Structural Order in Vinyl Chloride Polymers

by

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SUMMARY

Structural ordering in a commercial suspension poly(vinyl chloride), a low temperature synthesized vinyl chloride polymer and a vinyl chloride/vinyl acetate copolymer has been investigated.

The polymers were characterized as regards their molecular weight using gel permeation chromatography and their chain tacticity using 13 carbon nuclear magnetic resonance and infrared spectroscopy.

Following compounding with a low level of a lubricant-stabiliser the polymers were subjected to a number of heat treatments above and below their glass transition temperatures. Changes in structural ordering as a result of these heat treatments were examined using X-ray diffraction, differential thermal analysis, density measurements and solvent sorption techniques. These techniques revealed that crystallinity was present in the polymers. The low temperature polymer contained the highest level of crystallinity followed by the normal suspension polymer, and finally the copolymer.

The experimental data indicates that annealing below Tg causes changes in the structure of the amorphous phase. On treatment above Tg crystallization was shown to occur. The results also show that changes in the crystalline content can occur within times experienced during processing. X-ray diffraction and differential thermal analysis along with calculations using Flory's theory of crystallization of copolymers indicate the crystallites in poly(vinyl chloride) are small and imperfect.

Tensile properties of heat treated samples of the polymers were studied and found to be dependent on polymerization and thermal history.

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CHAPTER I - Introduction

1:1 Aim of the Research Project

The aim of this research project was to investigate the influence of heat treatment of vinyl chloride polymers. Changes expected to occur within the time scale of processing were to be examined in terms of structure and properties relevant to application.

It is known that polymerization history affects the ordering process in vinyl chloride polymers, consequently materials synthesized under differing conditions were chosen for the investigation. The first, a commercial suspension polymer, the second, a vinyl chloride/vinyl acetate copolymer in which the crystallizability would be expected to be small, and finally a low temperature polymer having a relatively high crystalline content.

The polymers were to be characterized in terms of their molecular weight and chain microstructure. Following compounding with a low level of stabiliser/lubricant the polymers were to be subjected to various heat treatments above and below the glass transition temperature. Resultant changes in structure would then be investigated using the techniques of differential thermal analysis, density measurement and X-ray diffraction. The mechanical properties as affected by heat treatment were also to be studied.

From the investigation it was hoped to arrive at a correlation between the properties of poly(vinyl chloride) as determined by polymerization and thermal history.

1:2 Introduction to the Material

The output of poly(vinyl chloride) PVC constitutes a large proportion of the total polymer production of the world; the range of properties which can be built into PVC products by selection of plasticisers and formulation ingredients are legion. It is, therefore, considered that a brief introduction to the history, polymerization and compounding technology of the polymer is necessary.

The work of Regnault, 1838, has been considered as the first example of vinyl chloride polymerization; however, the actual polymer produced was poly(vinylidene chloride). Following this Baumann, 1872, studied polymerization of several vinyl systems including ultraviolet initiation of vinyl chloride. The literature published between 1912 and 1929 by Ostromislensky contributed largely to the extent of knowledge on vinyl halide polymerization and by 1930 research on vinyl chloride polymers was becoming extensive, the polymer having been introduced as a commercial product in 1927.

Vinyl chloride may be polymerized by suspension, emulsion, bulk and solution techniques, the first three methods being the most important on a commercial preparative scale.

The molecular weight of the polymer affects both processability and the physical properties of the compound, generally the higher the molecular weight the greater the difficulty experienced in processing, and the greater the improvement in mechanical properties. For commercial polymers in use the weight and number average molecular weights are 70,000 - 330,000 and 30,000 - 82,000 respectively.

Owing to the lack of thermal stability of PVC certain compounding agents must be added before the material can be safely processed. These agents include stabilisers, lubricants and plasticisers which are mixed with the virgin polymer. The resulting mixture is subjected to heat and shearing forces such as milling or Banbury mixing. This compound can then be processed in the normal manner to yield the finished product. A comprehensive discussion of compounding and processing of PVC is available in the literature, notably in the monographs by Penn[1] and Matthews[2].

1:3 A review of the literature on structure in PVC

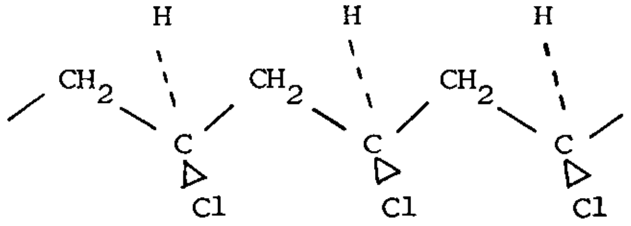
1:3:1 Introduction

This literature survey is intended to indicate the type and extent of evidence which exists showing that dimensional ordering in PVC systems occurs, and that it has a significant influence on the physical and mechanical properties of the polymer.

1:3:2 Polymer chain stereochemistry

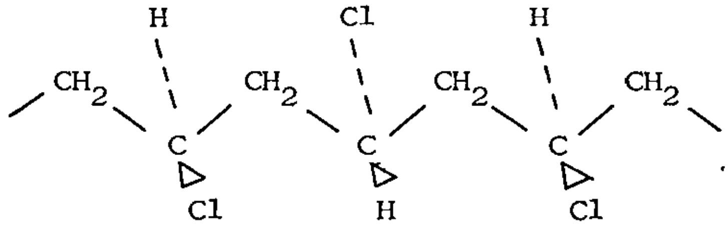
The ability of a polymer to undergo three dimensional ordering is primarily determined by the regularity of the polymer chains. In the case of PVC the major factors are tacticity, linearity, mode of monomer addition and molecular weight. These factors will now be dealt with in detail.

In vinyl polymers, as expressed by the general formula, $(CH_2CHR)_n$, it is possible for the R substituent to have two different arrangements about the polymer chain backbone. For PVC the R group is a chlorine atom. Consider the case where all the chlorine atoms are found in the same relative position; the resulting structure is known as an isotactic chain.



isotactic

If, on the other hand, the atoms are in alternating configurations, a syndiotactic chain is formed.



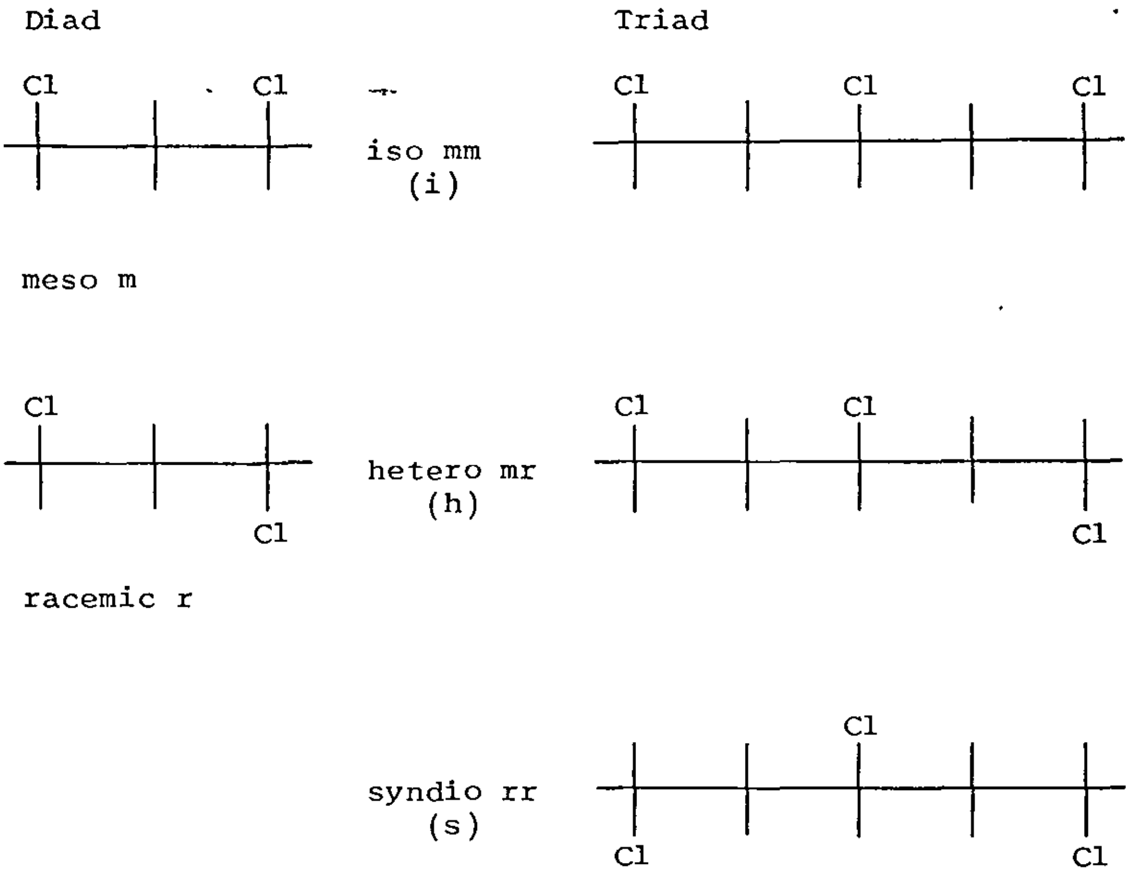
syndiotactic

It can be seen that the iso and syndiotactic sequences for vinyl polymers are regular and allow crystallization to occur. A third possibility is where the chlorine atoms are positioned randomly, hence the structure is termed atactic.

It has been shown theoretically by Fordham[3] that in radical polymerization of vinyl chloride syndiotactic placement is favoured over isotactic placement when the temperature is decreased. This has been shown to be true experimentally and will be discussed later (in depth).

The technique of high resolution nuclear magnetic resonance (N.M.R.) has proven to be an extremely useful means of studying polymer tacticity[4,5,6]. The distribution of configurational sequences, i.e. tacticity as measured by N.M.R. is usually expressed in terms "n" ad concentrations, which refer to the number of consecutive tactic units.

The nomenclature representing configurations of pairs of successive asymmetric carbon atoms, as outlined by Bovey[5], is a meso diad, m, and a racemic diad, r. This lettering system can then be extended to cover sequences of any length. Thus the diad and triad sequences are shown below for a PVC chain.



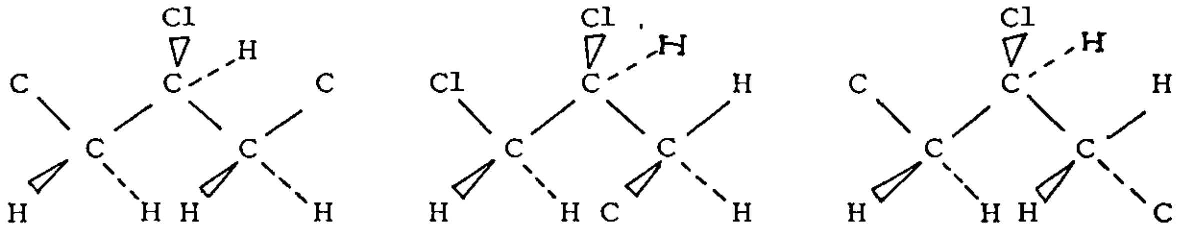
If it is assumed that the formulation of an m or r sequence is independant of the stereochemistry of the chain already formed, then the probability of forming a meso sequence is Pm. This is then referred to as a Bernoullian statistic[5], and requires only one parameter for its description. Thus the probability of forming a racemic sequence is 1 - Pm.

Generation of a triad sequence involves two monomer additions, the probabilities of obtaining iso, hetero and syndiotactic configurations are P^2m, $2Pm(1 - Pm)$ and $(1 - Pm)^2$ respectively. Free radical polymerizations in general obey Bernoullian statistics[7,8], whereas more advanced treatments are required for other polymerization systems[9,10].

There are a large number of papers dealing with the proton N.M.R. spectra of vinyl chloride polymers[11-28]. The analysis for tacticity has been involved because of the complexity of the proton spectrum due to spin coupling and the overlapping of the proton chemical shifts. The techniques of double resonance[15,16,20] and deuteration[21,24,27] have been employed to simplify the spectrum.

Relative intensities of the spectra of the α proton, the β proton and deuterated polymers have been used to measure syndiotactic and isotactic concentrations in vinyl chloride polymers. Recently carbon 13 nuclear magnetic resonance (^{13}C N.M.R.) spectra of PVC have shown advantages over proton spectra for determining tacticity. In o-dichlorobenzene[29,30] three distinct methine carbon resonances were assigned to syndio, hetero and isotactic triad configurations. These spectra were of sufficient quality to totally resolve the three peaks resulting in accurate measurement of the triad sequence concentrations. Additional ^{13}C N.M.R. spectra by Carman[31] and Pham et al[32] has enabled the observation of tetrad sequences.

Tacticity of PVC has also been studied using infrared spectroscopy. It will be appreciated that the position and intensity of the carbon-chlorine stretching vibration will be dependant on environment, and may therefore be used as a measure of chain conformation. (Shown schematically below).



SHH SHH^1 SCH

Conformations of PVC chain

This carbon-chlorine region in the infrared spectrum has been investigated by Krimm et al[33-37], Pohl and Hummel[38,39] and Glazkovskii et al[40]. From this published work the following table of diagnostic absorptions has been constructed, following Juijn et al[41].

Frequency (cm^{-1})	Type of Vibration	Conformation	Chain Conformation
603	SHH	S	syndiotactic straight chain, long segments
615	SHH	S	syndiotactic straight chain, short segments
635	SHH^1	i	isotactic straight chain
640	SHH	S	syndiotactic straight chain, long segments
690	SCH	S and i	isotactic straight chain, isotactic helix, syndiotactic helix

The ratio of the absorbances at 640 and 690 cm^{-1} has been used as a measure of the relative value of the syndiotactic portion of the polymer chain[18,19,42,43]. An absolute method for the determination of tacticity from infrared observations has been proposed by Germar et al[44] and has been used by several authors[45-47]. In this the temperature dependance of the vibrations at 1434 and 1428 cm^{-1} is used.

The syndiotactic fraction $\sigma = \frac{1 + \exp(- E/RT)}{1 + \lambda}$

where λ = Ratio of Absorbances $\frac{1434}{1428}$

T = Absolute Temperature

E = The Energy difference between the two syndiotactic conformations GG, TT

E is obtained by measuring λ at two temperatures T_1, T_2.

$$\frac{\lambda_2 + 1}{\lambda_1 + 1} = \frac{1 + \exp(- E/RT_2)}{1 + \exp(- E/RT_1)}$$

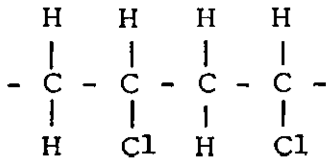
As stated earlier in this review it has been shown theoretically by Fordham[3] that decreasing the polymerization temperature favours syndiotactic placement over that of isotactic placement. Experimental data from N.M.R. and infrared estimates has revealed the increase in the degree of syndiotacticity with a decrease in polymerization temperature[22, 24,31,43-45]. A value of 55% syndiotacticity has been found for a polymer made at 50°C, this increases to 70 - 75% for one made at -60°C[48,126]. N.M.R. and infrared values of syndiotacticity are in agreement for commercial polymers, but for low temperature polymers infrared gives higher values. Differences are apparent between authors with regard to the infrared determined syndiotacticity as the temperature of polymerization is changed. Pezzin[48] considers that these discrepancies indicate that quantitative measurements from infrared are not as reliable as those from N.M.R.

By means of an Arrhenius type plot several authors[24,27,31,49,50] have determined the enthalpy and entropy differences between syndiotactic and isotactic placement, the values being of the order of 600 cal/mole and 1·4 e.u. respectively.

The degree of branching is considered to have an influence on ordering in PVC and has received attention in the literature. Estimates of branching in PVC have been carried out by reduction of the polymer with lithium aluminium hydride, followed by infrared measurements of the methyl band at 1378 cm^{-1} on the resultant polyolefin[51-57]. However, these results exhibit a degree of scatter, some authors obtained values of 15 - 20 branches/1,000 carbon atoms, whilst others found 2 - 5 branches/1,000 carbon atoms. Baker et al[57] in a recent publication state that it is necessary that the length of the side chain is required before an accurate estimate of branching can be made.

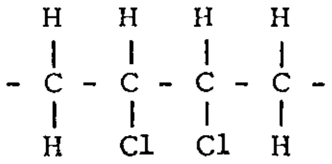
Evidence exists from X-ray diffraction on polyolefins[58] from which information can be deduced regarding the size and number of branches. This technique has been applied to reduced PVC[57], with the conclusion that the branches are only one or two carbon atoms long. Rigo et al[59] obtained large yields of methane in the gamma ray radiolysis of reduced PVC. From these data it is considered that the side branches in PVC are predominantly one carbon atom in length. Baker et al[57] from their own results and by recalculating published values of branching using an extinction coefficient for a side group of one carbon atom in length arrive at a figure of 5 - 6 branches per 1,000 carbon atoms for commercial PVC. A reduction in the polymerization temperature is accompanied by a corresponding decrease in the branched content. Burnett et al[54] in a study of vinyl chloride polymerized in several solvent media concluded that a decrease in branching is a contributing factor to increased crystallinity.

Using the analogy that vinyl chloride monomer has a "head" and a "tail", which are the carbon atom with the chlorine attached and the methylene group respectively, several structures can be visualised as shown below.



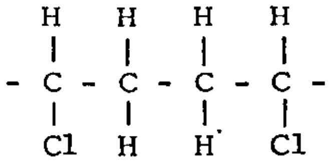
$$-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-$$

Head to tail



$$-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-$$

Head to head



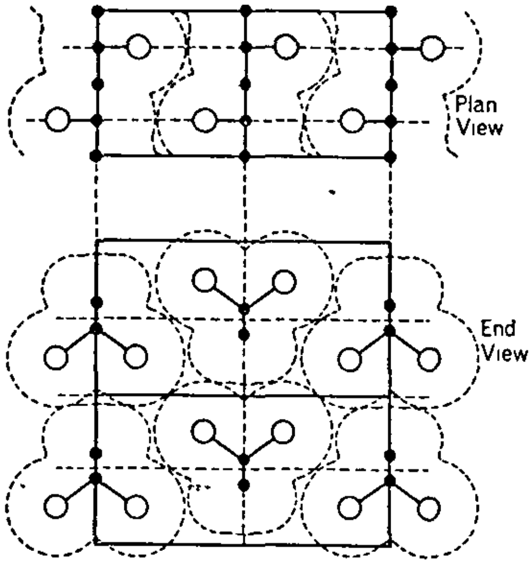
$$-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-$$

Tail to tail

Structures of the head to head and tail to tail types would be disruptive to the crystallization process. Marvel et al[60], Alfrey et al[61] and Harwood[62] have put forward evidence which strongly favours head to tail addition. This does not preclude the formation of some irregular structures, yet evidence in the literature is scanty in this respect. Koleske and Wartman[63] quote the results of Dawson et al, who suggested that 1·2 mole per cent of vinyl chloride adds in the tail to tail fashion. Ohtsu and Nakata reported that 1·5 mole per cent of the head to head structure is present in PVC.

1:3:3 Crystallinity

Pioneer work on the crystalline structure of PVC was carried out by Natta and Corradini[64]. Conformational analysis and X-ray measurements were interpreted in terms of an orthorhombic cell having the dimensions a = 10·6, b = 5·4 and c = 5·1 Å, the ordering being poor along the c axis. The crystal lattice was considered to consist of aligned extended syndiotactic chains the isotactic sequences being too short to give any degree of order.



PVC crystal lattice according to Natta and Corradini[64]

Growth of single crystals of PVC has been reported by Smith and Wilkes[65], Bort et al[66], Nakajima and Hayashi[67], and Wilkes et al[68]. The crystals were found to be lamellar in nature and of the order of 50 - 100 Å in length. Electron and X-ray diffraction evidence in these works also provides confirmation of the orthorhombic cell and the chains being in the extended form.

Juijn et al[41] quoting the X-ray work of Nardi[69,70] and their own investigations from differential scanning calorimetry and conformational analysis are of the opinion that part of the isotactic portion is capable of crystallizing. These authors consider that there are two types of crystallinity in PVC; these are referred to as primary and secondary crystallinity. The former is of the orthorhombic type and is created during the polymerization stage or following dissolution from a good solvent. On annealing the second type of crystallinity is formed, the nematic structure, which is similar to the orthorhombic type, but of a less perfect nature.

Quantitative estimates of the degree of crystallinity have been attempted by X-ray diffraction, infrared spectroscopy and density measurements. Essentially the same approach using X-ray diffraction procedures has been reported by Rayner and Small[71], D'Amato and Strella[72], Garbuglio et al[43] and Lebedev et al[73]. In this technique the intensity against scattering angle trace is obtained for the polymer being studied. The trace is then divided into crystalline and amorphous areas, the ratio of the crystalline to the total area yields a measure of the degree of crystallinity. This is not a totally satisfactory method as correction factors for Lorentz polarisation and changes in scattering factor with angle are required. However, polymers of varying degrees of crystallinity can be ranked in this way.

The correction procedure has been used for polyethylene[74], and Garbuglio et al have attempted to do this for PVC.

A direct correlation between the syndiotactic content and the degree of crystallinity has been demonstrated[43,45,75,76,126]. A typical commercial suspension polymer has a crystallinity value in the region of 10%; on reducing the polymerization temperature to -60°C the value increases to 25%. Calculation from X-ray measurements of the size of the crystallites has shown that they are in the range 50 - 100 Å[48].

Vinyl chloride polymers having high degrees of crystallinity can also be produced by polymerization in the presence of aldehydes[77,78], and by use of a urea-canal complex[79]. In the case of the polymer produced in aldehyde solution, it is considered that the increased crystallinity is due to a reduction in structural irregularities such as branching or a head to head addition as well as a high syndiotactic content. A further contributing factor is that in the polymerization chain transfer occurs resulting in a low value of molecular weight which facilitates crystallization[78]. PVCs of low molecular weight, degree of polymerization = 32, have been prepared in a series of solvents including n-butyaldehyde[80], and it was found that crystallinity increases with a decrease in molecular weight.

White[79] has outlined a method for polymerizing vinyl chloride in a urea-canal complex, initiation being carried out by high energy radiation. Polymers produced in this way are of low molecular weight, contain a syndiotacticity of 80% and a degree of crystallinity of 60%[76]. In the polymerization stage the vinyl chloride monomer is stacked in the channels of the complex such that the spatial arrangement protects against termination or branching.

A slight increase in crystallinity is also obtained when low concentrations of plasticisers are added to the polymer. By X-ray diffraction Horsley[81] and Lebedev et al[82] showed the increase in order goes through a maximum at approximately 10% plasticiser. The polymer chains are thought to have sufficient mobility to pack more efficiently; increased levels of plasticiser results in separation of the chains.

Witenhafer[83] using an infrared compensation technique on solvent cast films states that the ratio of the absorbances at 1250 and 2960 cm^{-1} can be used as a measure of crystallinity. He proceeded to use this method to study polymers of various thermal history. Kawasaki et al[84] have correlated various infrared bands with crystallinity as measured by density, for polymers made at room temperature and $-65^{\circ}C$. Using the $2920\ cm^{-1}$ band as a standard they consider that the optical densities of the absorptions at 1428, 1333, 1254, 1226 and $955\ cm^{-1}$ increase linearly with increasing crystallinity. An absolute method for determining infrared crystallinity of PVC is claimed by Lebedev et al[76].

$$X_{IR} = \frac{1{\cdot}5\ A\ 603}{\Sigma A\nu}$$

$A\ 603$ = Absorption at $603\ cm^{-1}$

$\Sigma A\nu$ = Sum of the absorptions of all the syndiotactic bands between 750 and $550\ cm^{-1}$

Crystallinity from density determinations has been published by Nakajima et al[45] and Manson et al[75], utilizing the formula.

$$X = \frac{\rho c}{\rho} \left(\frac{\rho - \rho a}{\rho c - \rho a} \right)$$

ρ = Density of the sample

ρc = Density of 100% crystalline polymer

ρa = Density of 100% amorphous polymer

The determined crystallinities are slightly higher than those obtained by X-ray diffraction. A contributing factor to this may be the non-uniformity of ρc and ρa values used in the determinations. Several values of ρc, ρa and range of samples along with the method of determination are given below.

		Range of Samples		
ρ_a Kg/m^3	ρ_c Kg/m^3	ρ Kg/m^3	Method	Ref
1385.0	1440.0	1391.0 - 1431.0	Density	45
-	-	1388.7 - 1403.1	Density	84
-	1440.0	-	X-ray	64
1412.0 - 1413.0	1440.0	-	X-ray	73
1373.0	-	1400.0 - 1440.0	Pyknometrically	85
1377.0	-	-	Pyknometrically	86
-	-1522.0	-	X-ray	77
-	1530.0	-	X-ray	68

1:3:4 Thermal Properties

A variety of methods have been used to evaluate the melting point of vinyl chloride polymers. Flory's theory of melting point depression relates the melting point of the pure polymer to that of a polymer/diluent system.

$$\frac{1}{Tm} - \frac{1}{Tm^o} = \left(\frac{R}{\Delta H}\right)\left(\frac{Vu}{V_1}\right)(v_1 - \chi_1 v_1^2)$$

where ΔH = Heat of fusion

Tm = Melting Point Polymer/Diluent

Tm^o = Melting Point of the Pure Polymer

Vu V_1 = The molar volume of the repeat unit and diluent respectively

v_1 = Mole fraction of the diluent

χ_1 = Polymer - diluent interaction parameter.

