viscometers at 25°C for at least three concentrations (0.05 to 0.15 g/dL). Knowing the flow time of the solvent and the solutions, the computation of the intrinsic viscosity $[\eta]$ is carried out with

$$[\eta] = \lim_{c \to 0} \eta_{sp/c} \qquad (1)$$

where

$$\eta_{sp/c} = \left(\frac{\text{flow time of solution}}{\text{flow time of solvent}} - 1 \right)$$

Huggins coefficient k_H is related to $[\eta]$ by the equation

$$\eta_{sp/c} = [\eta] + k_H[\eta]^2 c \qquad (2)$$

Mark-Houwink constants K and a for HPC in water, ethanol, and THF were calculated from the log-log plots of $[\eta]$ versus weight-average molecular weights $\overline{M}_w$. These values are listed in Table 1.

IR Analysis

The IR spectrum of degraded HPC sample was recorded from thin film on a Beckman Spectrophotometer Model 4250.

X-Ray

X-ray spectrum of the degraded HPC sample was recorded on a Warhus camera.

RESULTS AND DISCUSSION

In Table 1 are shown, besides the Mark-Houwink constants K and a, values of Huggins coefficient k_H. According to the hydrodynamic theory of Risemann and Ullman [18], the value of k_H should be 3/5 for a coil and 11/15 for rods. $k_H \geqq 1$ results from spherical particles. This would suggest that all HPC samples have a random coil configuration in ethanol and a rodlike structure in water. The two low molecular weight samples of HPC, viz., $\overline{M}_w = 6.0 \times 10^4$ and $\overline{M}_w = 1.0 \times 10^5$ have random coil configuration in THF. HPC sample with

TABLE 1. Intrinsic Viscosity $[\eta]$ and Molecular Weight Relationship for Hydroxypropyl Cellulose (HPC) at 25°C in Three Solvents

	Molecular characteristics of HPC samples									
	6.0×10^4		1.0×10^5		3.0×10^5		1.0×10^6			
Solvent	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$K \times 10^5$ (dL/g)	a
THF	1.32	0.78	1.38	0.72	3.1	1.42	8.0	2.57	24.0	0.75
Ethanol	1.2	0.65	1.35	0.50	3.75	0.48	14.4	0.76	9.3	0.85
Water	1.0	0.97	1.1	0.89	2.9	0.86	11.4	1.0	2.0	0.95

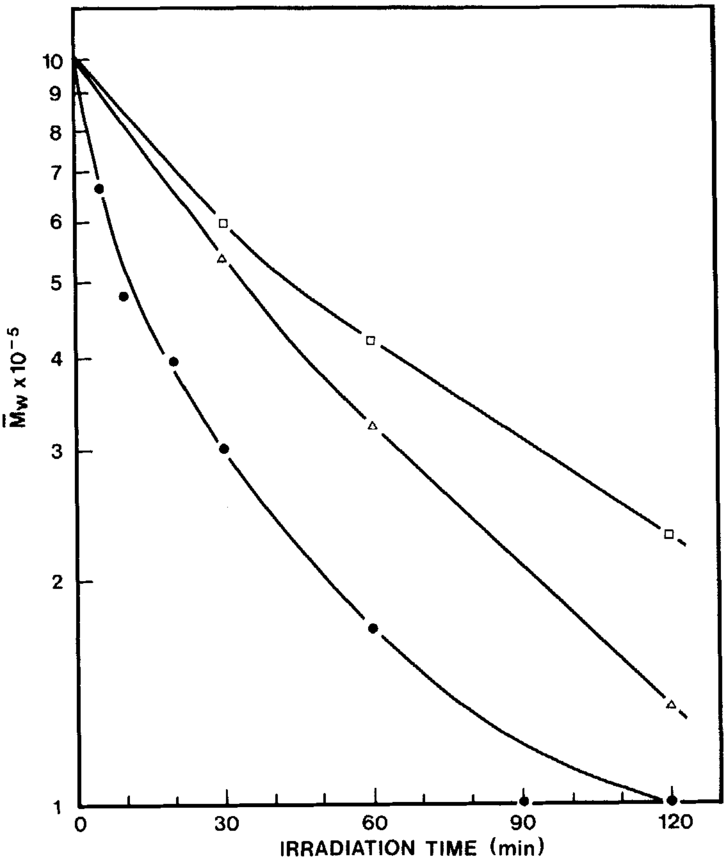

FIG. 1. Variation of molecular weight as a function of irradiation time for the 70-W ultrasonic degradation of 0.5% HPC ($\bar{M}_w = 1.0 \times 10^6$) water solutions of different volumes at 27°C: (●) 40, (△) 100, and (□) 150 mL.

$\bar{M}_w = 3.0 \times 10^5$ appears to have a sphere-like structure as shown by its high (1.42) k_H value. Huggins coefficient $k_H = 2.57$ for HPC sample of $\bar{M}_w = 1.0 \times 10^6$ suggests that the chains must be in extended form.

Degradation of HPC Solutions in Water

Effect of Solution Volume

In Fig. 1 are shown the variations of molecular weight as a function of irradiation time for the 70 W (frequency 20 kHz) ultrasonic degradation of 0.5% HPC ($\overline{M}_w = 1.0 \times 10^6$) water (distilled) solutions of different volumes at 27°C. After 30 min of irradiation time the $\overline{M}_w$ values for solution volumes of 150, 100, and 40 mL were 6.0×10^5, 5.4×10^5, and 3.0×10^5, respectively. After 60 min irradiation time, the $\overline{M}_w$ values for 150, 100, and 40 mL were 4.2×10^5, 3.2×10^5, and 1.72×10^5, respectively. It is quite clear from these data that the degradation of HPC in water solutions by this equipment is volume dependent. It must be added here that other factors, e.g., the ratio of probe diameter to reactor diameter and the immersion depth of the probe in solution, are also important in ultrasonic degradations. The volume dependence observed in this study is of only qualitative importance.

El'tsefon and Berlin [19, 20], who studied the influence of the shape of the vessel and the conditions of absorption of acoustic energy on kinetics of the ultrasonic degradation of polystyrene in benzene solutions, did introduce an energy q factor of degradation into their formal kinetics;

$$q = Ut/vc \tag{3}$$

where U is the intensity of irradiation, t is the time of exposure, v is the volume of sample, and c is the concentration of polystyrene. They found the q factor to be a more general parameter of the degradation process than time. Due to the low ultrasonic intensity used here, the q parameter does not define the HPC-water system well; however, the volume dependence of degradation found in the El'tsefon and Berlin [19, 20] study is qualitatively true in the present case as well.

Effect of Ultrasound Intensity

In Fig. 2 and Table 2 are shown the effects of ultrasound intensity (for three different volumes) on the degradation of 0.5% HPC ($\overline{M}_w = 1.0 \times 10^6$) water solutions for a fixed period of 120 min at 27°C. The minimum ultrasound intensity required to produce cavitation in 0.5% HPC-water solutions at 27°C depended on the volume of the solution used and were of the order of 35, 25, and 15-20 W for 150, 100, and 40 mL solutions, respectively. After the onset of cavitation the decrease in molecular weight as a function of ultrasound intensity was also volume dependent. The concept that cavitation brings about degradation in water solutions of HPC originates from the work of Weissler [6] who carried out ultrasonic degradation experiments as a function of ultrasonic intensity on solutions of hydroxyethyl cellulose and detected the presence of cavitation by intense transverse illumination.

In Fig. 3 and Tables 3 and 5 are shown the variation of molecular weight as a function of irradiation time for the ultrasonic degradation of 0.5% HPC (1.0×10^6) 40 mL water solutions at 27°C for ultrasound

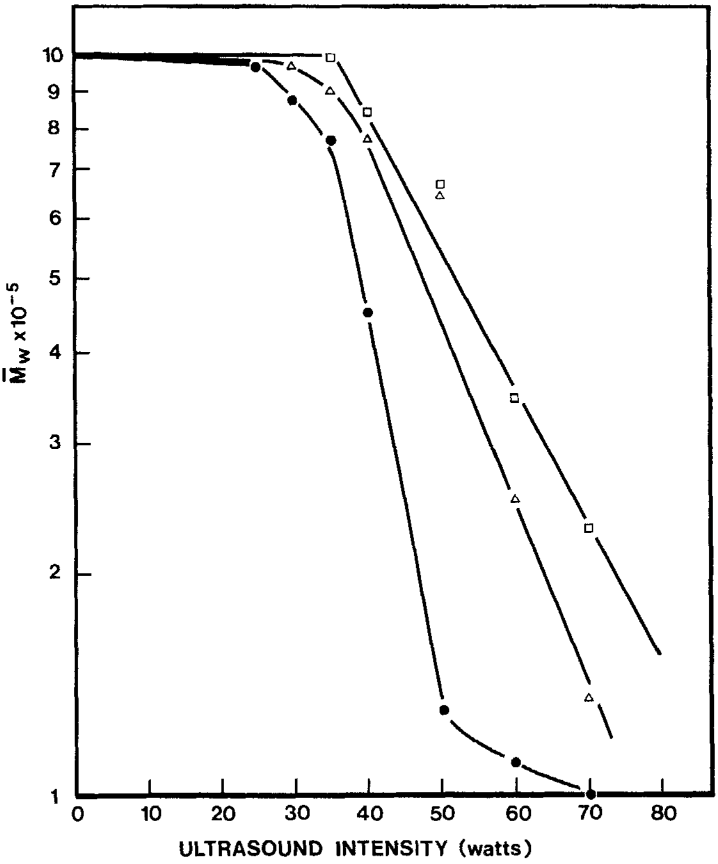

FIG. 2. Effect of ultrasound intensity on the degradation of 0.5% HPC ($\overline{M}_w = 1.0 \times 10^6$) water solutions for a fixed period of 120 min at 27°C: (●) 40, (△) 100, and (□) 150 mL. (See Table 2 for other data.)

