

SAFETY ISSUES

Methyl ethyl ketone is not toxic but should be disposed of properly, as instructed.

APPARATUS

One or more osmometers (complete with end plates, bolts, large test tube, drill rod, and stopper); membranes (uncoated cellophane, designated as PUT grade, is available from Flexil Corp., Covington, IN 47932), conditioned for use in methyl ethyl ketone; four 50-mL glass-stoppered volumetric flasks; 25-mL pipette; pipetting bulb; several beakers; 25-mL hypodermic syringe with long needle; constant-temperature bath (preferably with glass walls) set at 25°C; large clamp for mounting the osmometer; cathetometer; stop-watch; mercury (optional).

High-molecular-weight polystyrene powder; reagent-grade methyl ethyl ketone (500 mL).

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EXPERIMENT 28**Intrinsic Viscosity: Chain Linkage in Polyvinyl Alcohol**

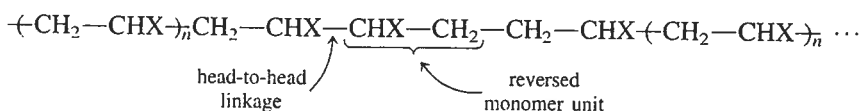
While the basic chemical structure of a synthetic polymer is usually well understood, many physical properties depend on such characteristics as chain length, degree of chain branching, and molecular weight, which are not easy to specify exactly in terms of a molecular formula. Moreover, the macromolecules in a given sample are seldom uniform

in chain length or molecular weight (which for a linear polymer is proportional to chain length): thus the nature of the distribution of molecular weights is another important characteristic.

A polymer whose molecules are all of the same molecular weight is said to be *monodisperse*; a polymer in which the molecular weights vary from molecule to molecule is said to be *polydisperse*. Specimens that are approximately monodisperse can be prepared in some cases by fractionating a polydisperse polymer; this fractionation is frequently done on the basis of solubility in various solvent mixtures.

This experiment is concerned with the linear polymer polyvinyl alcohol (PVOH), $(\text{CH}_2-\text{CHOH})_n$, which is prepared by methanolysis of the polyvinyl acetate (PVAc) obtained from the direct polymerization of the monomer vinyl acetate, $\text{CH}_2=\text{CH}-\text{OOCCH}_3$. As ordinarily prepared, polyvinyl alcohol shows a negligible amount of branching of the chains. It is somewhat unusual among synthetic polymers in that it is soluble in water. This makes polyvinyl alcohol commercially important as a thickener, as a component in gums, and as a foaming agent in detergents.

A characteristic of interest in connection with PVOH and PVAc is the consistency of orientation of monomer units along the chain. In the formula given above it is assumed that all monomer units go together "head to tail." However, occasionally a monomer unit will join onto the chain in a "head-to-head" fashion, yielding a chain of the form



where X is Ac or OH. The frequency of head-to-head linkage depends on the relative rates of the normal growth-step reaction α ,



and the abnormal reaction β ,



(where $\text{R}\cdot$ is the growing polymer radical, the arrow representing the predominant monomer orientation). The rates, in turn, must depend on the activation energies:

$$\frac{k_\beta}{k_\alpha} = \frac{A_\beta e^{-E_{\alpha\beta}/RT}}{A_\alpha e^{-E_{\alpha\alpha}/RT}} = S e^{-\Delta E_d/RT} \quad (2)$$

where $\Delta E_d = E_{\alpha\beta} - E_{\alpha\alpha}$ is the additional thermal activation energy needed to produce abnormal addition and S is the *steric factor* representing the ratio of the probabilities that the abnormally and normally approaching monomer will not be prevented by steric or geometric obstruction from being in a position to form a bond. Presumably the activation energy for the normal reaction is the lower one, in accord with the finding of Flory and Leutner^{1,2} that the frequency of head-to-head linkages in PVAc increases with increasing polymerization temperature. The quantities S and ΔE_d can be determined from data obtained at two or more polymerization temperatures by a group of students working together. It should be of interest to see whether steric effects or thermal activation effects are the more important in determining the orientation of monomer units as they add to the polymer chain.