Nakajima et al[45] and Anagnostopoulous et al[88] have used this theory to determine Tm^o, the melting point of the pure polymer. The former concluded that polymers made at -15° and -30°C have melting points of 285° and 310°C respectively.

Anagnostopoulous et al obtained a value of 176°C for a commercial type PVC, whilst for a similar polymer Lyngaae-Jorgensen[89], from studying plasticiser-polymer mixtures under shear conditions arrived at a value of 233°C.

Colbourne[90] studied a large number of commercially available polymers using a Köfler bar method and found a range of Tm varying from 174° to 232°C.

Reding et al[91] carried out stiffness modulus measurements over a range of temperatures on PVCs containing various levels of plasticiser. The Tm was taken as the temperature at which the sample had a stiffness of 10 p.s.i. By extrapolation to zero per cent plasticiser the Tm of the base polymer was found. The conclusions were that PVCs polymerized at temperatures of 155°, 40°, -10° and -80°C have melting points of 155°, 220°, 265° and more than 300°C respectively.

Finally, from X-ray diffraction measurements on a polymer progressively heat treated, (80° - 260°C), Michel and Guyot[92] found a value ot Tm between 250° and 260°C.

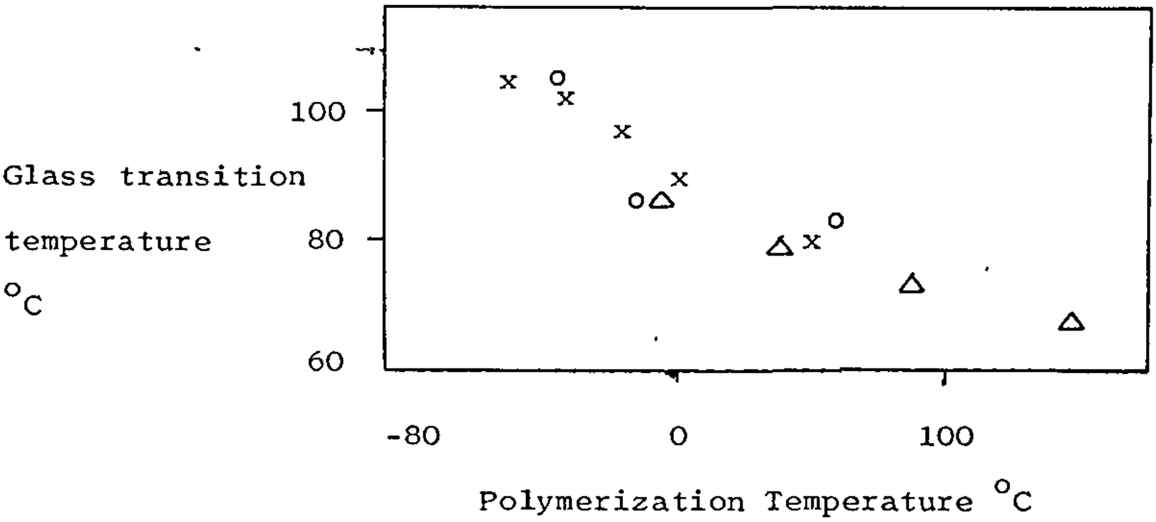
In the above published works determinations of the heat of fusion, ΔHf, have been made. These values are in the range 600 - 800 cal/mole[45,88,89] or slightly above[90]. Kockott[93], by considering that only the syndiotactic portion of the chains is capable of crystallizing, has applied Flory's theory of crystallization of copolymers. He found that the heat of fusion of a 100% crystalline polymer is 2700 cal/mole. It should be noted that this method is in doubt for measurement of ΔHf[127].

Illers[95] has extensively investigated the heat treatment of a commercial suspension polymer using differential scanning calorimetry, density, permeation and mechanical property measurements. The property changes observed from heat treatment below the glass temperature were considered to result from free volume changes. Changes occuring from treatment above the glass transition temperature are suggested to be due to crystallization. Illers quotes values of approximately 1·0 and 2·0 cal/gm for the heats of crystallization and fusion respectively.

McKinney and Foltz[96] using differential thermal analysis on PVC heat treated below the glass transition temperature observed an endotherm on the Tg step. They interpreted this phenomenon to alignment of the polymer chains of too short a length to be detected by X-ray diffraction. In a subsequent article[97] these authors studied heat treated vinyl chloride homopolymers and vinyl acetate copolymers. In this case they used a quenched sample of the polymer as the reference material, and considered this to be the amorphous phase of the material. Unfortunately, the sample was only quenched from 120°C, which is at variance with work on the melting of PVC discussed previously in this review.

Juijn et al[41] from differential scanning calorimetry and density measurements consider that heat treatment above the glass transition temperature results in the formation of a less perfect, secondary crystallinity. This secondary type is only formed after the primary, orthorhombic structure has been wholly or partially removed. The original primary crystallinity can be restored by slow precipitation of the polymer from a good solvent.

Crystalline vinyl chloride polymers have higher glass transition temperatures than commercial polymers[43,45,48,91]. The latter class have a glass transition temperature in the region of 80°C. The results from various sources are shown graphically below, with polymerization temperature as a variable.



x Pezzin[48] o Garbuglio[43] △ Reding et al[91]

The increased stereoregularity and crystallinity are thought to decrease the molecular mobility resulting in the increased glass transition temperatures.

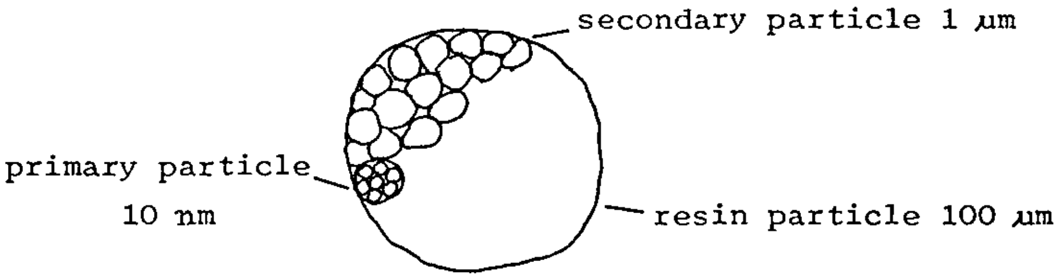
The heat treatment of PVC and its concomitant effects has been reported in the literature. Rybnikar[94], using density, differential thermal analysis and X-ray diffraction studied the crystallization and recrystallization of commercial suspension and emulsion polymers in the range 120 - 170°C. Plotting several of these variables against logarithm of time, (at constant temperature), he obtained S-shaped curves which are characteristic of crystallization isotherms. He also concluded that the crystallization process is very rapid, and a maximum rate occurs in the region of 140 - 150°C.

Michel and Guyot[92] by X-ray techniques studied the high temperature crystallization of a polymer made at 0°C. They found that crystallization occurs up to 240°C, the crystallinity changes little yet the crystallites increase in size. They took this as evidence that heat treatment results in perfection of existing crystallinity rather than additional crystallization from the amorphous mass.

1:3:5 Particulate Structure and Rheological Properties

The particulate character of PVC was first observed by Bort et al[98] who reported that the bulk polymerized polymer consists of 1 - 2 µm particles which had been formed during the polymerization process. Since then there has been a number of published articles on the particle nature of vinyl chloride polymers.

From work involving electron microscopy on samples of known shear and heat history[99-105] a model for PVC morphology has been put forward. Three types of particle have been observed, consisting of a primary particle, 10 nm diameter, which aggregates to form a secondary particle of 1 µm diameter. These secondary particles further agglomerate to give the final resin particle of 100 µm diameter.



Tsou and Geil[105], and Lyngaae-Jorgensen[89] have suggested that the primary particle contains a crystalline core. The particle contains between 10 - 15 single molecules which are held together by the crystalline core.

During processing the above particulate structures break down progressively under the combined effects of shear and heat, the process being complete in the region of 210°C.

From the preceding discussion of melting and particle structure breakdown, anomalous effects are expected and observed when studying the rheological properties of PVC. In a series of papers on the rheology of PVC by Berens and Folt[102-104], and Strella[106] the following summarised features were revealed. Two flow mechanisms may occur; particle flow, (flow of original unfused polymer particles), and molecular flow. The former is favoured by high molecular weight, low temperature and a large resin particle size. Additional evidence of two flow mechanisms has been provided by Collins and Krier[107]. In this work an Arrhenius plot of viscosity against reciprocal temperature yielded two different activation energies in the range 160°C to 230°C. The lower value of 10 K cal/mole was assigned to particle flow, the higher, 20 K cal/mole to molecular flow. The transitional region was considered to be the melting region of the crystallites in the polymer.

The work of Collins and Metzger[108] has shown that the temperature of the change in the activation energy is close to the temperature where the PVC particles change in structure. Also the transition temperature and the value of the activation energy itself can be shifted by changes in molecular weight.

The connection between crystallinity and particle flow has been demonstrated by Pezzin et al[109,110] on a PVC made at -30°C. Using electron microscopy on fracture surfaces of extrudates and Brabender Plastograph data it was shown that the primary particles fuse at a higher temperature than conventional PVC. The elasticity as measured by die swell of the extrudate is low, and independent of temperature and shear stress. With conventional PVC the die swell is higher and increases with temperature and shear stress, from which it was concluded that the contribution to molecular flow is less as crystallinity is increased.

Finally, a cautionary note on rheological properties is that in understanding flow data of PVC as determined by previous history, the influence of degradation must be considered[111,112]; as predictably the formation of crosslinks will affect values obtained of elasticity and viscosity.

1:3:6 Mechanical Properties

From the preceding discussion on particle structure, melting and thermal properties it can be appreciated that mechanical properties will vary according to polymerization and process history.

Malac[113] has examined the influence of pressing temperature and cooling rate on the tensile, impact and enbrittlement properties of PVC. A slow rate of cooling gives an increase in tensile strength, a low impact strength, and raises the enbrittlement temperature from -15°C to +15°C. He attributed the results to freezing-in of free volume in fast cooling. Phillips et al[114] found annealing above Tg causes a decrease in tensile strength and elongation whereas yield stress increases.

Retting[115] has studied the tensile behaviour between speeds of 10^{-3} and 1 cm/sec of a commercial polymer heat treated below Tg. He found that the modulus at low strain rates increases substantially with annealing time. At higher strains there was little effect of heat treatment. Illers[95] attributed changes in tensile behaviour to a decrease in free volume for samples heated below Tg, and crystallinity changes for those treated above Tg.

Pezzin et al have investigated the influence of processing history and crystallinity on the mechanical properties of PVC. A polymer made at -30°C has lower tensile strength, elongation at break and impact strength than a commercial PVC[110]. Room temperature modulus and yield are affected little by process history and crystallinity, whereas the elongation at break and fracture energy increase with milling temperature[116]. They considered from electron microscope evidence that this mechanical behaviour was a consequence of the retention of the particulate nature of the polymer.

The time dependant phenomena of creep and stress relaxation of vinyl chloride polymers has been investigated. Turner[117] found that creep results at 60°C could be varied greatly by prior treatment at 60°C. These differences at low values of elapsed time are modest, but become large at long periods of elapsed time. The changes could be removed by rapid cooling from temperatures close to that of the glass transition, which is consistent with free volume changes.

The 20°C creep compliance of PVC was shown by Wright[118] to be temporarily increased by prior annealing at temperatures above

45°C and below the Tg. This effect increases with decreasing annealing time. It was suggested that volume relaxation below 45°C proceeds by short range separation into regions of molecular order and disorder. This is rapidly disrupted at temperatures above 45°C.

Taylor and Tobolsky[119] made stress relaxation measurements at various temperatures on PVC containing a range of plasticiser types and levels. They concluded that PVC is semi-crystalline in nature; the crystallites can be considered to act as crosslinks. The action of plasticisers is similar to their effect on completely amorphous polymers, but the crystallites remain stable under their action. Hata et al[120] continued the above work and were of the opinion that partial crystallinity is the main cause of the higher modulus of plasticised PVC compared to that of plasticised pure glassy polymers. A "bump" in the modulus v's temperature curve was observed at 50°C, which was independent of plasticiser type and concentration. It's disappearance on reheating and rapid cooling pointed to a phenomenon associated with a separate, possibly crystalline phase.

Crugnola et al[121] investigated the stress relaxation of PVC between 120 - 180°C. The polymer was observed to respond elastically within this temperature range. The basis for this behaviour was linked to the partial crystalline nature of the material. From stress relaxation, creep measurements and by employing a semi-crystalline model as outlined above Sabia and Eirich[122,123] considered that two mechanisms occur in the viscoelastic behaviour of PVC. Firstly elongation of the amorphous regions, which is followed by deformation of the crystallites, so resulting in flow and set.

Anomalous behaviour of mechanical properties at low levels of plasticiser has been reported. At levels in the region of 10% a more rigid rather than a softer material is formed. Razinskaya et al[124] studied tensile and melt viscosity of suspension and emulsion polymers containing low levels of plasticiser. They concluded that stiffening occurs in suspension but not in emulsion polymers. Ghersa[125] from tensile and impact strength measurements concluded that there was little difference in the behaviour of suspension and emulsion resins. Horsley[81] carried out a similar study and also noted that the extra rigidity could be removed by quenching the material from a high temperature. Also, as stated earlier, X-ray evidence in this work provides confirmation that these low levels of plasticiser result in an increase in the crystalline content of the polymer.

CHAPTER II - Characterization of the Polymers studied

This chapter is devoted to the characterization of the polymers studied in the research project. The technique of Gel Permeation Chromatography was employed to measure the molecular weights of the polymers.

The literature review in Chapter I has shown that chain tacticity plays a significant role in the ordering of PVC. Consequently chain microstructure was assessed by Carbon-13 nuclear magnetic resonance and infrared spectroscopy.

As the polymers were to be subjected to various heat treatments above and below the glass transition their thermal stability and Tgs were measured using thermogravimetric and thermomechanical analysis respectively.

2:1 Materials and Compounding Conditions

Three vinyl chloride polymers were chosen for the study to give the range of high, intermediate and low order. The first material, a PVC homopolymer, supplied by Montecatini-Edison Ltd., synthesized at -30°C and having a higher than usual crystalline content. The second was a commercial suspension homopolymer, manufactured by B.P. Chemicals Ltd. This was supplied by the Polymer Supply and Characterization Centre of the Rubber and Plastics Research Association, and is referred to as PVC-2. From published literature the crystallinity in this polymer is expected to be in the region of 10%. The final material was a vinyl chloride/vinyl acetate copolymer (15% V.Ac. content), Breon As 60/41 x 15, manufactured and supplied by B.P. Chemicals Ltd. The presence of the acetate grouping is considered to be disruptive to the ordering process and thus crystallinity is thought to be minimal.

The research project was aimed at studying structural changes occuring during the processing of vinyl chloride polymers. Owing to its lack of thermal stability PVC must be mixed with certain additives prior to being processed. Commercial PVC formulations contain many ingredients such as stabilisers, lubricants, impact and flow modifiers, etc. and would create difficulties in a study of this type. Consequently a simple system containing four parts of dibasic lead stearate (DBLS) per hundred parts of PVC was used. (DBLS supplied by Polymer Supply and Characterization Centre, RAPRA). DBLS functions as both a stabiliser and a lubricant, the latter property being required to compound the material satisfactorily. Four parts per hundred is a relatively high level, however, this was considered necessary to provide adequate protection against thermal degradation during subsequent heat treatment.

The polymers were dry blended with the requisite amount of DBLS in a sigma-blade mixer at ambient temperature. The resulting formulations were then compounded on a two-roll mill. The materials took in the region of ten minutes to form a "band" on the mill, and were then milled for a further ten minutes with frequent cross blending to give an homogeneous mix. Following milling the materials were compression moulded in an electrically heated Bridge Press to give sheets of approximately 0·5 mm thick. The materials were given three minutes in the mould with contact pressure only, then five minutes with full pressure (4·5 MN/m^2) and finally the mould was cooled to room temperature over ten minutes, again under full pressure. Precise milling and moulding conditions are given in Table 1.

Table 1

Polymer	Mill Temp. °C	Mill Friction Ratio	Moulding Temp. °C
Vinyl Chloride/Vinyl Acetate Copolymer	140	1 : 1·5	140
PVC-2	160	1 : 1·5	180
Montecatini -30°C polymer	170	1 : 1·5	200

The milling conditions were chosen so as to achieve fusion of the 1 µm diameter particles present in PVC. A check on the extent of fusion was carried out by immersing the milled material in acetone. If adequate fusion has been attained the immersed sample swells but remains intact, whereas unfused material disintegrates.

2:2 Molecular Weight from Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) separates molecules according to their hydrodynamic volume in solution. Experimentally the technique uses a series of columns packed with crosslinked beads having a range of pore sizes. The columns are filled with a solvent and the sample to be studied is dissolved in the same solvent and introduced into the column. During elution larger molecules travel through the column quickly; small molecules take longer due to their larger effective path.

The molecular species as they are eluted are monitored by a detector, which is usually a differential refractometer. The displayed trace is in the form of recorder deflection against elution volume. A computer programme is used to interpret input data such as elution volume, recorder sensitivity, sample concentration, etc. to provide cumulative and differential molecular weight distributions, number, weight and viscosity average molecular weights.

Experimentally the determinations were carried out on the GPC apparatus at the laboratories of the Rubber and Plastics Research Association, Shawbury. This unit consists of a pumping system, a series of four columns containing Poragel* or Styragel*, automatic sample injection and an R401 differential refractometer*. The data was interpreted using an IBM 360 computer.

The instrument was operated under the following conditions:

Flow Rate	1 ml/min
Solvent	Tetrahydrofuran (THF) plus 0·1% 2,6-di-tert-butyl-p-cresol as inhibitor
Temperature	25°C
Concentration	0·2%
Calibration	Polystyrene standard

The commercial suspension polymer, PVC-2, and the vinyl chloride/vinyl acetate copolymer dissolved readily in THF at room temperature. The low temperature polymer apparently dissolved at ambient temperature but gave rise to two peaks in the chromatogram which is characteristic of associated molecules (see Chapter V Discussion). It was found necessary to heat this polymer in solution at 90°C in a sealed tube for five days in order to break down the aggregated molecules and obtain satisfactory GPC data.

Values obtained from the GPC measurements are shown in Table 2.

---

* Waters Associates Inc., Framingham, Mass.

Table 2

Polymer	Number Average Mol. wt. $\bar{M}_n$	Weight Average Mol. wt. $\bar{M}_w$
Vinyl Chloride/Vinyl Acetate Copolymer	34,800	77,020
PVC-2	23,300	59,200
Montecatini -30°C polymer	43,600	88,800

2:3 Assessment of Tacticity

2:3:1 Carbon 13 Nuclear Magnetic Resonance

The nucleus of an atom possesses the property of spin characterized by the spin quantum number I. When the spin quantum number is $\frac{1}{2}$ or greater the nucleus has a magnetic moment. When an external field, H_o, is applied the nucleus can occupy either of two energy levels corresponding to alignment of its magnetic moment with or against the field. The two orientations differ in energy by

$$\Delta E = h\nu_o = 2\mu H_o$$

where h = Planck's Constant and ν_o = Resonance Frequency which causes the transition between these energy levels. The quantity, ΔE of energy must be absorbed to raise the nuclei in the lower to a higher state and is emitted in the reverse process. The phenomenon of interaction of the magnetic fields of adjacent nuclei can occur, and this is referred to as spin-spin coupling. In general spin-spin coupling of a nucleus with a set of n equivalent nuclei splits the resonance band into n + 1 lines. The relative intensity of the lines within a band is given by the binomial coefficients.

Analysis of tacticity of PVC from proton NMR spectra has been complicated due to the overlapping of the proton chemical shifts, however, ^{13}C NMR has shown vast improvements in resolution[29-32].

These spectra are of sufficient quality to totally resolve the resonance bands enabling accurate measurement of tacticity.

Experimentally the measurements were recorded on a Nuclear Magnetic Resonance Ltd. XL-100 instrument at I.C.I. Plastics Division Laboratories, Welwyn Garden City. The operating conditions were as follows:

Observing	^{13}Carbon nuclei at 25·2 MHz
Lock	Hexadeuterated dimethyl sulphoxide
Solvent	o-dichlorobenzene
Temperature	PVC-2, Montecatini 140°C
	Vinyl Chloride/Vinyl Acetate copolymer 120°C
Sample Tube	12 mm outside diameter

Triad tacticity values were arrived at by measurement of the areas of the methine carbon resonances assigned to carbon atoms in the syndio, hetero and isotactic environments as outlined by Carman et al[30]. Assuming Bernoullian statistics the diad concentrations were calculated from the triad concentrations using the following formulae[5].

Diad Concentration Iso $m = I + \frac{H}{2}$

Syndio $r = s + \frac{H}{2}$

where I, H and s are the iso, hetero, and syndiotactic triad concentrations respectively.

The tacticity values obtained are given in Table 3 and the spectra in Figure 1.

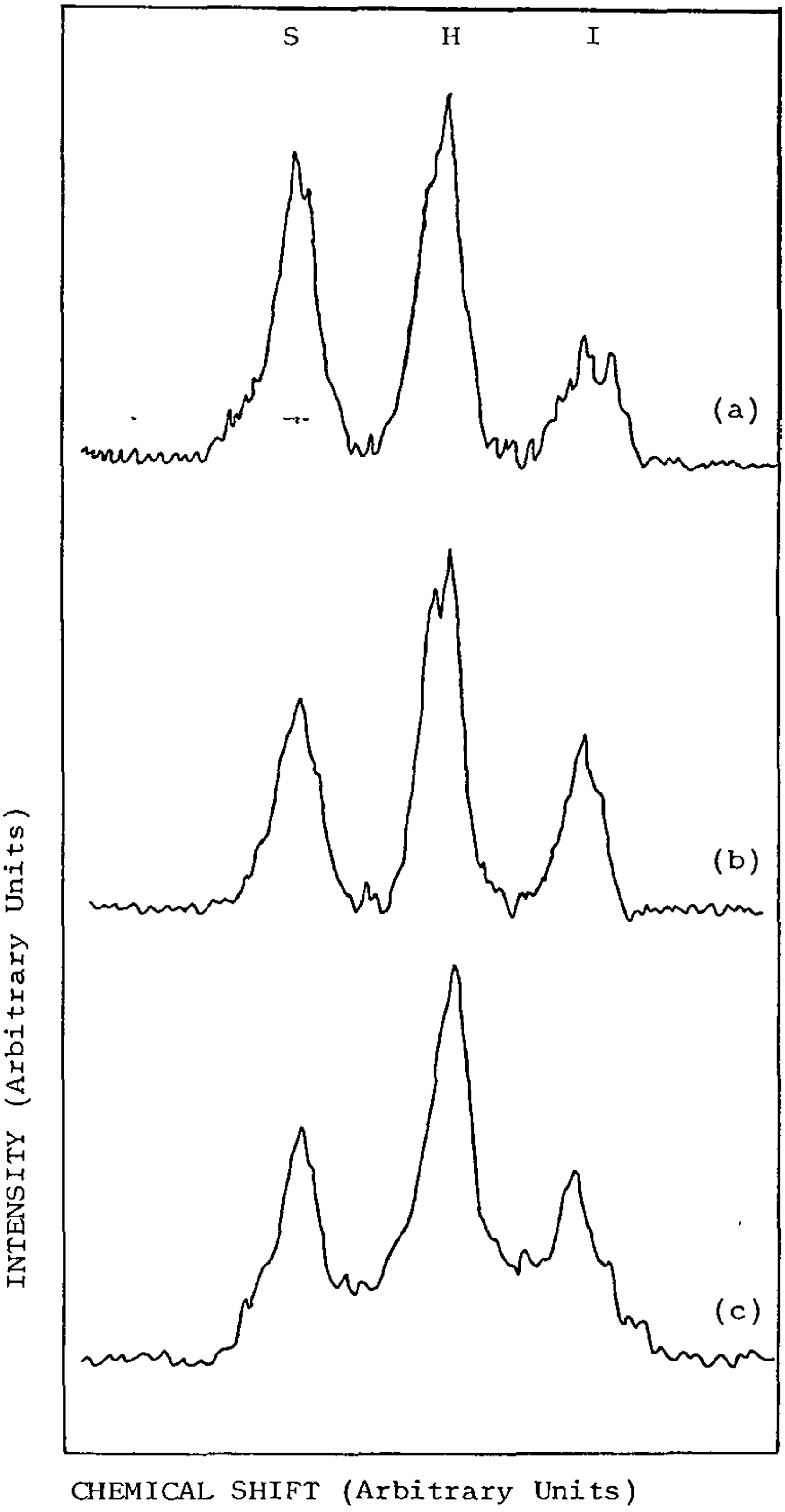


Figure 1 - ^{13}C NMR Spectra of syndio (S), hetero (H) and isotactic (I) methine carbon region

(a) Montecatini -30°C polymer

(b) PVC-2

(c) Vinyl Chloride/Vinyl Acetate copolymer

Table 3

	Triad Concentration %			Diad Concentration %	
Polymer	s	H	I	s	I
Vinyl Chloride/Vinyl Acetate Copolymer	24	51	25	49·5	50·5
PVC-2	34	48	18	58·0	42·0
Montecatini -30°C polymer	44	45	11	66·5	33·5

The vinyl chloride/vinyl acetate copolymer gave an atypical spectrum, with some peak overlap. This was considered a consequence of the vinyl acetate group resulting in additional spin-spin coupling with the nuclei of the main chain. The tacticity values for the polymer are thus approximate ones, however, they indicate that the polymer is virtually atactic. The values found for PVC-2, the commercial polymer and the low temperature polymer are in line with those published in the literature[48,126].

