

CHAPTER - IV

EXPERIMENTAL

A. PREPARATION OF SPECIMENS

A brief description of the preparation of the samples used in present investigations, is given in this section. The samples are studied in as-received condition and also after subjecting them to mechanical and thermal treatments. The base material used is GR grade pyrogallol, supplied by LOBA Chemie and is certified to have a purity of 99.9%.

Extreme care was taken with regard to the cleanliness and the purity while preparing (synthesizing) and handling the samples. All the glassware used during synthesis were cleaned by acetone. After cleaning they were dried thoroughly in an oven at 60°C.

(i) As received specimens

(a) Monomer

The synthesis of monomer has already been described earlier in Chapter-III. The monomer was crystallized twice from alcohol to ensure the purity of the sample. The melting point of the purified monomer tallies well with the literature one and the substance melts sharply. The crystals of the monomer were then dried and powdered. The monomer specimen prepared in this manner is designated "as received" monomer.

(b) Polymers

All the polymers were accomplished by the known method of solution polycondensation¹. The purification of polymers was carried out by solvent-nonsolvent method. The solvents in which the polymers are soluble and also insoluble are usually found out. It is observed that all the polymers used here are soluble in dimethyl formamide (DMF) and also in dimethyl sulphoxide (DMSO) but they are insoluble in alcohol. For purification some quantity of polymers was dissolved in dimethyl formamide. After complete dissolution, alcohol was poured in it, until the precipitates were formed. It was kept for overnight, so that finally, the complete precipitation takes place. The precipitates were filtered, dried and powdered. The polymers obtained thus, are called "as received" polymers.

(ii) Mechanically Deformed Specimens

Powdered 'as received' sample could be compressed to form the pellets. A stainless steel press was used for the compression. The pellets formed in this way were usually 1 cm in diameter and 0.1 mm thick. The average pressure applied to the specimens under which they are compressed is around 2500 kgcm^{-2} . Such specimens are called "mechanically deformed" specimens.

(iii) Thermal Annealing Treatments

Monomer and Polymer specimens are annealed in a muffle furnace at 100°C for 2 hrs. in a silica boat. On completion of

the annealing time, the specimen was quenched to room temperature by withdrawing the boat on to a block of aluminium and by a blast of cold air. Such specimens are designated "annealed and quenched" specimens.

B. INSTRUMENTATION

Description

The instrument used for the study of excitation and emission spectra of polymers is Aminco-Bowman-Spectrophoto-fluorometer (SPF) supplied by American Instrument Co., Inc.. The SPF consists of an optical unit, photomultiplier, microphotometer and a power supply. The optical unit includes an electrical panel, Xenon lamp with housing and blower, two monochromators, cell compartment, two slit holders (installed in monochromators), photomultiplier housing with manually operated rotary slit turret and filter holder with shutter control. The Xenon lamp power is supplied from the D.C. power supply, and the sweep power circuit is energized by a mercury battery contained within the optical unit. The Xenon lamp operates on 19.8 volts D.C. The photomultiplier microphotometer includes an electronic chassis, control panel and meters. The photometer operates on 115 volts A.C.

(a) Principles of Operation

Light from the Xenon lamp is dispersed by the excitation monochromator (grating type) into monochromatic radiation incident on the sample. Emitted light from the sample is dispersed by a

similar monochromator into monochromatic radiation incident on the photomultiplier. The light is then transformed to a weak electrical signal and fed to the photometer, where it is amplified. The photometer output is indicated on the self-contained meter. This output signal is connected to a strip chart recorder.

The gratings are oscillated by motor-driven cams to which are coupled graduated discs for visual observation and adjustment of wavelength. Provision is also made to adjust the wavelength manually. Spring loaded arms follow the continuous cam rotation and oscillate the gratings. The maximum and minimum angular positions of the gratings correspond to the high and low points of the cams and to the maximum and minimum wavelength of the monochromators namely, 800 and 200 nm respectively. The recorder could be started and stopped at any desired wavelength reading on the graduated scale. As the motor-driven cam moves with uniform speed, the intermediate wavelength values between two extreme readings on the chart could be determined by equally dividing the linear distance between two end points into the number of wavelengths involved in the corresponding range. The peak position of an excitation or an emission peak read from the chart was found to be coinciding with the position of the corresponding peak as observed by the manual operation of the graduated disc.

