# Characterization and Chain Stiffness of (Acetoxypropyl)cellulose

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ABSTRACT: A thermotropic cholesteric polymer, (acetoxypropyl)cellulose (APC), is prepared from (hydroxypropyl)cellulose and acetic anhydride. The unit ether and unit ester contents per anhydroglucose unit, determined by chromic acid oxidation and saponification, are 3.1 ± 0.3 and 1.9 ● 0.1, respectively. Fractions ranging in molar mass from $2.2 \times 10^4$ to $6.5 \times 10^5$ daltons, and of the same chemical composition as the unfractionated polymer, are obtained by fractional precipitation with *n*-heptane. The limiting viscosity numbers of APC and fractions are measured in dimethyl phthalate at 25, 105, and 150 °C. The exponent in the Mark-Houwink-Sakurada relationship decreases from 0.88 ± 0.05 at 25 °C to 0.57 ± 0.05 at 150 °C, reflecting the gradually increasing flexibility of the molecular chain. The chain conformation parameters (equivalent Kuhn segment length, diameter, and mass per unit length) are calculated from the viscosity data by means of recent hydrodynamic theories for wormlike chains. The axial ratio of the equivalent Kuhn segment decreases from 10.8 ± 0.8 to 5.6 ± 0.4 with a constant chain diameter of 1.2 nm over the temperature range at which the viscosities were measured.

(2-Hydroxypropyl)cellulose (HPC) was the first cellulosic derivative reported to form spontaneous anisotropic solutions when dissolved in aqueous[1-3] and organic solvents.[4,5] Many other cellulose derivatives (including cellulose itself[6-8]), when dissolved in suitable solvents, have since been reported to form ordered solutions.[9]

New cellulose derivatives have been prepared in order to study the effect of the substituents on the behavior of the liquid crystalline phase.[10,11] HPC is an ideal reactant as it is soluble in many different solvents, and it possesses reactive hydroxyl groups. The acetylation of (2-hydroxypropyl)cellulose yields (acetoxypropyl)cellulose (APC), which exhibits both lyotropic and thermotropic liquid crystalline properties.[10] HPC and its esters[11] share this unusual property of forming both thermotropic and lyotropic phases. The phase properties of these polymers with suitable high-boiling diluents are therefore measurable over a wide range of compositions and temperatures. In this paper we describe the preparation, fractionation, and characterization of (acetoxypropyl)cellulose. We also describe the observed changes in dilute solution viscosity with temperature for APC fractions and interpret them in terms of chain stiffness. Quantitative chain stiffness data are required for an understanding of the factors which govern ordered-phase formation from APC.[12]

(2-Hydroxypropyl)cellulose is prepared by the base-catalyzed reaction of cellulose and propylene oxide.[13] The propylene oxide molecule reacts with the hydroxyl groups on the anhydroglucose unit, with the result that hydroxypropyl substituents are attached to the cellulose backbone by ether linkages. Every chain hydroxyl which reacts with a propylene oxide molecule generates a new hydroxyl group, so many propylene oxide molecules can react per anhydroglucose unit. It is convenient to define the average number of ether groups per anhydroglucose unit as the *unit ether content* (UEC). In contrast, the *degree of etherification* (DE) is defined as the average number of cellulose hydroxyl groups per unit which have been etherified. The UEC of (hydroxypropyl)celluloses may have any value, but the DE has a maximum value of 3. Esterification of HPC can take place either at the hydroxyl groups of the hydroxyalkyl substituents or at unsubstituted hydroxyls on the anhydroglucose units. The average number of ester groups of both types per anhydroglucose unit may be defined as the *unit ester content* (UTC), and the average number of esters directly attached to each anhydroglucose unit is the *degree of esterification* (DT). The values for UTC and for (DS + DE) cannot exceed 3.

It is evident that characterization of the chemical composition of (hydroxyalkyl)cellulose ethers and their esters is rather complex. The reactivities of the hydroxyls in anhydroglucose units are not identical[14] and will differ from those of the hydroxyalkyl groups. Lee and Perlin[15] have elucidated the substitution *pattern* for HPC in a $^{13}C$ NMR study of oligomers and model compounds. Information on the *average* substitution of (hydroxyalkyl)celluloses may be derived from $^{13}C$[15] and $^1H$[16] NMR and from wet chemical methods. In this paper, $^1H$ NMR and IR analyses are supplemented by two quantitative but laborious wet chemical procedures. The ester content is measured by a saponification method,[17] and the total number of terminal methyl groups on the ester and ether substituents are analyzed by a chromic acid oxidation and titration procedure.[18,19] From these two methods, the UEC and UTC are found for the (acetoxypropyl)cellulose sample.

Two key variables in the formation of many polymeric liquid crystals are the chain contour length and the chain stiffness. The first quantity may be estimated from molar mass measurements, and the second from transport or viscosity measurements on fractions of known molar mass. Results for HPC have been reported by Wirick and Waldman.[20] The molar mass values for our APC fractions are measured by Rayleigh scattering from dilute solution with a low-angle laser light scattering (LALLS) photometer and the molar mass distributions are conveniently measured by size exclusion chromatography with a concentration-sensitive detector and a light scattering photometer (SEC-LALLS).[21]

The viscosities of the APC fractions are here measured conventionally over an unusually wide temperature range (25-150 °C) and are interpreted according to the theory of Yamakawa and co-workers for the transport and viscosity properties of wormlike chains.[22,23] In this theory, the limiting viscosity number $[\eta]$ is related to the diameter $d$, contour length $L$, and Kuhn segment length $k_w$ of the wormlike chain by

$$[\eta] = \Phi(L_r,d_r)L_r^{3/2}k_w/M \quad (1)$$

where the reduced chain parameters are $L_r = L/k_w$ and $d_r = d/k_w$ and $\Phi(L_r,d_r)$ is a function of $L_r$ and $d_r$, given by a set of approximate analytical expressions.[23] The contour length of the chain depends on the molar mass, with a shift factor, $M_L$, as the constant of proportionality.

$$L = M/M_L \quad (2)$$

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In the limit of very long chains ($L \rightarrow \infty$) the wormlike model is identical with the random-flight chain

$$k_w = (\langle r_0^2 \rangle / L)_\infty = (\langle r_0^2 \rangle / M)_\infty M_L \quad (3)$$

where $\langle r_0^2 \rangle$ is the mean square end-to-end distance of the chain. Values for $[\eta]$ as a function of $M$ may thus be calculated for given values of $d$ and $k_w$. The values for $d$ and $k_w$ which give the best agreement between calculated and experimental viscosities are sought. These values, derived from dilute solution measurements, may then be used to test theories for liquid crystalline phase formation from semiflexible polymers.