2:3:2 Infrared Spectroscopy

This spectroscopic technique is based upon the interaction of infrared electromagnetic radiation with mass. Such an interaction results in absorbtion of certain wavelengths of radiation, the energy of which corresponds to the energy of transition between various vibrational and rotational states of the molecule or group. The recorded trace is expressed in the form of the absorbtion intensity as a function of wave number or wavelength.

The three polymers in the form of potassium bromide discs were examined in the carbon-chlorine stretching region 800 - 550 cm^{-1}, using a Perkin-Elmer 457 Grating Infrared Spectrophotometer. The ratio of the absorbances of the bands at 640 and 690 cm^{-1} (syndiotactic and isotactic straight chain carbon-chloride stretching vibrations respectively) was used as a measure of tacticity[43,48]. The infrared spectra obtained are shown in Figure 2, the determined values of Absorbance 640/690 are given in Table 4.

Table 4

Polymer	Absorbance 640/690
Vinyl Chloride/Vinyl Acetate Copolymer	1·48
PVC-2	1·66
Montecatini -30°C polymer	1·99

The values of the absorbances shown are consistent with those published in the literature.

2:4 Thermomechanical and Thermogravimetric Analysis

2:4:1 Thermomechanical Analysis

The glass transition temperatures of the compounded materials were measured using the Du Pont 900 Thermal Analyser equipped with a Thermomechanical Analyser attachment. In this instrument the penetration of a probe into the sample is plotted against temperature as the material is heated at a linear rate.

The trace was recorded from -50°C, with a heating rate of 5°C/min and a 10g load on the probe. The glass transition temperatures found are given in Table 5.

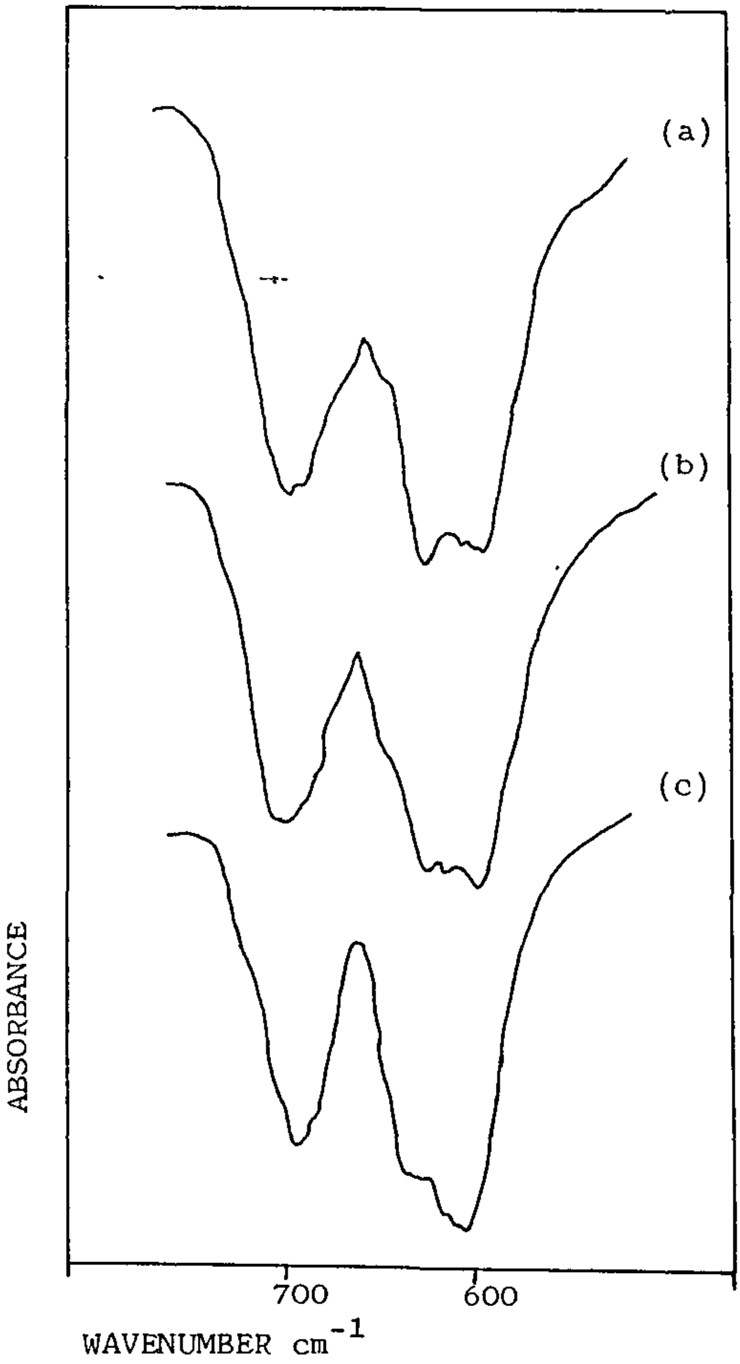


Figure 2 - Infrared Spectra of C-Cl stretching region

(a) Montecatini -30°C polymer

(b) PVC-2

(c) Vinyl Chloride/Vinyl Acetate copolymer

Table 5

Polymer	Tg°C
Vinyl Chloride/Vinyl Acetate Copolymer	75
PVC-2	82
Montecatini -30°C polymer	91

2:4:2 Thermogravimetric Analysis

As the polymers were to be subjected to a variety of thermal treatments then the thermal stability of the compounded material was examined using thermogravimetric analysis (TGA).

In this technique a preweighed sample is placed in a crucible holder suspended from a quartz arm; the whole assembly being surrounded by a furnace. A coil is actuated by the change in the sample weight providing a signal which is amplified and used as the input for the Y-axis of the recorder. The X-axis is used to indicate temperature by means of a thermocouple placed near the sample, or in isothermal experiments the X-axis displays time.

The instrument used was the Du Pont 900 Thermal Analyser in conjunction with the 950 TGA module. The apparatus was operated in a dynamic mode to study degradation as a function of temperature. Also under isothermal conditions to furnish information on time dependant degradation phenomena. The apparatus was operated under the following conditions.

Table 6

Mode	Sample Size mg	Heating Rate °C/min	Temp. Range °C	Atmosphere	Time h
Dynamic	5	10	Ambient-450	N_2	-
Isothermal	5	-	160 - 220	N_2	0 - 6

In the dynamic mode the thermogram consisted of two plateau regions. Only a slight weight loss occurred in all cases when the temperature had reached 220°C. At approximately 250°C a steep drop in the thermogram occurred which was assigned to quantitative loss of HCl from the vinyl chloride repeat unit. A further large weight loss commencing at approximately 400°C was considered to be due to the polymer being reduced to carbon.

With the isothermal experiments with temperatures up to 180°C for the low temperature polymer and PVC-2, and 160°C for the vinyl chloride/vinyl acetate copolymer the weight loss after six hours was found to be less than one per cent. Using temperatures higher than these much higher weight losses were observed.

To compliment the above isothermal measurements of thermal stability the samples studied were retained for visual inspection of colour change and microscopic examination. After six hours at 180°C for PVC-2 and the low temperature polymer, and 160°C for the copolymer, a brown colouration had resulted. On microscopic examination of sectional samples, voids could be seen, particularly in the case of the copolymer. The observations were considered to be due to minor amounts of degradation.

CHAPTER III - Examination of Structural Ordering

The experimental procedures and results obtained on the assessment of structural ordering are given in this Chapter. The polymers were subjected to heat treatments above and below their glass transition temperatures for a variety of temperatures and times. Differential thermal analysis, density measurement, X-ray diffraction and solvent sorption techniques were used to examine resultant changes. From the above analyses it was anticipated that the effects of changes which might occur in the time scale of processing could be observed.

3:1 Thermal Treatments

In order to provide a uniform thermal history the three compounded polymers (as in Chapter II) were subjected to a pretreatment prior to being annealed; the temperatures and times used are given in Table 7.

Table 7

Polymer	Temperature °C	Time min.
Vinyl Chloride/Vinyl Acetate copolymer	175	3
PVC-2	200	3
Montecatini -30°C polymer	220	3

These conditions were chosen following studies of the thermal stability of the materials and the literature review of the melting of PVC. The intention was to use the highest temperature possible in an attempt to remove existing order whilst keeping degradation to a minimum. The pretreatments were carried out under an atmosphere of oxygen free nitrogen and after the three minute period the polymers were immediately quenched into an ice/water mixture. The quenched samples were then annealed under nitrogen at temperatures between 40 and 160°C for times varying from 0·5 to 5 hours and again quenched into ice/water. With the vinyl chloride/vinyl acetate copolymer, voids occurred in the sample at temperatures in excess of 130°C. Consequently, this was the highest annealing temperature that was employed.

The materials to be annealed were wrapped in aluminium foil to prevent them sticking together and to maintain their shape. They were then packed into a glass tube which was immersed in a thermostatted bath controlled to ± 0·15°C. Some samples were stored at ambient temperature for a long period of time. The heat treated samples were either examined immediately or stored at a temperature of approximately -50°C, subsequent analysis showed that no changes occurred during this storage period.

3:2 Differential Thermal Analysis

Differential thermal analysis (DTA) measures the heat changes occurring as a function of temperature. The sample to be examined is heated at a linear rate alongside an inert reference, the temperature difference between the two is monitored by thermocouples situated underneath the sample and reference.

The instrument used was the Du Pont 900 Thermal Analyser fitted with a DSC cell. (The technique used was DTA the above description of the cell is according to Du Pont nomenclature). The thermograms were recorded from -40°C to 200°C using a heating rate of 30°C/minute and a sample weight of 10 ± 1 mg. An empty aluminium sample pan was used as the inert reference.

The area of the peaks observed were found by weighing tracings on a balance capable of measuring to four decimal places. To obtain values of these areas in energy units the cell was calibrated using Indium, melting point 157°C, heat of fusion ΔH_f 28·4 kJ/kg. A check on the reproducibility of this method was performed by carrying out ten determinations on a heat treated sample and the standard deviation was found to be 5% of the mean.

The thermograms obtained for a quenched sample and those annealed for 5 hours are shown in Figure 3 for PVC-2. In the case of the quenched sample the thermogram consists of a baseline shift at approximately 84°C which is assigned to the glass transition. This is followed by an exothermic peak at 107°C which is in turn followed by a broad endothermic peak starting at 120°C and extending to 200°C. Note that all the transitions merge into one another. Also the glass transition temperature is higher than that in Chapter II, this is considered a consequence of the relatively high heating rate used.

The thermogram obtained for a quenched sample of the Montecatini -30°C polymer was similar to that of PVC-2, however, the exothermic change was smaller and the endotherm extends to 220°C. Values obtained for the exo and endothermic changes are given in Table 8.

With the heat treated samples sharper endothermic changes are observed and appear at approximately 20°C above the annealing temperature. The temperature at which the maximum occurs for PVC-2 and the low temperature polymer are given in Tables 9 and 10 respectively. From these Tables it is noted that the peak maxima increase with annealing time.

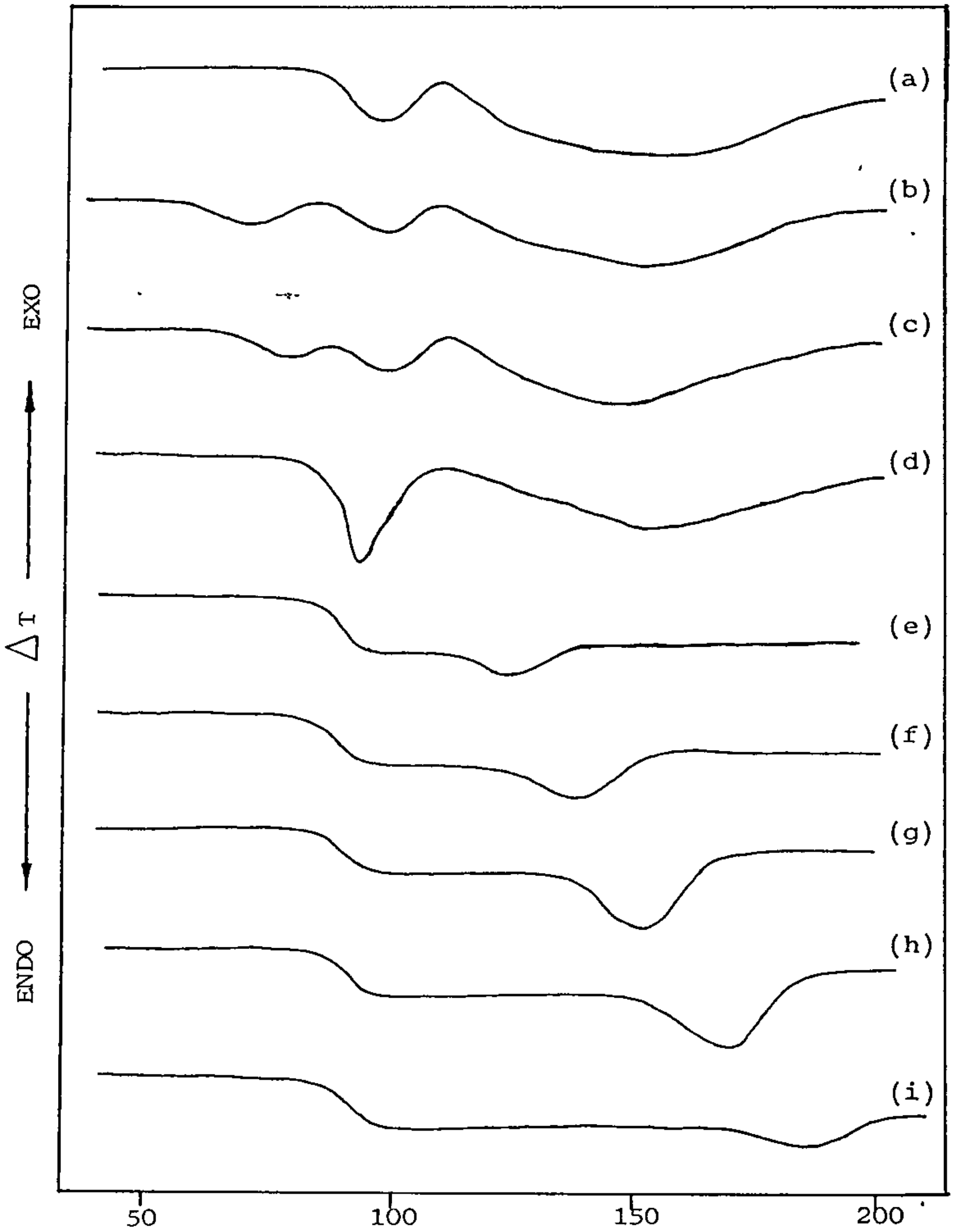


Figure 3 - DTA traces for PVC-2

(a) Quenched and annealed 5h at (b) 40°C (c) 55°C
(d) 70°C (e) 100°C (f) 115°C (g) 130°C (h) 145°C
(i) 160°C

Table 8 - Enthalpy Change values for quenched polymers

Polymer	Exothermic kJ/kg	Endothermic kJ/kg
PVC-2	1·9	4·8
Montecatini -30°C polymer	1·0	7·0

Table 9 - Effect of annealing on Endothermic peak temperature for PVC-2

Annealing Time h	Annealing Temp. °C	40	55	70	100	115	130	145	160
0·5	Peak Temp°C	-	-	-	121	134	148	162	176
1·0	"	-	-	-	121	135	148	163	177
1·5	"	-	-	-	122	137	150	164	179
3·0	"	-	-	-	123	138	151	164	180
5·0	"	72	83	94	125	139	152	166	180

Table 10 - Effect of annealing on Endothermic peak temperature for Montecatini -30°C polymer

Annealing Time h	Annealing Temp. °C	40	55	70	100	115	130	145	160
0·5	Peak Temp°C	-	-	-	117	135	148	164	178
1·0	"	-	-	-	118	136	149	165	179
1·5	"	-	-	-	120	137	150	166	181
3·0	"	-	-	-	121	138	152	167	181
5·0	"	71	85	96	122	139	153	168	182

Samples annealed between 40 - 70°C, that is below Tg, the exotherm which occurs in the quenched sample is still present. For annealing temperatures of 55° and 70°C the exotherm occurs very close to the Tg, and hence makes accurate measurement of the enthalpy changes difficult. In these instances, the areas were arrived at by superimposing thermograms of the quenched samples over those of annealed samples. For materials heat treated between 100 and 160°C the exotherm is absent.

In Figures 4 and 5 ΔH, the endothermic enthalpy change occurring is plotted against annealing temperature for PVC-2 and the Montecatini -30°C polymer. These Figures show the effect of temperature of heat treatment on the magnitude of the enthalpy change. The results of samples stored at room temperature for a long period of time are given in Table 11.

The influence of annealing time on the endothermic peak is shown in Figures 6 and 7. Endothermic enthalpy changes were observed with annealed samples of the vinyl chloride/vinyl acetate copolymer. These were, however, much smaller than those in the case of the two other polymers. The values of ΔH and the temperature at which the maximum occurs are given in Table 12.

Table 11 - Enthalpy changes and DTA peak temperatures for quenched samples stored at room temperature

Polymer	Storage Time day 5	Endothermic ΔH kJ/kg	Temperature at which maximum occurs °C
PVC-2	81	0·766	69
Montecatini -30°C polymer	77	0·576	69

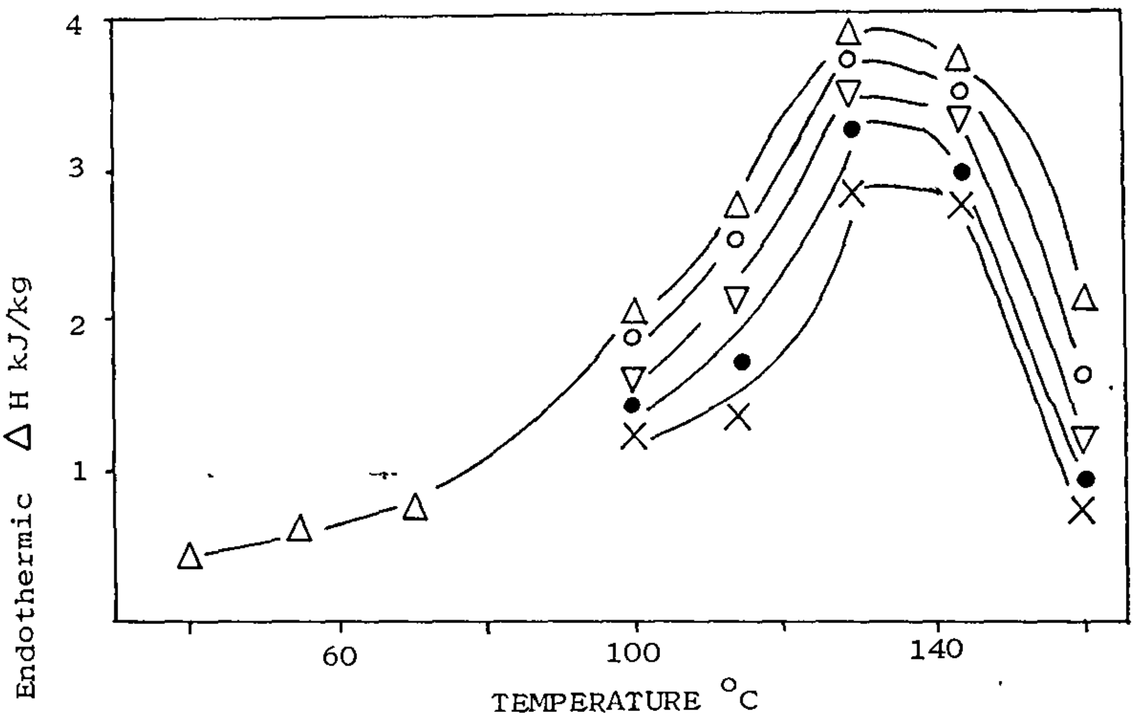


Figure 4 - PVC-2

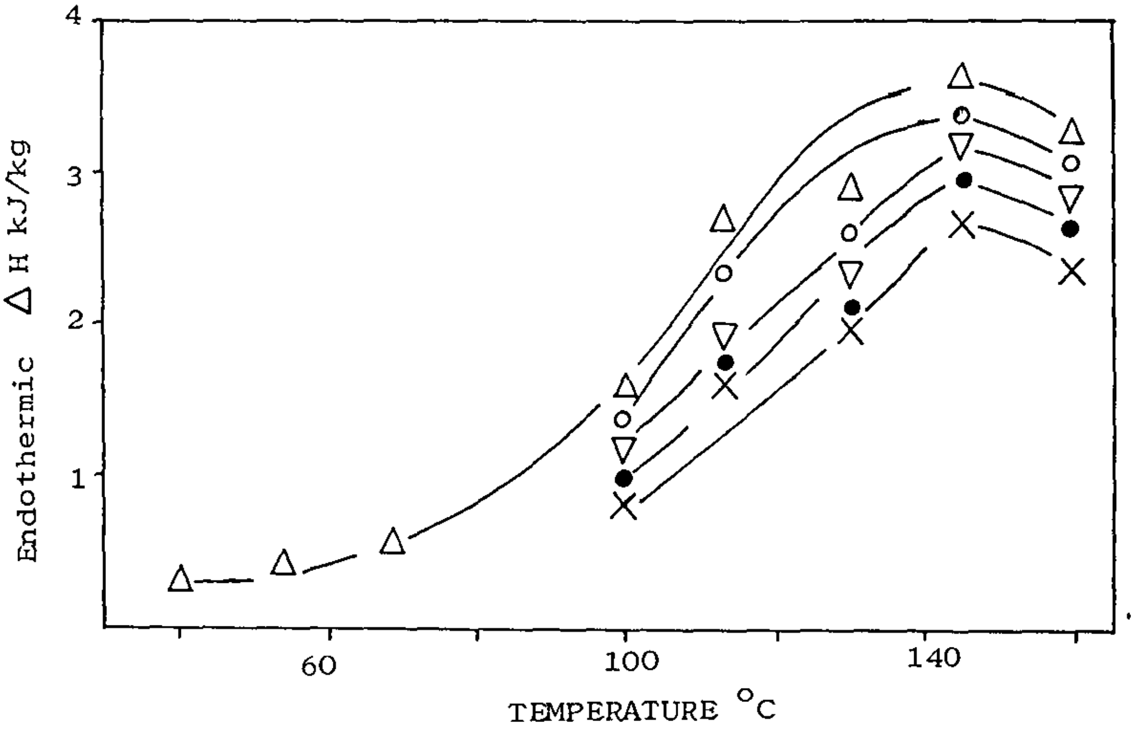


Figure 5 - Low Temperature Polymer

Enthalpy change as a function of annealing temperature.

Times × 0·5h, ● 1.0h, ▽ 1·5h, ○ 3·0h, △ 5·0h

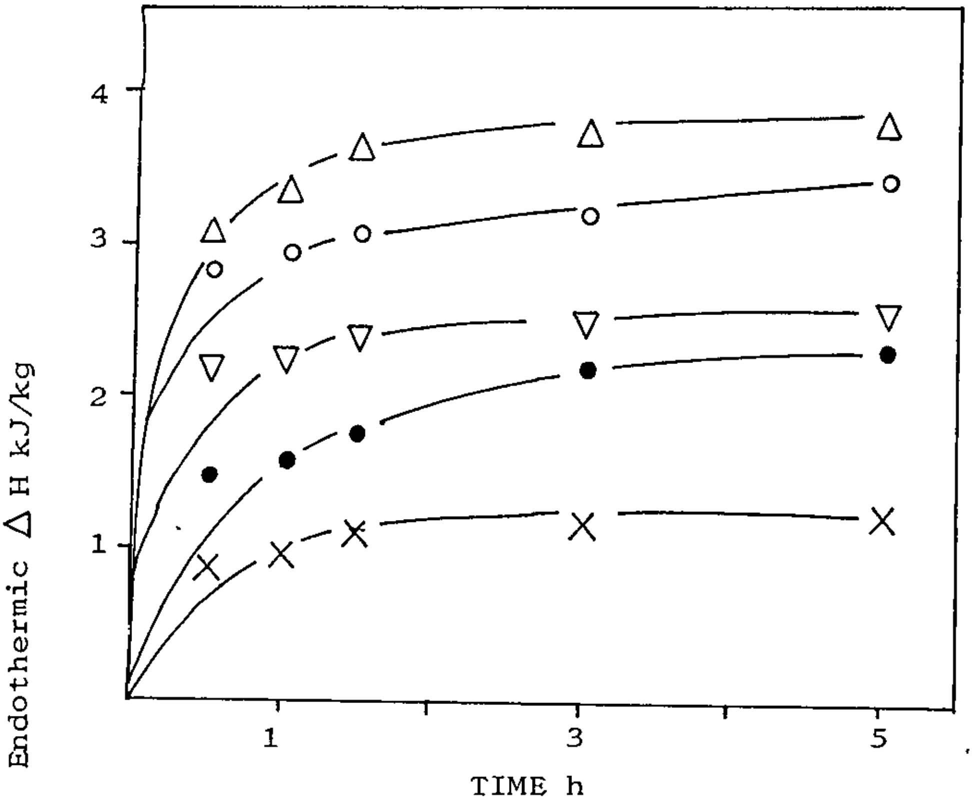


Figure 6 - Low Temperature Polymer

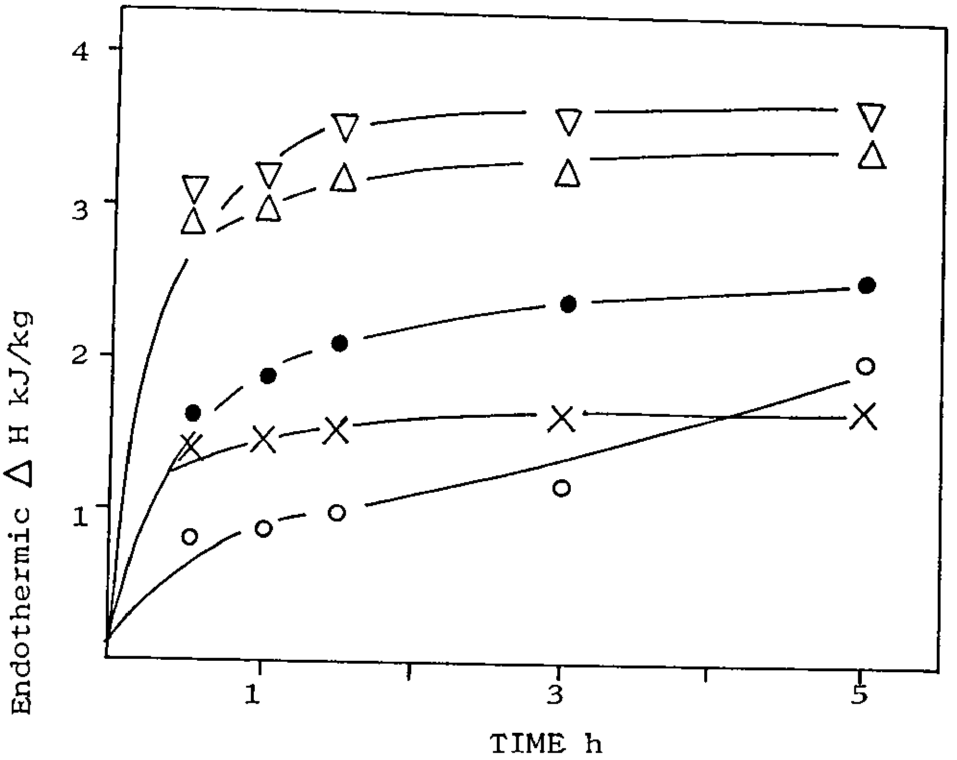


Figure 7 - PVC-2

Enthalpy change as a function of annealing time.