intensities of 40, 50, 60, and 70 W, respectively. The variation of $\overline{M}_w$ vs irradiation time is intensity dependent. These results agree well with those reported by Akiya et al. [4] for methyl cellulose and cotton cellulose, by Weissler [6] on hydroxyethyl cellulose, by Melville and Murray [21], by Prudhomme and Graber [2], by Hirose [22], and by Mostafa [23]. These results also agree with those of Thomas and Alexander [9] who studied the ultrasonic degradation of cellulose nitrate in ethyl acetate at radio frequency powers of 50 and 120 W. They found out that for equal degradations, lower intensity would

TABLE 2. Effect of Ultrasound Intensity on the Degradation of 0.5% Water Solutions of HPC ($\bar{M}_w = 1.0 \times 10^6$) during a Fixed Period of 120 min at 27°C

Volume of solution (mL)	25 W		30 W		35 W		40 W		50 W		60 W		70 W	
	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
40	10.0	1.23	9.0	1.10	8.0	1.01	4.5	1.12	1.3	1.66	1.1	1.80	1.0	3.48
100	-	-	10.0	0.96	9.2	0.90	8.0	1.10	6.7	0.85	2.7	0.61	1.4	1.90
150	-	-	-	-	11.0	1.05	8.6	1.04	6.9	0.84	3.6	0.99	2.4	1.16

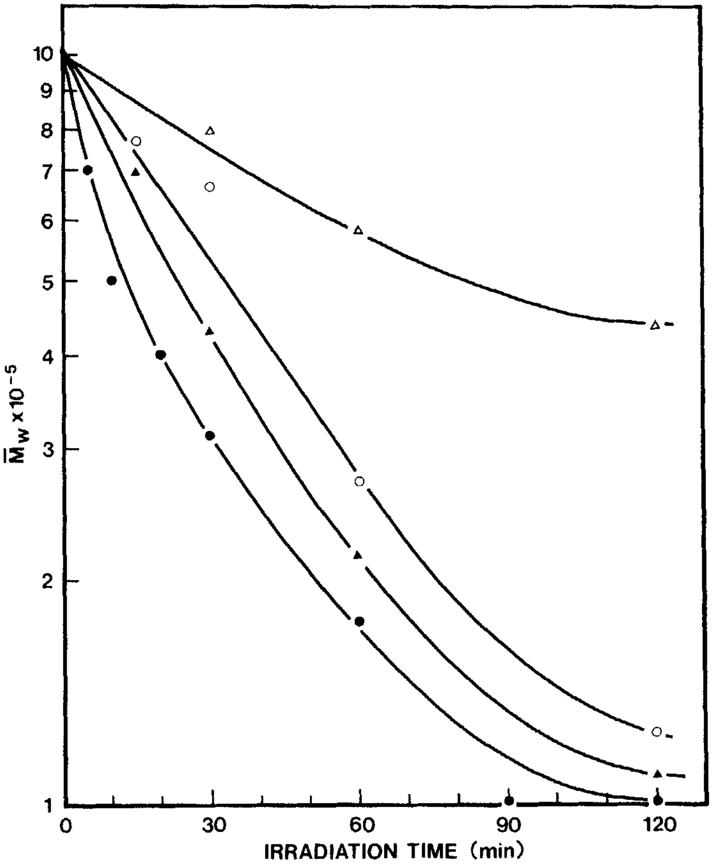

FIG. 3. Variation of molecular weight as a function of irradiation time for the ultrasonic degradation of 0.5% HPC ($\bar{M}_w = 1.0 \times 10^6$) water solutions (40 mL) at 27°C for ultrasound intensities of (△) 40, (○) 50, (▲) 60, and (●) 70 W. (See Tables 3 and 5 for other data.)

require longer times. However, the conclusions from the present work do not agree with those of Thomas and Alexander [9] when they state that "the rate of degradation is independent of power as long as cavitation is present." The present conclusions agree well with those of Hirose [22] that cavitation intensity does not increase linearly with the increase in sound intensity, because there exists a lower threshold of ultrasonic intensity below which cavitation does not occur [23].

Effect of Temperature

In Fig. 4 and Table 4 are shown the variation of molecular weight as a function of irradiation time for the 70 W ultrasonic degradation

TABLE 3. Effect of Ultrasound Intensity on the Degradation of 0.5% Water Solutions (40 mL) of HPC ($\overline{M}_w = 1.0 \times 10^6$) at 27°C

Ultrasound intensity (W)	Time of irradiation (min)	$[\eta]$ at 25°C (dL/g)	$\overline{M}_w \times 10^{-5}$	Huggins coefficient k_H
50	15	8.0	7.7	1.29
	30	7.0	6.75	0.96
	60	2.8	2.70	0.79
	120	1.3	1.25	1.66
60	15	7.0	6.75	0.96
	30	4.3	4.20	0.96
	60	2.15	2.10	1.17
	120	1.1	1.05	1.80
70	5	7.1	6.75	1.16
	10	5.0	4.8	1.12
	20	4.0	3.9	0.89
	30	3.1	3.0	0.83
	60	1.75	1.72	1.24
	90	1.0	0.95	2.10
	120	1.0	0.95	3.48

of 0.3% HPC ($\overline{M}_w = 1.0 \times 10^6$) 40 mL water solutions at 27 and 12°C. The data obtained at two temperatures fit a single curve, suggesting that under these conditions temperature has no effect on the degradation of HPC in water. These results are in agreement with those obtained by Simionescu and Rusan [24] on the degradation of agar-agar solutions in water at 16, 20, and 36°C. Thomas and Alexander [10], while studying the effect of temperature on ultrasonic degradation, found that cavitation and hence degradation did not take place below and above two initial temperatures. Keeping in mind the results of Thomas and Alexander [10], effect of temperature was reevaluated by making studies at low ultrasound intensity.

In Fig. 5 and Table 5 are shown the variation of molecular weight as a function of irradiation time for 40 W ultrasonic degradation of 0.5% HPC ($\overline{M}_w = 1.0 \times 10^6$) 40 mL water solutions at 27 and 4°C. It was remarked that degradation improved on lowering the temperature. This would suggest that the temperature dependence of

TABLE 4. Effect of Temperature on the Degradation of 0.3% Water Solutions (40 mL) of HPC ($\overline{M}_w = 1.0 \times 10^6$) at High (70 W) Ultrasound Intensity

Time of irradiation (min)	Temperature of degradation					
	27°C			12°C		
	[η] (dL/g)	$\overline{M}_w \times 10^{-5}$	k_H	[η] (dL/g)	$\overline{M}_w \times 10^{-5}$	k_H
5	6.8	6.5	0.86	6.8	6.5	0.86
10	5.0	4.8	0.87	4.65	4.6	0.55
15	4.2	4.0	0.85	3.80	3.6	0.64
30	2.5	2.4	0.57	2.50	2.4	0.69
60	1.8	1.75	0.44	1.40	1.35	1.00
90	1.0	0.95	1.33	-	-	-
120	0.8	0.77	1.56	0.90	0.86	2.05

TABLE 5. Effect of Temperature on the Degradation of 0.5% Water Solutions (40 mL) of HPC ($\overline{M}_w = 1.0 \times 10^6$) at Low (40 W) Ultrasound Intensity

Time of irradiation (min)	Temperature of degradation					
	27°C			4°C		
	[η] (dL/g)	$\overline{M}_w \times 10^{-5}$	k_H	[η] (dL/g)	$\overline{M}_w \times 10^{-5}$	k_H
30	8.2	8.0	1.38	6.6	6.3	1.18
60	6.1	5.85	1.16	3.5	3.4	0.86
120	4.5	4.4	1.12	-	-	-
129	-	-	-	1.75	1.72	1.24

sonodegradation and sonoluminescence follow similar trends. This also supports the theory of Borgstedt [25] who refuted the idea that dissolved polymer molecules could act as nuclei for cavitation proposed by Langton and Vaughan [26, 27]. Improved degradation at lower temperatures is also contradictory to that proposed by Hirose [22] who suggested that at low temperatures the viscosity of the