A simplified version of the Yamakawa–Fujii theory has recently been proposed by Bohdanecky.[24] Equations 1–3 may be rewritten as

$$[\eta] = [\Phi_\infty (\langle r_0^2 \rangle / M)_\infty^{3/2} M^{1/2}] F_1 \quad (4)$$

where $F_1 = \Phi/\Phi_\infty$ and $\Phi$ takes the limiting value $\Phi_\infty$ ($=2.86 \times 10^{23}$) for $L \rightarrow \infty$.[22] Evaluation of $(\langle r_0^2 \rangle / M)_\infty$ requires extrapolation of $F_1$ to infinite chain length. According to Bohdanecky, the value of $F_1$ may be approximated by the analytical expression

$$F_1 = (B_0 + A_0 / L_r^{1/2})^{-3} \quad (5)$$

where

$$B_0 = 1.00 - 0.0367 \log d_r \quad (6)$$

and

$$A_0 = 0.46 - 0.53 \log d_r \quad (7)$$

Combining eq 4 and 5 gives

$$(M^2/[\eta])^{1/3} = A_\eta + B_\eta M^{1/2} \quad (8)$$

where

$$A_\eta = A_0 M_L \Phi_\infty^{-1/3} \quad (9)$$

and

$$B_\eta = B_0 \Phi_\infty^{-1/3} (\langle r_0^2 \rangle / M)_\infty^{-1/2} \quad (10)$$

Thus the slope of a plot of $(M^2/[\eta])^{1/3}$ against $M^{1/2}$ gives $B_\eta$. Equation 10 allows measurement of $(\langle r_0^2 \rangle / M)$, because $B_0$ is a very weak function of $d_r$ (eq 6) and can be replaced in the first approximation by the numerical constant 1.05.[24]

The estimation of $d_r$ from the Yamakawa–Fujii treatment of viscosity is not very precise. Bohdanecky presents an alternative approach based on the assumption that the hydrodynamic volume occupied by 1 g of the wormlike chain is equal to the partial specific volume, $\bar{v}$, of the polymer. This gives

$$d_r^2 / A_0 = (4\Phi_\infty / 1.215\pi N_{Av})(\bar{v}/A_\eta) B_\eta^4 \quad (11)$$

where $N_{Av}$ is the Avogadro constant. The quantity $d_r^2/A_0$ may be related to $d_r$ by the empirical expressions

$$\log (d_r^2/A_0) = 0.173 + 2.158 \log d_r \qquad (d_r \leq 0.1) \quad (12)$$

$$\log (d_r^2/A_0) = 0.795 + 2.78 \log d_r \qquad (0.1 \leq d_r \leq 0.4) \quad (13)$$

With $d_r$ thus calculated, $k_w$ and $M_L$ can be found from the slope and intercept of a plot of $(M^2/[\eta])^{1/3}$ against $M^{1/2}$.

## Experimental Section

**(a) Preparation of APC.** To 630 mL of distilled acetic anhydride (bp 144–145 °C), 248 g of (hydroxypropyl)cellulose (Aldrich, nominal molar mass 100 000 daltons) was added with gentle stirring. Acetic acid (20 mL), a catalyst for the nucleophilic reaction, was added and the mixture was heated continuously at 50–60 °C for 7 days with occasional stirring. The (acetoxypropyl)cellulose solution was poured into water to precipitate the polymer. Prolonged washing of the precipitate with water was required to remove untreated acetic anhydride. The (acetoxypropyl)cellulose was further purified by dissolution in 1500 mL of acetone and reprecipitation in distilled water to yield a pearly white product, which was washed twice with distilled water. The polymer was spread out on glass sheets and dried in an oven at 60 °C under reduced pressure for 4 days. The procedure yielded 296 g of APC, which was cut into small thin pieces and stored in a freezer.

**(b) Spectroscopic Characterization.** Fourier transform $^1H$ nuclear magnetic resonance spectra for unfractionated APC and for two of the fractions were measured with a Varian XL-200 spectrometer. Solutions (~5%) were prepared by dissolving accurately weighed samples of the polymer in deuterated chloroform with tetramethylsilane as internal standard. Infrared spectra were measured with a Nicolet 7000 series Fourier transform infrared spectrometer on thin films of APC cast from dilute acetone solutions onto a sodium chloride plate. The ultraviolet spectra of solutions of dry APC in spectrograde tetrahydrofuran (1–5 g/L) were measured with a Pye-Unicam SP8-150 spectrophotometer.