Temperatures ╳ 100°C, ● 115°C, ▽ 130°C,
△ 145°C, ○ 160°C.

Table 12 - Enthalpy changes and DTA peak temperatures for vinyl chloride/vinyl acetate copolymer annealed 5h

Annealing Temp. °C	Endothermic ΔH kJ/kg	Temperature at which maximum occurs °C
110	1·104	126
115	1·021	142
130	1·058	152

3:3 Density Measurements

The densities of heat treated samples were measured using a Davenport density gradient column at 23 ± 0·1°C. The column was filled with aqueous calcium nitrate and was calibrated with glass floats whose density was known to four places of decimals. Prior to being placed in the column, samples were cleaned with ethanol, dried with a tissue, then dipped in a solution of calcium nitrate, and finally gently dropped into the column. The process of dipping in calcium nitrate prevents air bubbles adhering to the sample surface.

Four determinations were carried out for each annealing condition and the mean value was recorded. The samples were given three hours after being dropped into the column to reach equilibrium; it was thought that no significant changes occurred during this period.

The polymers had been compounded with four parts per hundred of DBLS, consequently to obtain the density value of the PVC alone, a correction procedure was applied using

$$\rho_{DBLS} = 2000 \text{ kg/m}^3 \quad ^{128}$$

From these corrected values the density determined degree of crystallinity, Xd, was calculated using the formula.

$$Xd = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right) \times 100\%$$

where ρ_c = Density of 100% crystalline polymer 1530 kg/m^3 68
ρ_a = Density of 100% amorphous polymer 1373 kg/m^3 85
ρ = Density of sample

The density values obtained and the calculated crystallinities are given in Table 13. The time and temperature dependance is seen to be similar to those of the enthalpy changes, however, the density results for PVC-2 show a degree of scatter. The lower reliability of the density measurement is thought to be partly due to the very small density changes being measured. Also minor amounts of degradation could have a significant effect on density, but much less effect on enthalpy changes.

In Table 13 it is noted that the quenched polymers still have relatively high Xd values, that is the thermal pretreatment has not totally removed the crystallinity originally present. The amount of crystallinity introduced by the annealing process is given in Table 14. These values were obtained by subtracting the value of the quenched sample crystallinity Xd quench from that of Xd.

Table 13 - Effect of annealing on density ρ kg/m^3 and crystallinity Xd% for PVC homopolymer

Annealing Time h	Annealing Temp. °C	Quenched		100		115		130		145		160		40	
	Polymer	ρ	Xd	ρ	Xd	ρ	Xd	ρ	Xd	ρ	Xd	ρ	Xd	ρ	Xd
0·5	PVC-2			1397·2	16·88	1397·6	17·16	1397·4	17·02	1394·1	14·79	1392·8	13·88	1390·8	12·48
1·0	"			1398·2	17·58	1397·3	16·95	1397·6	17·16	1394·5	15·07	1392·8	13·88		
1·5	"	1389·1	11·35	1398·4	17·72	1398·3	17·65	1397·9	17·37	1394·7	15·15	1392·5	13·67		
3·0	"			1398·5	17·79	1398·3	17·65	1397·7	17·23	1395·0	15·35	1392·6	13·74	1391·4	12·90
5·0	"			1398·9	18·07	1398·1	17·51	1397·9	17·37	1395·5	15·70	1392·9	13·54	1391·7	13·11
0·5	Montecatini			1401·5	19·80	1402·7	20·63	1403·6	21·25	1403·4	21·11	1401·5	19·80	1397·2	16·88
1·0	-30°C			1401·7	19·94	1403·0	20·84	1403·0	20·84	1403·3	21·04	1401·9	20·08		
1·5	polymer	1396·2	16·26	1402·1	20·22	1403·3	21·05	1403·5	21·18	1404·1	21·60	1401·8	20·02		
3·0	"			1402·7	20·63	1403·5	21·18	1403·7	21·32	1403·6	21·25	1400·1	18·90	1397·7	17·23
5·0	"			1403·0	20·84	1403·6	21·25	1403·4	21·11	1403·8	21·39	1402·3	20·35	1397·9	17·37

Table 14 - Change of density determined crystallinity Xd-Xdquench% on annealing

Annealing Time h	Annealing Temp. °C	100	115	130	145	160
	Polymer	Xd-Xdq	Xd-Xdq	Xd-Xdq	Xd-Xdq	Xd-Xdq
0·5	PVC-2	5·53	5·81	5·67	3·44	2·53
1·0	"	6·23	5·60	5·81	3·72	2·53
1·5	"	6·37	6·30	6·02	3·80	2·32
3·0	"	6·44	6·28	5·88	4·00	2·39
5·0	"	6·72	6·16	6·02	4·35	2·19
0·5	Montecatini	3·54	4·37	4·99	4·85	3·54
1·0	-30°C	3·68	4·58	4·58	4·78	4·82
1·5	polymer	3·96	4·79	4·92	5·34	3·76
3·0	"	4·37	4·92	5·06	4·99	2·64
5·0	"	4·58	4·99	4·85	5·13	4·09

3:4 X-ray Diffraction

3:4:1 Introduction

If a beam of X-rays is incident upon a crystal, the radiation will be scattered by the extra nuclear electrons of the atomic array; in certain directions the scattered rays will reinforce to produce a diffracted beam. The condition for reinforcement is the total path difference for rays scattered by successive units separated by lattice translations is equal to a whole number of wavelengths of the radiation considered. This condition is expressed in the Bragg equation.

$$n\lambda = 2d \sin\theta$$

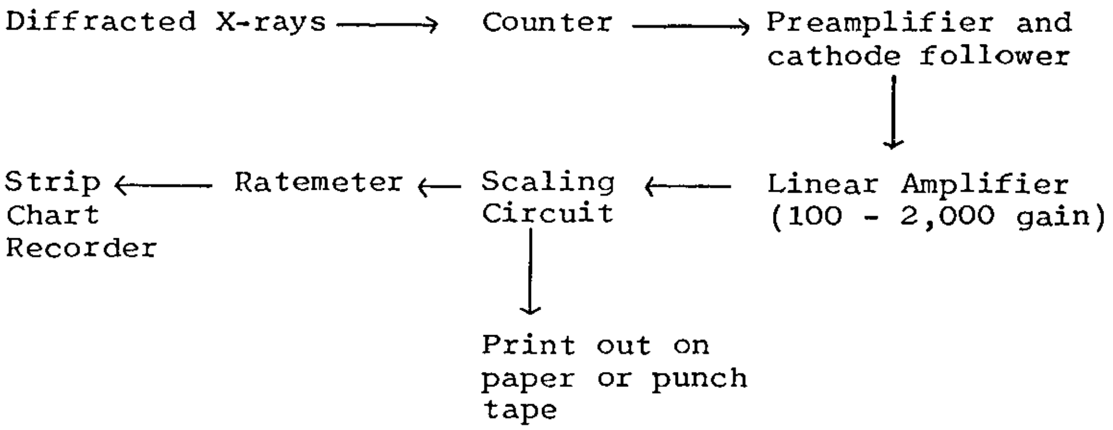
n = An integer
d = Lattice translation
λ = Wavelength of radiation
θ = Angle of incident radiation

Observation of the X-ray pattern of PVC is difficult owing to the very low diffraction intensity. The reason for the low observed pattern is due to a number of contributing factors. Firstly, as outlined in the literature review, the crystallinity in PVC is derived from the syndiotactic portions of the polymer chains, the amounts of these syndiotactic sequences, therefore, imposes a limitation on the diffraction intensity. From the above it may also be appreciated that the isotactic and atactic fractions will contribute to the amorphous background. Secondly, there is a lack of ordering within the syndiotactic crystal lattice in the c axis. This causes a decrease in intensity due to a lower number of reflection planes being available. Thirdly, there may also be some incomplete ordering in the a and b axes, which will add to the amorphous background. Finally, the crystallites present in PVC are very small, which will result in an additional contribution to line broadening.

A consequence of the above considerations is that investigation of crystallinity in PVC using X-rays requires special experimental methods.

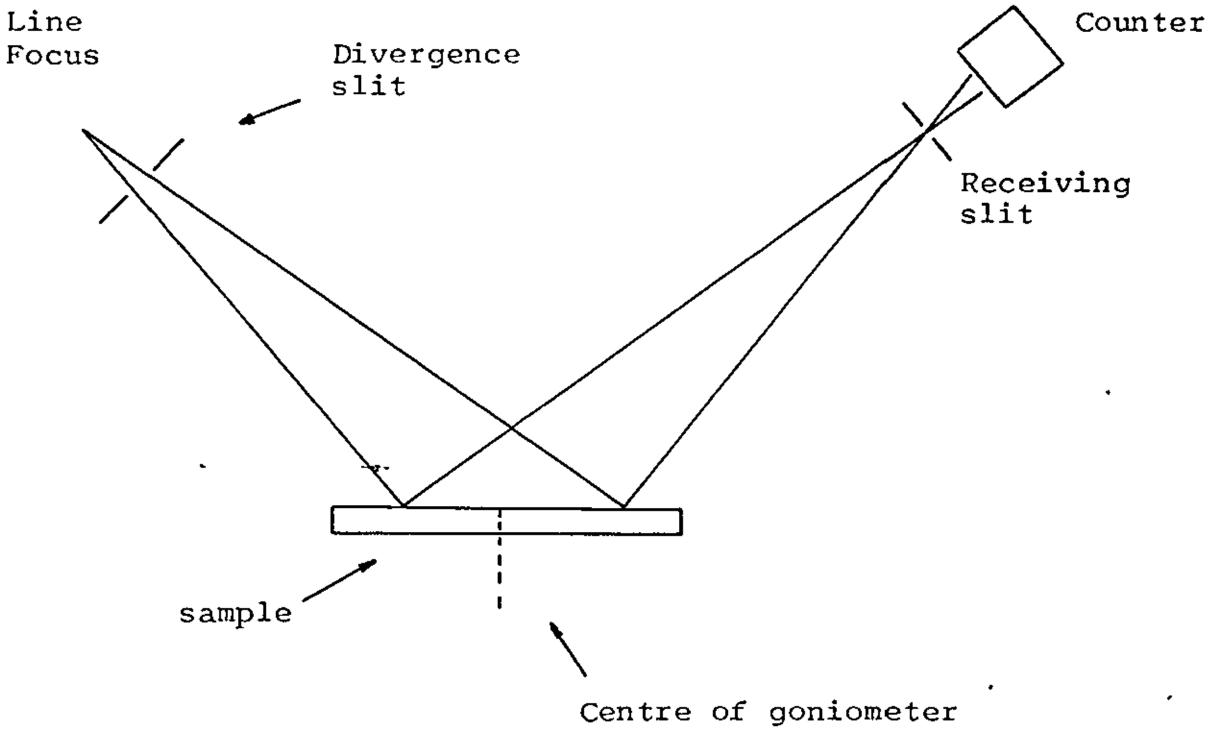
3:4:2 Experimental Procedure

The X-ray diffraction measurements were performed using the Philips wide range goniometer PW 1050/25 in an air atmosphere. The instrument is fitted with shields around the X-ray tube and goniometer to protect the user from scattered radiation. A schematic representation of the components of a modern diffractometer are shown below.



The intensity of the diffracted radiation is monitored by a counter, which scans the sample at various scattering angles. The signal from the scaler is usually fed to a pulse-integrating circuit, this activates a counter-rate meter. The intensity of the scattered radiation can be displayed as a digital print-out, or more simply the output current from the pulse-integrating circuit is fed to a potentiometer strip-chart recorder. The recorder is driven at a constant speed during the scan of the prescribed angular range, thus a plot of intensity against scattering angle 2θ is obtained.

Samples of heat treated PVC, 4 x 1·5 cms, held in an aluminium holder were examined in the symmetrical mode (see below).



The X-ray source was obtained from a copper target anode and the K β radiation was removed by means of a nickel filter. The detector used was a Geiger-Müller tube fixed to the goniometer carriage and set at a distance of 170 mm from the goniometer centre. The carriage is driven by a synchronous motor across the desired angular range, the speed of scanning being controlled by means of a gear system.

A strip chart recorder was used to obtain the trace of intensity against scattering angle. A second pen on the recorder marked the chart at $\frac{1}{2}^{\circ}$ 2θ intervals, thus enabling calibration of the angular position.

Detection of the scattered radiation by a counter technique was chosen rather than a photographic method. Briefly, the advantages are that shorter exposure times are required, in general, with counter techniques. Secondly, intensities from photographic detection cannot be determined with highest quantitative accuracy due to difficulties that affect conversion of photographic-film blackening to intensity.

As outlined in the introduction to this section the X-ray diffraction pattern of PVC is of low intensity and, therefore, necessitates special experimental conditions. To increase the diffraction response the instrument is operated at a high energy output. For the experiments the voltage and current settings were the maximum for the X-ray tube used, these settings were 40 kV and 20 mA respectively.

The detected energy of the diffracted radiation can also be increased by changing to a larger receiving slit. The receiving slit defines the width of the reflected beam that can be detected by the counter. The resolution decreases slightly, however, the peak intensity increases markedly when the slit width is increased.

Earlier experiments using four degree divergence and receiving slits resulted in an extremely intense signal being detected at scattering angles less than 12 2θ . This was attributed to scattering of radiation from other parts of the goniometer, due to the large "flood" area of the incident beam. On changing to two degree divergence and receiving slits, satisfactory X-ray traces were obtained.

The operating conditions of the diffractometer are summarised in Table 15.

Table 15

X-ray Tube	40 kV 20 mA
Divergence Slit	2^o
Receiving Slit	2^o
Time Constant	8 secs.
Scan Speed	$\frac{1}{2}^o$/min.
Angular Range	10 - 35^o 2θ

3:4:3 Diffractometer Trace Interpretation

As stated in the literature review section, several authors have published data on the degree of crystallinity of PVC as determined by X-rays. Essentially, all the techniques used are the same, and are based on resolving the experimental diffraction trace into areas of scattering due to the crystalline and amorphous fractions of polymer. The ratio of the crystalline area to that of the total is then used as a measure of crystallinity.

In the present work the method of Rayner and Small[71] was used to resolve the diffraction traces into their crystalline and amorphous components. In the method described by the above authors, a sample of PVC is obtained by quenching the material into cold water from a high temperature. An X-ray diffraction trace of this sample is then obtained, and is considered to be the pattern for amorphous PVC. A series of amorphous diffraction patterns are presented in reference 71. These curves were redrawn to the same horizontal scale as the diffraction traces performed in this work to provide a series of amorphous templates.

D'Amato and Strella[72] have investigated several ways of obtaining the diffraction pattern for amorphous PVC. One of the procedures described was the same as that of Rayner and Small, and produced an equivalent diffraction pattern. It is, therefore, considered that the amorphous templates prepared from data supplied by Rayner and Small can be used with some degree of confidence.

The diffraction patterns obtained from the chart recorder contained a high degree of noise. An attempt was made to reduce this by employing a relatively large value of the time constant. The patterns were then "smoothed out" by drawing a line through the mid-point of the diffraction pen tracing.

The next stage in the interpretation of the diffraction trace is to draw a base line joining the points 10 and 35° 2θ . This straight line indicates the background level of intensity and the area below this line is ignored in the subsequent calculations.

An amorphous template is then chosen such that the trough in the curve just touches that of the sample trace at 21° 2θ (see Figure 8). At this fitting point it is assumed there is no contribution to the crystalline diffraction. The experimental X-ray diffraction trace is now divided into its amorphous, A_a, and crystalline, A_x, component areas. Typical traces of heat treated samples are reproduced in Figure 8.

The amorphous and crystalline areas were measured using a polar planimeter and an X-ray order factor calculated according to the formula shown below.

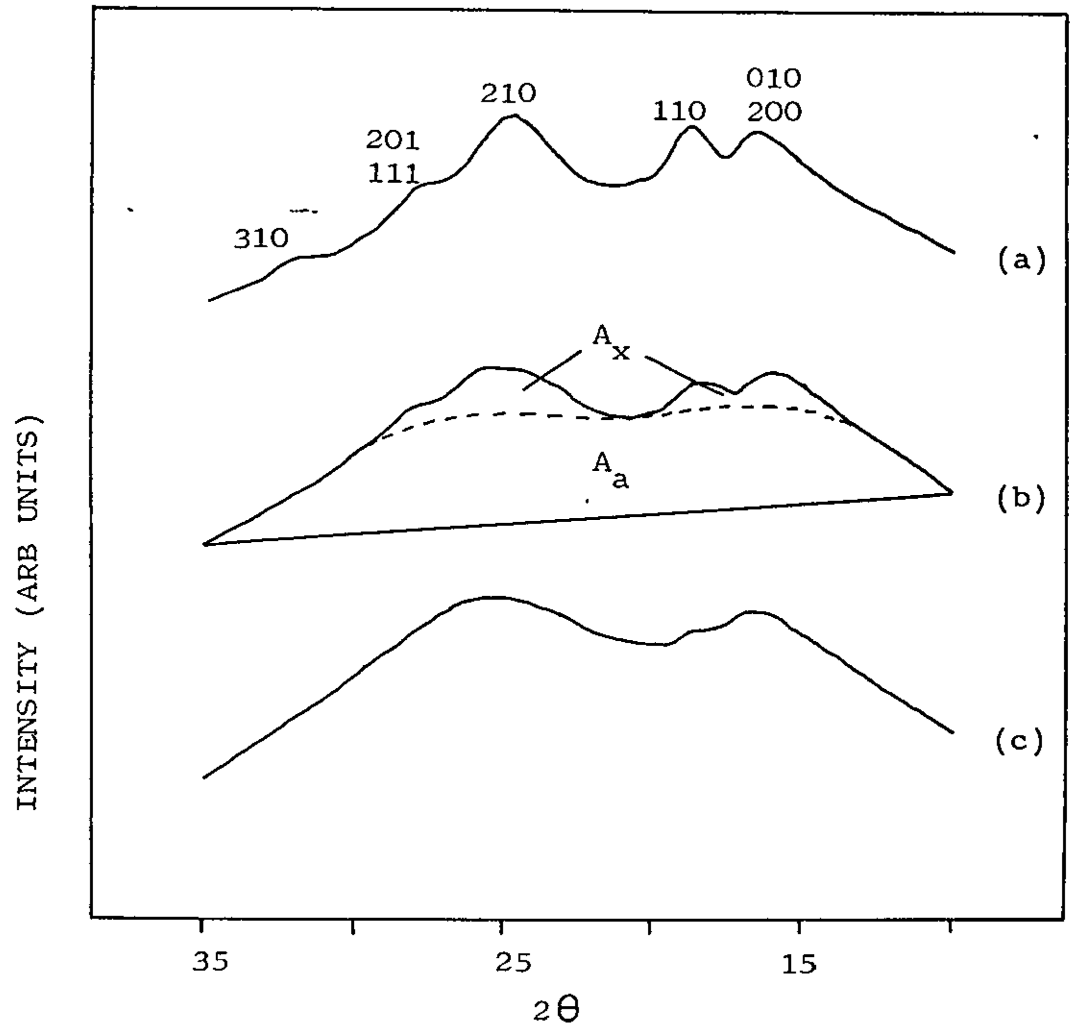


Figure 8 - X-ray Diffraction Traces

(a) Low Temperature Polymer 5h 100°C

(b) PVC-2 5h 100°C

(c) PVC-2 5h 40°C

Lattice reflection assignment after Garbuglio et al[43].

$$\text{Order Factor} \quad X_{XR} = \frac{A_x}{A_x + A_a} \times 100\%$$

where A_x = Area of crystalline portion

A_a = Area of amorphous portion

In the above expression no corrections were made for variations in observed intensity with change in scattering angle. In light of the resolution obtained with the experimental traces, it was considered that such corrections were not justified. The calculated quotient of the crystalline to the total diffracted area is, therefore, not strictly the absolute degree of crystallinity, and hence the term order factor is used. This fact in no way invalidates the data, and X-ray determined order factor can be used satisfactorily to rank samples of varying crystallinity.

During the interpretation of the experimental data it was found that some samples gave rise to shallow traces of the detected intensity. (The term shallow refers to the intensity difference between the base line and the point of maximum intensity.) This has the result that no unique template can be used to fit all the experimentally determined traces, and this may be a possible source of error. The variation in intensity may arise from the surface finish of the samples. Following heat treatment with some samples the previously smooth compression moulded surface became slightly roughened. The diffracted radiation may then be scattered at random angles from such an irregular surface. This will thus result in an overall reduction in magnitude of the signal detected by the counter.

The calculated values of order factor $X_{XR}\%$ for polymers annealed for 0·5 and 5·0 hours are given in Table 16. As anticipated, the copolymer has the lowest value of order factor, a sample annealed for 5·0 hours had a value of 2%. The low temperature polymer gave the highest value.

Annealing the polymers in the range 40 - 70°C did not significantly alter the order factor, but heat treatment at temperatures greater than 100°C, (i.e. above Tg), did result in increased values. The size of the increases on annealing are shown in Table 17; these were obtained by subtracting X_{XR} from $X_{XRquench}$. The increases obtained are approximately a factor of 1·6 for PVC-2 and 1·2 for the low temperature polymer. There was no appreciable increase of order factor on increasing the annealing time from 0·5 to 5·0 hours, nor between those samples annealed at temperatures above the glass transition.

An estimation of the mean crystallite size perpendicular to the hkl reflection planes can be obtained using the equation shown below[129].

$$D_{hkl} = \frac{0{\cdot}9\lambda}{B_{\frac{1}{2}}\ \cos\theta}$$

where λ = Wavelength of X-radiation

$B_{\frac{1}{2}}$ = Breadth at half maximum intensity

θ = Bragg Angle

Contribution to X-ray peak broadening can result from changes in crystallite size and from lattice imperfections. Separation of broadening into these components is possible, and the principles have been discussed in depth in the literature[165]. The procedure, however, requires that at least two well-resolved orders of diffraction are present in the observed diffraction pattern. In the diffraction pattern of PVC this requirement is not always satisfied. Consequently, in applying the above equation to analyse the X-ray traces only a crystallite size effect is considered. In light of this conclusion values of crystallite size which are calculated from the equation are approximate.

In Table 18 the values of the mean crystallite size calculated from the 110 and 210 reflections are given. From this it can be seen that the size of the crystallites remains relatively constant for the various heat treatments, and the value for the low temperature polymer is as expected, slightly higher than that of the suspension polymer.

3:5 Solvent Sorption

The solvent sorption behaviour of the polymers has been investigated as a function of annealing temperature and time. Heat treated strips, 40 x 13 x 0·5 mm, were used for the observations. The weight and average thickness of the sample was recorded and the sample was immersed in toluene for a selected time in a stoppered tube at 30 ± 0·1°C. After the selected time had elapsed the sample was removed, dabbed lightly with a tissue and its weight recorded over a period of approximately five minutes. By extrapolation to zero time of the weight against time plot the weight gain of the sample on removal from the solvent was determined.