(b) Optical Unit

The optical unit incorporates two gratings monochromators of the basic type first described by Elbert². Properties of this

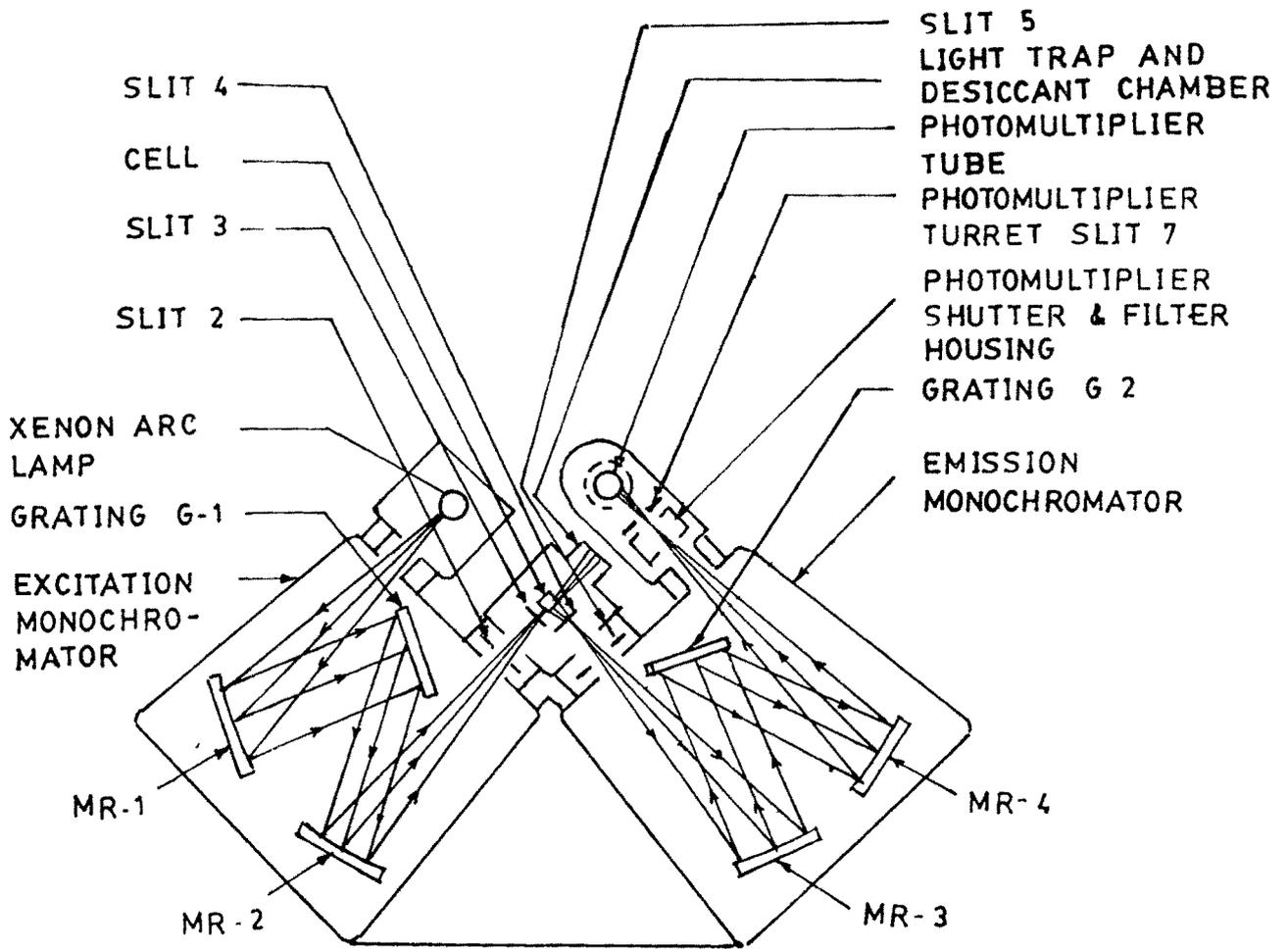


FIG IV-1 OPTICAL UNIT SHOWING POSITION OF SLITS

mounting are discussed fully in two articles by W. G. Fastie³. The schematic diagram of the optical system is shown in Figure IV-1 which illustrates the following :

- (i) The excitation monochromator selects light of monochromatic wavelength from the Xenon arc lamp and focuses it on the sample holder. The light emitted from the sample is received by the emission monochromator and directed on the photo-multiplier tube.
- (ii) Monochromators are optically identical except for a difference in "blaze" wavelength between the two gratings. The excitation grating is blazed at 300 nm (1st order) to strengthen the output from the Xenon lamp which decreases below 400 nm. The emission grating is blazed at 500 nm (1st order) to improve the response to the emission at wavelength from 400-600 nm.
- (iii) The Xenon arc lamp, located at the focus of the spherical mirror, MR-1 (vide Figure IV-1), produces a continuous spectrum peaking at 400 nm and again at 900 nm (beyond the range of the instrument). Light from the lamp, indicated by the three rays, strikes MR-1, which renders it parallel and directs it to the plane grating. Dispersed light from the grating is redirected to the second mirror MR-2 (identical to MR-1), which focuses a monochromatic image of the lamp on the centre of the sample holder. The magnification of

the system is unity, resulting in an image equal in size to the Xenon arc (1.8 mm wide by 3.5 mm high). Emitted light from the sample is similarly dispersed by the emission monochromator and imaged on the photomultiplier slit. Five slit positions are provided in an optical unit. Slits 2 and 3 determine the band-width and the resolution for excitation spectra, whereas, slits 5 and 4 decide the band-width and the resolution in the case of emission spectra. The photomultiplier slit turret controls the intensity. A convenient arrangement of the slits was found out by trial. This arrangement remains unchanged throughout all the measurements, thereby keeping the band-width and resolution constant.