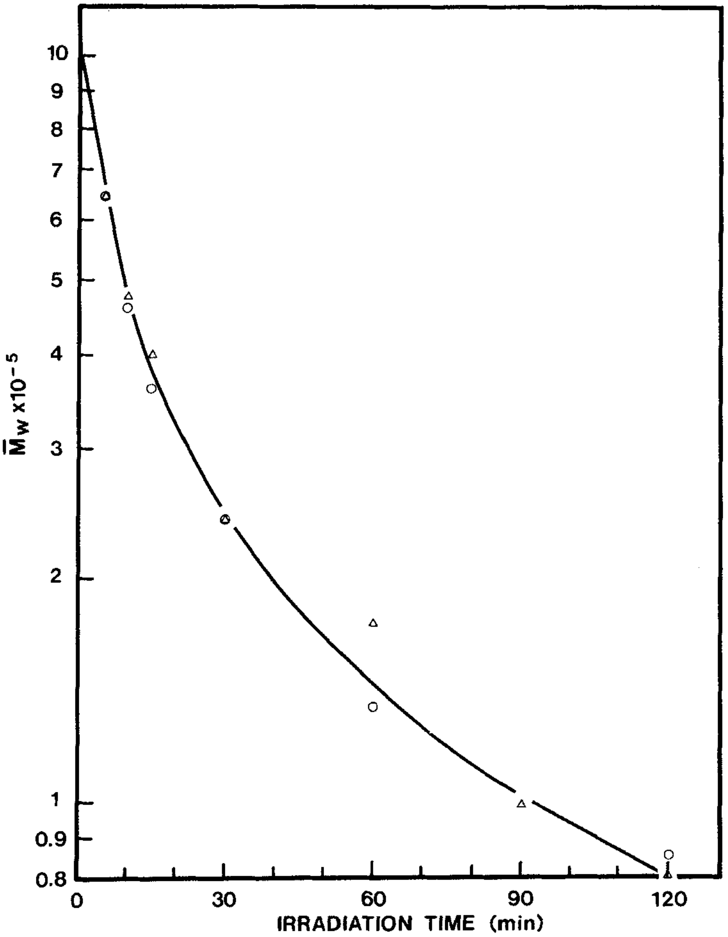

FIG. 4. Variation of molecular weight as a function of irradiation time for the 70-W ultrasonic degradation of 0.3% HPC ($\bar{M}_w$ = 1.0 × 10^6) water solutions (40 mL) at (△) 27 and (○) 12°C. (See Table 4 for other data.)

polymer solution increases and may become viscous enough to prevent cavitation and hence degradation.

The reason as to why changes in the 70 W degradation of HPC ($\bar{M}_w$ = 1.0 × 10^6) 40 mL water solutions at 27 and 12°C were not noted stems from the fact that degradation at 27°C is near ideal due to relatively high intensity 70 W, considering the 40 mL volume of solution used, and consequently cannot be improved. The effect of

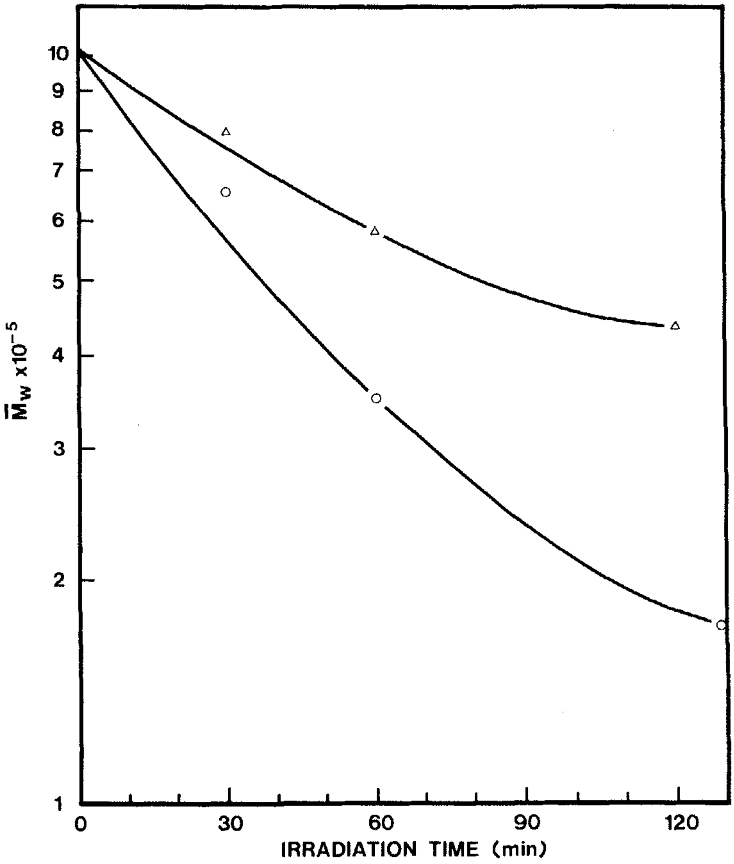

FIG. 5. Variation of molecular weight as a function of irradiation time for the 40-W ultrasonic degradation of 0.5% HPC ($\overline{M}_w = 1.0 \times 10^6$) solutions (40 mL) at (△) 27 and (○) 4°C. (See Table 5 for other data.)

temperature in the HPC degradations in ethanol and THF is far more pronounced and will be dealt with later on.

Variations in Huggins Coefficient of HPC in Water Solutions after Irradiation

In Table 1 are shown the Huggins coefficients k_H in the non-degraded samples of HPC, and in Tables 2 to 5 values are listed for the degraded HPC samples. In general k_H decreases initially, becomes near constant, and then increases as the molecular weights tend to reach the limiting values. The decrease in k_H values is often noted on shear degradation as the molecular weights decrease. However, increased values of k_H are sometimes evidenced as signs of branching reactions [28, 29]. These results are somewhat different than those of Sato and Nalepa [12] who showed that in the ultrasound degradation of hydroxyethyl cellulose (HEC) the k_H values remain unchanged at 0.6, suggesting that the viscosity changes in their studies were strictly due to random scissions and that there were no changes in polymer-solvent interactions. Their 0.6 values for sonicated HEC agree with those reported by Brown [30].

Rate Constants for the Degradation of HPC in Water Solutions

The relation [31, 32] between the number-average degree of polymerization P_n and the time (t) in a random degradation process is given by

$$-\ln (1 - 1/P_{n,t}) = kt - \ln (1 - 1/P_{n,0}) \qquad (4)$$

where $P_{n,t}$ and $P_{n,0}$ are the number-average degree of polymerization at times t = t and t = 0 respectively, and k is the rate constant.

According to Sato and Nalepa [12], Eq. (4) can be rendered to the form

$$\frac{1}{\overline{M}_{n,t}} = \frac{1}{\overline{M}_{n,0}} + k't \qquad (5)$$

here $k' = k/M_0$. M_0 is the average molecular weight of each monomer unit.

From the knowledge of $\overline{M}_n$ at various time t, plots of $1/\overline{M}_n$ versus t can be traced to obtain k' and consequently k.

Values of $\overline{M}_n$ for HPC can be conventionally obtained by osmometry, or even by a gel permeation chromatograph [33]. This, however, is cumbersome and sometimes not even possible. That is why the degradation reactions have been, for a long time, followed by viscometry. In the present study as well, the ultrasonic degradation reactions have been monitored by viscosity. The rate constants have been computed from the plots of $1/\overline{M}_w$ as a function of irradiation time (Eq. 6). Thus these rate constants k" have a built-in error which must be kept in mind prior to making any comparisons with other literature data.

$$\frac{1}{\overline{M}_{w,t}} = \frac{1}{\overline{M}_{w,0}} + k''t \qquad (6)$$

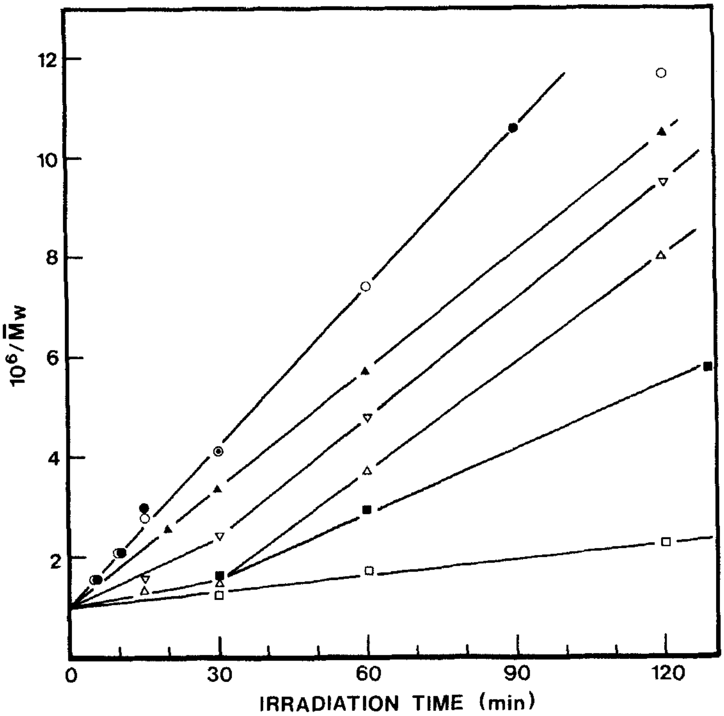

FIG. 6. Variation of $1/\overline{M}_w$ as a function of irradiation time for the ultrasonic degradation of HPC ($\overline{M}_w = 1.0 \times 10^6$) water solutions (40 mL): (○) 70 W, 0.3%, 27°C; (●) 70 W, 0.3%, 12°C; (▲) 70 W, 0.5%, 27°C; (▽) 60 W, 0.5%, 27°C; (△) 50 W, 0.5%, 27°C, (■) 50 W, 0.5%, 4°C; and (□) 40 W, 0.5%, 27°C. (See Tables 3, 4, and 5 for other data.)