In Figures 9 - 11 the percentage weight gain for quenched samples and those annealed for eight hours at 70 and 110°C is plotted against $t^{\frac{1}{2}}/l$, where t is the immersion time and l is the average sample thickness. The expression $t^{\frac{1}{2}}/l$ is used to eliminate effects due to variations in sample

Table 16 - Effect of annealing on order factor for vinyl chloride polymers

Annealing Temp °C	40		55		70		100		115		130		145		160		Quenched
Annealing Time h	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	
PVC-2	8·5	8·4	9·3	9·8	7·8	7·8	15·0	14·4	16·8	11·9	14·4	14·6	14·1	14·3	11·6	11·9	8·7
Montecatini -30°C polymer	20·7	19·5	23·7	15·0	19·6	21·2	23·2	25·2	23·7	24·6	26·9	20·8	23·7	24·0	27·5	23·1	20·1
Vinyl Chloride/ Vinyl Acetate Copolymer	-		-		-		-		-			2·0	-		-		-

Table 17 - Change of Order Factor $X_{XR} - X_{XRq}$% on annealing

Annealing Time h	Annealing Temp °C	100	115	130	145	160
	Polymer	$X_{XR}-X_{XRq}$	$X_{XR}-X_{XRq}$	$X_{XR}-X_{XRq}$	$X_{XR}-X_{XRq}$	$X_{XR}-X_{XRq}$
0·5	PVC-2	6·3	8·1	5·7	5·4	2·9
5·0	"	5·7	3·2	5·9	5·6	3·2
0·5	Montecatini -30°C	3·1	3·6	6·8	3·6	7·4
5·0	polymer	5·1	4·5	0·7	3·9	3·0

Table 18 - Mean Crystallite Size of PVC-2 and Montecatini -30°C polymer

	Annealing Temp °C	40		55		70		100		115		130		145		160	
Crystallite size nm		D_{110}	D_{210}	D_{110}	D_{210}	D_{110}	D_{210}	D_{110}	D_{210}	D_{110}	D_{210}	D_{110}	D_{210}	D_{110}	D_{210}	D_{110}	D_{210}
Annealing Time h	PVC-2																
0·5		6·2	5·9	6·7	6·6	5·4	5·0	5·8	4·5	4·6	4·2	5·0	4·0	5·4	5·0	6·2	5·4
5·0		6·1	5·8	6·2	6·1	6·9	5·4	6·9	5·6	5·8	4·0	6·7	4·0	4·5	4·0	6·7	5·8
	Montecatini -30°C polymer																
0·5		5·4	4·0	7·9	6·6	5·4	7·9	6·2	4·7	7·9	6·1	7·3	6·1	5·0	4·2	7·9	4·5
5·0		5·8	5·8	6·2	6·6	7·9	7·9	7·9	7·9	7·3	7·9	7·9	7·2	7·3	4·7	6·2	5·6

thickness[130]. From these plots the influence of the heat treatment temperature is shown. The sorption behaviour for the vinyl chloride/vinyl acetate copolymer appears to be linear with time. Also the percentage weight gain for this polymer was over 90% after one hour's immersion, compared with less than 1% for PVC-2 and the low temperature polymer over the same time.

For PVC-2 the sorption curves all reached an equilibrium value between 50 - 60%. The rates of solvent uptake for this polymer also varied according to the thermal history of the sample. With the low temperature polymer the sorption curves again differed with the type of heat treatment and were of much lower rates than the commercial polymer.

A comparison of the sorption behaviour of all the polymers annealed for eight hours at 110°C is given in Figure 12. This demonstrates clearly the effect of changing polymer type on the sorption characteristics. The effect of the time of heat treatment is given in Figures 13 and 14 for PVC-2 and the -30°C polymer respectively. In these Figures the weight gain is plotted against annealing time at 110°C for samples immersed for a constant time; the times were four hours for PVC-2 and seventy two hours for the low temperature polymer. These curves give information on the rate of the ordering process in PVC.

To document fully the results obtained on the assessment of the ordering of PVC and to provide a reference source for subsequent research work, numerical values of data presented graphically in this Chapter are given in Appendix 1.

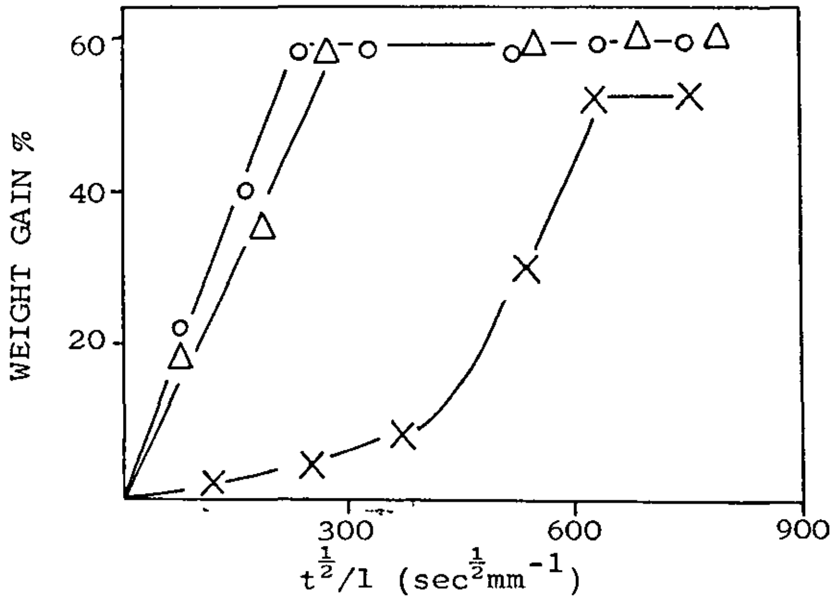


Figure 9 - PVC-2

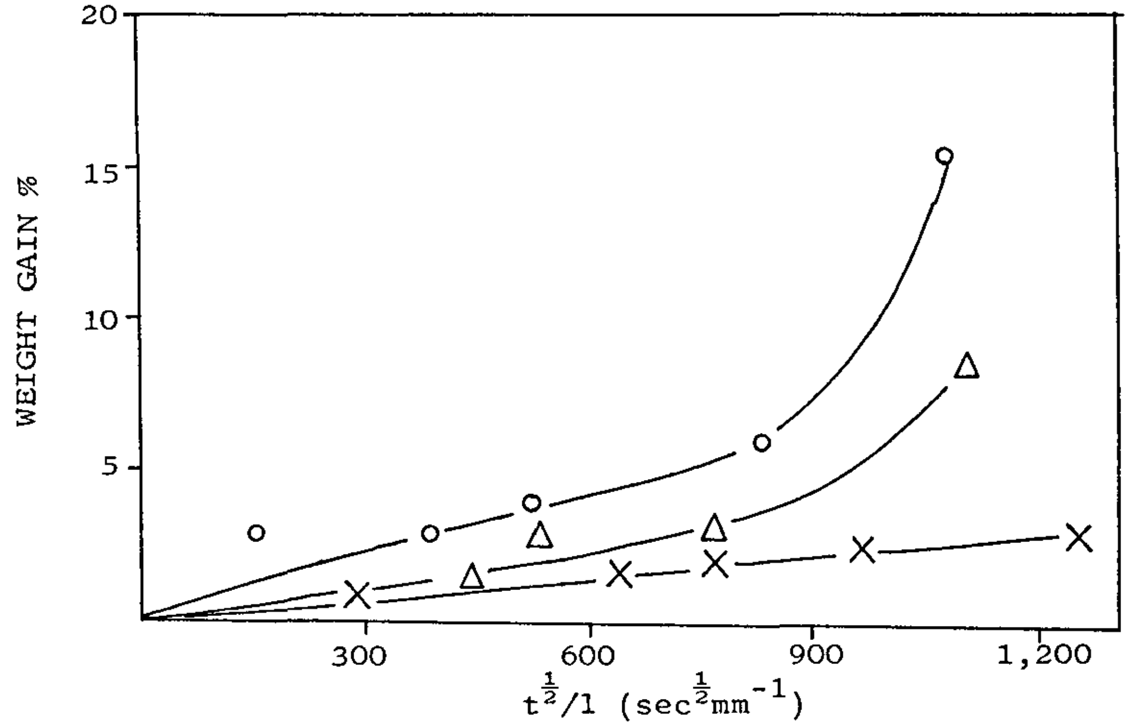


Figure 10 - Low temperature polymer

Sorption Curves for heat treated polymers.

o Quenched

Δ Quenched and annealed 8h 70°C

X Quenched and annealed 8h 110°C

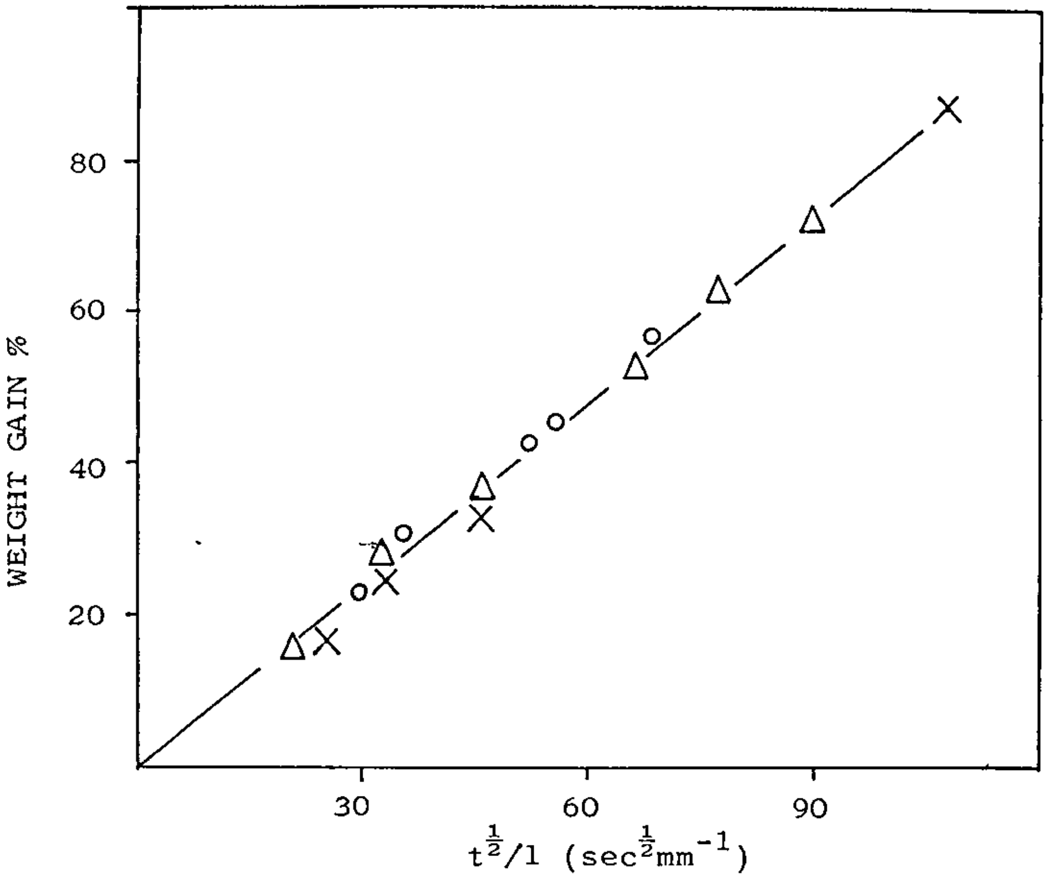


Figure 11 - Sorption Curve for heat treated Vinyl Chloride/ Vinyl Acetate Copolymer (symbols as with Figures 9&10)

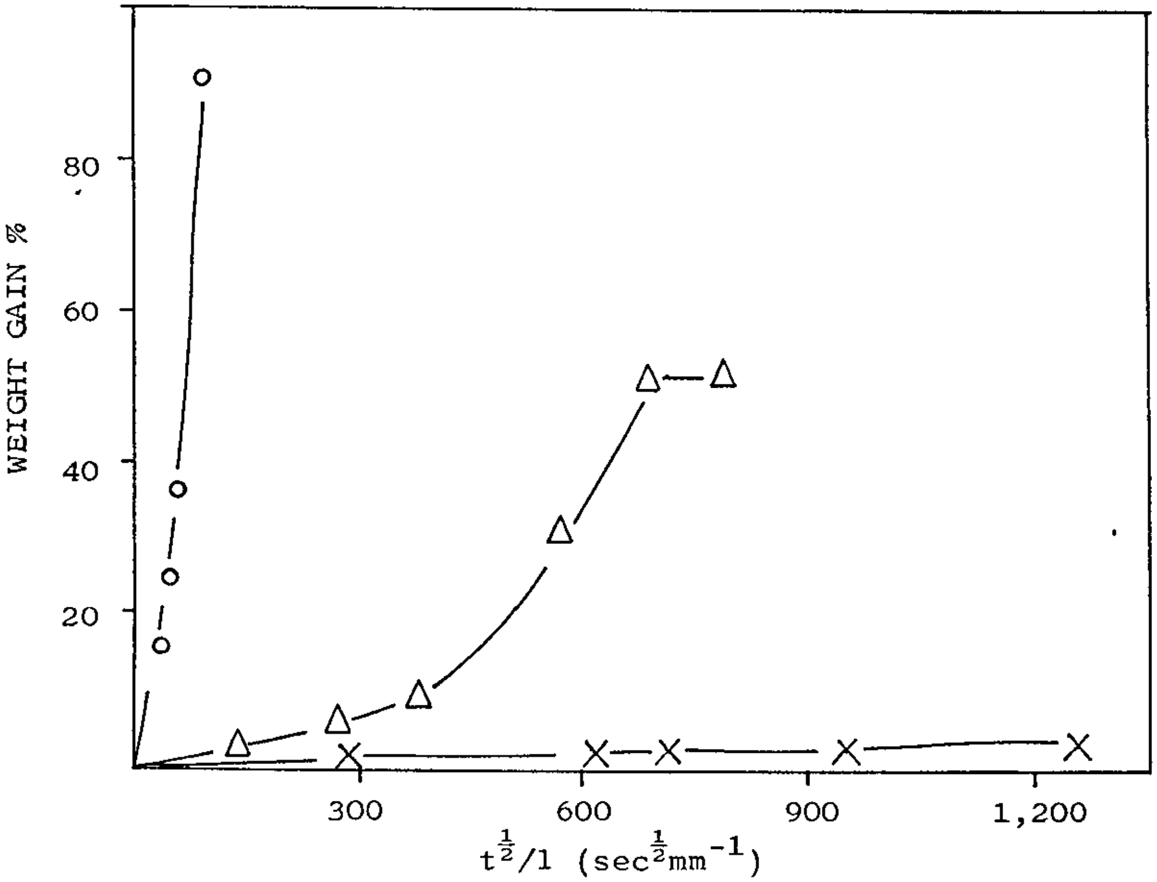


Figure 12 - Sorption Curves for all polymers annealed 8h 110°C.

○ Vinyl Chloride/Vinyl Acetate Copolymer, Δ PVC-2 and

× Low temperature polymer.

Figure 13 - PVC-2

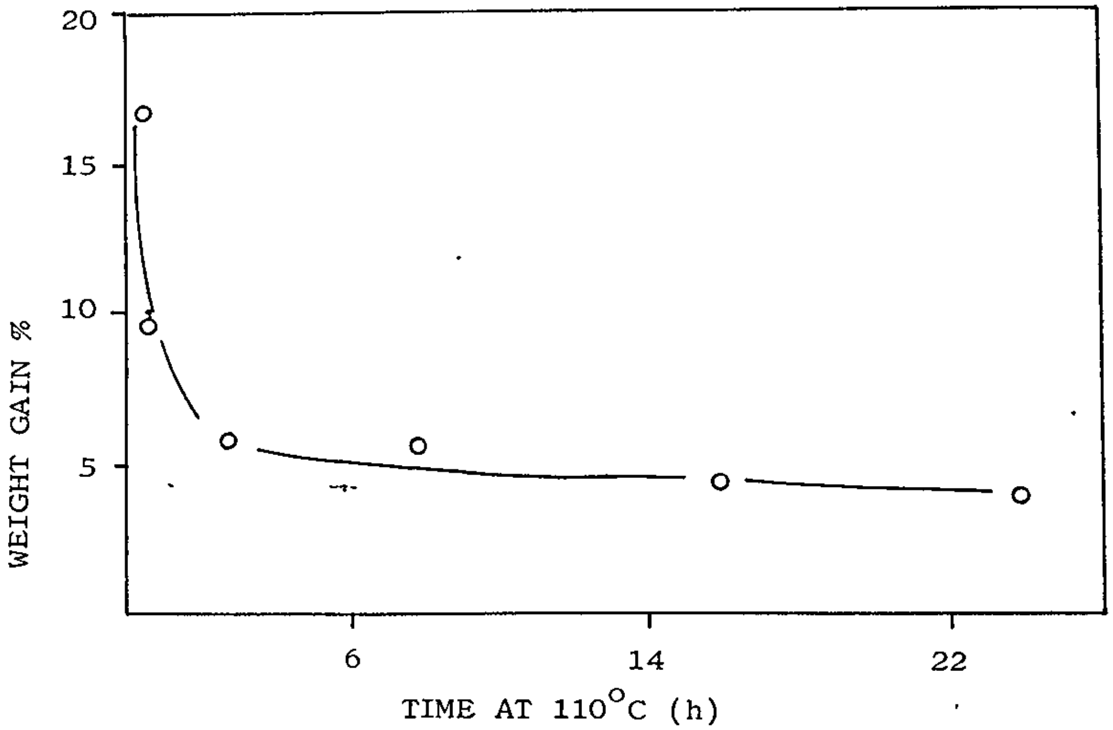
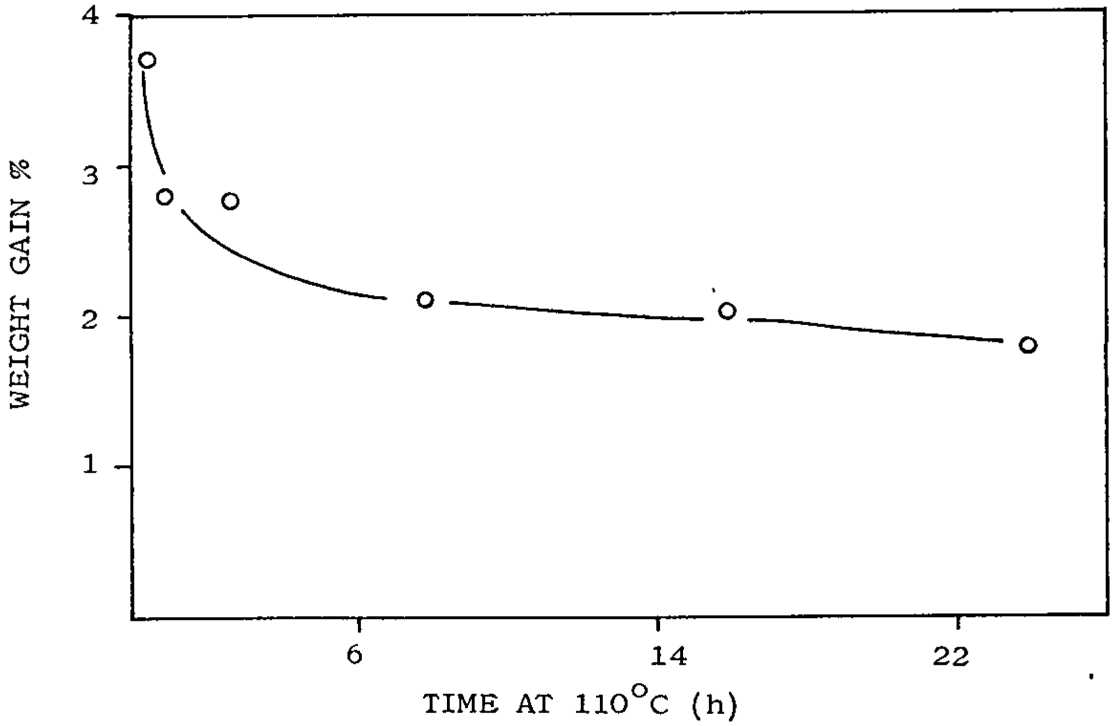


Figure 14 - Low Temperature Polymer



Sorption behaviour two homopolymers as a function of treatment time at 110°C for a constant immersion time.

Immersion time	PVC-2	4h
	Low temperature polymer	72h

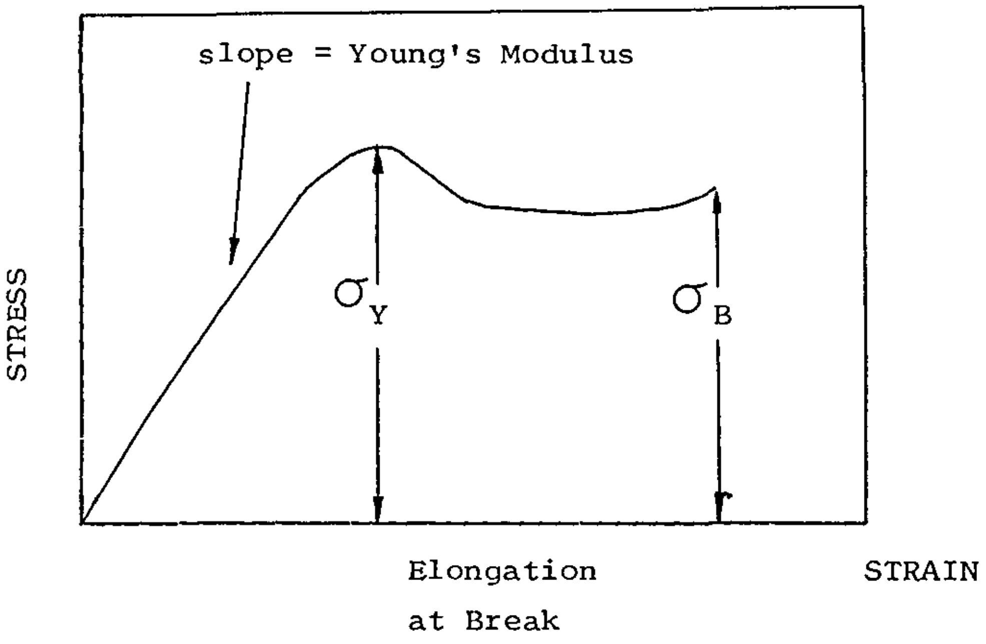
CHAPTER IV - Tensile Properties

It is known that the physical properties of polymers depend on their composition and thermal history. Consequently, in this Chapter, a report of mechanical property differences of vinyl chloride polymers as a function of their polymerization and heat history is presented.

4:1 Introduction

Considerable information can be obtained about polymers by studying the plot obtained from a load-deformation test. The results of such a test are usually expressed in terms of a stress-strain diagram. The nature of the polymer, the rate of strain and the temperature of the test can greatly influence the form of the stress-strain diagram, however, plastics in general conform to a curve of the type shown schematically in Figure 15.

Figure 15



where σ_Y = Yield Stress

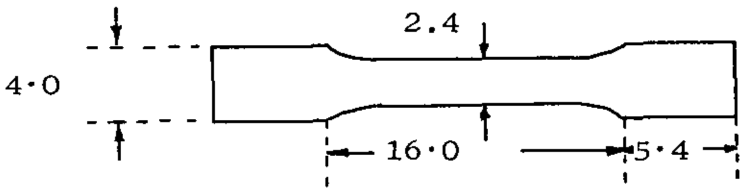
σ_B = Tensile Strength

The values of modulus, tensile strength, yield stress and elongation at break can be used to characterize the material under test.

4:2 Experimental

The tensile behaviour of the three polymers has been investigated using an Instron Universal Testing Machine at 23°C. Owing to the limited quantity available of the low temperature polymer, a microtensile sample was used, the dimensions of which are given below in Figure 16.

Figure 16 - Tensile Sample (all dimensions mm)



Samples were cut from quenched sheets of the compression moulded materials. These were then heat treated as outlined in Section 3:1. The nominal yield stress, nominal tensile strength and elongation at break were used to characterize the tensile behaviour of the polymers. (The term nominal is used as the yield stress and tensile strength were calculated using the initial cross-sectional area.)

Five determinations on each heat treatment condition were carried out, the mean value of parameter was recorded. A consequence of the small dumbell sample used was that an extensometer was too large to be fitted to the wasted portion. Thus values of elongation were calculated using the initial gauge and final crosshead separation.

The operating conditions of the Instron are given in Table 19.

Table 19

CTM Load Cell Full Scale Deflection	20 Kg
Gauge Length	16 mm
Cross Head speed	20 mm/min
Chart speed	200 mm/min

4:3 Results

The presence of orientation can greatly influence the tensile behaviour of polymers. In the instance of uniaxial orientation, if the applied force is in the direction parallel to the molecular orientation the modulus, tensile strength and elongation at break increase over the values found with an unoriented polymer.

Orientation may change a polymer from a brittle material to a ductile one which has a yield point. Where the tensile load is applied in a direction perpendicular to the molecular orientation, the modulus, tensile strength and elongation are found to be less than for the unoriented material.

It is considered that during the thermal pretreatment and annealing stages any orientation which may have been introduced in the milling and moulding operations has been removed.

In the literature review the influence of the extent of PVC particle structure breakdown on the properties of the polymer was discussed. Such influences are considered absent in this study as processing conditions were chosen to achieve breakdown of the 1 μm secondary particles.

Consequently, the mechanical properties quoted in this Chapter are attributed to variations due to polymerization and thermal history.

Typical stress-strain curves for quenched samples of the materials and those annealed above and below the glass transition are given in Figures 17 - 19. The results for all the heat treatment conditions are given in Tables 20 - 22.