**(c) Chemical Composition. Acetyl Content.** The acetyl ($COCH_3$ group) content of cellulosic polymers can be determined reliably and quantitatively by saponification.[17] The ester groups are treated with a known amount of base. The number of moles of base consumed corresponds to the number of moles of ester which have been hydrolyzed. An accurately weighed sample (~0.5 g) of (acetoxypropyl)cellulose, which had been previously dried at 70 °C overnight in a vacuum oven, was dissolved in 50 mL of absolute ethanol. Ten milliliters of 1 M sodium hydroxide was pipetted into the solution. After 3 h, the excess sodium hydroxide was back-titrated with standardized sulfuric acid to a colorless phenolphthalein end point. Blanks were measured by titrating 10 mL of sodium hydroxide in 50 mL of absolute ethanol with sulfuric acid. The weight fraction of acetate groups, $w_{acetate}$, was calculated from

$$w_{acetate} = 43(N_{NaOH}V_{NaOH} - N_{H_2SO_4}V_{H_2SO_4})/(\text{sample weight}) \quad (14)$$

where $N$ and $V$ are the normality and volume of the standard solutions, respectively, and 43 is the molar mass of the acetate group. The method was tested on a sample of cellulose acetate (Eastman, ASTM Visc. 45); the measured acetate content was 39.5 ± 0.2%, in excellent agreement with the supplier's value of 39.4%.

**Terminal Methyl Group Analysis.** The chemical analysis of terminal methyl substituents on carbohydrates is a rather complex procedure developed by Purves and Lemieux.[18] The method consists of the oxidation of the terminal methyl group to acetic acid with a hot aqueous solution of chromium trioxide. The acetic acid is distilled, collected, and titrated with standardized sodium hydroxide. An iodide–thiosulfate titration is necessary to correct for acidic oxidizing impurities carried over with the acetic acid.

The sample to be analyzed was dried at 70 °C overnight in a vacuum oven. An appropriate quantity of the sample (~0.03 g for APC, ~0.05 g for HPC) was accurately weighed and introduced into the 50-mL reaction vessel. The chromium trioxide reagent, ~10 mL of a solution consisting of 30 g of $CrO_3$ and 70 g of water, was introduced into the flask. Nitrogen flowed through the distillation apparatus at 20 mL/min. Distillation commenced at 130–140 °C. Once 5 mL of distillate was collected, an additional 5–10 mL of distilled water was added from the dropping funnel. This process was continued until 50 mL of distilled water had been added. The distillate was collected until the residue in the 50-mL vessel was dry. The entire distillation process required 2.5–3 h. Condensate remaining in the still was rinsed with water to give a total of 125–175 mL of a pale yellow distillate.

The distillate was titrated with standardized $CO_2$-free sodium hydroxide (~0.02 M) until the pink phenolphthalein end point slowly faded. The solution was then boiled, cooled, and titrated to the end point. Following the titration, 0.5 g of sodium bicarbonate was added. Once dissolution had occurred 10 mL of

a 10% sulfuric acid solution was added, and the solution was shaken until carbon dioxide evolution had ceased. One gram of iodate-free potassium iodide was added, and the solution was kept in the dark for a 5-min reaction period. The yellow solution was titrated with standardized sodium thiosulfate until the solution was pale yellow. At this point, 2 mL of 1% starch solution was added. The resulting blue solution was titrated to a colorless end point.

Blank determinations were performed identically, except that the sample was Whatman no. 1 filter paper. The thiosulfate titration determines the quantity of reducible species carried over with the distillate. Titration with sodium hydroxide quantifies the acidic species in the blank. The ratio of the number of equivalents of NaOH to $Na_2S_2O_3$ required to titrate the blank is defined as a factor $K$.[18] This ratio represents the fraction of the reducible species which are acidic and is assumed to be constant for all sample titrations.

The primary source of error in the chromic acid oxidation technique results from the uncertainty in the $K$ value. The four blank determinations gave $K = 1.0 \pm 0.2$. The variability in the $K$ factor may be caused by variations in the heating rate.[18] A dependence of $K$ upon the nitrogen flow rate was also detected. The error introduced by the uncertainty in the $K$ value becomes larger as the correction for acidity represented by $KN_{Na_2S_2O_3}V_{Na_2S_2O_3}$ becomes significant.

The terminal methyl analysis was tested with cellulose acetate of known acetyl content. The acetyl content was calculated from

$$w_{acetone} = 43(N_{NaOH}V_{NaOH} - KN_{Na_2S_2O_3}V_{Na_2S_2O_3})/(\text{sample weight}) \quad (15)$$

where $N$ and $V$ are the normality and volume, respectively, of the sodium hydroxide and sodium thiosulfate solutions. The term $K$ was determined from blank experiments, and 43 is the molar mass of the acetate group. Four replicate measurements of the acetate content of a cellulose acetate (Eastman, ASTM Visc. 25) by terminal methyl oxidation gave values of 39.5 ± 0.8% acetate content, in excellent agreement with the manufacturer's value of 40.0% for this sample.

The terminal methyl group oxidation also allows analysis of the propoxy content of (hydroxypropyl)cellulose:

$$w_{propoxy} = 58(N_{NaOH}V_{NaOH} - KN_{Na_2S_2O_3}V_{Na_2S_2O_3})/(\text{sample weight}) \quad (16)$$

The propoxy content is related to the unit ether content by

$$w_{propoxy} = 58(UEC)/[58(UEC) + 162] \quad (17)$$

where 58 and 162 are the molar masses of the propoxy and unsubstituted anhydroglucose groups, respectively, and UEC is the unit ether content of the polymer.

(Acetoxypropyl)cellulose contains terminal methyl groups on both acetate and on propoxy substituents. Chromic acid oxidation gives the total of both methyl-containing substituents. The saponification method gives the acetate content, and the propoxy content is found from the difference. The weight fraction of propoxy units, $w_{propoxy}$, is related to the unit ether content UEC and unit ester content UTC by

$$w_{propoxy} = \frac{58(UEC)}{58(UEC) + 42(UTC) + 162} \quad (18)$$

where 58 and 162 are the molar masses of the propoxy and unsubstituted anhydroglucose units, respectively, and 42 is the molar mass of the ester group, corrected for the loss of one hydrogen for each ester substituent. The weight fraction of acetate units in APC is related to the UTC and UEC by

$$w_{acetate} = \frac{43(UTC)}{58(UEC) + 42(UTC) + 162} \quad (19)$$

Thus the unit ester content and unit ether content of an (acetoxypropyl)cellulose sample can be calculated from these last two relationships.