In this experiment, the method of Flory and Leutner will be used to determine the fraction of head-to-head attachments in a single sample of PVOH. The method depends on the fact that in PVOH a head-to-head linkage is a 1,2-glycol structure, and 1,2-glycols can

be specifically and quantitatively cleaved by periodic acid or periodate ion. Treatment of PVOH with periodate should therefore break the chain into a number of fragments, bringing about a corresponding decrease in the effective molecular weight. All that is required is a measurement of the molecular weight of a specimen of PVOH before and after treatment with periodate.

METHOD³

For the determination of very high molecular weights, freezing-point depressions, boiling-point elevations, and vapor-pressure lowerings are too small for accurate measurement. Osmotic pressures are of a convenient order of magnitude, but measurements are time-consuming. The technique to be used in this experiment depends on the determination of the intrinsic viscosity of the polymer. However, molecular-weight determinations from osmotic pressures are valuable in calibrating the viscosity method.

Two other methods, light scattering and gel permeation chromatography (GPC), could also be used as alternatives or in addition to the viscosity technique. Light scattering is a classical method for determining molecular weights and, if scattering as a function of angle is measured, it is also possible to learn something of the polymer shape, i.e., to distinguish rodlike from spherical forms. Bettleheim⁴ and White⁵ describe experiments of this type. In the case of gel permeation chromatography, molecules of different sizes are carried by a liquid solvent over a substrate gel network of uniformly sized pores which can be chosen in a range from 10 to 100 000 nm. Smaller solute molecules diffuse into and out of the pores and hence exhibit a longer retention time than larger solute molecules, which are not retained and travel through the column with the solvent. This method is simple, but to obtain accurate molecular weights of a given polymer type from the retention times it is necessary to reproduce the flow rates carefully and to calibrate the column with polymers of known weight and similar chemical composition.⁵

The coefficient of viscosity η of a fluid is defined in Exp. 4. It is conveniently measured, in the case of liquids, by determination of the time of flow of a given volume V of the liquid through a vertical capillary tube under the influence of gravity. For a virtually incompressible fluid such as a liquid, this flow is governed by Poiseuille's law in the form

$$\frac{dV}{dt} = \frac{\pi r^4 (p_1 - p_2)}{8\eta L}$$

where dV/dt is the rate of liquid flow through a cylindrical tube of radius r and length L and $(p_1 - p_2)$ is the difference in pressure between the two ends of the tube. In practice a viscosimeter of a type similar to that shown in Fig. 1 is used. Since $(p_1 - p_2)$ is proportional to the density ρ , it can be shown that for a given total volume of liquid,

$$\frac{\eta}{\rho} = Bt \quad (3)$$

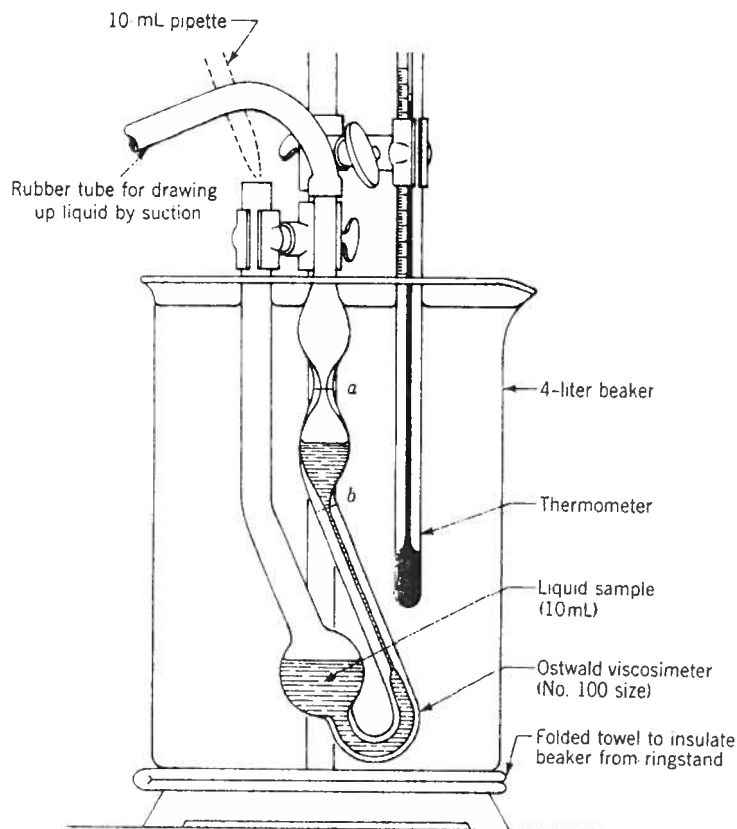
where t is the time required for the upper meniscus to fall from the upper to the lower fiducial mark (a to b) and B is an apparatus constant that must be determined through calibration with a liquid of known viscosity (e.g., water). The derivation of this equation is similar to that given for Eq. (4-10). For high-precision work, it may be necessary to consider a kinetic-energy correction to Eq. (3). As in Eq. (4-16), we can write