The mode of deformation for all three polymers was similar in that yielding occurred in the region of 5 - 7% strain followed by cold drawing and finally fracture. However, the measured parameters of yield stress, tensile strength and elongation at break varied with polymer type. These parameters were also changed by annealing when compared with the quenched material.

In the case of PVC-2 and the Montecatini -30^{0}C polymer the yield stress increased by approximately 13% and 8% respectively, for heat treatment both above and below Tg. A differing response of yield stress due to treatment above and below Tg was given by the copolymer. An increase in the region of 11% was observed after treatment above Tg, whereas a decrease of the same magnitude was recorded for treatment above Tg.

The values of tensile strength for PVC-2 remain relatively constant for treatments below the Tg and decrease by approximately 9% for those above Tg. For the low temperature polymer decreases of 10% and 6% were recorded respectively for heat treatments below and above Tg. Annealing below the Tg for the copolymer resulted in a slight increase in tensile strength, whereas for treatment above the Tg the values remained constant.

The elongation at break of all the polymers was affected by heat treatment. Decreases of 42% and 23% were observed for PVC-2 and the low temperature polymer respectively. A drop of 70% for samples treated below the Tg and 32% for those treated above the Tg were found for the vinyl chloride/vinyl acetate copolymer.

The observed effects for treatment below the Tg did seem to show a dependence on the time of annealing. However, the values for samples treated above Tg showed an erratic response with respect to time.

The elongational behaviour of the annealed polymers and the mechanism of deformation and fracture will be discussed in greater detail in Chapter V.

able 20 - Effect of annealing on the nominal yield stress MN/m^2

nnealing emp °C	Quenched	40		55		70		100		115		130		145		160	
nnealing ime h		0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0
VC-2	39·07	43·14	44·24	45·80	45·72	46·61	49·37	46·79	45·55	45·30	44·90	44·84	44·69	44·32	41·58	42·19	43·4
ontecatini 30°C olymer	51·41	47·11	55·62	52·90	57·05	55·89	56·06	55·30	59·35	56·37	53·85	55·50	55·19	52·84	54·62	53·89	53·1
inyl hloride/ inyl cetate opolymer	45·26	47·11	50·71	50·77	54·80	51·32	50·82	42·96	43·76	38·06	36·74	-		-		-	

Table 21 - Effect of annealing on Nominal Tensile Strength MN/m^2

nnealing emp°C	Quenched	40		55		70		100		115		130		145		160	
nnealing ime h		0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·C
VC-2	46·49	40·00	46·82	43·73	44·54	44·19	47·74	44·85	44·27	42·46	43·50	43·71	43·28	43·64	43·50	42·72	43·6
ontecatini 30°C olymer	49·01	39·53	44·01	45·41	46·16	44·11	42·91	47·54	47·86	44·97	49·90	47·95	48·64	47·61	46·21	46·30	46·9
inyl hloride/ inyl cetate opolymer	33·00	32·19	34·01	33·25	34·97	34·55	35·04	34·27	33·35	31·71	29·08	-		-		-	

Table 22 - Effect of annealing on Elongation at Break %

Annealing Temp °C	Quenched	40		55		70		100		115		130		145		160	
Annealing Time h		0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0	0·5	5·0
PVC-2	237	108	130	127	137	132	126	131	130	142	140	146	142	133	156	152	133
Montecatini -30°C polymer	58	32	41	27	31	25	22	38	26	32	22	41	33	33	31	43	32
Vinyl Chloride/ Vinyl Acetate Copolymer	201	62	85	46	59	74	52	138	114	133	142	-		-		-	

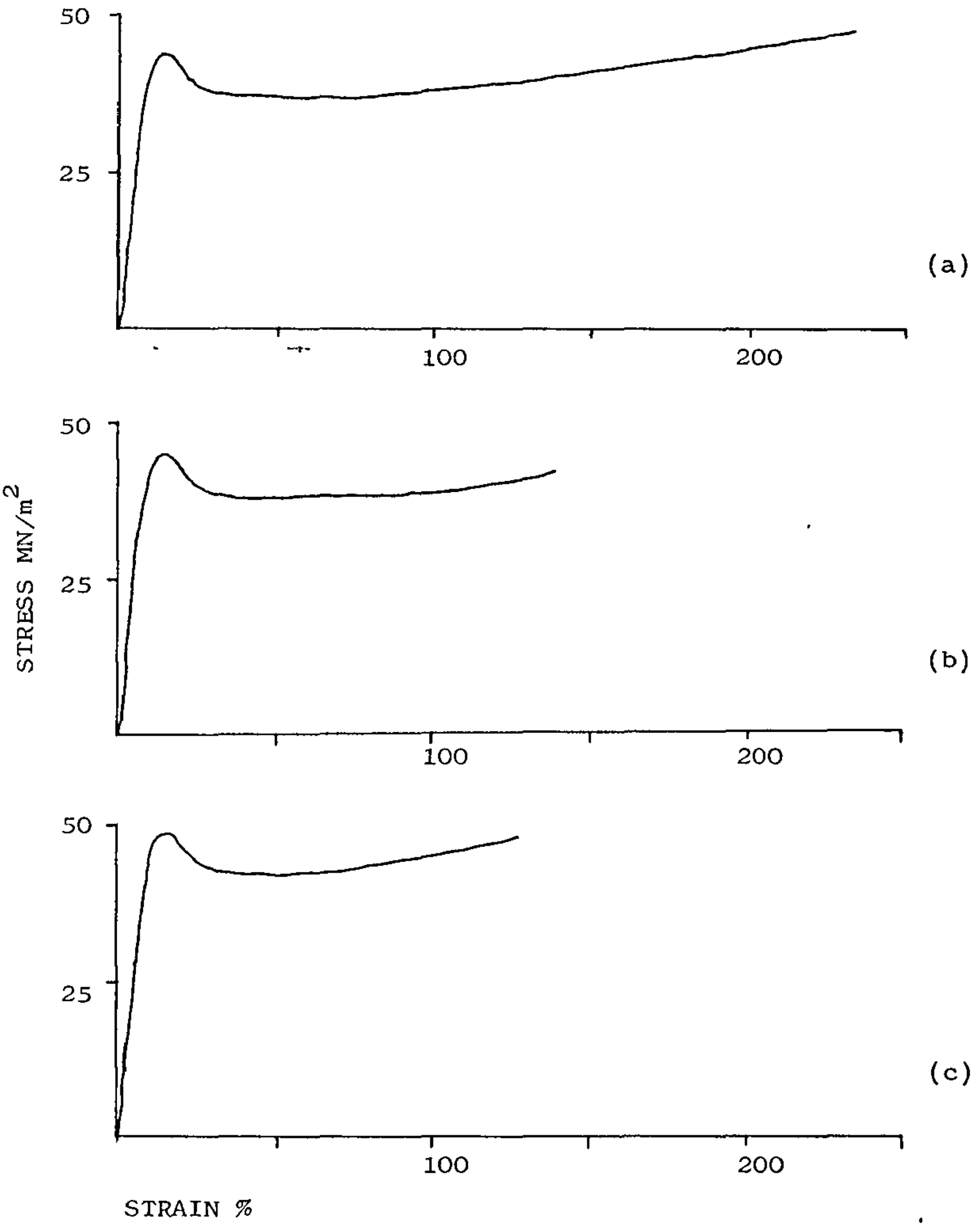
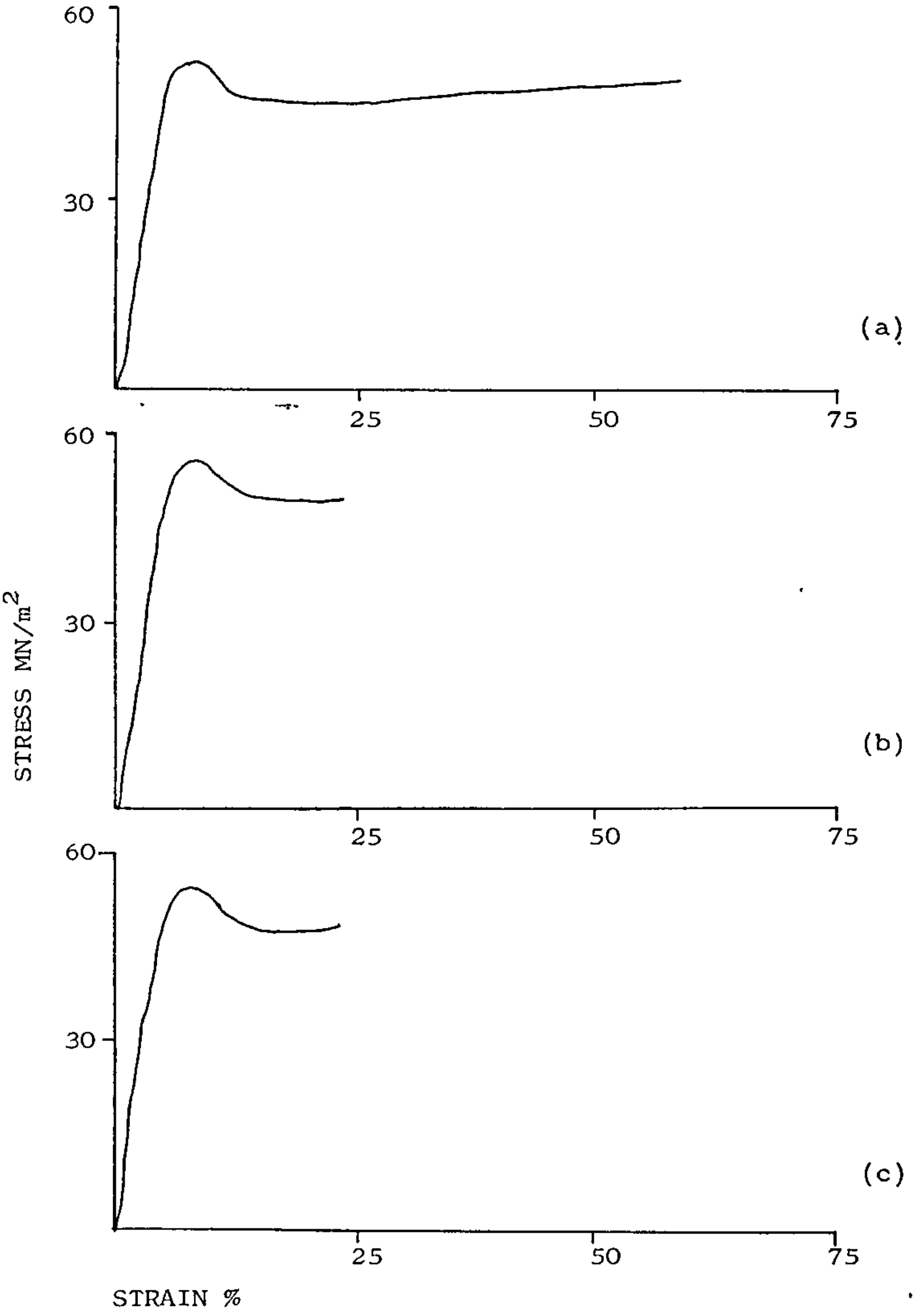


Figure 17 - Stress-strain curves for PVC-2

(a) Quenched

(b) 5h 70°C

(c) 5h 115°C



<u>Figure 18</u> - Stress-strain curves for Montecatini -30°C polymer

(a) Quenched

(b) 5h 70°C

(c) 5h 115°C

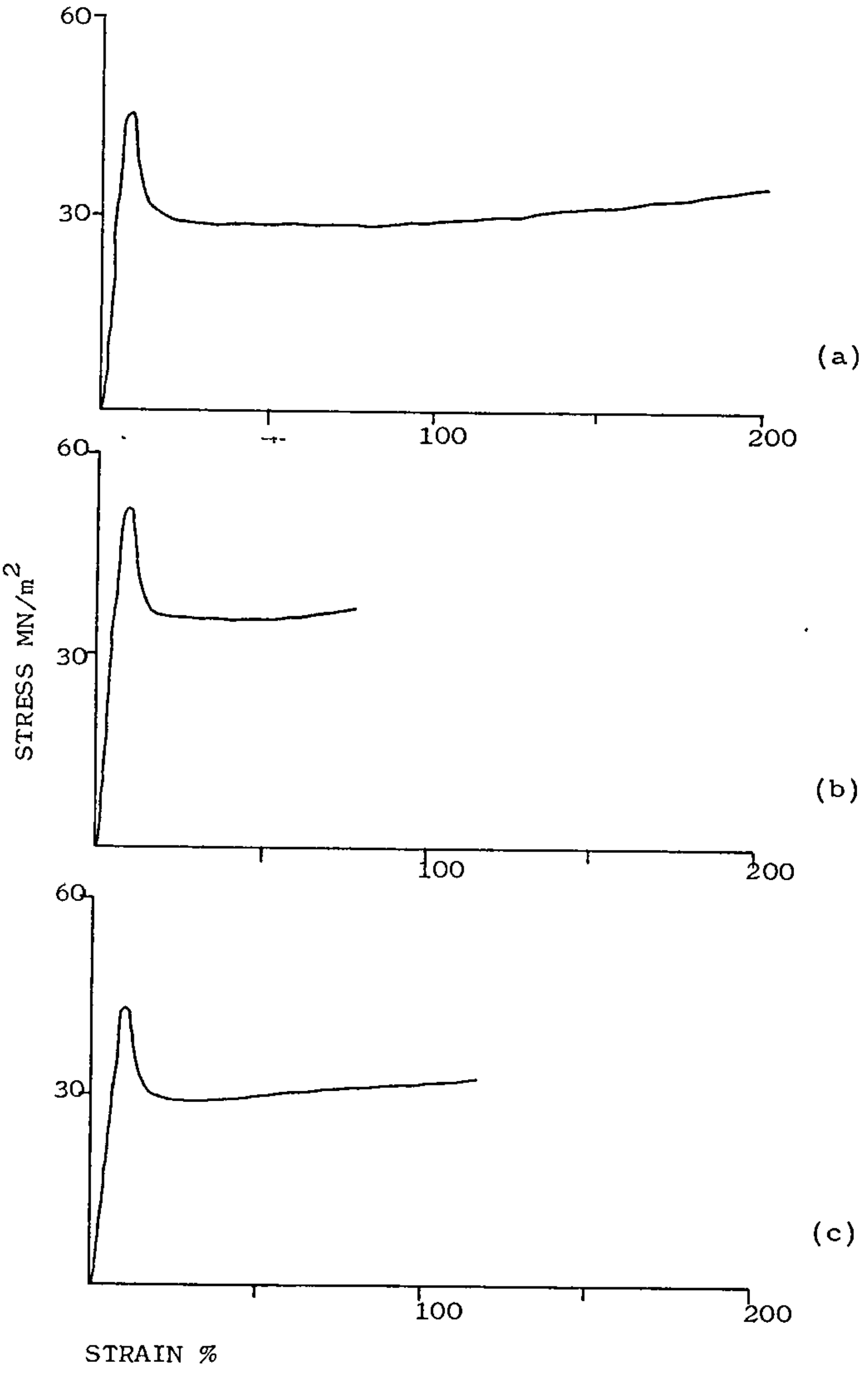


Figure 19 - Stress-strain curves for Vinyl Chloride/Vinyl Acetate copolymer

(a) Quenched

(b) 5h 70°C

(c) 5h 115°C

CHAPTER V - Discussion

5:1 Proposed Mechanisms for structural changes

Before embarking upon discussion of the results obtained, two mechanisms will be put forward to explain the ordering processes in PVC. The two mechanisms will then be tested by seeing if they are instrumental in the analysis and interpretation of the experimental data obtained.

The first mechanism describes ordering taking place below the glass transition and uses the "hole theory" of liquids as proposed by Eyring[131]. This theory has been developed by Hirai and Eyring[132], and Wunderlich[133] for polymers and considers the non-equilibrium nature of the amorphous state. It is considered that polymer chain movement can occur by jumping of portions of the chains into vacant "holes", the process of jumping thus creates a vacancy for subsequent occupation.

In the liquid state the number of holes increases with temperature and expansion occurs. On cooling from the liquid state a stage will be reached where chain mobility is lost and the liquid will be transformed into the glassy state. At this point a certain equilibrium hole concentration is frozen-in. If the cooling process is fast compared to the time required for holes to diffuse out, then an excess concentration is frozen-in, resulting in a lower glass transition temperature.

This results in a dependence of properties on the rate of reheating. Where the reheating is slow the material first of all seeks its equilibrium vacancy concentration and volume decreases before subsequently increasing. Where a fast heating rate is used the vacancy concentration is unable to increase quickly enough and cannot attain its equilibrium value, consequently overheating of the glass occurs[95,134].

Annealing of the amorphous state below the glass transition will cause a gradual escape of the excess frozen-in hole concentration. The vacancy concentration will, therefore, reach an equilibrium state depending on the annealing temperature. The rate of the vacancy relaxation is related to segmental mobility, and thus will be greater as the annealing temperature approaches Tg. It can be seen that the vacancy concentration will, therefore, be dependent greatly on the thermal history and will be reflected in terms of the physical properties of the polymer.

The second mechanism of ordering is that of formation of crystallites in the temperature range between the glass transition and the melting point. The literature review has shown that the syndiotactic content plays a significant role in the ordering of PVC. Hence the results will be assessed in terms of the amount of syndiotactic material available for crystallization.

5:2 Discussion of Results

5:2:1 Chain Microstructure

The 13 carbon NMR spectra for the methine resonance region are reproduced in Figure 1. The spectra exhibit a high degree of discrimination between the stereochemical configurations. The advantages of 13 carbon NMR are that the range of chemical shifts is larger than the corresponding proton spectra. Also the technique directly observes the carbon chain backbone, rather than the attached protons[6]. The spectra were proton decoupled, that is the coupling between the 13 carbon and hydrogen nuclei has been erased. This has the effect of increasing the effective signal-to-noise ratio, resulting in the resolution of the fine structure of the polymers. The overlap of the resonances of the vinyl chloride/vinyl acetate copolymer is attributed to additional spin-spin coupling of the acetate grouping with the main chain nuclei.

The values of the tacticity concentrations calculated from the spectra, Table 3, and the infrared absorbance ratios, Table 4, show the influence of polymerization history on chain microstructure. On decreasing the polymerization temperature to -30°C from that ~~of~~ a normal suspension condition, (40 - 60°C), an increase in the syndiotactic placement is given. The measurements for the vinyl chloride/vinyl acetate copolymer indicate this material is virtually atactic.

The relative amount of the stereochemical arrangements of the polymer chains is considered to have a significant influence on the ordering process and properties of materials. The first instance of such an influence is that exerted on the GPC measurements of molecular weight.

The phenomenon of aggregation of PVC molecules in dilute solution has been known for a number of years[135]. Molecular weight information derived from PVC solutions may, therefore, be distorted because the polymer is not molecularly dispersed. Hengstenberg and Schuch[136] found that the aggregates consist of a number of single molecules and considered these are held together by crystallites. Later work by Vidotto et al[137] supports this hypothesis by showing that during fractional precipitation the initial fractions exhibit higher crystallinity than following fractions.

Abdel-Alim and Hamielec[50] have used area distortion of GPC traces to measure the total mass of the aggregates. They found the mass could be correlated with the syndiotactic content and thus the degree of crystallinity of the polymer.

Heating of dilute solutions of PVC will destroy the aggregates[50,138,139] and result in GPC traces consisting only of a peak for single PVC molecules. Dissolution is found to be more difficult the lower the polymerization temperature. Similar distortion of the GPC trace has been observed in this present work with the low temperature polymer (Section 2:2). A heat treatment of five days at 90°C of the solution was found necessary to obtain satisfactory molecular weight data. These observations are indicative of the pronounced effect of syndiotacticity and crystallinity on the solution properties of PVC.

5:2:2 Examination of Ordering

As outlined in Section 3:1, prior to annealing the polymers were subjected to a three minute pretreatment. This was done firstly to destroy existing order and secondly to create a uniform thermal history. Subsequent examination revealed that residual order was present in the polymers. Density values of 1389 kg/m^3 and 1396 kg/m^3 were obtained for quenched samples of PVC-2 and the low temperature polymer. These values give calculated crystallinities of 11·35% and 16·26%, respectively. X-ray diffraction order factor values for the quenched materials, 8·7% and 20·1%, also confirmed that order was retained. Both techniques indicated a greater amount of crystallinity is retained in the case of the low temperature polymer. From these observations, it may be considered that the pretreatment temperatures and times used are too low to destroy the order present in the polymers. It could also be concluded that the recrystallization process may occur so rapidly, as to prevent quenching resulting in a totally amorphous state. Further discussion of the rapidity of the ordering process will be given later in the text.

The DTA thermograms of the quenched polymers can be interpreted in terms of the amount of crystallinity retained. An example of a typical thermogram obtained for PVC-2 is reproduced in Figure 3. This consists of a base-line shift at approximately 84°C, followed by an exothermic peak and finally a very broad endothermic peak. The base-line shift is attributed to the glass transition temperature. The exothermic peak following the Tg, is considered to be due to crystallization. This observation is in agreement with DSC data published by Illers[95] on heat treatment of a commercial suspension polymer. The final broad endothermic peak is ascribed to the melting of crystallites remaining from the pretreatment and those formed during crystallization. All three transitions in the DTA trace occur very close together, making calculation of the enthalpy changes difficult. However, approximate values of the magnitude of the transition has been made.

The form of the thermogram for the low temperature polymer was similar to that of PVC-2, but there were several notable differences, which are apparent in the calculated enthalpy change values. For PVC-2 the exothermic peak corresponds to 1·9 kJ/kg, whereas the value for the low temperature polymer is 1·0 kJ/kg. The endothermic enthalpy values were 4·8 kJ/kg and 7·0 kJ/kg for PVC-2 and the -30°C polymer, respectively. The exothermic enthalpy change was equivalent to 40% of the endotherm for PVC-2 and 15% for the low temperature polymer. The smaller value in the latter case is in line with data from density and X-ray diffraction measurements. The higher amount of crystallinity remaining after the quenching process in the low temperature polymer limits that available for crystallization.

A greater value of the temperature range of melting was obtained for the low temperature polymer compared with PVC-2; 120 - 220°C as opposed to 120 - 200°C. This fact coupled with the difference in melting endotherm values indicates the effect of decreasing polymerization temperature on crystallinity in PVC.

Although relatively high pretreatment temperatures were employed, there was a failure with PVC-2 and the -30°C polymer to transform large portions of crystalline material into the amorphous state. The presence of these relatively high levels of crystallinity may be considered to significantly influence properties.

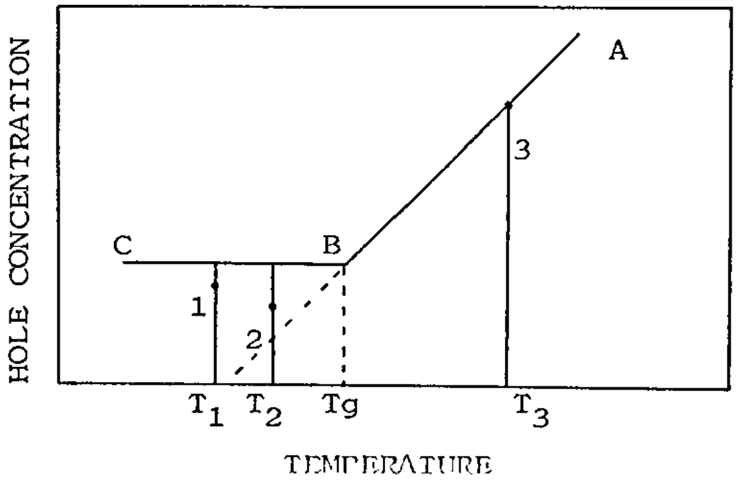
In the case of heat treatment below the glass transition temperature, crystallization would not be expected to occur due to restricted chain mobility. This fact is borne out by X-ray diffraction measurements, which show no significant increase in order factor with treatment below Tg. However, there is still the appearance of endothermic peaks in the DTA thermograms and changes in the density of the polymer. Thus an alternative mechanism is required to explain the observed phenomenon. The experimental results may be interpreted by considering the effects of annealing on the amorphous phase.

As outlined in Section 5:1 the vacancy concentration of the amorphous state is greatly dependent on the thermal history of the sample. The vacancy concentration cannot be measured directly, however, it may be assessed by the corresponding change in the enthalpy of the system.

In a second heating cycle to above Tg overheating of the glass will result if the vacancy concentration cannot increase quickly enough to attain equilibrium. This will result in the appearance of an endothermic peak in the DTA trace on or near the Tg step. From the penultimate sentence it may be concluded that the heating rate employed will affect the magnitude of the resulting endotherm. Such observations have been reported for PVC by Illers[95] and for polystyrene by Wunderlich et al[134] and Petrie[140].

With reference to Figures 4 and 5, it has been demonstrated that a constant annealing time below the glass transition results in an increase in size of the observed endotherm. This observation may be explained using the concept of the change in the vacancy concentration. Referring to Figure 20, AB is the equilibrium vacancy state for the system above Tg; on reaching the Tg a certain concentration will be frozen in, BC. Annealing below Tg at two temperatures T_1 and T_2 for the same time ($T_1 < T_2$) will allow the vacancy concentration to approach its equilibrium values at these temperatures.

Figure 20



On the basis of reduced segmental mobility at T_1 the system will be further away from its equilibrium state, that is, at point 1. At T_2 the vacancy state will be closer to its equilibrium, point 2. Consequently, on reheating the system above Tg to some temperature T_3 the system at point 2 will be further away from the equilibrium state at 3 and will, therefore, give rise to a larger endothermic peak.