**(d) Fractionation.** An APC sample (10.6 g) was fractionated from 750 mL of a 2:1 ethanol–methanol solution by the addition of $n$-heptane. After each addition, the suspension was stirred for several hours and then allowed to settle. Seven fractions were precipitated from solution; the eighth fraction was obtained by rotary evaporation of almost 2 L of residual solution. The first fraction was a solid white mass. Subsequent fractions were increasingly tacky, as the molecular weight decreased. The final fraction resembled an oily substance and exhibited violet cholesteric iridescence. The yields of the precipitated fractions are tabulated with the incremental volume of nonsolvent required to effect precipitation (Table I).

**Table I**
**Fractional Precipitation of (Acetoxypropyl)cellulose from Ethanol–Methanol Solution at 25 °C**

| fraction | inc vol of $n$-heptane added, mL | mass collected, g | % of total recovered |
|---|---|---|---|
| A | 800 | 0.11 | 1.2 |
| B | 25 | 0.57 | 6.1 |
| C | 24 | 0.88 | 9.5 |
| D | 110 | 1.57 | 16.9 |
| E | 45 | 1.39 | 15.0 |
| F | 75 | 1.51 | 16.2 |
| G | 225 | 2.25 | 24.2 |
| H | | 1.01 | 10.9 |

**(e) Molecular Weight.** The (acetoxypropyl)cellulose fraction was dried overnight in a vacuum oven at 60 °C prior to use. Solutions of $\sim 10^{-3}$ g mL$^{-1}$ were prepared by dissolving the (acetoxypropyl)cellulose in 10 mL of HPLC grade tetrahydrofuran (Caledon Laboratories) and were stirred overnight prior to use. A known aliquot of solution, ~100 μL, was introduced into the injector loop. A Waters Model 6000A pump maintained a uniform tetrahydrofuran flow rate of 1.0 mL min$^{-1}$ through a set of μStragel columns (Waters) with nominal pore diameters of $10^6$, $10^5$, $10^4$, $10^3$, and 500 Å. A 0.2-μm Millipore filter, Type FGLP, was inserted before the light scattering cell to remove any foreign particles. A Chromatix KMX-6 LALLS photometer with flow cell was used as a molecular weight sensitive detector. A Hewlett-Packard Model 79877A refractive index detector thermostated at 25 °C in a water jacket was used to measure polymer concentration. The chromatographic data were acquired and treated with a Chromatix LDS data system and software.

The refractive index increment, $dn/dc$, and the second virial coefficient, $A_2$, are required to calculate molar masses for the SEC–LALLS data. Refractive index increments, $dn/dc$, at a wavelength of 546 nm were obtained for the polymer at 25.0 ± 0.1 °C with a Brice-Phoenix differential refractometer. Five solutions whose concentrations varied from $\sim 2 \times 10^{-3}$ to $8 \times 10^{-3}$ g mL$^{-1}$ were prepared by dissolving accurately weighed samples of dried (acetoxypropyl)cellulose in 10 mL of solvent. The $dn/dc$ values for unfractionated APC were 0.1003 in acetone and 0.0565 in tetrahydrofuran. These values for the fractions were assumed to be the same as for the unfractionated polymer.

The second virial coefficient, $A_2$, was calculated from low-angle laser light scattering data. A stock solution of concentration $10^{-3}$ g mL$^{-1}$ was prepared by dissolving an accurately weighed sample of dried (acetoxypropyl)cellulose in 25 mL of solvent and stirring overnight. Solutions ranging in concentration from 0.1 to 0.7 of the stock were prepared and passed through a 0.2-μm Millipore FGLP filter and the Chromatix KMX-6 cell at a rate of 0.05 mL min$^{-1}$. Measurements on four or five dilutions were performed for each of the eight (acetoxypropyl)cellulose fractions analyzed.

**(f) Viscosity.** Two Ubbelohde viscometers were selected to give flow times of 100–200 s for the solvent, dimethyl phthalate, at 25 and 150 °C. A water bath (Townson and Mercer) was used for viscosity measurements at 25.0 °C. The temperature was maintained to within ±0.02 °C of this value by a proportional temperature controller (Yellow Springs Instruments Ltd.) For the experiments at 105 and 150 °C, a thermostated bath containing Dow Corning 200 poly(dimethylsiloxane) fluid was used. A minor vertical temperature gradient of less than 0.5 °C was observed. The quoted temperature was at the middle of the capillary tube. The viscometer was immersed to the same depth for each measurement.

Stock solutions were prepared by the addition of an appropriate quantity of dimethyl phthalate (Fisher) to a preweighed quantity of an (acetoxypropyl)cellulose fraction, so that the specific viscosity of solutions ranged between 0.8 and 0.2. For the experiments

performed at 105 and 150 °C, 0.2% by weight of an antioxidant, 2,6-di-*tert*-butylcresol, was dissolved in the solvent. The solution was blanketed with nitrogen and was stirred for a day while the polymer dissolved. For measurements at 150 °C, an acid acceptor, thiosemicarbazide (Aldrich), was added directly to the viscometer at a 1% concentration by weight to inhibit degradation; the viscometer and solution were immersed in the bath for 20–30 min prior to flow time measurements. Nitrogen was bubbled through the solutions at 150 °C to aid in dissolving the thiosemicarbazide. After measuring flow times for the first concentration, the viscometer was removed and a predetermined quantity of solvent was added. Nitrogen gas was bubbled through the solution for 10 min prior to reimmersion in the bath. The flow times for four dilutions, five concentrations in all, were obtained for each fraction. Despite the precautions to minimize thermal degradation, a slight decrease in the flow time was noticed for the high molecular weight fractions. The decrease in the flow times was under 3% in all cases and generally under 1% at 150 °C. A rapid decrease in flow times was noted when the precautions were not observed.