A certain amount of scatter is always present in varying degree in any optical instrument. This is especially true for instruments which measure fluorescence. In the design of the equipment presently being used, though the scatter has been reduced to a practical minimum, a certain amount of scatter still exists. Thus, one observes scatter or reflection peaks whenever the excitation and emission wavelengths are equal. Due to uneliminated second order light from the gratings a noticeable amount of apparently spurious signal will frequently be present at high wavelengths. For example, if emission is maximum at 300 nm, there will be an indication also at 600 nm. This spurious indication should be ignored, since it will usually not

interfere with the shape of the peaks (both excitation and emission spectra). It can be eliminated with the use of suitable optical filters. Thus whether a given peak is genuine or not can be verified by using the appropriate optical filters.

- (iv) A dessicant chamber mounted on the sample housing of the SPF performs two functions. It serves as a light trap for the excitation wavelength and prevents condensation on the sample, especially under conditions of high humidity. The solid sample is fixed on the sample holder with the help of a non-fluorescent grease, and placed diagonally in the sample compartment such that the sample faces both the excitation and emission monochromator slits. The sample holder is made of Ebonite, the surface being covered with black paper, further it does not show any excitation or emission peaks without the phosphor. The position of the sample holder is adjusted in such a way that it gives the maximum emission.

(c) Photomultiplier Microphotometer Unit

This assembly essentially consists of a light sensitive photomultiplier tube with associated circuitry and an amplifier which responds to a small current produced by the photomultiplier tube and registers the amplified current on a microphotometer. The photometer sensitivity is controlled by the meter multiplier switch and sensitivity knob. Coarse adjustments are made with meter multiplier

switch which reduces the meter readings in steps of 1, 3, 10, 30, 100, 300 and 1000. The photomultiplier tube used in this set up is IP 21 with S_4 spectral response.

Operating Procedure for Recording the Spectra

Excitation spectra are obtained by recording the luminescence intensity at fixed wavelength as a function of the wavelength of the exciting source, whereas, emission spectra are records of the spectral distribution of luminescence at fixed excitation wavelength.

- (a) The photomultiplier shutter was opened after inserting the sample in the sample chamber.
- (b) The emission monochromator wavelength disc was then allowed to rotate slowly with the help of slow-fast control.
- (c) The photometer was set for high sensitivity. Subsequently, the excitation wavelength disc was changed manually in steps of 20 nm at the completion of each emission scan until a maximum is indicated on the photometer.
- (d) When the excitation wavelength was located, the emission scan was stopped and the emission wavelength was adjusted for maximum emission indicated on the meter.
- (e) The excitation wavelength disc was again adjusted until a new maximum on-scale meter reading was obtained.

Knowing the excitation peak wavelength and placing the excitation monochromator wavelength disc at this known value, the emission spectrum was recorded. Similarly, knowing the emission peak wavelength, the emission monochromator wavelength disc was adjusted at this known value, and the excitation spectrum was recorded. During the above procedure the sensitivity was adjusted with the help of metermultiplier, so that the photometer reading was within the range of the meter.

Whenever, the instrument was switched 'ON' for measurements a warm-up period of about half an hour was allowed for the stability. The excitation and emission spectra were recorded immediately one after another to avoid the effect of voltage fluctuations. These fluctuations were kept to a minimum with the help of a voltage stabilizer.

C. SOLUTION VISCOSITY AND MOLECULAR SIZE

The usefulness of solution viscosity as a measure of polymer molecular weight has been recognized ever since the early work of Staudinger⁴. Solution viscosity is basically a measure of the size or extension in space of polymer molecules. It is empirically related to the molecular weight of linear polymers. The simplicity of the measurement and the usefulness of the viscosity-molecular weight correlation are so great that the viscosity measurement constitutes an extremely valuable tool for the molecular characterization of polymers.

(i) Experimental Method

The polymer solutions have been characterized by measuring their intrinsic viscosity. Viscosity measurements are carried out in a standardized Ostwald suspended level viscometer, at 30°C. The solvent is introduced into the clean and dry viscometer held vertically in constant temperature bath at 30°C. After the temperature equilibrium is attained, the efflux time is noted down for the solvent. Three independent readings are taken and an average of the three readings is noted.

, A measured amount of powdered polymer is dissolved in a suitable solvent (DMF) to make 1% solution. The clear solution is then filtered through G-3 sintered glass funnel. The solution thus prepared is introduced in the viscometer. After the solution inside the viscometer attains thermostat temperature, the flow time is measured in seconds. At least three observations are made and the average flow time is measured. From the mean efflux time, the viscosity is determined.