The changes in the vacancy concentration due to annealing will also explain the observed densification of the polymers due to volume relaxation. Although density determined degrees of crystallinity were calculated for the polymers heat treated below Tg, it is considered that their true crystallinity values are equal to those of the quenched polymers.

The appearance of endothermic peaks for heat treatment below the Tg of vinyl chloride polymers has been attributed by McKinney and Foltz[96] to melting of crystallites of too small a size to be detected by X-ray techniques. Structural changes may be expected to occur on annealing below Tg, however, formation of crystalline regions would not be expected. Observations of the endothermic peaks can be satisfactorily explained using vacancy change concepts in the amorphous state. It is of interest to note that larger enthalpy and density changes were found for PVC-2 than with the low temperature polymer on annealing below Tg (this includes storage at room temperature). That is, larger changes occur in a polymer containing a greater amorphous content.

Endothermic peaks in DTA and DSC traces and density changes have been reported for atactic polystyrene[134,140], amorphous polycarbonate[141] and suspension PVC[95] and interpreted using vacancy change type models.

X-ray measurements have shown that crystallization on annealing above Tg occurs with PVC-2 and the low temperature polymer. On examining the X-ray diffraction traces in Figure 8, it is noticed that larger and sharper reflections are obtained with the low temperature polymer. This fact indicates the greater overall percentage crystallinity and slight increase in the mean crystallite size of the latter. Unfortunately, the technique is unable to show any significant change in the level or perfection of the crystalline phase as the time of heat treatment is increased. For the low temperature polymer treated above Tg the X_{XR} values were erratic with respect to time and temperature. The values of the increase in crystallinity on annealing, $X_{XR} - X_{XRquench}$, are larger for PVC-2 than the low temperature polymer. This is not totally unexpected due to the relatively high degree of crystallinity remaining in the latter, following pretreatment and quenching.

Endothermic peaks are observed in the DTA traces of samples treated above Tg. These are assigned to the melting of crystallites formed during annealing. These peaks are considered as thermodynamic equilibrium transitions, rather than overheating phenomena. This conclusion is reached firstly because definite X-ray evidence exists showing changes in the crystalline content on annealing (Table 17, References 72,94). Secondly, it has been reported in the literature that the size of such transitions is less dependent on the heating rate[95].

In Figures 4 and 5 the enthalpy changes observed for treatment above Tg for PVC-2 and the low temperature polymer are plotted as a function of annealing temperature. The plots for both polymers go through a maximum as is the case with other crystallizable polymers. The density as a function of annealing temperature for the low temperature polymer also exhibited the above behaviour. Similar observations have been reported by Rybnikar[94] for commercial emulsion and suspension polymers. Unfortunately, for PVC-2 the density values exhibited a large amount of scatter, thus posing questions of degradation with this polymer. However, no voids could be detected in sectioned samples of the heat treated material using optical or scanning electron microscopy. Thus the observed scatter for PVC-2 may tentatively be considered as a surface degradation phenomenon.

The temperature of the maximum rate was found to be greater for the low temperature polymer. This may be expected on the basis that the glass transition temperature for the latter is higher, and as a consequence of the larger syndiotactic content the melting point of the crystallites will also be higher.

Kockott[93] has reported a value of 180·75 kJ/kg (2,700 cal/mole) for the heat of fusion of a 100% crystalline vinyl chloride polymer. Using this value calculated crystallinities for the two homopolymers from their total melting endotherms gives very low figures. Heats of fusion for PVC-2 and Montecatini polymer of 4·8 and 7·0 kJ/kg yield crystallinities of 2·7 and 3·8%, respectively, and these values seem unrealistic. The value of 180·75 kJ/kg reported by Kockott, however, may be questioned on the grounds of the relatively high values of syndiotacticity used in his calculations (0·80 and 0·69 for polymers made at -70 and -25°C respectively).

The density and enthalpy changes showed a dependence on the time of annealing, for example Figures 6 and 7. The values increase steadily with time and then level off; it may, therefore, be concluded that the extent of crystallization is approaching its equilibrium value at that temperature.

From Tables 9 and 10 the peak maxima of the endotherms are seen to shift to a higher temperature as the time of annealing is increased. This can be viewed, as expressed in the previous paragraph, as a greater extent of crystallization and of perfection of the crystallites. Regrettably, the X-ray technique does not furnish conformatory evidence as to the change of order factor or crystallite size with time.

Evidence for the DTA work indicates that crystallization is rapid in PVC. At 100°C half the crystallization has occurred within less than 0·5h. The exotherm obtained in DTA traces of quenched samples using a relatively fast heating rate also points to the rapidity of the process. Illers[95] states that only a few moments annealing above Tg is necessary to produce pronounced endothermic peaks in the DSC trace.

Endothermic peaks were also obtained with the vinyl chloride/ vinyl acetate copolymer, however, these peaks were much smaller in size than those of the two homopolymers. This fact and the low value of X-ray order factor indicate that the inclusion of vinyl acetate as a comonomer greatly hinders crystallization. The reduction in ordering may be explained due to the steric effect of the bulky acetate group and a reduction in the proportion of syndiotactic material. Changing a vinyl chloride unit for vinyl acetate will also bring about a reduction in the polar attractive forces between the polymer chains.

It is of interest to compare the crystallinity with the amount of crystallizable material available. If the assumption that only the syndiotactic portion of the chains may crystallize then Flory's theory of crystallization of copolymers can be employed[142].

In this theory a copolymer consisting of units, A, which are capable of crystallizing and of co-units, B, which do not crystallize is considered. The polymer will contain crystallites of varying lengths, denoted by a number N of A type units in a single chain running from one end of the crystallite to the other. Longitudinal growth of existing crystallites will be restricted by B units which occur in some chains where they protrude from the ends of the crystallites. Growth in the lateral direction, however, will be restricted only by the availability of sequences of A units in the amorphous regions.

Growth of crystallites of a certain size in the above manner will be determined by the availability of A sequences in the melt, and on the decrease in standard free energy to be gained on crystallization. At equilibrium crystallites of every length N must be in equilibrium with the amorphous sequences of A units. The acquisition of an additional chain may be initiated at any site on the lateral surface of a crystallite. For this to occur the amorphous unit occupying a particular site shall be an A unit which is suitably situated within a sequence of at least N units. If the site in question is next to a terminal unit of the crystallite, then the site must be occupied by an A unit which is followed by a sequence of at least N - 1 units. The probability of fulfilling the conditions is represented by P_N. At equilibrium with crystallites of length N this concentration P_N^e of acceptable A units in the amorphous phase can be related to the standard free energy of fusion, ΔF_N, of a sequence of N units from a crystallite of length N.

$$P_N^e = \exp(-\Delta F_N/RT) \tag{1}$$

The standard free energy of fusion per mole of units is given by

$$F_u = \Delta H_u - T\Delta S_u$$

$$= \Delta H_u (1 - (T/T^om) \tag{2}$$

where ΔH_u, ΔS_u are the heat and entropy of fusion per unit. T^om is the melting point of the pure polymer.

Assuming the change in $\Delta H_u/\Delta S_u$ with temperature over the range from T to T^om may be neglected, then

$$\Delta F_N = N\Delta F_u - 2\sigma_e \tag{3}$$

where σ_e is the free energy per mole associated with a terminal unit at the end of the crystallite. From 1 - 3

$$P_N^e = (1/D)\exp(-N\theta) \tag{4}$$

$$\text{where}\quad \theta = (\Delta H_u/R)({}^1/T - {}^1/T^om) \tag{5}$$

$$D = \exp(-2\sigma_e/RT) \tag{6}$$

The probability P_N can be related to the composition of the melt as follows:-

W_j represents the probability that a unit chosen from the melt is an A unit which is a member of a sequence j units in length, bounded by B units. Further, if $P_{N,j}$ is the probability that the specific A unit selected is followed in a given direction by at least N - 1 addition A units. Then:-

$$P_{N,j} = \left(\frac{j - N + 1}{j}\right) W_j \qquad j \geqslant N \tag{7}$$

$$P_{N,j} = 0 \qquad j < N$$

$$\text{and}\quad P_N = \sum_{j=N}^{\infty} P_{N,j} = \sum_{j=N}^{\infty} \left(\frac{j - N + 1}{j}\right) W_j$$

solving the above gives:-

$$W_N = N(P_N - 2P_{N+1} + P_{N+2}) \tag{8}$$

The quantities P_N and W_N can be related to the constitution of both the initially molten polymer and the partially crystalline one. The conditions for equilibrium can then be established. For a completely molten polymer

$$W_N^o = \frac{X_A N \nu_N^o}{N_A} \qquad (9)$$

where N_A is the total number of A units, X_A the corresponding mole fraction; and ν_N^o the number of sequences of NA units initially present in the melt. The assumption is made that the probability of an A unit being followed by another A group is independent of the number of preceding A groups in sequence. This probability is denoted by P. Then (9) may be written:

$$W_N^o = \frac{N X_A (1 - P)^2 P^N}{P} \qquad (10)$$

By combination with (7):-

$$P_N^o = X_A P^{N - 1} \qquad (11)$$

If crystallites of length N, N + 1 and N + 2 are present and are in equilibrium with the melt, then combining (4) and (8) gives:-

$$W_N^e = N D^{-1} \left[1 - \exp(-\Theta)\right]^2 \exp(-N\Theta) \qquad (12)$$

which is the expression for the residual concentration in the melt of sequences of A units which are N units long.

From the above, the necessary and sufficient condition for crystallization can be stated as

$$P_N^o > P_N^e$$

for one or more values of N. Similarly, the condition $W_N^o > W_N^e$ for one or more N is a necessary but sufficient condition for crystallization. Equations (10) and (12) describe the initial and equilibrium distributions of sequences in the melt, are both functions of the sequence length N. There is, therefore, a critical value of N at which these two distributions are equal. This can be written as:

$$N_{critical} = -\left\{ \frac{\ln (DX_A/P) + 2\ln \left[(1 - P)/(1 - e^{-\theta}) \right]}{\theta + \ln P} \right\}$$

For values of $N < N_{critical}$, W_N^e is greater than W_N^o while for $N > N_{critical}$ the converse is true. Thus the critical N value represents the limiting size above which crystallites cannot be maintained in equilibrium. This critical value of N will from now onwards be described as ξ min.

The theory also allows for an estimate of the fraction of the A units that are crystalline at temperatures less than Tm. This estimate is obtained by totalling all the sequences of A units involved in crystallites. This procedure is a slight overestimate of the degree of crystallinity since units greater than N in length may participate in crystallites only N units long. The value derived from such a summation may, therefore, be considered the maximum crystallinity obtainable[41].

For random copolymer propagation the probability P in (10) is equal to X_A[142]. This latter equation then becomes equivalent to that stated by Fordham[3].

$$F^N_{SYNDIO} = N\ (1 - \alpha)^2 \alpha^N$$

where F^N_{SYNDIO} = Fraction of the total polymer in syndiotactic sequences

N = Number of repeat units in a syndiotactic sequence

α = Degree of syndiotacticity

In order to compare the experimentally determined values of crystallinity and tacticity with those predicted by the above theory certain calculations were performed. The theoretical syndiotactic sequence distribution as determined by the degree of tacticity and the value of N have been calculated using Fordham's relationship. The value of F^N_{SYNDIO} was computed for values of $\alpha = 0{\cdot}5$ to $0{\cdot}8$, and N values varying from 1 to 20; larger N values were not considered as the value of F^N_{SYNDIO} becomes very small for $N > 20$.

The theoretical degree of crystallinity obtainable was calculated by the summation of all the sequences of syndiotactic units involved in crystallites, with ξ min values varying from 1 to 20, i.e.

$$\sum_{\xi \text{min} = 1 - 20}^{20} F^N_{SYNDIO}$$

The actual calculations of F^N_{SYNDIO} and $\sum F^N_{SYNDIO}$ were carried out using a Hewlett-Packard 9820A calculator. The flow chart and computer programme used are given in Appendix 2.

In Figure 21 the calculated crystallinity is plotted against syndiotacticity. Density determined crystallinities and X-ray order factors are also plotted against 13C NMR tacticity values on this graph. The experimentally determined ranges intersect the theoretical curves at values for the minimum number of sequences necessary for crystallization of 5 - 6. These values are in agreement with Lebedev et al[76], Talamini and Vidotto[22], and Iobst[143]. However, Kockott[93] found a value of 12 for ξ min, which according to Lebedev et al is due to the former's low estimation of the degree of crystallinity, for example, a zero value was reported for a commercial PVC.

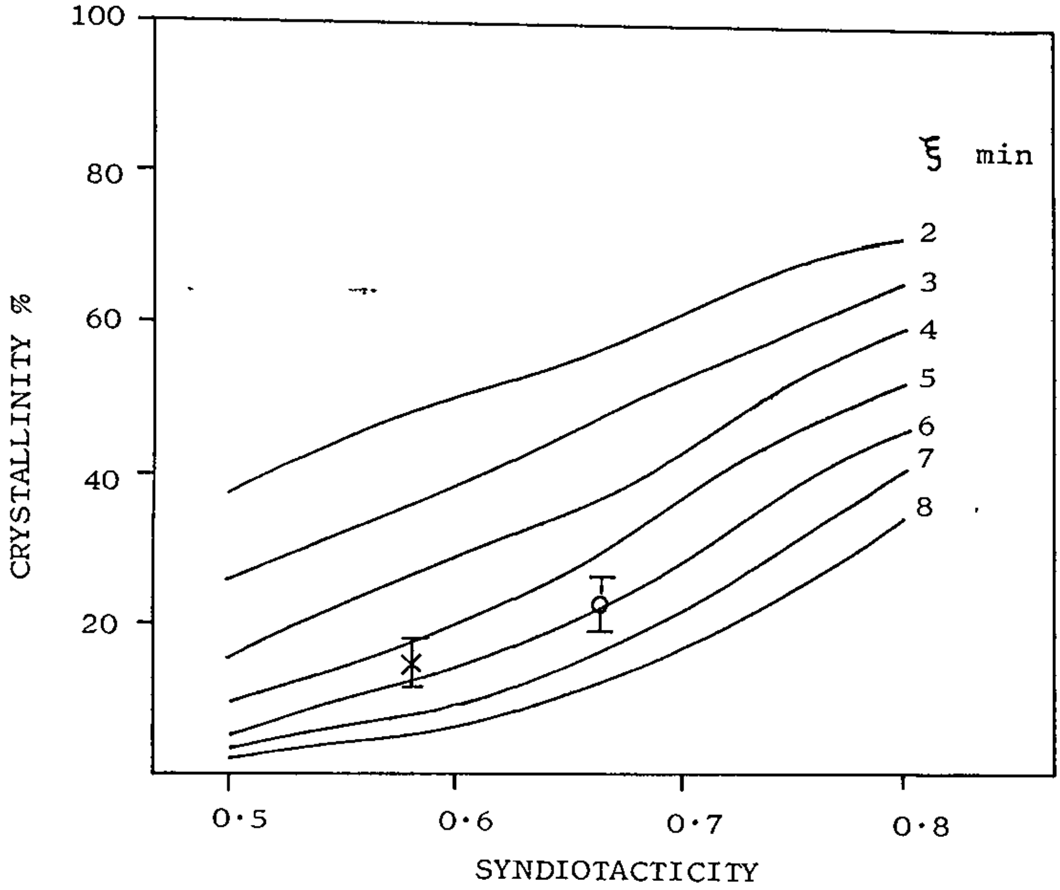
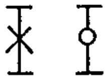


Figure 21 - Calculated crystallinity against syndiotacticity, with ξ min as a variable



Experimental range of density determined crystallinity and X-ray Order Factor for PVC-2 and low temperature polymer against 13C NMR syndiotacticity.

Juijn et al[41], using values of $\alpha = 0{\cdot}55$ and ξ min = 12 for commercial PVC, obtained a low crystallinity figure of 0·45%. This result was explained by showing that the isotactic structure could also be incorporated into the crystal lattice. The value of 12 for ξ min was used as it was "in agreement with values for other polymers". However, X-ray evidence in this work and reported literature shows that the crystallites in PVC are in the region 5 - 10 nm, which is smaller than other crystalline polymers. Thus a lower value of ξ min does not seem unreasonable. Using a figure of 0·251 nm for the size of the repeat distance of the vinyl chloride unit, then a sequence of 5 - 6 units will be 1·25 - 1·50 nm in length. This is lower than the X-ray determined mean crystallite size, however, the latter technique is only capable of resolving structures 2·5 - 3·0 nm and above. It is also important to stress that the ξ min value represents the minimum sequence length capable of crystallizing. The very broad melting endotherm observed in the DTA traces indicate further that a wide range of crystallite size and or perfection exists.

The techniques of DTA, density measurements and X-ray diffraction have so far shown that heat treatment can have a pronounced effect on ordering in PVC. It is anticipated that a change in the molecular arrangement may affect solvent sorption behaviour.

It is the intention that interpretation of such changes in behaviour may serve as a tool for studying polymer morphology.

It has been found experimentally that the rate of diffusion J is proportional to the concentration gradient.

$$J = - D \frac{\partial c}{\partial x} \qquad \text{(a)}$$

where J = Rate of Diffusion

D = Diffusion Coefficient

c = Concentration.

In many systems, however, D has been found to depend markedly on the concentration, c. Thus considering the X direction, the diffusion process can be expressed by:

$$\frac{\partial c}{\partial x} = \frac{\partial}{\partial x} (D \frac{\partial c)}{\partial x} \qquad \text{(b)}$$

Equations (a) and (b) are Fick's first and second laws of diffusion; systems which follow these equations are referred to as Fickian.

The data from sorption experiments are usually expressed by plotting the amount absorbed or desorped per unit mass or area against the square root of time. Such a plot is referred to as the sorption curve. Sorption curves which show Fickian behaviour are in the initial stage linear, then level out to an equilibrium value. However, frequent anomalous or non-Fickian behaviour is found to occur experimentally. (For example in the monographs of Meares[144] and Crank and Park[145]).

Crank and Park[146], and later Crank[147] have developed a theory which considers the time dependence of the diffusion coefficient in terms of the chain conformation in a volume element of polymer and the stress exerted on this element by the surroundings. When diffusion occurs in a polymer the chain conformation changes to a new equilibrium state. However, this change does not occur immediately. The chain conformation is determined not only by the concentration of the diffusant, but also on the elapsed time.

Stresses may be set up in the material as the diffusing molecules swell the polymer. These stresses will change with time as the polymer chains attempt to relieve the stress by changing conformation. This represents a second mechanism by which the diffusion coefficient becomes dependent on time.

Temperatures above Tg enable the polymer to take up an equilibrium conformation almost instantaneously following sorption. Thus the time dependence of the diffusion coefficient associated with conformational changes is eliminated. The dependence also on internal stress should also disappear as in this extremely mobile state any stresses developed will be dissipated very quickly. The situation where the polymer is above Tg, thus represents the condition for Fickian sorption.

From the preceding paragraphs it may be concluded that those factors which influence chain conformation such as vacancy relaxation, reduction in attractive forces and crystallinity will affect sorption behaviour. As the crystalline phase is considered impermeable changes in crystallinity will alter the amount of swellable material available. This point also raises the question of the affect on sorption by the increased diffusive path[148] as the number or size of such impermeable sites increases. Finally the role of the glass transition is considered important as it can significantly influence sorption behaviour[149,150].

In Figures 9 - 11 the sorption curves for all the three polymers are given. These curves show that heat treatment and polymer type greatly affect the sorption behaviour. For the vinyl chloride/vinyl acetate copolymer all instances of heat treatment the sorption curves are linear with time, i.e. Fickian behaviour. DTA and X-ray diffraction measurements have shown that crystallinity is very low in this polymer. The inclusion of the vinyl acetate group will also bring about a reduction in the polar forces between the polymer chains. Consequently, the main restriction imposed upon segmental mobility will be due to a decrease in the vacancy concentration. The glass transition temperature for this polymer is also the lowest for all of the three materials studied. It is thought that the diffusant quickly penetrates the polymer, plasticising the layers below the surface and so reducing the Tg of the polymer-diffusant system. It seems that this effect predominates over the conformational changes resulting from annealing and linear sorption is found in all cases.

For PVC-2 the sorption curves showed a different response according to the thermal history. The quenched sample, in which crystallinity from the X-ray measurements was found to be lowest, absorbs solvent most rapidly. The samples which were heat treated below Tg absorb solvent at a slightly lower rate, but the equilibrium weight gain reached the same value. The material annealed above Tg gave a completely different S-shaped curve and a lower equilibrium value than the other two samples. The low temperature polymer also showed a differing response with a change in thermal history. The curves in this case appear to be S-shaped, although the experiments were not carried out to equilibrium. (Subsequent work, however, has shown this to be the case[151]).

These observations may be interpreted in terms of the changes occurring in ordering. The sorption curves for PVC-2 samples quenched and treated below Tg were linear. These curves are again characteristic of polymers above their glass transition temperature. The slight decrease in the rate for the sample treated below Tg can be attributed to the constraint imposed on the diffusing molecules by the reduced vacancy concentration. The crystallinity in the samples is not changed, thus the amount of swellable material is unaltered. The restricting effect of the crystallites on the mobility of the polymer chains will also be the same, as a result the same equilibrium value is reached. This condition is not found for a sample annealed above Tg, as crystallization has been shown to occur. The additional crystallinity will reduce the amount of swellable material available and impose restrictions on the chain mobility and effective diffusion path length. Similar arguments can be used to explain the sorption behaviour of the low temperature polymer.

The S-shaped curve for PVC-2 samples annealed above Tg and all the low temperature samples are characteristic of diffusion below the glass transition. The tentative explanation offered for the sorption phenomena[144] is that when the diffusant is brought into contact with the polymer swelling of the surface layer tends to immediately set up a sorption equilibrium. The swelling, however, is restrained by entanglement with unswollen layers beneath. The equilibrium condition cannot be attained until sufficient diffusant has penetrated and plasticised the layers below the surface. When the latter state is reached the rate of sorption increases giving rise to the S-shaped curves. It is thought that the presence of crystallinity will impose additional constraints on swelling. The molecular weight of the polymer may also contribute to the observed behaviour. A higher molecular weight would mean a greater degree of chain entanglement, which would restrict swelling. Such an effect would be greatest with the low temperature polymer as this has the largest molecular weight.

It is concluded that the increase in crystallinity due to annealing above Tg for PVC-2 is responsible for the S-shaped sorption curve.

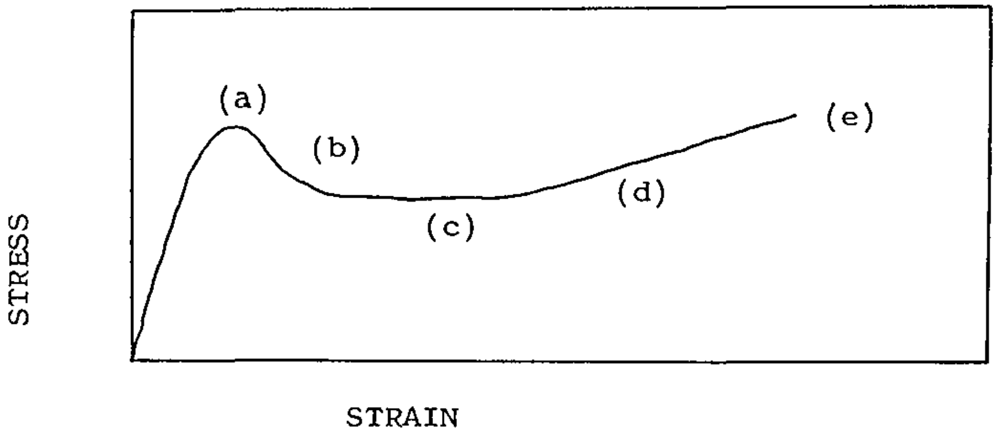
For samples quenched and treated below Tg the lowering of the Tg by the penetrant appears to predominate, giving rise to Fickian curves. The occurrence of S-shaped curves for all cases of the low temperature polymer is attributed to the relatively high levels of crystallinity remaining in these samples following pretreatment and quenching. This polymer also has the highest glass transition temperature, and so will require a greater extent of penetration to lower the Tg of the polymer - diffusant system. At this point, it is considered pertinent to note that Blackadder and Vincent[130] have recently published sorption data on crystalline poly(propylene) and these curves were also S-shaped. The pronounced effect of a change in the polymer type on sorption is clearly demonstrated in Figure 12. Here sorption data for all three polymers annealed above Tg are plotted together.

In Figures 13 and 14 sorption behaviour of PVC-2 and the low temperature polymer annealed above Tg for various lengths of time but immersed for a constant time are presented. The curves illustrate the increase in the extent of crystallization of the polymers with increasing time of heat treatment. The curves also to a certain extent indicate the rapidity of the crystallization process.

5:2:3 Tensile Properties

The stress-strain curves for the three polymers heat treated under various conditions are reproduced in Figures 17 - 19. These curves can be represented by one of the type given below in Figure 22.

Figure 22



In Figure 22 the initial portion of the curve is linear and the specimen extends uniformly, until after a few per cent strain the sample yields, (a), and a constriction or neck forms. The basic reason for necking in tensile samples is non-uniformity. If part of the sample is slightly thinner than the rest, then the stress will be slightly higher. Consequently, further deformation will be concentrated at this point and increase the local stress, thus the system becomes unstable and a neck is formed. (A more rigorous treatment of the necking phenomenon is given by the construction of Considère[152]). Following the yield point the stress drops, (b), to a nearly constant level, this portion of the curve being referred to as stress softening. As stretching continues the sample cold draws, (c), and the shoulders of the neck travel along the sample. The portion (d) of the stress-strain curve involves further straining of the cold drawn polymer and the curve rises steeply due to orientation hardening. Finally, at the point (e), the sample breaks.