According to Ranby and Rabek [34], k'' is $\frac{1}{2}$ of k' for a random distribution.

In Fig. 6 are shown plots for the variation of $1/\overline{M}_w$ as a function of irradiation time for the ultrasonic degradation of HPC ($\overline{M}_w = 1.0 \times 10^6$) 40 mL water solutions. The overall rate constants k'' calculated from the linear part of the plots in Fig. 6 are presented in Table 12. These yielded the following information.

(a) Ultrasound intensity, solution concentration and temperature remaining constant, degradation rates decrease with increasing volume of solution but not linearly.

TABLE 6. Effect of Ultrasound Intensity on the Degradation of Ethanol Solutions (40 mL) of HPC ($\overline{M}_w = 1.0 \times 10^6$)

		Intensity			
		60 W		70 W	
Concentration (g/dL)	Time of irradiation (min)	[η]	$\overline{M}_w \times 10^{-5}$	[η]	$\overline{M}_w \times 10^{-5}$
0.12	60	10.0	8.0	3.7	3.0
	120	8.2	6.4	3.1	2.15
0.075	30	9.5	7.5	4.75	3.5
	90	8.0	6.2	3.20	2.2
0.031	20	9.5	7.5	4.5	3.3
	40	8.2	6.4	4.0	2.8

(b) Solution volume, temperature and concentration remaining constant, degradation rates increase exponentially with increasing intensity of ultrasound.

(c) Solution volume, temperature and ultrasound intensity remaining constant, degradation rates decrease with increasing concentration.

(d) Solution volume, concentration remaining constant for low ultrasound intensity, degradation rates increase with decreasing temperature.

Making use of the concept of El'tsefon and Berlin [19, 20], the data on rate constants obtained at 27°C for various intensities, concentrations, and volumes were normalized [to eliminate concentration and volume effects and replace them by the weight of the polymer and reduce the ultrasonic intensity (U) from watts to watts per gram (U/g) of the polymer]. A log-log plot of rate constants k" versus U/g yielded a straight line with the relation

$$k'' = 6.4 \times 10^{-12}\ (U/g)^{0.9} \qquad (7)$$

This relation is valid at 27°C for HPC samples of $\overline{M}_w = 1.0 \times 10^6$ in water. The value of $6.4 \times 10^{-12}\ s^{-1}$ increases as the temperature is lowered.

TABLE 7. Ultrasound Irradiation (60 W) of Hydroxypropyl Cellulose in Ethanol (40 mL) at 27°C

Sample molecular weight $\overline{M}_w$	[Concentration] (g/dL)	Time of irradiation (min)	$[\eta]$	$\overline{M}_w \times 10^{-5}$	k_H, Huggins coefficient
1.0×10^6	0.12%	0	14.4	10.0	0.76
		15	11.0	9.0	0.53
		30	10.4	8.5	0.49
		60	10.0	8.0	0.43
		90	8.0	6.2	0.41
1.0×10^6	0.075%	0	14.4	10.0	0.76
		5	12.0	9.5	0.63
		15	10.5	8.5	0.41
		60	8.5	6.7	0.10
		120	7.5	5.8	0.19
1.0×10^6	0.031%	0	14.4	10.0	0.76
		10	11.4	9.3	0.56
		30	8.65	7.0	-
		60	7.70	6.0	-
		120	7.00	5.4	-
3.0×10^5	0.25%	0	3.75	3.0	0.48
		60	3.75	3.0	0.18
		120	3.75	3.0	-
1.0×10^5	0.40%	0	1.35	1.0	0.50
		60	1.35	1.0	0.47
		120	1.35	1.0	-

Degradation of HPC Solutions in Ethanol

Effect of Solution Concentration and Ultrasound Intensity

In Table 6 are listed some of the data obtained at different irradiation times for HPC ($\overline{M}_w = 1.0 \times 10^6$) ethanol solutions (40 mL) with concentrations of 0.12, 0.075, and 0.031 g/dL at two ultrasound intensitites of 60 and 70 W. It may be observed that, unlike in water, in ethanol solutions ultrasonic degradations are strongly dependent on ultrasound intensity and solution concentration. A 10-W increase in ultrasound intensity, from 60 to 70 W, improves degradation significantly.

Table 7 carries 60 W ultrasonic degradation of HPC samples

($\overline{M}_w = 1.0 \times 10^6$, 3.0×10^5, and 1.0×10^5) in 40 mL ethanol solutions at 27°C. HPC samples with $\overline{M}_w = 3.0 \times 10^5$ (0.25 g/dL) and 1.0×10^5 (0.4 g/dL) could not be degraded even for reaction times of 120 min. Their Huggins coefficient k_H, however, did decrease with time of irradiation. HPC ($\overline{M}_w = 1.0 \times 10^6$) solutions in ethanol degraded as a function of time of irradiation but reached only a limiting value of $\overline{M}_w = 5.0 \times 10^5$ beyond which there was no further decrease in $\overline{M}_w$. HPC solutions of lower concentration in ethanol degrade better and faster than those having high concentrations. Rate constants k" were calculated from the plots $1/\overline{M}_w$ versus time of irradiation at 60 W for HPC ($\overline{M}_w = 1.0 \times 10^6$) 40 mL ethanol solutions of concentrations 0.031, 0.075, and 0.12 g/dL. k" values increased from 1.05×10^{-10} to 1.33×10^{-10} to 1.75×10^{-10} as the concentration decreased from 0.12 to 0.075 to 0.031 g/dL, respectively. A plot of k" vs concentration yielded a rough value of 8.0×10^{-11} s^{-1} for k" at 0.3 g/dL for the 60-W degradation of HPC (1.0×10^6) ethanol solutions (40 mL). The experimental k" at 0.3 g/dL for 70 W degradation of ethanol solution was 6.6×10^{-10} s^{-1}, showing clearly the effect of an additional 10 W ultrasound intensity on degradation. If one compares these results with those obtained with water solutions, one notes that the minimum ultrasonic energy to generate cavitation at 27°C in ethanol solution would be higher (~40 W) than that in water solutions (20 W).

Effect of Temperature

In Fig. 7 and Table 8 are shown the variation of molecular weight as a function of time for the ultrasonic degradation of HPC ($\overline{M}_w = 1.0 \times 10^6$) ethanol solutions at different temperatures. One notes that ultrasonic degradation of HPC in ethanol solution is improved noticeably as the temperature decreases. This would suggest that cavitation or the quality of cavitation improves as the temperature is lowered, due to a better coupling between the transducer and the medium.

Variations in Huggins Coefficient of HPC in Ethanol Solutions after Irradiation

In Table 1 are presented the Huggins coefficients k_H of the nondegraded samples in ethanol and in Tables 7 and 8 values are listed for the degraded HPC samples. k_H decreases regularly with increasing degradation. Unlike in water, where after an initial decrease k_H increased, suggesting the presence of cross-links, in ethanol k_H values do not increase even for $\overline{M}_w$ in the range of 1.0×10^5.