## Results and Discussion

The initial characterization of the product obtained from the reaction of (hydroxypropyl)cellulose and acetic anhydride was performed by IR and NMR. Detailed infrared band assignments for (hydroxypropyl)cellulose can be found in the literature.[25] The most apparent differences between the spectra of APC and HPC are the reduction in the size of the broad hydroxyl stretching peak in the 3700–3200-$cm^{-1}$ region and the appearance of a strong carbonyl peak at 1736 $cm^{-1}$. A strong peak centered at 1240 $cm^{-1}$ is consistent with the asymmetric C–O–C stretching peak of an acetate ester. An incomplete esterification reaction is probable, as a reduced but still a significant hydroxyl stretching band is observed. The absence of peaks that are characteristic of anhydrides in the region from 1850 to 1750 $cm^{-1}$ implies that the excess acetic anhydride was removed by the washing procedures.

The major difference in the $^1H$ nuclear magnetic resonance spectrum of HPC and that of APC is the appearance of a singlet centered at 2.02 ppm due to the acetate methyl protons in the spectrum of the derivative (Figure 1). The signals due to the protons of the ether terminal methyl groups occur at 1.14 and 1.23 ppm. The appearance of the two signals for the terminal methyl group of the propoxy unit indicates that the chemical environment of this group is not identical throughout the molecule. This nonequivalence may be caused by incomplete acetylation or may reflect the differing extension of the branches. The peak at 5.0 ppm in the (acetoxypropyl)cellulose spectrum is not clearly visible in the spectrum of (hydroxypropyl)cellulose.[16] This peak may result from the anomeric proton whose carbon atom is bonded to two oxygen atoms and one carbon atom. In addition, acetylation of the side-chain hydroxyl shifts the position of the methine proton from ~3.5 to 5 ppm. All other protons should appear in the broad multiplet centered at 3.48 ppm.

The sample of APC displayed an ultraviolet absorption maximum at 227 nm. A linear Beer–Lambert plot was obtained, with an extinction coefficient of 12.5 mL $g^{-1}$ $cm^{-2}$.

**Chemical Composition.** The acetyl content of (acetoxypropyl)cellulose was analyzed by saponification of the acetate ester linkage in dilute alkali. The method gave excellent results on a cellulose acetate of known composition. The weight percentage of acetyl ($H_3CCO$) groups in the APC sample was found to be 19.0 ± 0.2%, based on five separate determinations. These esters may be attached either to unsubstituted hydroxyl groups on the cellulose backbone or to the hydroxypropyl substituents. The number of ester groups per anhydroglucose unit cannot be deduced directly from the weight fraction; information on the number of ether substituents is also required.

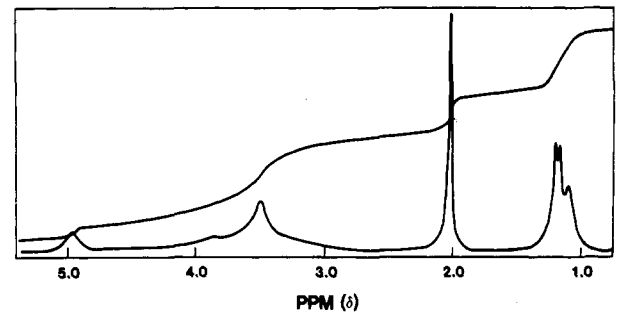


**Figure 1.** $^1H$ NMR spectrum of unfractionated (acetoxypropyl)cellulose in deuterated chloroform.

The propoxy ($H_3CCHOCH_2$) content of (hydroxypropyl)cellulose and the combined acetyl and propoxy contents of (acetoxypropyl)cellulose were analyzed by the terminal methyl oxidation method.[18] The propoxy content of the (hydroxypropyl)cellulose starting material was found to be 55.1 ± 0.3%, based on four analyses. This corresponds to a unit ether content of 3.4 ± 0.1. In other words, each anhydroglucose unit in the cellulose chain is attached to an average of 3.4 ether groups. A UEC value greater than 3 indicates that some of the anhydroglucose units have side chains more than one ether unit long. Some information on the substitution pattern of HPC (Klucel E, Hercules Inc.) is presented in a recent $^{13}C$ NMR study by Lee and Perlin.[15] The unit ether content for their sample was estimated to be 4.1. The degree of etherification at the O-2 and O-6 positions was found to be 0.95 while at the O-6 position it was only 0.6, to give an overall value for the DE of 2.5. Thus the average number of propoxy units attached to other propoxy units was 4.1 − 2.5 = 1.6 per anhydroglucose unit.

The (acetoxypropyl)cellulose sample was analyzed by oxidation of the terminal methyl groups in the acetyl and propoxy substituents. The results, when combined with those for the saponification analysis for acetyl groups, give values of 1.86 ± 0.10 for the unit ester content and 3.14 ± 0.30 for the unit ether content. The unit ester content of this sample is considerably lower than the maximum value of 3; nearly 40% of the hydroxyl groups remain unesterified, with the potential of forming hydrogen bonds. The unreacted hydroxyl groups may well affect the physical properties of the polymer. The unit ether content of the APC sample is the same within experimental error as the value for the HPC from which it was prepared. Thus the acetylation does not cleave ether links. Taking the above values for the unit ether and ester contents, the yield of APC from HPC is essentially quantitative, with a molar mass of 423 daltons per APC anhydroglucose residue.

The wet-chemical analyses of the average substitution of APC are supported by quantitative $^1H$ NMR results. The ratio of the terminal methyl proton signal of the propoxy group (1.2 ppm) to that of the acetyl protons (2.02 ppm) should correspond to the ratio of the unit ether content to the unit ester content. A value of 1.63 ± 0.09 was obtained for the ratio of these peak areas based on five APC spectra. This is in good agreement with the ratio of the UEC and UTC values from the chemical analyses of (acetoxypropyl)cellulose (1.7 ± 0.25). However, the NMR method does not give the individual UEC or USC values. (The $^1H$ NMR methods proposed to measure the UEC of HPC[16] are less suitable for APC.)