Measurements⁵ of solution viscosity are usually made by comparing the efflux time 't', required for a specified volume of polymer solution to flow through a capillary tube with the corresponding efflux time (t_0) for the solvent. From t, t_0 and the solute concentrations the following viscosities are derived :

(a) Relative viscosity (viscosity ratio), η_{rel} :

$$\eta_{rel} = \eta/\eta_0 = t/t_0$$

In this expression, η and t refers to solution and solvent viscosity, respectively, in poise which are proportional to the corresponding flow times, t and t_0 , through the viscometer capillary. Relative viscosity is dimensionless.

(b) Specific viscosity, η_{sp} :

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$$

specific viscosity is also dimensionless.

(c) Reduced viscosity (viscosity number), η_{red} :

$$\eta_{red} = \frac{\eta_{sp}}{C}$$

(d) Inherent viscosity (logarithmic viscosity number), η_{inh} :

$$\eta_{inh} = \frac{\ln \eta_{rel}}{C}$$

(e) Intrinsic viscosity (limiting viscosity number), $[\eta]$:

$$[\eta] = \lim_{C \rightarrow 0} (\eta_{sp}/C) = \lim_{C \rightarrow 0} (\eta_{inh})$$

Concentration, C , in the above expressions is in grams per 100 ml of solvent; therefore reduced, inherent, and intrinsic

viscosities have units of deciliters per gram. The intrinsic viscosity (η) is independent of concentration by virtue of extrapolation to $C \rightarrow 0$, but is a function of the solvent used. The intrinsic viscosity at a specified concentration, usually 0.5 g/dl is sometimes used as an approximation.

(ii) Precautions

The viscometer used here is the Ostwald viscometer. Because it has the advantage that the measurement is independent of the amount of solution in the viscometer; measurements at a series of concentrations can easily be made by successive dilution.

For highest precision, the following precautions are usually observed. The viscosity measurement has been made in a constant temperature bath regulated at an accuracy of $\pm 0.02^\circ\text{C}$. The efflux time is kept long (preferably greater than 100 sec.) to minimize the need for applying corrections to the observed data. For accuracy in extrapolating to $C \rightarrow 0$, the solution concentration is restricted to the range which gives relative viscosities between 1.1 and 1.5.