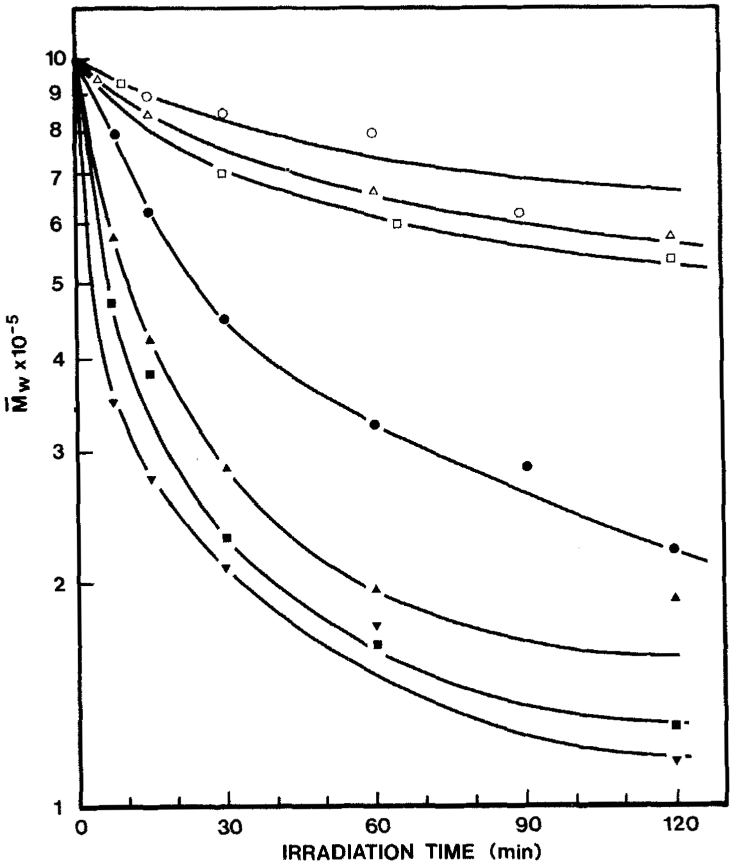

FIG. 7. Variation of molecular weight as a function of irradiation time for the ultrasonic degradation of HPC ($\bar{M}_w = 1.0 \times 10^6$) ethanol solutions (40 mL): (○) 60 W, 0.12%, 27°C; (△) 60 W, 0.075%, 27°C; (□) 60 W, 0.031% 27°C; (●) 70 W, 0.3%, 27°C; (▲) 70 W, 0.3%, 12°C; (■) 70W, 0.3%, 2°C; and (▼) 70 W, 0.3%, -15°C. (See Tables 6, 7, and 8 for other data.)

Rate Constants for the Degradation of HPC in Ethanol

In Fig. 8 are shown plots for the variation of $1/\bar{M}_w$ as a function of time for the ultrasonic degradation of HPC ($\bar{M}_w = 1.0 \times 10^6$) 40 mL ethanol solutions. The overall rate constants k" calculated from the linear part of the plot in Fig. 8 are presented in Table 12. These rate constants increased remarkably with decreasing temperature, jumping from a value of 6.6×10^{-10} s^{-1} at 27°C to 31.0×10^{-10} s^{-1} at -15°C.

TABLE 8. Effect of Temperature on the Degradation of 0.3% Ethanol Solution (40 mL) of HPC ($\overline{M}_w$ = 1.0 × 10^6) at 70 W Ultrasound Intensity

Temperature (°C)	Time of irradiation (min)	[η] (dL/g)	$\overline{M}_w \times 10^{-5}$	k_H
27	8.5	10.0	8.0	0.49
	15	8.0	6.25	0.47
	30	6.0	4.5	0.48
	60	4.5	3.3	0.46
	90	4.0	2.85	0.51
	120	3.4	2.2	0.40
12	7.5	7.5	5.8	0.47
	15	5.7	4.25	0.39
	30	4.0	2.85	0.60
	60	2.9	1.95	0.49
	120	2.8	1.90	0.38
2	7.5	6.3	4.75	0.43
	15	5.1	3.80	0.50
	30	3.3	2.30	0.44
	60	2.45	1.65	0.36
	120	1.85	1.20	0.29
-15	7.5	4.75	3.50	0.55
	15	3.85	2.75	0.44
	30	3.0	2.10	0.39
	60	2.55	1.75	0.31
	120	1.80	1.15	0.29

Degradation of HPC in THF Solutions

Ultrasonic degradations of HPC ($\overline{M}_w$ = 3.0 × 10^5) THF solutions (0.25%) and HPC ($\overline{M}_w$ = 1.0 × 10^5) THF solutions (0.4%) were tried at 27°C for periods of 15, 60, and 120 min. In the case of HPC ($\overline{M}_w$ = 3.0 × 10^5), the Huggins coefficient of 1.42 came down to 0.71 in 15 min and remained constant after that. The Huggins coefficient for the HPC ($\overline{M}_w$ = 1.0 × 10^5) remained unchanged after irradiation. The molecular weight of these two HPC samples did not change as shown by their intrinsic value data (not shown here).

In Table 9 and Fig. 9 are presented the data on 70 W ultrasound irradiation of HPC (1.0 × 10^6) at different temperatures for solution concentrations of 0.18 g/dL.

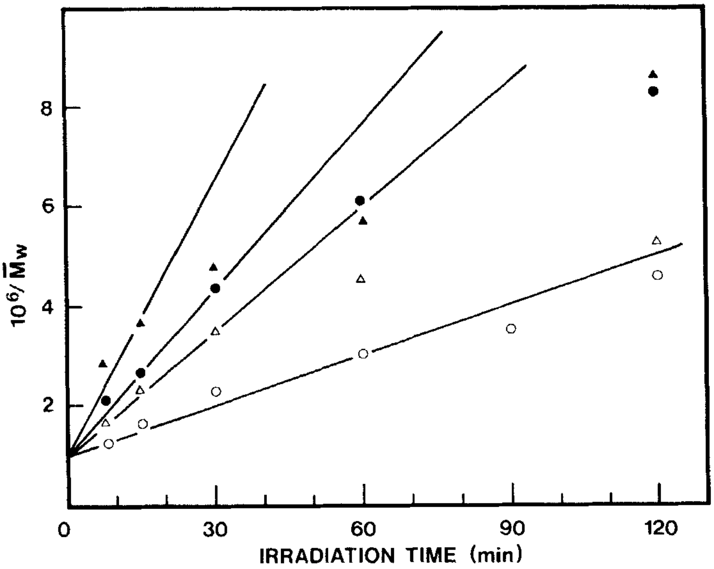

FIG. 8. Variation of $1/\overline{M}_w$ as a function of irradiation time for the 70-W ultrasonic degradation of 0.3% HPC ($\overline{M}_w = 1.0 \times 10^6$) ethanol solutions (40 mL): (○) 27, (△) 12, (●) 2, and (▲) -15°C. (See Table 8 for other data.)

At 27°C there was no change in viscosity of 8.0 for irradiation time of 15 min. During this period, however, the Huggins coefficient k_H decreased from 2.57 to 1.50. After 30 min of irradiation there was a decrease in $[\eta]$ from 8.0 to 7.0 and the Huggins coefficient k_H decreased to 0.78. At 120 min irradiation the $\overline{M}_w$ value reached a plateau of 5.8×10^5 as was also noted for 60 W irradiation of HPC ethanol solutions. Degradations at lower temperature were much improved and no significant induction periods were noted as was observed at 27°C for the first 15 min. The Huggins coefficient decreased abruptly from 2.57 to 0.3 ± 0.1 after 15 min irradiations at lower temperatures of 12, 2, and -15°C. This would suggest that solvent-polymer bondings, which take a long time to disrupt at 27°C, break faster at lower temperatures.

With a view of having a better idea of these solvent-polymer interactions, ultrasonic degradations were studied with 0.3 g/dL HPC-THF solutions. The data obtained are listed in Table 10 and shown in Fig. 10. One notes that for 27°C degradations, the induction period has reached to about 60 min. In the first 30 min of degradation there

TABLE 9. Ultrasound Irradiation (70 W) of Hydroxypropyl Cellulose ($\overline{M}_w = 1.0 \times 10^6$, 0.18%, 40 mL) in THF at Various Temperatures for Different Periods of Time

Temperature (°C)	Time of irradiation (min)	[η] in THF at 25°C	$\overline{M}_w \times 10^{-5}$	k_H, Huggins coefficient
-15	Nonirradiated	8.0	10.00	2.57
	15	3.9	4.20	0.33
	30	1.5	1.20	0.35
	60	1.85	1.55	0.23
	120	1.45	1.15	0.53
2	15	4.55	5.00	0.21
	30	3.5	3.60	0.41
	60	2.45	2.20	0.37
	120	1.7	1.40	0.63
12	15	6.5	8.00	0.42
	30	4.7	5.40	0.32
	60	3.5	3.40	0.40
	90	3.5	3.40	0.40
	120	2.8	2.70	0.28
27	15	8.0	10.0	1.50
	30	7.0	9.0	0.78
	60	5.5	6.50	0.64
	120	5.0	5.80	0.67

was no decrease in [η] and the Huggins coefficient k_H decreased from 2.57 to 2.50. After a 60-min degradation period, [η] decreased from 8.0 to 7.8 and k_H decreased to 1.0. At 120 min degradation the $\overline{M}_w$ reached a plateau of 5.4×10^5 and so did the k_H value. At a temperature of 12°C there was still an induction period, though short, and in 15 min of irradiation [η] was lowered to 7.4 and k_H decreased to 1.24. At 30 min irradiation [η] and k_H decreased sharply. At lower temperatures of 2 and -15°C, degradations were rapid and no induction periods were observed. k_H decreased abruptly from 2.57 to 0.20, indicating that the solvent-polymer interactions decrease at lower temperatures.