$$\frac{\eta}{\rho} = Bt - \frac{V}{8\pi Lt}$$

but the correction term is usually less than 1 percent of Bt and may be neglected in this experiment.

FIGURE 1

Viscosimeter arrangement to be used if a glass-walled thermostat bath is not available.



THEORY

Einstein showed that the viscosity η of a fluid in which small rigid spheres are dilutely and uniformly suspended is related to the viscosity η_0 of the pure fluid (solvent) by the expression⁶

$$\frac{\eta}{\eta_0} - 1 = \frac{5}{2} \frac{v}{V}$$

where v is the volume occupied by all the spheres and V is the total volume. The quantity $(\eta/\eta_0) - 1$ is called the *specific viscosity* η_{sp} . For nonspherical particles the numerical coefficient of v/V is greater than $\frac{5}{2}$ but should be a constant for any given shape provided the rates of shear are sufficiently low to avoid preferential orientation of the particles.

The *intrinsic viscosity*, denoted by $[\eta]$, is defined as the ratio of the specific viscosity to the weight concentration of solute, in the limit of zero concentration:

$$[\eta] \equiv \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \left(\frac{1}{c} \ln \frac{\eta}{\eta_0} \right) \quad (4)$$

where c is conventionally defined as the concentration in grams of solute per 100 mL of solution. In this case, the units for $[\eta]$ are $10^2 \text{ cm}^3 \text{ g}^{-1}$. Both η_{sp}/c and $(1/c)(\ln \eta/\eta_0)$ show a reasonably linear concentration dependence at low concentrations. A plot of $(1/c)(\ln \eta/\eta_0)$ versus c usually has a small negative slope, while a plot of η_{sp}/c versus c has a positive and larger slope.³ Careful work demands that either or both of these quanti-

ties be extrapolated to zero concentration, although $(1/c)(\ln \eta/\eta_0)$ for a single dilute solution will give a fair approximation to $[\eta]$.

If the internal density of the spherical particles (polymer molecules) is independent of their size (i.e., the volume of the molecule is proportional to its molecular weight), the intrinsic viscosity should be independent of the size of the particles, and hence of no value in indicating the molecular weight. This, however, is not the case; to see why, we must look into the nature of a polymer macromolecule as it exists in solution.

Statistically Coiled Molecules. A polymer such as PVOH contains many single bonds, around which rotation is possible. If the configurations around successive carbon atoms are independent and unrelated, it will be seen that two parts of the polymer chain more than a few carbon atoms apart are essentially uncorrelated in regard to direction in space. The molecule is then "statistically coiled" and resembles a loose tangle of yarn:



Simple statistical treatments² show that the mean distance between the two ends of the chain, and indeed also the effective mean diameter d of the coiled molecule regarded as a rough sphere, should be proportional to the square root of the chain length and thus to the square root of the molecular weight:

$$d \propto M^{1/2}$$

The volume v_m occupied by a molecule should then vary as $M^{3/2}$. The number of molecules in a given weight of polymer varies inversely with the molecular weight; hence the total volume of the spheres is

$$v \propto \frac{cV}{M} M^{3/2} = cVM^{1/2}$$

Therefore,

$$[\eta] = KM^{1/2} \quad (5)$$

where K is a constant. This treatment is much simplified; it ignores, among other things, the problem of "excluded volume"; that is, the fact that the chain cannot coil altogether randomly because it is subject to the restriction that no two parts of the chain may be at the same point in space at the same time. This restriction becomes more and more important the higher the molecular weight. Even more serious is the effect of solvent: the above treatment tacitly assumes a "poor solvent" which would barely get the polymer into solution. A "good solvent," by solvating the polymer, makes the size of the statistical coil

increase faster with chain length than it otherwise would, owing to enhancement of the excluded volume effect. Accordingly, instead of Eq. (5) we might write

$$[\eta] = KM^a \quad (6)$$

where K and a are empirical parameters characteristic both of the polymer itself and of the solvent. The exponent a varies from about 0.5, for well-coiled polymer molecules in a poor solvent, to as much as 1.7, for a rigidly extended "rodlike" polymer molecule.