Several theories have been put forward to explain the yield and cold drawing behaviour of polymers. One theory of the phenomenon is that during the stretching process a large amount of heat is generated. This goes largely into heating the region of the neck, and hence yielding and cold drawing occur[153-155]. Vincent[152], however, explains the phenomenon by stating that the stress in the polymer lowers the softening temperature to about the temperature at which drawing occurs, rather than the straining process generating heat which raises the temperature of the material to the softening temperature. Vincent, however, does not offer a molecular mechanism for this temperature lowering process. Lazurkin[156] and Robertson[157] have formulated a theory based on the Eyring model[131] to describe yielding and cold drawing. The former theory states that the phenomenon occurs when stresses or strains have sufficiently increased the mobility to allow large scale configurational changes.

The Eyring-Lazurkin-Robertson concept appears to explain the phenomenon most satisfactorily as certain objections have been put forward to the other theories. The extent of temperature rise can be lowered by reducing the stretching speed and increasing the heat transfer to the surroundings. Under such conditions yielding and cold drawing still occur[156]. The yielding phenomenon is also observed in shear[158,159] and in compression[160,161]. Such observations are not explained by the tensile force affecting the softening temperature of the material.

To summarize the models formulated, it may be considered that yielding will occur when stresses or strains have sufficiently increased segmental mobility. The magnitude of the force required to cause this increase will be greatly dependent on the initial chain mobility of the sample to be deformed. Changing the segmental mobility by heat treatment will be expected to alter the values of the forces necessary to deform the material.

On annealing below Tg the vacancy concentration decreases, so decreasing mobility. This, therefore, should result in larger values of stress required to bring about yielding. This was found to be the case with all the polymers. Effects of crystallinity on the tensile behaviour of polymers may be interpreted by assuming that the crystallites act as stress concentrators, but at the same time they behave as cross-links, reducing the movement of molecular segments[162].

For PVC-2 and the low temperature polymer, the presence of crystallites remaining and the slightly larger polar attractive forces between the chains, may contribute further to the increase of stress to yield. On examination of the values of the yield stress for samples annealed below the Tg, the low temperature polymer had the highest value, next the copolymer and finally PVC-2. The higher value for the copolymer yield stress over that of PVC-2 is contrary to expectation. The greater amorphous content and hence greater decreased chain mobility on annealing with the former may partly explain this observation.

Lowering the vacancy concentration will reduce the capacity of the polymer to relax applied stresses by virtue of a reduction in the number of alternative conformational sites available for occupation. Thus a drop in the elongation at break will be expected to occur. The presence of crystallites is also expected to cause a reduction in elongation due to a cross-link type effect. The amorphous regions are thought to deform to a greater extent under an applied stress, thus reducing the amorphous content will reduce the ability to extend and orientation harden, so decreasing elongation at break. These considerations are borne out by the experimentally observed decreases in elongation at break.

Following the development of the neck in a sample, the drawn region has a much higher stress than the undrawn material, due to the drop in cross-sectional area. If hardening did not occur, (portion (d) Figure 22), the sample would break soon after development of the neck as the stress continues to rise as the cross-sectional area decreases. Thus the hardening process comes about by orientation of the molecules, so the material will become progressively stronger as the extension proceeds. Reducing segmental mobility by decreasing the vacancy concentration will thus result in a greater force necessary to orient the molecules, so giving an increase in tensile strength.

On annealing above Tg crystallization has been shown to occur, thus imposing additional constraints on chain conformational changes. This should be reflected in increases in yield stress and decreases in elongation at break. However, this situation is complicated by the fact that on quenching from above Tg an excess vacancy concentration will be frozen in, tending to increase mobility. Thus for annealing above Tg, the two factors of crystallinity and vacancy concentration come into direct opposition as regards their effect on tensile behaviour.

The cross-link type influence of crystallinity appears to predominate for PVC-2 and the low temperature polymer over the excess vacancy concentration effect on annealing above Tg, with the values of yield stress and elongation at break. For the vinyl chloride/vinyl acetate copolymer, where the crystallinity is low, the yield and elongation values should be affected only slightly on treatment above Tg. The yield stress values were of the same magnitude as the quench value, and elongation at break, however, was surprisingly reduced.

The tensile strength values for PVC-2 and the low temperature polymer after annealing above Tg, were found to decrease when compared with a quenched sample. It seems correct to assume, therefore, that the stress concentration effect of the crystallites increases the probability of fracture, resulting in a lower value of tensile strength. The presence of crystallites will also reduce the extent to which the material will orientation harden, contributing further to a reduction in tensile strength. The percentage change in the value was smaller for the low temperature polymer than PVC-2, this is attributed to the smaller increase of crystallinity with the former on annealing. The values of tensile strength for the copolymer remain approximately constant, this can be viewed as the effect of the excess vacancy concentration balancing the effect of the small level of crystallinity in this polymer. The results for treatment above Tg reported here are in agreement with those published by Phillips et al[114] on a commercial PVC.

The values of the expected changes in tensile parameters for treatment below Tg did show a correlation with the time and temperature of treatment. However, as in the case of the X-ray measurements, an erratic response was observed with respect to time with annealing above Tg.

In comparing the overall behaviour of the three polymers, it is noticeable that the vinyl chloride/vinyl acetate copolymer showed a larger degree of stress softening than the other polymers (Figures 17 - 19). This is not surprising as the constraining forces due to crystallinity and polar attraction are less for this polymer, so it will stress soften to a greater extent. Although softening of the material due to heat generation on stretching has been disregarded as a mechanism for yielding the occurrence of a heating effect is considered significant[163]. Softening of the material due to heat generation will favour cold drawing, high elongation and result in a decrease of the force required to extend the polymer. Such an effect will be greatest in the case of the copolymer as this has the lowest softening temperature.

The cross-link effect of the crystallites is thought to be responsible for the very low values of elongations at break obtained for the low temperature polymer as compared with the other materials.

Tensile behaviour to an extent may be considered to be affected by molecular weight on the basis of a larger molecular weight, creating a greater degree of chain entanglement. Where such greater entanglement exists, larger forces may be required to extend the network. As shown in Table 2, the molecular weight is highest for the low temperature polymer, followed by the copolymer and finally PVC-2. This order is that expected by which molecular weight characteristics will influence tensile behaviour. The molecular weight influence is offered as a tentative explanation for the difference in yield stress values between PVC-2 and the copolymer, and tensile strength differences between PVC-2 and the low temperature polymer.

In Appendix 3 a statistical analysis of the variability of the tensile data is given. The large variation for the among treatment values indicates the significance of the shift obtained with changing annealing conditions. However, in the analysis there are some instances where there is some overlap in the range of the determined values, thus reducing the significance of the comparison of the data. These facts also indicate the overall variability to which tensile test data is subject.

In conclusion, the previous discussion has shown that interpretation of tensile behaviour with changes in polymer type and annealing treatments is complex. The influence on tensile behaviour of crystallinity and secondary attractive forces often come into opposition with vacancy concentration changes. Effects due to molecular weight characteristics and heat generated during stretching must also be considered as they may contribute to the observed tensile behaviour.

CHAPTER VI - Conclusions and Recommendations for Further Study

6:1 Conclusions

Attempts to convert the polymers into the amorphous state by quenching from temperatures well above the glass transition were not totally successful. Evidence from X-ray diffraction, density measurements and DTA have shown significant levels of crystallinity remain after the above pretreatments and quenching. It may, therefore, be concluded that the melting point of PVC is well in excess of the pretreatment temperatures employed, or that recrystallization is so rapid that the material cannot be quenched into the amorphous state.

Following various thermal treatments above and below the glass transition changes in structural ordering of the three polymers studied were found to occur. Two mechanisms for ordering in PVC above and below Tg have been proposed. It is considered that treatment below Tg results in changes in the vacancy concentration of the amorphous phase. For samples annealed above Tg it is suggested that crystallization occurs. No significant change in the X-ray determined crystalline content in the former case, and distinct increases in the latter case provide strong evidence to support the two proposed mechanisms. Further substantiating evidence is provided by data from density measurements, DTA and solvent sorption.

The appearance of the exotherm in the DTA thermogram when employing a relatively fast heating rate and the observed large extents of crystallization, as measured by enthalpy of fusion, indicate crystallization in PVC may occur after short elapsed times. It may be appreciated that such rapid changes in crystalline order can occur well within time scales experienced in processing.

The solvent sorption techniques outlined in the study provide a novel method for investigating small changes in order in PVC. The techniques have the advantage of requiring no sophisticated apparatus, yet provide a high degree of discriminative ability.

The experimentally determined values of the amount of crystallizable, i.e. syndiotactic material, and the crystalline content have been compared with those calculated from Flory's theory of crystallization of copolymers. From this comparison a value of 5 - 6 for the minimum sequence length capable of crystallization was obtained. This figure along with the broad X-ray diffraction maxima and the very broad melting DTA endotherms indicate that the crystallites in PVC are small and have a wide range of perfection.

The tensile behaviour of vinyl chloride polymers was shown to be greatly influenced by changes in polymerization and thermal history. It may be concluded that structural changes occurring during processing of commercial PVC may have a bearing on performance properties.

The merits of the various techniques for studying structural ordering in PVC have been assessed. It has been shown that by employing a number of techniques simultaneously, a complimentary picture of the ordering process can be built up.

6:2 Recommendations for Further Study

The pretreatment and quenching process was unsuccessful in totally removing the crystallinity present in the polymers. To determine whether the pretreatment temperature used was too low or that recrystallization was occurring extremely rapidly, pretreatments of increasing severity should be carried out, and the crystallinity remaining measured. These pretreatments could take the form of heat treatment for various times and increasing temperatures followed by quenching into liquid nitrogen.

The X-ray method used in this present study on samples treated above Tg was unable to show any correlation between the extent and perfection of crystallinity with temperature or time. By employing step-scanning or data-averaging techniques as outlined by Brunner[164] and using a low-scattering atmosphere[43,72] resolution should be improved making the above correlation possible.

Heat treatment both above and below Tg were found to alter structure. Hence a study of dual heat treatment, i.e. annealing above as well as below Tg may provide useful information whereby an optimum physical property could be obtained by judicious choice of thermal treatment.

Changes in crystallinity on annealing above Tg were shown to take place rapidly. Thus a thorough investigation using the techniques employed in this study should be undertaken to determine the significance of structural changes occurring within the short time scales experienced in processing.

A major study into structure changes and mechanical properties of PVC as a function of formulation and process history. Such a study, though involved, would be of direct commercial significance as it would furnish performance property data as determined by fabrication history.

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APPENDIX 1

Table 23 - Endothermic Enthalpy Change Values, kJ/kg for PVC-2

Annealing Temperature°C	40	55	70	100	115	130	145	160
Annealing Time h								
0.5	-	-	-	1.383	1.525	3.084	2.940	0.759
1.0	-	-	-	1.458	1.879	3.316	3.154	0.863
1.5	-	-	-	1.581	2.205	3.648	3.422	1.044
3.0	-	-	-	1.874	2.563	3.783	3.532	1.422
5.0	0.378	0.594	0.762	1.930	2.729	3.837	3.665	2.093

Table 24 - Endothermic Enthalpy Change Values, kJ/kg for the low temperature PVC

Annealing Temperature°C	40	55	70	100	115	130	145	160
Annealing Time h								
0.5	-	-	-	0.839	1.564	2.232	2.955	2.764
1.0	-	-	-	0.936	1.638	2.319	3.279	2.917
1.5	-	-	-	1.148	1.875	2.571	3.638	3.132
3.0	-	-	-	1.249	2.439	2.770	3.754	3.238
5.0	0.372	0.418	0.516	1.339	2.791	2.977	3.830	3.543

APPENDIX 1 contd.

Table 25 - Sorption behaviour of PVC-2 as a function of heat treatment

	% wt. gain	22.37	40.33	57.80	58.29	57.85	59.21	57.18
Quenched	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	91.17	148.49	208.52	271.42	537.72	628.74	755.39
8h 70°C	% wt. gain	18.48	35.61	58.73	58.31	59.50	57.84	-
	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	86.98	134.85	253.68	548.49	671.50	772.89	-
8h 110°C	% wt. gain	0.925	6.00	11.05	34.18	52.96	53.90	-
	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	116.81	270.87	382.18	554.69	627.11	767.39	-

Table 26 - Sorption behaviour of the low temperature polymer as a function of heat treatment

	% wt. gain	1.90	2.10	3.69	6.26	15.4
Quenched	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	164.67	398.99	515.18	848.34	109.10
8h 70°C	% wt. gain	0.79	2.33	2.59	8.20	-
	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	466.77	526.03	754.53	1101.48	-
8h 110°C	% wt. gain	0.19	1.23	2.18	2.33	2.50
	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	296.68	630.45	969.72	743.84	1270.49

APPENDIX 1 contd.

Table 27 - Sorption behaviour of Vinyl Chloride/Vinyl Acetate Copolymer as a function of heat treatment

Quenched	% wt. gain	24.70	29.40	43.60	45.70	56.80	-
	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	32.14	36.09	52.98	55.15	65.37	-
8h 70°C	% wt. gain	16.60	28.90	36.10	51.60	66.66	75.16
	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	22.85	35.78	46.94	64.06	78.07	90.16
8h 110°C	% wt. gain	16.70	25.80	34.10	92.00	-	-
	$t^{\frac{1}{2}}/l$ ($sec^{\frac{1}{2}}mm^{-1}$)	24.55	36.25	47.17	106.35	-	-

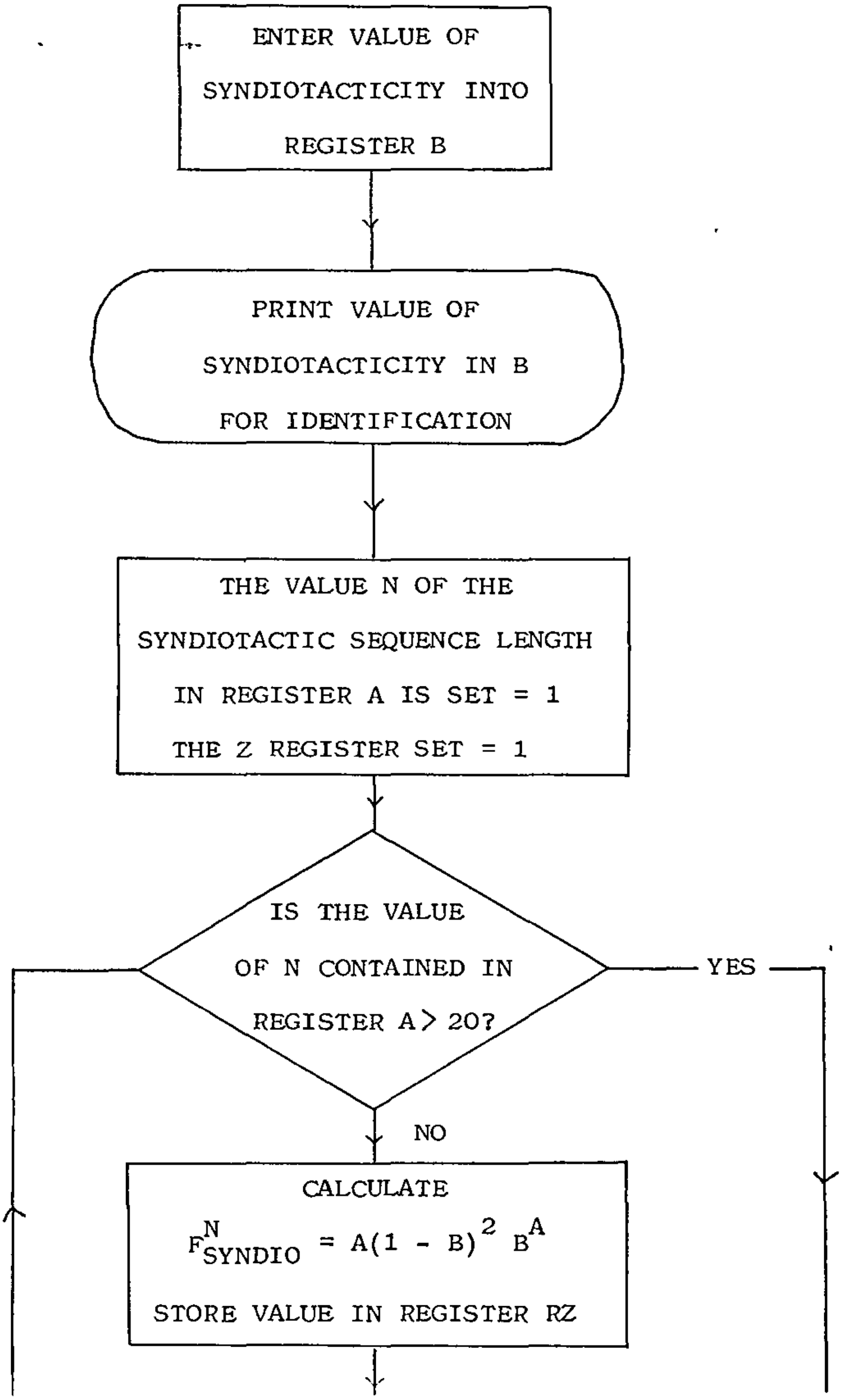
Table 28 - Solvent Sorption for PVC-2 immersed 4h and the low temperature polymer immersed for 72h as a function of heat treatment time at 110°C

PVC-2	% wt. gain	17.10	9.30	6.30	6.00	4.40	4.00
	Time h	0.16	1.00	3.00	8.00	16.00	24.00
Low Temperature Polymer	% wt. gain	3.73	2.82	2.73	2.18	2.01	1.67
	Time h	0.16	1.00	3.00	8.00	16.00	24.00

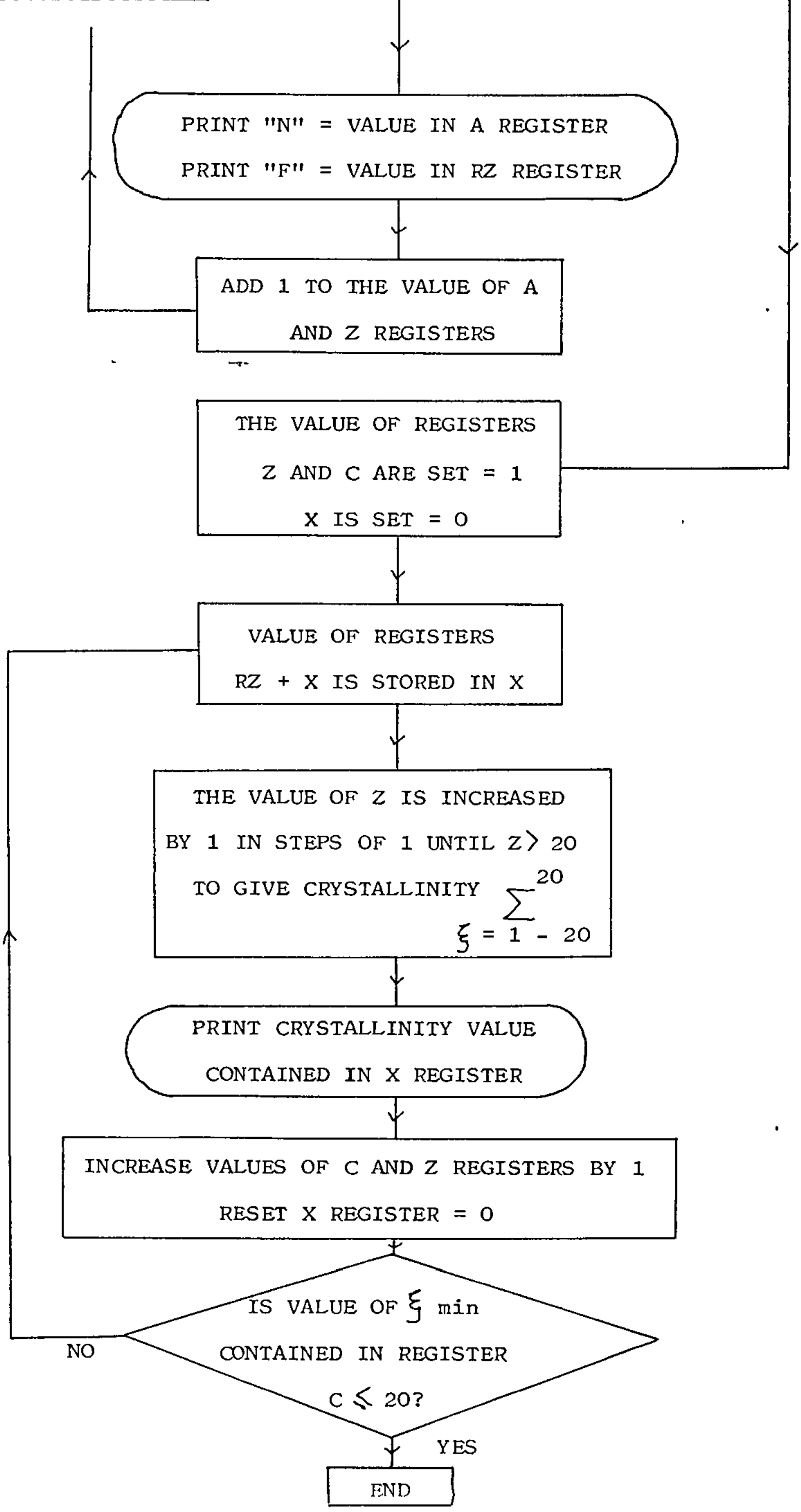
APPENDIX 2

Flow chart and computer programme used to calculate the fraction of the total polymer in syndiotactic sequences F^N_{SYNDIO} and $\sum F^N_{SYNDIO}$ for N = 1 - 20.

Flow Chart



Flow Chart contd.



Computer Programme

```
1.      FXD 6
2.      ENT "SYNDIO ALPHA?", B
3.      1 → A → Z
4.      SPC 2;  PRT "SYNDIO ALPHA =", B; SPC 2
5.      IF A > 20; GTO 9
6.      A (1-B) (1-B) B ↑ A → RZ
7.      PRT "N=", A, "F=", RZ; Z=1 → Z
8.      A+1 → A= GTO 5
9.      1 → Z → C; O → X
10.     RZ+X → X; JMP (Z+1 → Z) > 20
11.     PRT "CRYSTALLINITY", "SUM N=", C, "TO N=20", X
12.     C+1 → C → Z; O → X; IF C ≤ 20; GTO 10
13.     END
```

APPENDIX 3

Analysis of Variance of Tensile Data

The mean square estimates the variance caused by variability in r treatments and m replications. The total number of observations n = rm.

Source of Variation	Sum of Squares	Mean Square
Among Treatments	$s_2 = r\sum_i (\sum_i x_{it})^2 - (\sum_{it} x_{it})^2$	$s_2^2 = \frac{s_2}{r-1}$
Within Treatments	$s_3 = s_2 - s_1$	$s_3^2 = \frac{s_3}{n-r}$
Total	$s_1 = n\sum_{i,t} x^2_{it} - (\sum_{i,t} x_{it})^2$	$s_1^2 = \frac{s_1}{n-1}$

Abbreviations

T.S.D. = Estimated Standard Deviation caused by variability of total treatments.

S.D.A. = Estimated Standard Deviation caused by variability among treatments.

S.D.W. = Estimated Standard Deviation within treatments.

Y.S. = Yield Stress

E.B. = Elongation at Break

T.S. = Tensile Strength

APPENDIX 3 contd.

Table 29 - Analysis for treatments below Tg

Annealing Time h		0·5			5·0		
Polymer		T.S.D.	S.D.A.	S.D.W.	T.S.D.	S.D.A.	S.D.W.
PVC-2	Y.S.	4·13	7·90	2·64	2·12	3·60	1·61
	E.B.	21·57	19·05	22·09	15·02	2·60	16·56
	T.S.	5·29	8·02	4·46	3·87	0·51	4·27
Low Temperature Polymer	Y.S.	4·81	7·64	2·55	4·77	0·81	5·26
	E.B.	12·71	16·41	11·73	16·70	31·53	10·89
	T.S.	3·84	5·58	3·33	3·76	1·73	4·08
Vinyl Chloride Vinyl Acetate Copolymer	Y.S.	3·16	5·58	2·30	2·32	3·85	1·82
	E.B.	23·00	33·80	19·82	21·28	10·32	23·03
	T.S.	2·29	3·69	1·83	1·72	1·06	1·83

Table 30 - Analysis for treatments above Tg

Annealing Time h		0·5			5·0		
Polymer		T.S.D.	S.D.A.	S.D.W.	T.S.D.	S.D.A.	S.D.W.
PVC-2	Y.S.	4·94	10·34	1·56	2·23	3·48	1·75
	E.B.	27·92	22·93	29·10	20·15	24·37	18·86
	T.S.	2·77	3·35	2·59	2·93	2·98	2·91
Low Temperature Polymer	Y.S.	3·46	5·07	2·88	3·45	5·39	2·69
	E.B.	7·51	9·54	6·87	9·10	10·33	8·75
	T.S.	2·75	2·58	2·80	3·43	4·24	3·19
Vinyl Chloride Vinyl Acetate Copolymer	Y.S.	3·00	5·88	2·16	3·92	9·07	2·06
	E.B.	127·15	16·62	42·90	30·81	57·62	23·54
	T.S.	2·25	2·23	2·25	2·64	5·05	1·96