**Characterization of the Fractions.** The $^1H$ NMR spectra of the fractions resembled that of the unfraction-

**Table II**
**Relative Magnitude of the $^1H$ Group Integration Signals for APC Samples As Percentage of Total $^1H$ Signal**

| | APC sample | | |
|---|---|---|---|
| group chem shift, ppm | % unfractionated | % frac A | % frac F |
| 1.24 | 36 | 37 | 37 |
| 2.03 | 22 | 21 | 23 |
| 3.53 | 36 | 36 | 33 |
| 5.00 | 6 | 6 | 7 |

**Table III**
**Molecular Weights and Virial Coefficients for (Acetoxypropyl)cellulose Fractions**

| | static LALLS[a] | | SEC–LALLS[b] | |
|---|---|---|---|---|
| frac | $\bar{M}_w/10^5$, daltons | $10^4A_2$, mol mL $g^{-2}$ | $\bar{M}_w/10^5$, daltons | $\bar{M}_n/10^5$, daltons |
| A | | | 6.5 ± 0.2 | 3.1 ± 0.2 |
| B | | | 7.7 ± 1.0 | 3.1 ± 0.1 |
| C | 4.6 | 3.6 | 4.3 ± 0.2 | 2.8 ± 0.4 |
| D | 2.8 | 4.6 | 2.8 ± 0.2 | 2.3 ± 0.3 |
| E | 1.94 | 5.8 | 1.9 ± 0.4 | 1.5 ± 0.3 |
| F | | | 1.3 ± 0.05 | 1.1 ± 0.05 |
| G | 0.69 | 4.5 | 0.76 ± 0.1 | 0.62 ± 0.1 |
| H | | | 0.22 ± 0.01 | 0.16 ± 0.01 |
| whole polymer | 2.14 | 5.2 | 2.3 ± 0.1 | 1.18 ± 0.1 |

[a] Low-angle laser light scattering in acetone. [b] Size exclusion chromatography in tetrahydrofuran with low-angle laser light scattering detector. Values indicate mean and range of three measurements.

ated polymer (Figure 1). The chemical shifts were identical with those of the unfractionated (acetoxypropyl)cellulose and the percentages of the total integration curve for each signal were also similar (Table II). These data indicate that the composition of the APC fractions are close to that of the unfractionated polymer (UEC = 3.14, UTC = 1.86).

The molecular weights and distributions for the fractions calculated from low-angle laser light scattering (LALLS) and size exclusion chromatography coupled with low-angle laser light scattering (SEC–LALLS) in tetrahydrofuran are presented in Table III. The number-average molecular weight calculated by the SEC–LALLS technique is very often too high (resulting in too low a polydispersity ratio, $\bar{M}_w/\bar{M}_n$) because of imperfect fractionation by the size exclusion columns.[26] A second source of error in the $\bar{M}_n$ value may be the decreased sensitivity of the light scattering photometer to the lower mass species. Thus the accuracy of $\bar{M}_n$ may be lower than indicated by the precision given in Table III. In contrast, the value for $\bar{M}_w$ should be independent of column performance, and good agreement between SEC–LALLS and static LALLS measurements is in fact observed.

Included in the table are the weight-average molar mass and the second virial coefficient for some fractions, measured by low-angle light scattering in acetone.

The (acetoxypropyl)cellulose solutions did not display behavior characteristic of aggregation; the light scattering intensities did not change with time, the appropriate plots of light scattering intensity vs. concentration were linear, and the second virial coefficients of solutions were positive. No pressure buildup due to clogging of the filters was noted. This APC sample thus shows none of the difficulties in light scattering previously encountered with HPC solutions.[4]

**Viscosities of Fractions.** The limiting viscosity number, $[\eta]$, of each (acetoxypropyl)cellulose fraction in dimethyl phthalate was obtained from the intercepts of the Huggins and Kraemer plots of the viscosity data

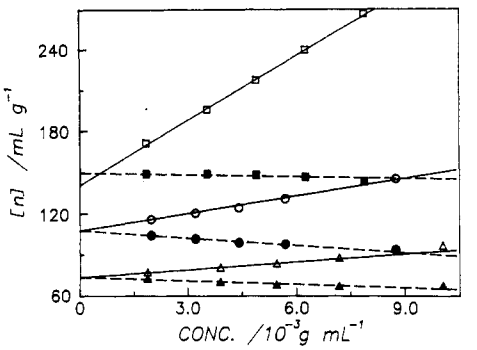


**Figure 2.** Huggins (open symbols) and Kraemer (filled symbols) plots for (acetoxypropyl)cellulose (fraction D) in dimethyl phthalate at 25 (squares), 105 (circles), and 150 °C (triangles).

**Table IV**
**Limiting Viscosity Number of APC Fractions in Dimethyl Phthalate at 25, 105, and 150 °C**

| | limiting viscosity number, mL/g | | |
|---|---|---|---|
| frac | 25 °C | 105 °C | 150 °C |
| C | 203 ± 4 | 136.5 ± 1.5 | 85.0 ± 1.5 |
| D | 146 ± 5 | 107.2 ± 1.0 | 71.8 ± 1.0 |
| E | 129 ± 2 | 83.3 ± 0.5 | 61.0 ± 0.6 |
| F | 96 ± 1 | 59.6 ± 0.6 | 50.8 ± 0.5 |
| G | 45 ± 2 | 39.4 ± 0.4 | 34.0 ± 0.4 |
| H | 14 ± 0.5 | | 13.5 ± 0.25 |
| unfractionated | 104 ± 2 | 78.2 ± 0.4 | 55.0 ± 1.0 |

$$\eta_{sp}/c = [\eta] + K'_H[\eta]^2c \quad (20)$$

$$\ln (n_r)/c = [\eta] + K'_K[\eta]^2c \quad (21)$$

where $c$ is the concentration, $\eta_{sp}/c$ is the viscosity number, and $\ln (n_r)/c$ is the logarithmic viscosity number. Typical Huggins and Kraemer plots are illustrated in Figure 2 for fraction D in dimethyl phthalate at the three temperatures. When the intercepts of the two equations did not coincide, the average value of the limiting viscosity numbers was taken. The limiting viscosity numbers for each fraction as a function of temperature are presented in Table IV.