In order to show the magnitude of solvent-polymer interactions, in Fig. 11 are shown the variation of $\eta_{sp/c}$ as a function of c for

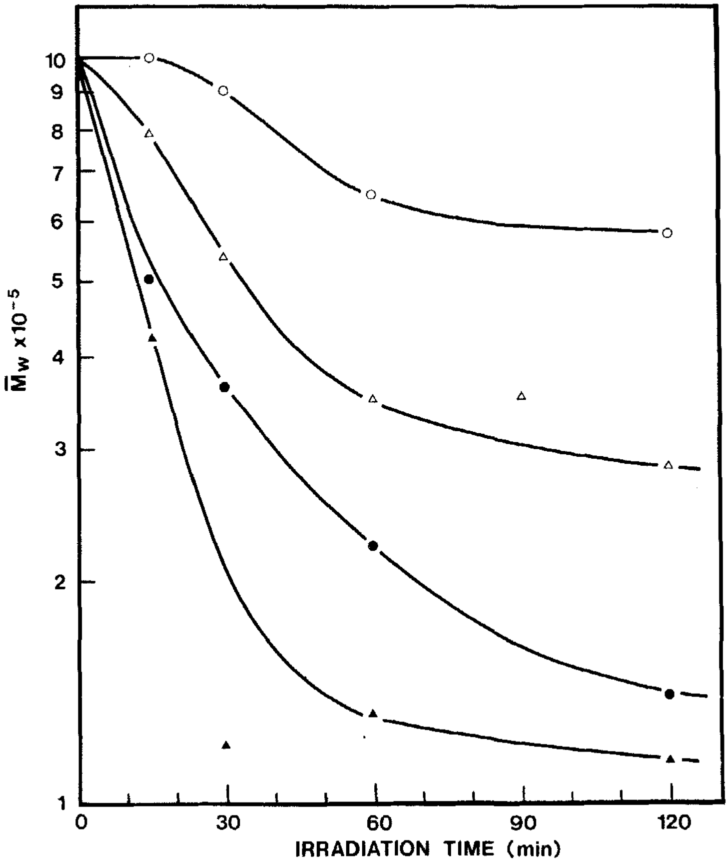

FIG. 9. Variation of molecular weight as a function of irradiation time for the 70-W ultrasonic degradation of 0.18% HPC ($\bar{M}_w = 1.0 \times 10^6$) THF solutions (40 mL) for four different temperatures: (○) 27, (△) 12, (●) 2, and (▲) -15°C. (See Table 9 for other data.)

nondegraded HPC ($\bar{M}_w = 1.0 \times 10^6$) THF solutions and degraded HPC solutions for various periods of time. For 30 min degradation $\eta_{sp/c}$ for degraded samples fit the same line as that for nondegraded. After 60 min irradiation $\eta_{sp/c}$ for c = 0.12, 0.09, and 0.06 g/dL decreased from 27.2, 22.3, 17.5 to 15.0, 13.4 11.5, respectively; however, $[\eta]$ decreased from 8.0 to 7.8 only. This would suggest that during this period of 60 min, ultrasound energy is being consumed in breaking solvent-polymer interactions of some types, e.g., hydrogen bonding

TABLE 10. Ultrasound Irradiation (70 W) of Hydroxypropyl Cellulose ($\overline{M}_w = 1.0 \times 10^6$, 0.3%, 40 mL) in THF at Various Temperatures for Different Periods of Time

Temperature (°C)	Time of irradiation (min)	[η] in THF at 25°C	$\overline{M}_w \times 10^{-5}$	k_H Huggins coefficient
-15	Nonirradiated	8.00	10.00	2.57
	15	5.20	6.00	0.18
	30	3.50	3.70	0.17
	60	2.05	2.00	0.51
	90	1.80	1.50	0.31
	120	1.70	1.40	0.23
2	15	6.30	7.50	0.21
	30	4.10	4.40	0.15
	60	2.85	2.80	0.25
	90	2.20	1.90	0.50
	120	1.90	1.60	0.18
12	15	7.40	9.50	1.24
	30	5.60	6.50	0.44
	60	3.60	3.80	0.22
	90	3.20	3.20	0.30
	120	3.80	4.00	0.33
27	30	8.00	10.00	2.50
	60	7.80	9.70	1.00
	75	6.00	7.20	1.07
	90	5.00	5.80	1.12
	120	4.80	5.40	1.26

between HPC and THF. After the breaking of hydrogen bonds the degradations proceed normally as is evidenced by the changes in the Huggins coefficient values.

In order to see whether the nondegraded HPC-THF solutions themselves show some confirmation changes at different temperatures, their intrinsic values and Huggins coefficients were found at 40, 25, 10, and 0°C. These are shown in Table 11. Although [η] increases considerably (from 7.0 at 40°C to 10.0 at 0°C) with decreasing temperature, the Huggins' coefficient k_H changed from 2.78 at 40°C to 2.07 at 0°C. These values of Huggins' coefficient suggest that there are only minor conformational changes with temperature in the nondegraded HPC-THF solutions.

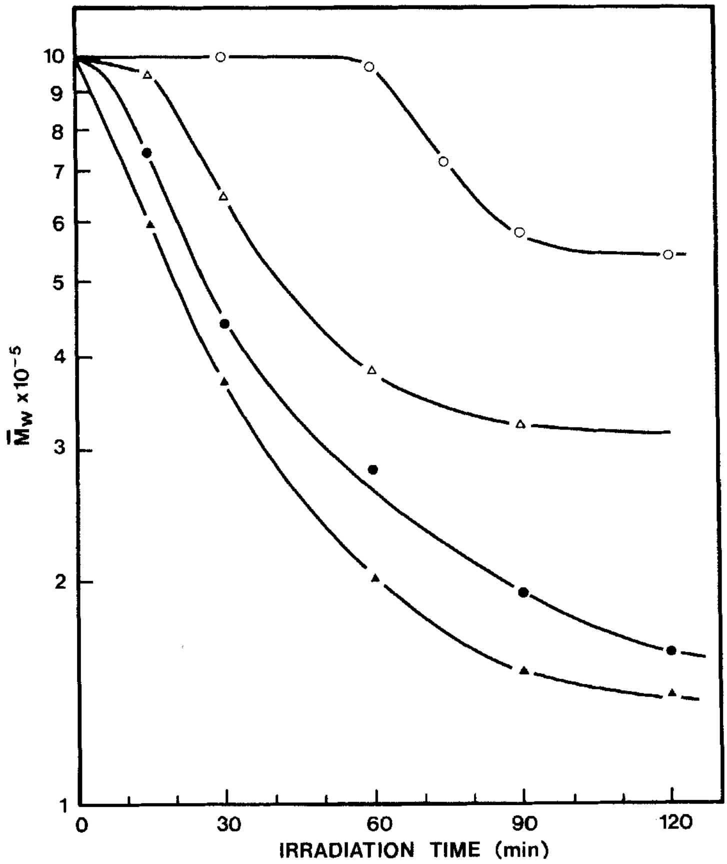

FIG. 10. Variation of molecular weight as a function of irradiation time for the 70-W ultrasonic degradation of 0.3% HPC ($\overline{M}_w = 1.0 \times 10^6$) THF solutions (40 mL) for four different temperatures: (○) 27, (△) 12, (●), 2 and (▲) -15°C. (See Table 10 for other data.))

Rate Constants for the HPC-THF System

In Fig. 12 are shown the variation of $1/\overline{M}_w$ as a function of irradiation time for the 70-W ultrasonic degradation of HPC ($\overline{M}_w = 1.0 \times 10^6$) THF solutions (40 mL) at different temperatures. The overall rate constants k'' calculated from the linear parts of the plots in Fig. 12 are presented in Table 12. These yield the following information:

(a) Ultrasound intensity, solution concentration and volume

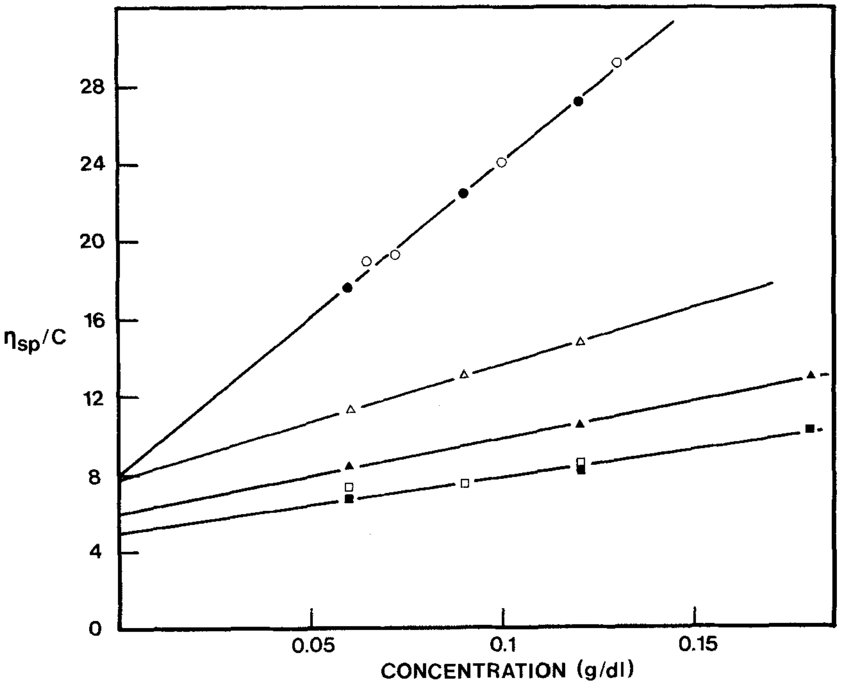

FIG. 11. Variation of $\eta_{sp/c}$ as a function of c for nondegraded HPC ($\overline{M}_w = 1.0 \times 10^6$) THF solutions and degraded HPC solutions for various periods of time: (○) nondegraded, (●) 30, (△) 60, (▲) 75, (□) 90, and (■) 120 min.