Flory and Leutner,¹ working with monodisperse specimens of PVOH differing from one another in molecular weight over a wide range (obtained by fractionating polydisperse commercial PVOH), established a correlation between the molecular weight, as determined from osmotic pressure measurements, and the intrinsic viscosity. They found that for PVOH in aqueous solution at 25°C,

$$\begin{aligned} [\eta] &= 2.0 \times 10^{-4} M^{0.76} \\ M &= 7.6 \times 10^4 [\eta]^{1.32} \end{aligned} \quad (7)$$

Equation (7) also holds for a polydisperse sample of PVOH, but the molecular weight in this case is \bar{M}_v , the viscosity-average molecular weight defined below.

Number-Average and Viscosity-Average Molecular Weight. For a polydisperse polymer, any determination of molecular weight must yield an average of some sort. When a colligative property such as osmotic pressure is used, the average is a number average:

$$\bar{M}_n = \frac{\int_0^{\infty} MP(M) dM}{\int_0^{\infty} P(M) dM} \quad (8)$$

where $P(M)$ is the molecular-weight distribution function; that is, $P(M) dM$ is proportional to the number of molecules with molecular weights between M and $M + dM$. However, the average obtained from intrinsic viscosity is not the same kind of average. It is called the viscosity average and is given by

$$(\bar{M}_v)^a = \frac{\int_0^{\infty} M^{1+a} P(M) dM}{\int_0^{\infty} MP(M) dM} \quad (9)$$

For a monodisperse polymer, $\bar{M}_v = \bar{M}_n = M$; for a polydisperse polymer the two kinds of averages are not equal but are related by a constant factor that depends on the distribution function $P(M)$ and the parameter a . A commonly encountered distribution function, and one that is likely to be valid for PVOH, is one that arises if the probability of a chain-termination reaction during the polymerization is constant with time and independent of the chain length already achieved. It is also the most likely function for the product resulting from cleavage with periodate if the head-to-head structures can be assumed to be randomly distributed along the PVOH chains. This distribution function is

$$P(M) = \frac{1}{\bar{M}_n} e^{-M/\bar{M}_n} \quad (10)$$

When this function is used as the weighting function in evaluating averages, it can be shown^{3,7} that

$$\frac{\bar{M}_v}{\bar{M}_n} = [(1+a)\Gamma(1+a)]^{1/a}$$

where Γ is the gamma function. For $a = 0.76$ (the value given above for polyvinyl alcohol),

$$\frac{\bar{M}_v}{\bar{M}_n} = 1.89 \quad (11)$$

If a much exceeds 0.5, \bar{M}_v is much closer to a weight-average molecular weight.

$$\bar{M}_w = \frac{\int_0^\infty M^2 P(M) dM}{\int_0^\infty M P(M) dM} \quad (12)$$

than it is to the number average \bar{M}_n . In fact, when $a = 1$, \bar{M}_v and \bar{M}_w are identical, and with the distribution assumed in Eq. (10), their ratio to \bar{M}_n is 2.

Determination of Frequency of Head-to-Head Occurrences. We wish to calculate the fraction of linkages that are head to head (that is, the ratio of "backward" monomer units to total monomer units), on the assumption that degradation arises exclusively from cleavage of 1,2-glycol structures and that all such structures are cleaved. Let us denote this ratio by Δ . It is equal to the *increase* in the number of molecules present in the system, divided by the total number of monomer units represented by all molecules in the system. Since these numbers are in inverse proportion to the respective molecular weights,

$$\Delta = \frac{1/\bar{M}'_n - 1/\bar{M}_n}{1/M_0} \quad (13)$$

where \bar{M}'_n and \bar{M}_n are number-average molecular weights before and after degradation, respectively, and M_0 is the monomer weight, equal to 44 g mol^{-1} . Thus,

$$\Delta = 44 \left(\frac{1}{\bar{M}'_n} - \frac{1}{\bar{M}_n} \right) \quad (14)$$

Making use of Eq. (11), we can write

$$\Delta = 83 \left(\frac{1}{\bar{M}'_v} - \frac{1}{\bar{M}_v} \right) \quad (15)$$

which permits viscosity averages to be used directly.