The limiting viscosity number is often related to the shape of the polymer molecule in solution by the Mark–Houwink–Sakurada (MHS) equation.

$$[\eta] = K\bar{M}^a \quad (22)$$

where $K$ is a parameter which is independent of the solvent and molar mass of the fractions. The MHS exponent, $a$, decreases from 0.88 ± 0.05 at 25 °C to 0.75 ± 0.03 at 105 °C and 0.57 ± 0.05 at 150 °C. The value of the MHS exponent at 150 °C is typical of a nondraining Gaussian coil rather than a semiflexible wormlike chain. These values suggest that as the temperature increases, the (acetoxypropyl)cellulose molecule becomes more flexible. The conformation changes gradually with increasing temperature from a semirigid rod to a flexible coil at 150 °C.

The chain stiffness of a polymer molecule is reflected in the exponent, $a$, of the MHS equation only in a qualitative manner. Many theories relate the limiting viscosity number of a polymer to its molecular conformation; selected is the recent hydrodynamic theory of Yamakawa and co-workers for the limiting viscosity number of a wormlike cylinder.[22,23] The variables in the treatment are the Kuhn segment length, $k_w$, the diameter of the chain, $d$, and the mass per unit length, $M_L$ (eq 1–3). Chain

Table V
Values at Three Temperatures for the Kuhn Segment Length $k_w$ at Given Values of Chain Diameter $d$ from a Wormlike Chain Treatment of the Viscosity Data[a]

| | 25 °C | | 105 °C | | 150 °C | |
|---|---|---|---|---|---|---|
| $d$, nm | $k_w$, nm | $\sigma$[b] | $k_w$, nm | $\sigma$[b] | $k_w$, nm | $\sigma$[b] |
| 0.2 | 17.2 | 0.11 | | | 8.7 | |
| 0.4 | 15.0 | 0.095 | 10.8 | 0.119 | 8.0 | 0.0365 |
| 0.5 | *14.3* | | | | | |
| 0.6 | 13.6 | 0.099 | 9.9 | 0.080 | 7.3 | 0.0284 |
| 0.8 | 12.8 | 0.103 | 9.3 | 0.051 | 6.9 | 0.0223 |
| 1.0 | 12.3 | 0.109 | *8.8* | 0.029 | 6.6 | 0.0166 |
| 1.2 | 11.8 | 0.121 | 8.4 | 0.032 | 6.3 | 0.0147 |
| 1.4 | 11.3 | 0.128 | 8.0 | 0.053 | 6.0 | 0.0112 |
| 1.6 | 10.9 | 0.138 | 7.6 | 0.081 | 5.8 | 0.0099 |
| 1.8 | 10.4 | 0.144 | 7.3 | 0.114 | 5.5 | 0.0121 |
| 2.0 | 10.0 | 0.155 | 6.9 | 0.150 | 5.3 | 0.0154 |

[a] The root mean square differences $\sigma$ between experimental viscosities and those calculated for the given $k_w$ and $d$ values are listed. [b] The value of $k_w$ for the best fit ($k_w$, $d$) pair at each temperature is italicized. $\sigma = \{\sum_{i=1}^{6}([\eta]_i - [\eta]_{i,cal})^2/6[\eta]_i^2\}^{1/2}$, where $[\eta]_i$ and $[\eta]_{i,cal}$ are the measured and calculated limiting visocity numbers, respectively, for each of the six fractions.

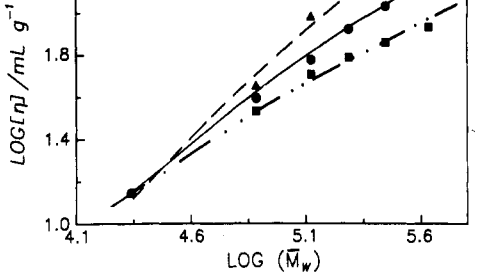


**Figure 3.** Limiting viscosity number as a function of molar mass for (acetoxypropyl)cellulose in dimethyl phthalate. Experimental points at 25 (triangles), 105 (circles), and 150 °C (squares) are shown. Theoretical curves are drawn for the wormlike model with $d$ = 0.4 nm, $k_w$ = 15 nm (broken line), $d$ = 1 nm, $k_w$ = 8.8 nm (solid line), and $d$ = 1.6 nm, $k_w$ = 5.8 nm (dotted line).

contour lengths and mass per unit length were assumed to be the same as those of the seven (acetoxypropyl)cellulose fractions. By adjusting the Kuhn segment length and diameter, the limiting viscosity numbers were calculated according to equations in ref 22, with revised coefficients from ref 23. The calculated limiting viscosity numbers were compared to the experimental values for the seven (acetoxypropyl)cellulose fractions. (The excluded volume effect for cellulose derivatives is small[27] and is ignored here.)

The Kuhn segment lengths which resulted in the minimization of the average deviation between calculated and measured limiting viscosity numbers for a range of diameter values are compiled in Table V. An overall minimum in the average deviation occurred for a particular pair of Kuhn segment length and diameter values at each temperature. For example, at 105 °C, a wormlike chain with a diameter of 1.0 nm and a Kuhn segment length of 8.8 nm best represented the experimental limiting viscosity numbers of the (acetoxypropyl)cellulose fractions. The Kuhn segment lengths which form a part of the best fit pair are italicized in Table V.