TABLE 11. Solution Properties of Hydroxypropyl Cellulose ($\overline{M}_w = 1.0 \times 10^6$) in THF

Temperature (°C)	Intrinsic viscosity $[\eta]^a$	Huggins coefficient k_H
40	7.0	2.78
25	8.0	2.57
10	9.0	2.24
0	10.0	2.07

$^a[\eta]$ values are difficult to obtain at -15°C due to frequent clogging of the viscometric capillaries.

TABLE 12. Rate Constants k'' for the Degradation of HPC ($\overline{M}_w$ = 1.0 × 10^6) in Different Solvents

Solvent	Solution concentration (g/dL)	Volume of solution ultrasounded (mL)	Ultrasound intensity (W)	Temperature (°C)	k'' × 10^{10} s^{-1}
Water	0.5	40	40	4	6.00
Water	0.5	40	40	27	1.66
Water	0.5	40	50	27	8.00
Water	0.5	40	60	27	10.00
Water	0.5	40	70	27	13.90
Water	0.5	100	70	27	5.55
Water	0.5	150	70	27	3.80
Water	0.3	40	70	27	17.40
Water	0.3	40	70	12	17.40
THF	0.3	40	70	27	1.20
THF	0.3	40	70	12	3.85
THF	0.3	40	70	2	7.36
THF	0.3	40	70	-15	10.40
THF	0.18	40	70	27	1.25
THF	0.18	40	70	12	5.00
THF	0.18	40	70	2	9.72
THF	0.18	40	70	-15	15.00
Ethanol	0.3	40	70	27	6.60
Ethanol	0.3	40	70	12	14.70
Ethanol	0.3	40	70	2	18.50
Ethanol	0.3	40	70	-15	31.00
Ethanol	0.12	40	60	27	1.05
Ethanol	0.075	40	60	27	1.33
Ethanol	0.031	40	60	27	1.75

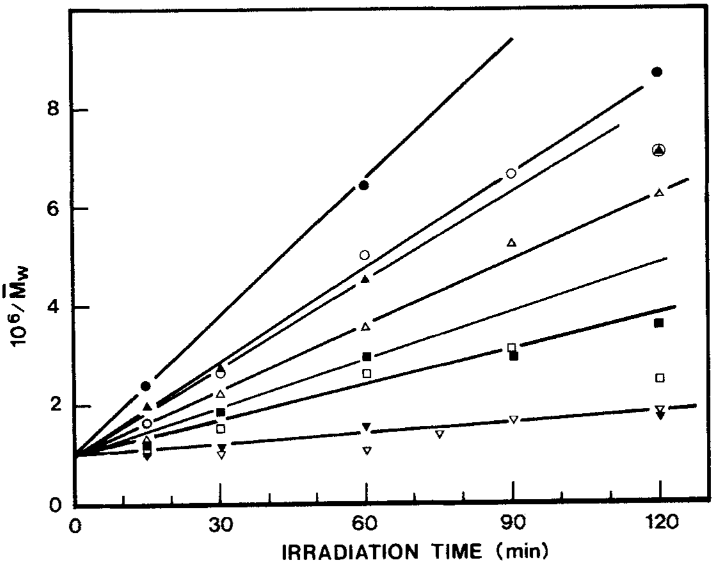

FIG. 12. Variation of $1/\overline{M}_w$ as a function of irradiation time for the 70-W ultrasonic degradation of HPC ($\overline{M}_w = 1.0 \times 10^6$) THF solutions (40 mL) at different temperatures: (●) 0.18%, -15°C; (○) 0.3%, -15°C; (▲) 0.18%, 2°C; (△) 0.3%, 2°C; (■) 0.18%, 12°C; (□) 0.3%, 12°C; (▼) 0.18%, 27°C; and (▽) 0.3%, 27°C.

remaining constant, degradation rates increase with decreasing temperature as was seen for HPC-ethanol solutions.

(b) Ultrasound intensity, temperature and solution volume remaining constant, degradation rates increase with decreasing concentration as was also seen in HPC-water and HPC-ethanol solutions.

Based on all these studies, the parameter (besides intensity) which is very prominent in enhancing the quality of cavitation is the temperature. Thus it was thought of interest to correlate the variables which control cavitation to the temperature parameter.

In his book Ultrasonics, The Low and High Intensity Applications, Ensminger [35] suggests that the onset of cavitation occurs at intensities, or cavitation thresholds, that depend upon such factors as the sizes of nuclei, ambient pressure, amount of dissolved gases, vapor pressure, viscosity, surface tension, and the frequency as well as duration of ultrasonic energy. To have effective cavitation, the bubble must be capable of expanding with the rarefaction part of the cycle of the impressed field and collapsing before the total pressure reaches its minimum value. That is, the bubble must reach a catastrophic size in less than one-quarter cycle of the impressed wave. Thus the generation of intense cavitation depends upon the relation between the dimensions of the nuclei, the wavelength of the sound field, and the intensity of the sound field. Frederick [36] gives the following relationship for the critical radius R_c (bubbles larger than critical radius do not yield intense cavitation) as

$$R_c = \frac{1}{\omega}\sqrt{3\gamma P_0/\rho} \qquad P_0 \gg 2\,\sigma/R_c \tag{8}$$

$$= \frac{1}{\omega}\sqrt{6\gamma\sigma/\rho R_c} \qquad P_0 \ll 2\sigma/R_c \tag{9}$$

where R_c is the critical bubble radius (cm), γ is the ratio (C_p/C_v) of specific heats of the gas in the bubble, P_0 is the hydrostatic pressure (atm), and ρ is the density of the liquid (g/cm^3).

The effect of surface tension on bubble size is indicated by

$$P_i = P_0 + \frac{2\sigma}{R_0} \tag{10}$$

where P_i is the vapor pressure inside the bubble and R_0 is the radius of the bubble which is stable under these conditions.

Analyses of Eq. (8)-(10) reveal that the factors which might influence the formation of the critical size bubbles in HPC solutions of THF and ethanol at low temperatures are the increased surface tension σ and the increased density ρ of the medium because ω, which is $2\pi f$ (f is the frequency of ultrasound), will not change at a constant ultrasound frequency. C_p/C_v can be considered not to change dramatically in this temperature range, and the hydrostatic pressure P_0 is constant as the depth of reaction vessel and the volume of the solution used are not changed.

Out of the two parameters, i.e., surface tension and density, thought to be responsible for improved cavitation, surface tension is considered to be of greater importance in controlling the critical bubble size. In their work on the effect of density on ultrasound degradations, Schmid and Beuttenmuller [1] concluded that density had little or no effect. In the present work at 27 °C, HPC solutions in water degrade much better as compared to that in ethanol, in spite of the fact that this characteristic impedance, ρC (where ρ is the density of the medium and the C is the velocity of sound), of water is higher at

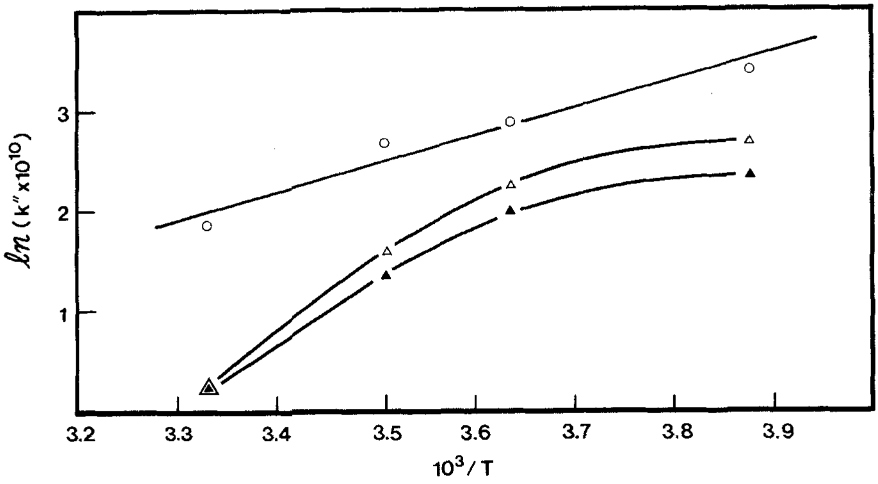

FIG. 13. Plot of ln k″ versus 1/T for the 70-W ultrasonic degradation of HPC ($\overline{M}_w = 1.0 \times 10^6$) in ethanol and tetrahydrofuran: (○) ethanol solutions, 0.3%; (△) THF solutions, 0.18%; and (▲) THF solutions, 0.3%.