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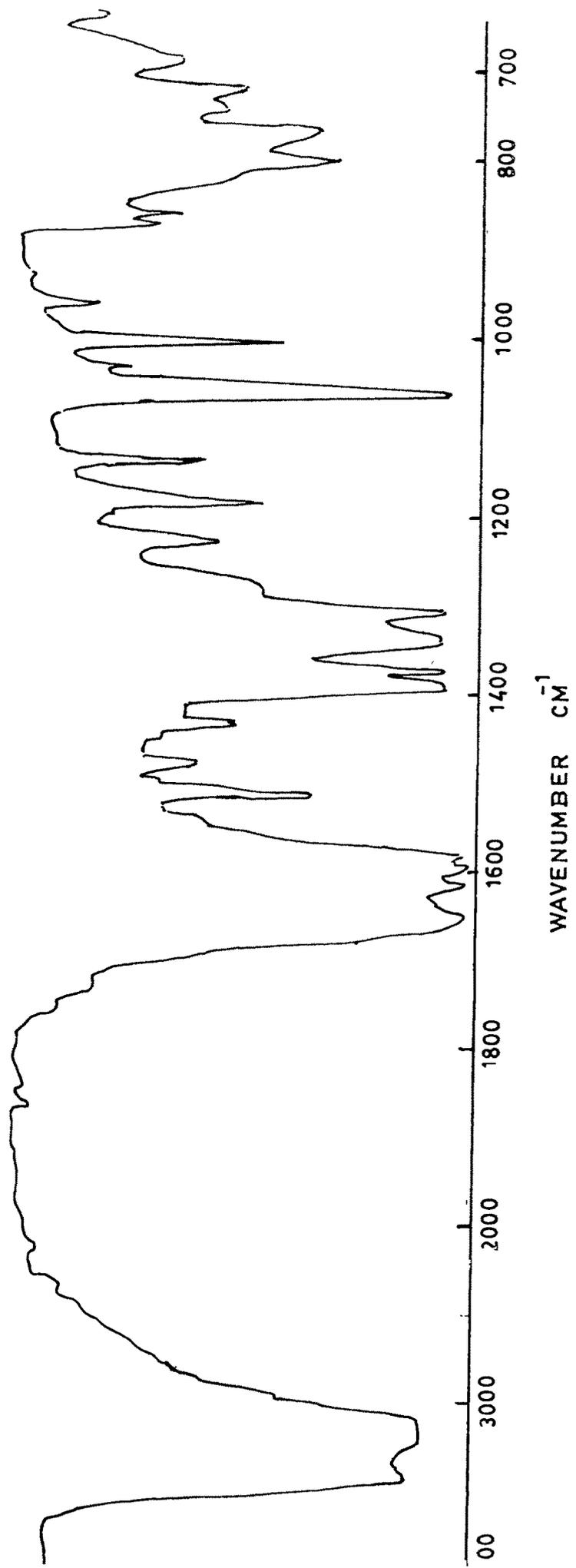
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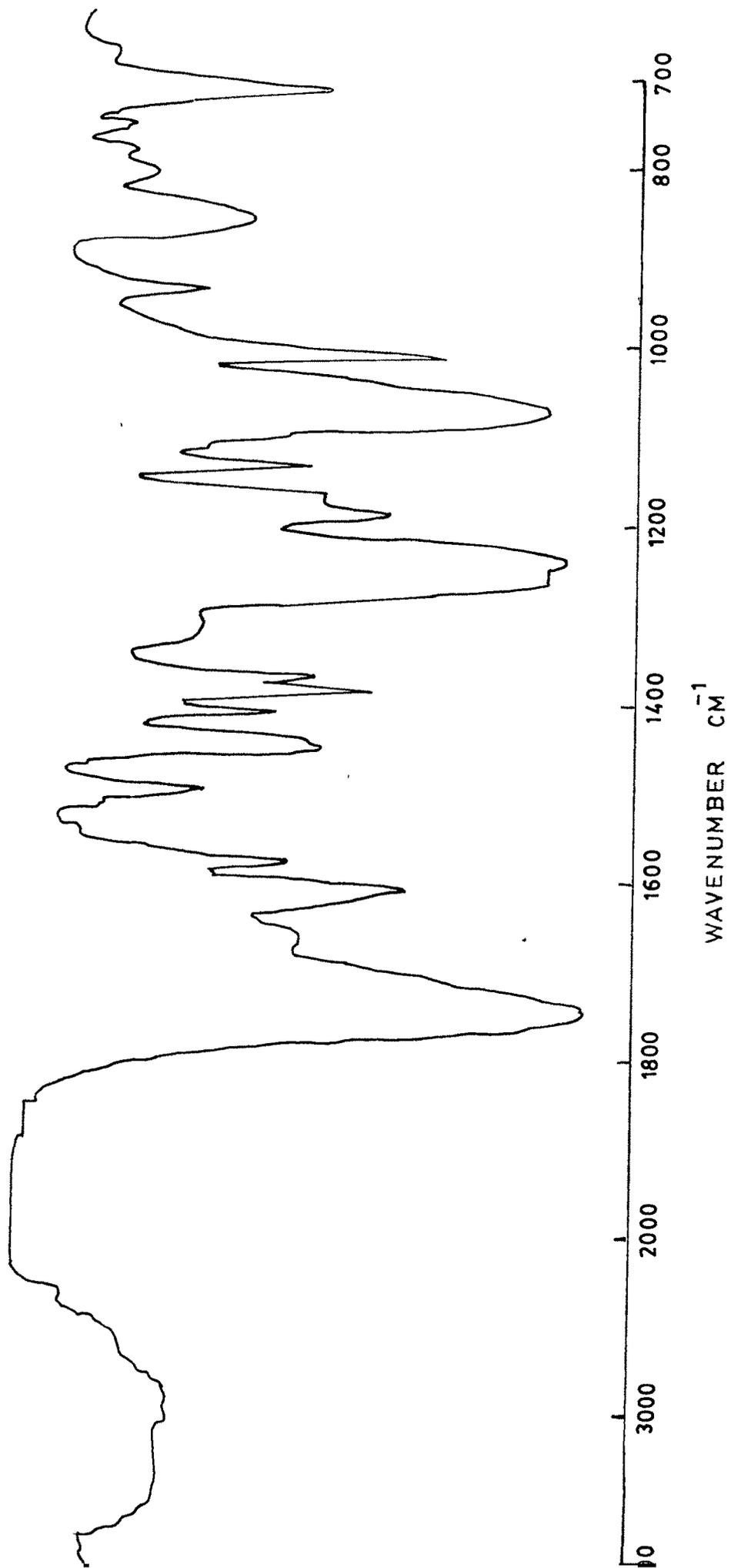
VISCOSITY DATA OF POLYMERS

Solvent Dimethyl sulphoxide (DMSO)
 Concentration 1 %.
 Temperature 30° C.