EXPERIMENTAL

Clean the viscosimeter thoroughly with cleaning solution,† rinse copiously with distilled water (use a water aspirator to draw large amounts of distilled water through the capillary), and dry with acetone and air. Immerse in a 25°C thermostat bath to equilibrate.

† The cleaning of glassware is discussed in Chapter XXI. An excellent cleaning solution is chromic acid, but this must be handled with care (see p. 688). Alternative choices are hot 50-50 nitric + sulfuric acid (caution in handling also required), alcoholic KOH, or a commercial cleaning solution such as MICRO.

Place a small flask of distilled water in a 25°C bath to equilibrate. Equilibration of water or solutions to bath temperature, in the amounts used here, should be complete in about 10 min.

If a stock solution of the polymer is not available, it should be prepared as follows. Weigh out accurately in a weighing bottle or on a watch glass 4.0 to 4.5 g of the dry polymer. Add it slowly, with stirring, to about 200 mL of hot distilled water in a beaker. To the greatest extent possible "sift" the powder onto the surface and stir gently so as not to entrain bubbles or produce foam. When all of the polymer has dissolved, let the solution cool and transfer it carefully and quantitatively into a 250-mL volumetric flask. Avoid foaming as much as possible by letting the solution run down the side of the flask. Make the solution up to the mark with distilled water and mix by *slowly* inverting a few times. If the solution appears contaminated with insoluble material that would possibly interfere with the viscosity measurements, filter it through Pyrex wool. (Since making up this solution may take considerable time, it is suggested that the calibration of the viscosimeter with water be carried out concurrently.)

In all parts of this experiment, avoid foaming as much as possible. This requires careful pouring when a solution is to be transferred from one vessel to another. It is also important to be meticulous about rinsing glassware that has been in contact with polymer solution promptly and *very thoroughly*, for once the polymer has dried on the glass surface it is quite difficult to remove. Solutions of the polymer should not be allowed to stand for many days before being used, as they may become culture media for airborne bacteria.

Pipette 50 mL of the stock solution into a 100-mL volumetric flask, and make up to the mark with distilled water, observing the above precautions to prevent foaming. Mix, and place in the bath to equilibrate. In this and other dilutions, rinse the pipette *very thoroughly* with water and dry with acetone and air.

To cleave the polymer, pipette 50 mL of the stock solution into a 250-mL flask and add up to 25 mL of distilled water and 0.25 g of solid KIO_4 . Warm the flask to about 70°C, and stir until all the salt is dissolved. Then clamp the flask in a thermostat bath and stir until the solution is at 25°C. Transfer quantitatively to a 100-mL volumetric flask, and make up to the mark with distilled water. Mix carefully, and place in the bath to equilibrate. (This operation can be carried out while viscosity measurements are being made on the uncleaved polymer.)

At this point, two "initial" solutions have been prepared: 100 mL of each of two aqueous polymer solutions of the same concentration (~ 0.9 g/100 mL), one cleaved with periodate and one uncleaved. To obtain a second concentration of each material, pipette 50 mL of the "initial" solution into a 100-mL volumetric flask and make up to the mark with distilled water. Place all solutions in the thermostat bath to equilibrate. The viscosity of both solutions of each polymer (cleaved and uncleaved) should be determined. If time permits, a third concentration (equal to one-quarter of the initial concentration) should also be prepared and measured.

The recommended procedure for measuring the viscosity is as follows:

1. The viscosimeter should be mounted vertically in a constant-temperature bath so that both fiducial marks are visible and below the water level. If a glass-walled thermostat bath which will allow readings to be made with the viscosimeter in place is not available, fill a large beaker or battery jar with water from the bath and set it on a dry towel for thermal insulation. The temperature should be maintained within $\pm 0.1^\circ\text{C}$ of 25°C during a run. This will require periodic small additions of hot water.
2. Pipette the required quantity of solution (or water) into the viscosimeter. Immediately rinse the pipette copiously with water, and dry it with acetone and air before using it again.

