

Shear Degradation of Cellulose Derivatives

INTRODUCTION

The relationship between the number-average degree of polymerization (P_n) and the time in a random degradation process (t) is given by¹⁻³

$$-\ln \left(1 - \frac{1}{\bar{P}_{n,t}} \right) = kt - \ln \left(1 - \frac{1}{\bar{P}_{n,0}} \right) \quad (1)$$

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

When \bar{P}_n is large, eq. (1) may be approximated by

$$\frac{1}{\bar{P}_{n,t}} = \frac{1}{\bar{P}_{n,0}} + kt \quad (2)$$

Since the number-average molecular weight (\bar{M}_n) is expressed by

$$\bar{M}_n = \bar{M}_0 \cdot \bar{P}_n$$

where \bar{M}_0 is the average molecular weight of each monomer unit, eq. (2) is reduced to

$$\frac{1}{\bar{M}_{n,t}} = \frac{1}{\bar{M}_{n,0}} + k't \quad (3)$$

where $\bar{M}_{n,t}$ and $\bar{M}_{n,0}$ are the number-average molecular weight of polymer at $t = t$ and $t = 0$, respectively, and $k' = k/\bar{M}_0$. Equation (3) may be applied to any mode of degradation in which polymer molecules are being broken up in a continuous process of random scissions of the chain.

In the present work, the applicability of this theoretical equation to the ultrasonic degradation of cellulose derivatives in water was examined. The degradation was followed by the determination of the change in molecular weight by measuring the intrinsic viscosity.

EXPERIMENTAL

Materials

Cellulose derivatives used in this work are commercial hydroxyethyl cellulose (HEC, Cellosize QP-4400) and hydroxypropylmethyl cellulose (HPMC, Methocel F-4M) supplied by Union Carbide Corporation and Dow Chemical Company respectively. Their properties are given in Table I.

Procedure

Two liters aqueous solution of the cellulose derivatives (1 g/100 ml) were subjected to ultrasonic wave irradiation at 55 kHz with 0.8 W/cm² intensity in a stainless steel tank (23.5 cm × 13.7 cm × 9.5 cm) for various periods. The change in molecular weight of the polymers was determined by measuring the intrinsic viscosity $[\eta]$ with an Ubbelohde viscometer at 20° and 25°C.

The number-average molecular weight \bar{M}_n was calculated from the following equations: for HEC⁴

$$[\eta]_{25^\circ\text{C}} = 4.70 \times 10^{-4} \bar{M}_n^{0.80}$$

for HPMC⁵

$$[\eta]_{20^\circ\text{C}} = 3.39 \times 10^{-4} \bar{M}_n^{0.88}$$

TABLE I
Property of Cellulose Derivatives

	HPMC ⁵	HEC ⁶
Trade name	Methocel F4M	Cellosize QR-4400
Manufacturer	Dow Chemical Company	Union Carbide Corp.
Chemical structure	Hydroxypropylmethyl ether	hydroxyethyl ether
Molar substitution ^a	0.1-0.2	1.67
Degree of substitution ^b	1.7-1.9	0.88
$[\eta]$ 20°C, dl/g	5.5	8.5
$[\eta]$ 25°C, dl/g	—	8.2
\bar{M}_n	57.5×10^3	182.0×10^3

^a Average number of ethylene oxide molecules per anhydroglucose unit.

^b Average number of hydroxyls substituted per anhydroglucose unit.

RESULTS AND DISCUSSION

The change in molecular weight \bar{M}_n and the reciprocal of the molecular weight $1/\bar{M}_n$ of cellulose derivatives with time of ultrasonic irradiation, t , is shown in Figure 1. A linear relationship between $1/\bar{M}_n$ and t obeys eq. (3), indicating that the shear degradation by ultrasonic irradiation is caused by a random scission of the polymer chain.

The rate constants for HEC and HPMC obtained from the slopes of the curves are $6.1 \times 10^{-8} \text{ sec}^{-1}$ and $2.6 \times 10^{-8} \text{ sec}^{-1}$, respectively.

The greater rate of degradation of HEC relative to HPMC is probably due to the greater molecular weight of HEC, since the probability of chain breaks occurring increases with increase in chain length. This result is in good agreement with that of Sues and Hanke.⁷

The greater shear stability of HPMC was confirmed in a practical running test in which the aqueous solution of the cellulose derivatives were circulated in a tank by a pump through nozzles. It appears that the evaluation of shear resistance of polymers by ultrasonic energy is applicable to any processes such as stirring, agitation, pumping, etc., which might mechanically degrade the polymer molecules.

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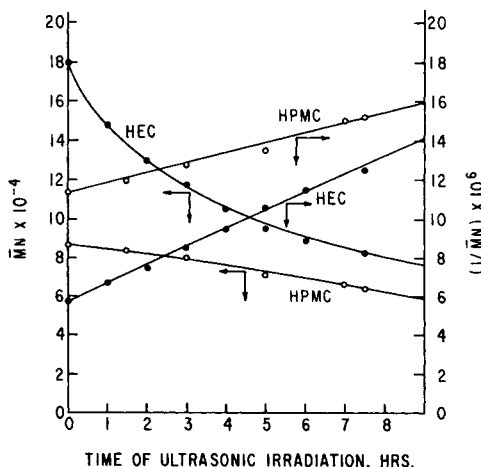


Fig. 1. Change in molecular weight and reciprocal of molecular weight of polymers with time of ultrasonic irradiation.

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