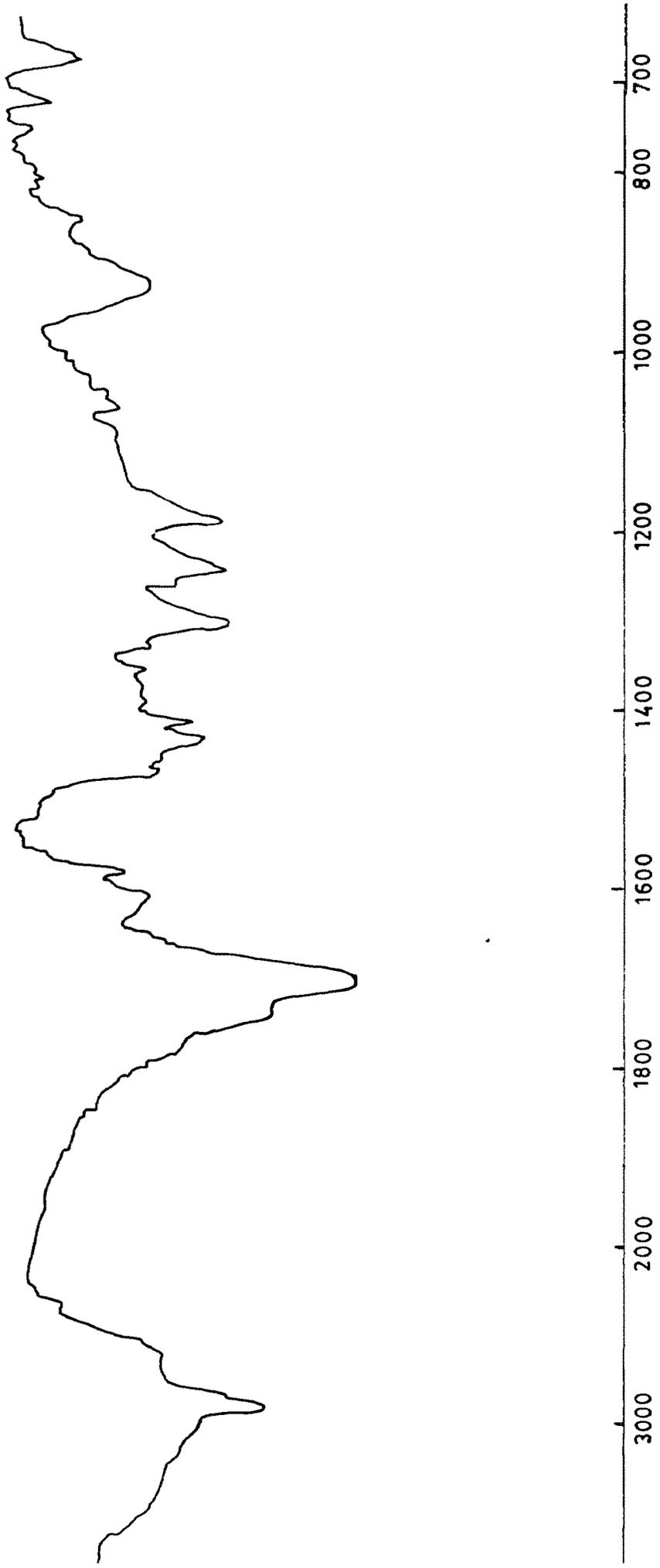
	Relative viscosity	Specific viscosity	Reduced viscosity	Inherent viscosity
	η_r	η_{sp}	η_{red}	η_{inh}
A ₁	1.042	0.042	0.042	0.0179
A ₂	1.032	0.032	0.032	0.0139
A ₃	1.046	0.046	0.046	0.0193
A ₄	1.042	0.042	0.042	0.0179
A ₅	1.036	0.036	0.036	0.0153