- By suction with a pipette bulb through a rubber tube, draw the solution up to a point well above the upper fiducial mark. Release the suction and measure the flow time between the upper and lower marks with a stopwatch. Obtain two or more additional runs with the same filling of the viscosimeter. Three runs agreeing within about 1 percent should suffice.
- Each time the viscosimeter is emptied, rinse it *very thoroughly* with distilled water, then dry with acetone and air. Be sure to remove *all* polymer with water before introducing acetone.

If time permits, the densities of the solutions should be measured with a Westphal balance. Otherwise, the densities may be taken equal to that of the pure solvent without introducing appreciable error.

CALCULATIONS

At 25°C, the density of water is 0.9970 g cm^{-3} and the coefficient of viscosity η_0 is 0.8937 cP. Using your time of flow for pure water, determine the apparatus constant B in Eq. (3).

For each of the polymer solutions studied, calculate the viscosity η and the concentration c in grams of polymer per 100 mL of solution. Then calculate η_{sp}/c and $(1/c)(\ln \eta/\eta_0)$. Plot η_{sp}/c and $(1/c)(\ln \eta/\eta_0)$ versus c and extrapolate linearly to $c = 0$ to obtain $[\eta]$ for the original and for the degraded polymer.

Calculate \bar{M}_v and \bar{M}_n for both the original polymer and the degraded polymer, then obtain a value for Δ . Report these figures together with the polymerization temperature for the sample studied. Discuss the relationship between Δ and the rate constants k_α and k_β .

If a group of students have studied a variety of samples polymerized at different temperatures, it will be possible to obtain estimates of the difference in thermal activation energies ΔE_a and the steric factor S [see Eq. (2)]. It may be difficult to obtain a quantitative interpretation unless the details of the polymerization (amount of initiator, polydispersity, etc.) are well known. However, you should comment qualitatively on your results in the light of what is known about the theory of chain polymerization.^{2,8}

DISCUSSION

Equations (14) and (15) were derived on the assumption that a 1,2-glycol structure will result from every abnormal monomer addition. What is the result of two successive abnormal additions? Can you derive a modified expression on the assumption that the probability of an abnormal addition is independent of all previous additions? Would such an assumption be reasonable? Are your experimental results (or, indeed, those of Flory and Leutner) precise enough to make such a modification significant in experimental terms?

SAFETY ISSUES

Chromic acid or nitric + sulfuric acid cleaning solutions are corrosive and need to be handled with care; see p. 688. Wear safety goggles and gloves while cleaning the viscosimeter.

APPARATUS

Ostwald viscosimeter; two 100- and two 250-mL volumetric flasks; a 10- and a 50-mL pipette; pipetting bulb; 250-mL glass-stoppered flask; one 100- and two 250-mL beakers; stirring rod; bunsen burner; tripod stand and wire gauze; 0 to 100°C thermometer; length of gum-rubber tubing. If polymer stock solution is to be prepared by student: weighing bottle; funnel; Pyrex wool.

Glass-walled thermostat bath at 25°C or substitute; polyvinyl alcohol (M.W. ~60 000 to 80 000; 5 g of solid or 200 mL of solution containing 18 g L⁻¹); KIO₄ (1 g); chromic acid or other cleaning solution (50 mL); Westphal balance, if needed. The polyvinyl alcohol can be obtained from Polysciences Inc., 400 Valley Road, Warrington, PA 18976, and many other suppliers.

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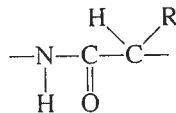
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EXPERIMENT 29

Helix-Coil Transition in Polypeptides

Polymer molecules in solution can be found in many different geometric conformations, and there exist a variety of experimental methods (e.g., viscosity, light scattering, optical rotation) for obtaining information about these conformations.¹ In this experiment, the measurement of optical rotation will be used to study a special type of conformational change that occurs in many polypeptides.

The two important kinds of conformation of a polypeptide chain are the helix and the random coil. In the helical form the amide hydrogen of each "amide group."



EXPERIMENTS IN PHYSICAL CHEMISTRY

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Cover illustration: The top trace is the NMR proton free induction decay of a gaseous mixture of HCl and HBr. (See Exp. 43) The middle trace is the spectrum after Fourier transformation. The lower trace is the corresponding deuteron spectrum of DCl and DBr in the sample. The inset shows potential energy curves for these molecules.