1.48×10^{-5} g/cm^2·s at 20°C than 0.93×10^{-5} 8/cm^2·s for ethanol at the same temperature [35]. Based on these observations, one can only say that at 20 or 27°C the ultrasonic degradations do not follow the order of their characteristic impedances. The role of increasing density of the medium on the formation of critical size bubbles, however, cannot be minimized.

In Fig. 13 are shown plots of ln (k″ × 10^{10}) as a function of 1/T (where T is absolute temperature) for calculating the activation energy of the cavitation phenomenon. Although one can draw a straight line from the data obtained with the HPC-ethanol system, the data of the HPC-THF system fit a curve. A closer examination of the HPC-ethanol data also suggests that ln k″ as a function of 1/T is not exactly linear.

In Fig. 14 are shown plots of rate constants k″ obtained at different temperatures for HPC-ethanol and HPC-THF systems. k″ varies linearly with temperature.

Linear dependence of rate constants with temperature as shown in Fig. 14 support the earlier concept of surface tension and density being the factors responsible for better cavitation as these also vary with temperature linearly in the small temperature range studied.

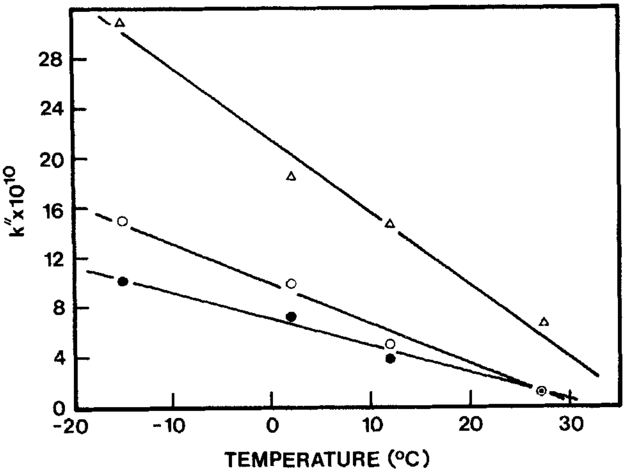

FIG. 14. Variation of rate constant k'' as a function of temperature for the 70-W ultrasonic degradation of HPC ($\overline{M}_w$ = 1.0 × 10^6) in ethanol and THF: (●) THF, 0.3%; (○) THF, 0.18%; and (△) ethanol, 0.3%.

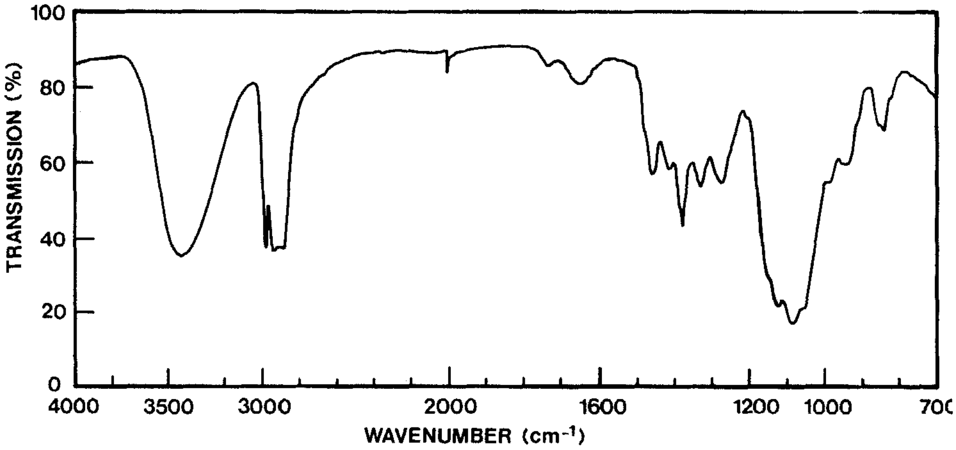

FIG. 15. Typical IR spectrum of HPC ($\overline{M}_w$ = 1.0 × 10^6) ultrasounded in ethanol solution for 120 min at 27° C.

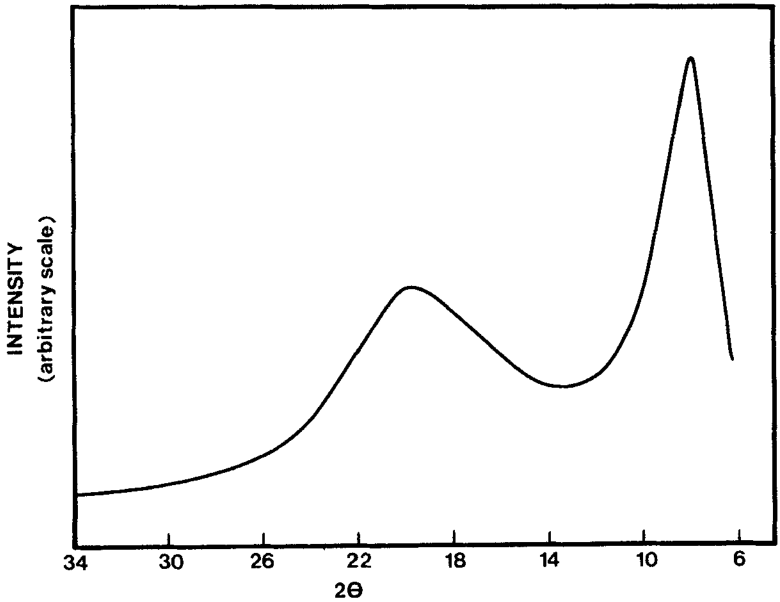

FIG. 16. Typical x-ray spectrum of HPC ($\overline{M}_w = 1.0 \times 10^6$) ultrasounded in ethanol solution for 120 min at 27°C.

Structural Analysis of Degraded HPC Sample

During the ultrasonic degradation of HPC in different solvents, the changes in $\overline{M}_w$ on irradiation have been attributed to random scission. In order to verify whether there were chemical or physical changes after ultrasonic treatments, a degraded HPC sample film of the HPC-ethanol system was analyzed for IR as shown in Fig. 15. This IR spectrum resembles those published by Samuels [37] for nontreated sample of HPC. In Fig. 16 is shown an x-ray diffraction pattern of the sonicated HPC film from the HPC-ethanol system which also resembles the equitorial scan obtained by Samuels [37] for a stretched (250%) HPC (molar substitution = 4.0) film. Contrary to the findings of Polcin et al. [13] who reported structural changes in cellulose fibers under the influence of ultrasonic degradation, no significant changes were noted for ultrasounded HPC in the present study.

CONCLUSIONS

The principal conclusions to be drawn from the present study may be summed up as follows:

(a) Out of the three solvents, viz., water, ethanol, and THF, in which the ultrasonic degradations of HPC have been studied at 27° C, water yields the best results. The rate of degradation follows the order water > ethanol > THF, which is not in line with their characteristic impedance values.

(b) In the HPC-water system, cavitation intensity did not increase linearly with ultrasound intensity because of a lower threshold of ultrasonic intensity (U_L) below which cavitation does not occur. The value of U_L depends on the concentration and volume of solution used. A log-log plot of U_L versus volume V for 0.5 g/dL concentration yielded the equation for HPC as follows:

$$U_L = 3V^{0.5} \tag{11}$$

Based on this equation, a U_L value of 95 W is reached for a 1-L solution (0.5%) of HPC in water, suggesting that for pilot-plant scale operations (1 to 5 L) ultrasound generators of very high intensity (W-2500) need be used. The maximum available intensity 75 W from W-375 is not even sufficient to degass a 1-L solution.

(c) 0.3% HPC solutions in ethanol and THF, which do not degrade as well as HPC-water solutions, can be made to do so at low temperatures because of the increased surface tension (decreased vapor pressures) and increased density of the media.

(d) The decreases in intrinsic viscosity on ultrasonic irradiation of HPC solutions arise because of the lowering of $\overline{M}_w$ due to random scission of the chains. There are no chemical modifications of HPC as shown by the IR spectrum. Similar decreases in the Huggins coefficients can be attributed to physical changes (decrease in molecular weight or branching) in the degraded HPC samples.

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