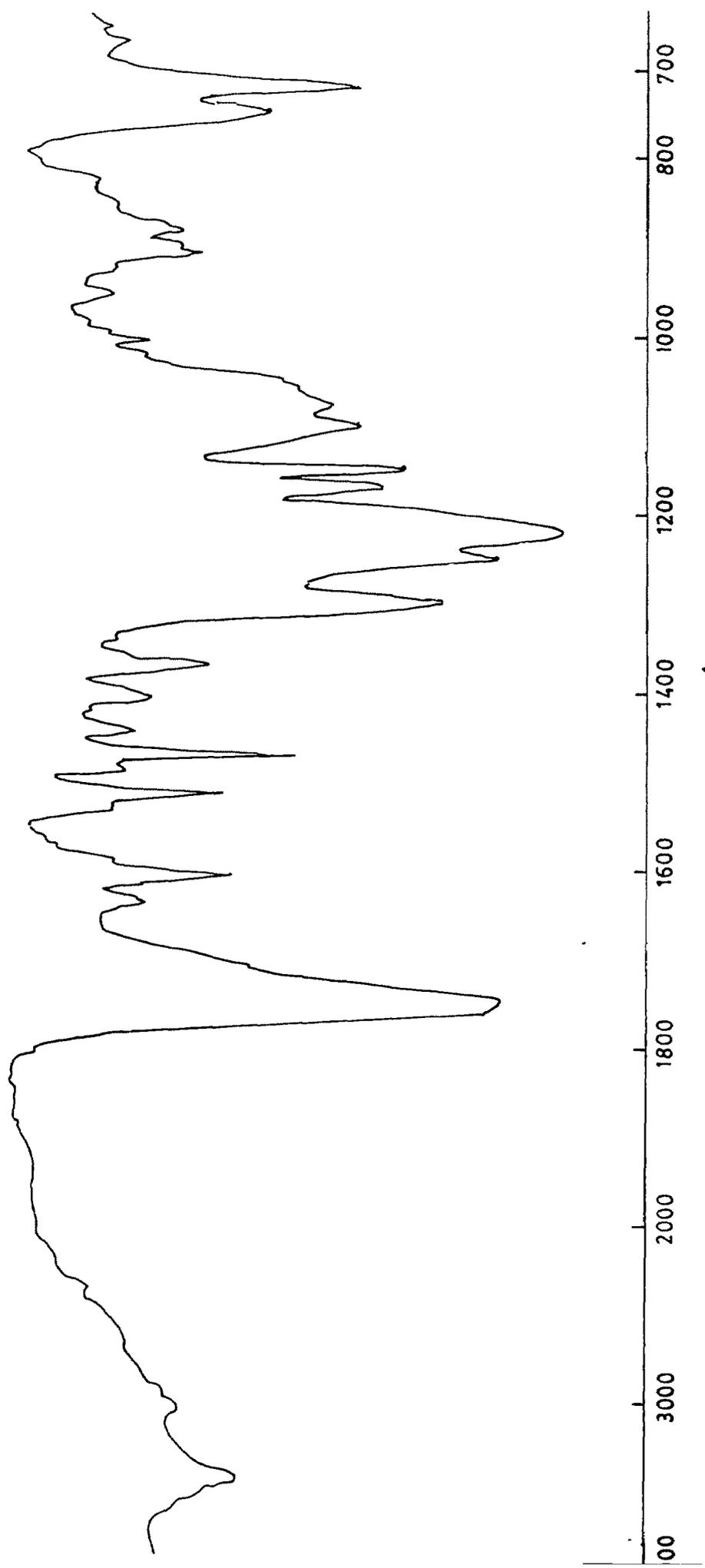
IR SPECTRA FOR SPECIMEN A



IR SPECTRA FOR SPECIMEN A1

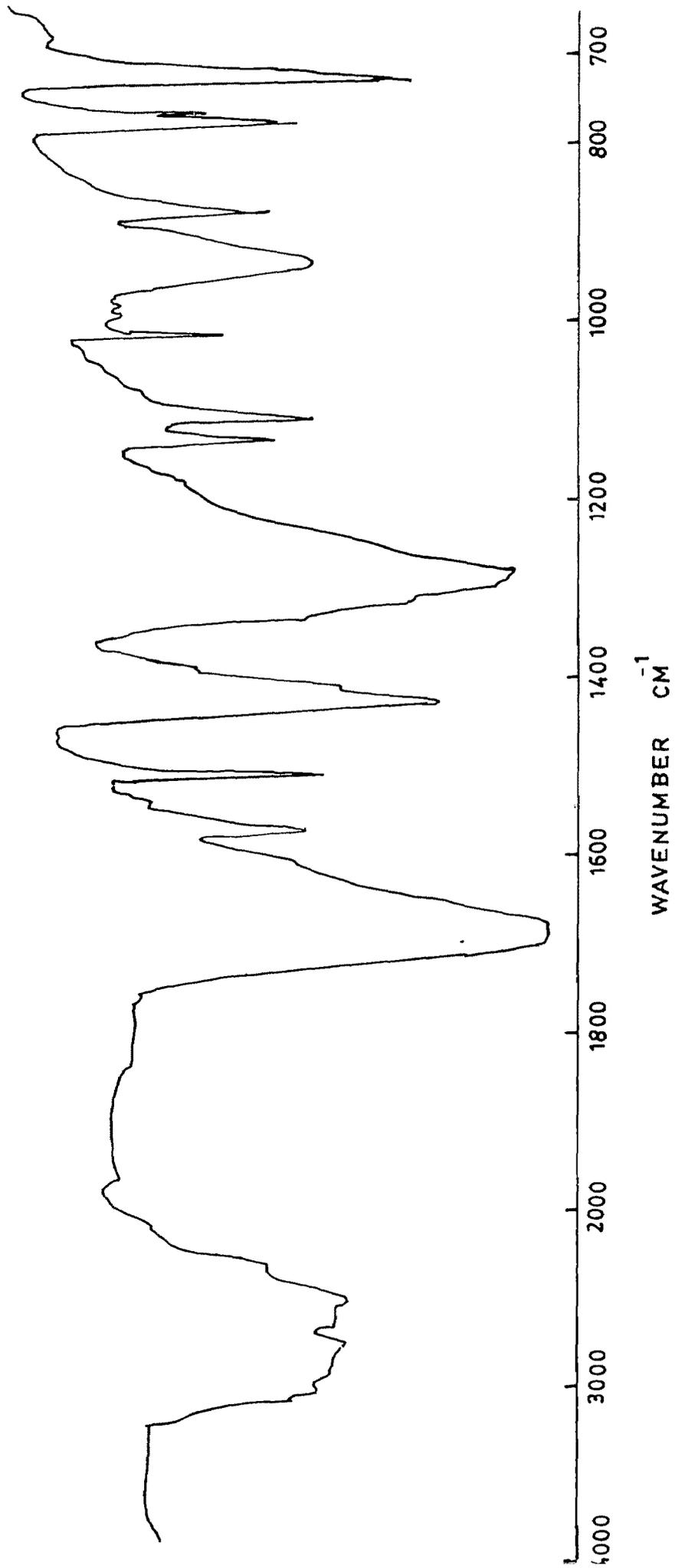


IR SPECTRA FOR SPECIMEN A2

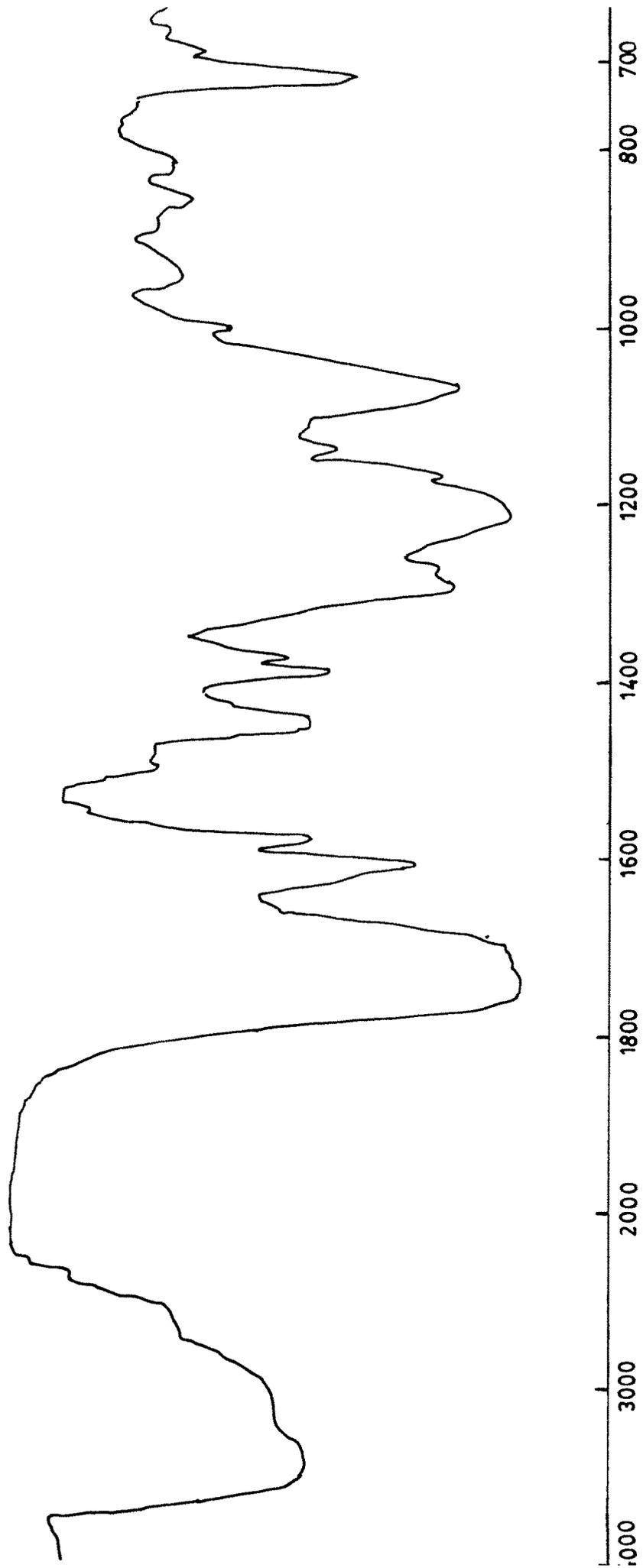


WAVENUMBER CM⁻¹

IR SPECTRA FOR SPECIMEN A3



IR SPECTRA FOR SPECIMEN A4



WAVENUMBER cm^{-1}

IR SPECTRA FOR SPECIMEN A5

IR SPECTRAL DATA

IR Stretching Vibrations (cm^{-1}) for Specimens

A	A ₁	A ₂	A ₃	A ₄	A ₅
1640	1740	1700	1750	1680	1745
3400-3200	3500-2900	2800	3400	3000-2500	3500-3300
1340	1610	1610	1605	1575, 1510	1610
1310	1390	1430	1470	1430	1450
1190	1250	1300	1300	1280	1390
1060	1080	1240	1230, 1150	1110	1215
800	860	1060	745	780	1070
760	710	720	720	730	720

R E F E R E N C E S

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