The best fit pair of diameter and Kuhn segment length values for each temperature is plotted and compared with the experimental values in Figure 3. The fit is best at 105 °C. The parameters obtained from the Yamakawa formulation for (acetoxypropyl)cellulose in dimethyl phthalate at 25 °C ($k_w$ = 14.3 ± 1.2, 0.5 ± 0.2 nm) are compatible with published data for other cellulose derivatives at ambient temperatures.[22,28,29]

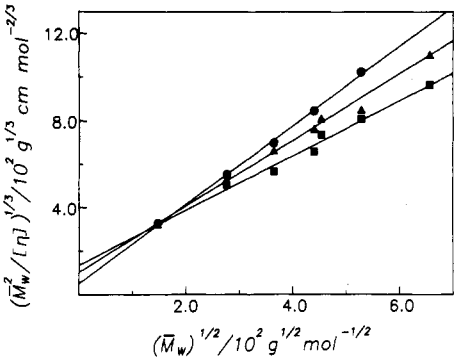


**Figure 4.** Bohdanecky plots of dilute solution viscosity data for (acetoxypropyl)cellulose in dimethyl phthalate. Experimental points at 25 (squares), 105 (triangles), and 150 °C (circles) are shown.

X-ray diffraction from an APC film gave a diffuse ring with an intensity maximum which corresponded to a $d$ spacing of 1.22 ± 0.01 nm. To a first approximation this may be taken as the chain diameter for the nematic-like phase. The molecular diameter calculated from the Yamakawa equation at ambient temperatures is significantly smaller than the X-ray value. This discrepancy coupled with the observation that the Yamakawa theory yields low diameter values for other cellulose derivatives[22] leads to the conclusion that the theory underestimates the chain diameter. The data in Table IV indicate that the Kuhn segment length is relatively insensitive to the assumed diameter of the wormlike chain. It is of course also possible to fix the diameter at an independently measured value and then select a value for the Kuhn segment length that gives best agreement with the measured viscosities.

The best fit pair of Kuhn segment length and diameter values show a marked temperature dependence. The Kuhn segment length corresponding to the best fit diameter decreases from 15 nm at 25 °C, through 8.8 nm at 105 °C, to 5.8 nm at 150 °C, while the diameter increases from 0.4 nm through 1.0 nm to 1.6 nm in the same temperature range. This represents a very marked decrease in the stiffness of the (acetoxypropyl)cellulose molecule as the temperature is elevated. The decrease in the Kuhn segment length is still evident if a temperature-independent diameter is assigned to the chain. For example, assuming a diameter of 12 Å, the Kuhn segment length decreases from 11.8 nm at 25 °C to 6.3 nm at 150 °C.

More realistic values for the chain diameter are given by Bohdanecky's simplified treatment of the Yamakawa–Fujii theory.[24] The intrinsic viscosities for the APC fractions were plotted as $(M^2/[\eta])^{1/3}$ vs. $M^{1/2}$. The relationship was linear for the three temperatures (Figure 4), as required by eq 8. The values for $(\langle r_0^2\rangle/M)_\infty$ may be determined from the slopes of the lines by means of eq 10. The treatment also relates the reduced chain hydrodynamic diameter to the partial specific volume of the polymer by eq 11–13. Unfortunately reliable measurements of the partial specific volume of the APC sample in dimethyl phthalate at 25, 105, and 150 °C have not yet been made; a value of 0.825 cm³/g for the apparent specific volume of APC in acetone at 25 °C[10] will be used as a first approximation for $\bar{v}$. Values for $d$, $M_L$, and $k_w$ derived from the slopes and intercepts of Figure 4 and eq 3 and 8–12 are listed in Table VI. The values for the equivalent Kuhn length are in good agreement with those calculated by the iterative method (Table V). It is evident that the con-

**Table VI**
**Chain Dimensions for (Acetoxypropyl)cellulose in Dimethyl Phthalate from Viscosity Data according to Bohdanecky's Formulation of the Yamakawa–Fujii Wormlike Chain Model**

| | temp | | |
|---|---|---|---|
| | 25 °C | 105 °C | 150 °C |
| $M_L$, daltons/nm | 900 | 860 | 630 |
| $d$, nm | 1.26 | 1.22 | 1.46 |
| $k_w$, nm | 14.4 | 9.46 | 5.30 |
| $d$, nm[a] | 1.14 | 1.16 | 1.49 |
| $k_w$, nm[a] | 13.5 | 9.3 | 7.1 |

[a] For $M_L$ = 821 daltons/nm (see text).

straints placed on possible values for $d_r$ by the APC specific volume term in eq 11 result in much more reasonable values for the chain diameter than those in Table V; the values at 25 and 105 °C in Table VI are close to the observed X-ray $d$ spacing (1.22 nm) for the bulk mesophase. The shift factor, $M_L$, at 25 and 105 °C is also close to the value of 821 daltons/nm which may be estimated from the molar masses (423 daltons) and length (0.515 nm) of the anhydroglucose residues. The results at 150 °C show an increase in the hydrodynamic diameter and a decrease in $M_L$. If real, these changes may indicate an extension of the side chains and of the main chain with increasing temperature. A change in $M_L$ seems rather unlikely; therefore included in Table VI are values for $d$ and $k_w$ calculated for a temperature-independent $M_L$ of 821 daltons nm$^{-1}$. More work on this point is required, but in general the treatment of the viscosity data by Bohdanecky's version of the Yamakawa–Fujii theory readily gives physically reasonable values for the equivalent Kuhn length and chain diameter. The most important result is the measured decrease in $k_w$ with temperature for APC in the phthalate ester solvent. The strong temperature dependence of cellulosic chain dimensions has long been known;[30] in terms of the wormlike chain model the magnitude of the temperature dependence indicates that the bending force constant for the cellulose chain varies with temperature.[31] The decrease in $k_w$ with temperature for APC in dibutyl phthalate will be related in the following paper to the anisotropic–isotropic phase transition for this system.

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